FINAL REPORT

I. URANIUM GEOCHEMISTRY

II. THERMOLUMINESCENCE

CONTRACT AT (11-1)-178

U. S. ATOMIC ENERGY COMMISSION

WITH THE

UNIVERSITY OF WISCONSIN

BY

FARRINGTON DANIELS

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FINAL REPORT

Uranium Recovery, Uranium Geochemistry,
Thermoluminescence and Related Studies

Contract AT(11-1)-178

Atomic Energy Commission

with the

University of Wisconsin

by

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I. History of the Project

When crystals are exposed to intense radiation, such as gamma rays, they frequently emit light later when heated to temperatures well below red heat. This thermoluminescence was a rather obscure phenomenon on which research was started ten years ago at the University of Wisconsin. A grant from the Atomic Energy Commission, Contract AT(11-1)-27, supported the program from July 1, 1949 to June 30, 1951. The final report under this contract was published late in 1951 by Farrington Daniels and Donald F. Saunders. It contained 26 chapters and was entitled "The Thermoluminescence of Crystals". The first four chapters of that report summarize the early studies on thermoluminescence and the work at the University of Wisconsin.

The investigation started with the purpose of studying kinetics in the solid state through measurements of thermoluminescence and expanded to the study of radiation damage in crystals by gamma and alpha rays and the search for uses of thermoluminescence as a research tool. It was found that many rocks exhibit thermoluminescence even without the exposure to gamma rays, a fact which had previously been recognized, but considered as a mineralogical curiosity. Studies quickly proved that the thermoluminescent rocks, such as limestones, fluorites and granites, were activated by high energy radiation in the form of alpha rays from the traces of uranium which they contained. The effects are of course very small, but they are accumulative. One part per million of uranium in limestone sending out alpha particles for millions of years can give enough displaced and trapped electrons to produce rather bright thermoluminescent light. This discovery shifted part of the emphasis of the research to geology and the geochemistry of uranium. An important part of the program was the development of improved apparatus and special techniques for measuring very feeble thermoluminescent light as a function of temperature, for measuring very low alpha counts of 1 to 10 alpha particles per hour, and for analyzing rocks for very low concentrations of uranium in parts per million and less.

This research led to studies on the geochemistry of uranium and to an expansion of the program with extensive field trips. These in turn led to a proposal for trying to develop a uranium extraction process so simple that it could be taken to the mine and thus reduce the heavy expense of hauling a ton of low grade uranium ore over long distances to a processing plant for the recovery of a few pounds of uranium. This expanded program resulted in a new contract, AT(11-1)-178, on July 1, 1951 which continued for five years until June 30, 1956. The present report summarizes this work which has followed along several different directions and has led to the publication of thirty-five articles in the scientific journals of geology, chemistry, physics, and botany.

The range of researches may be seen from the list of titles and the abstracts of these publications. They include chemical and mining engineering studies on the recovery of uranium from low grade ores, and hypotheses for the geochemical origins of uranium in both igneous and sedimentary rocks. The program included field trips to uranium deposits in Canada and the Rocky Mountains, to the granites of the Canadian shield, to the carnotite deposits of the Colorado plateau and to the uraniferous lignites of South Dakota. Studies on the geochemistry of uranium led to trips to volcanic deposits at Mt. Lassen, California and Paricutin, Mexico and elsewhere, to the examination of ground and surface waters in Wisconsin and in uraniferous areas of the West, and to measurements of uranium and radioactivity in the ashes of plants collected in Wisconsin and the Smoky Mountains. The measurements of uranium content and alpha particle radioactivity of limestone in exposed cliffs and outcrops, led to extensive field trips throughout the Midwest and the western part of the United States. The radioactivity and uranium content of a stratum of Bentonite clay was traced through several states, and clays and sandstones of the Grand Canyon and elsewhere were also collected.

Over seven thousand samples have been collected and most of them have been studied for thermoluminescence, uranium content or alpha ray activity. Much effort has been spent in trying to correlate thermoluminescence glow curves with the

stratigraphy of limestone deposits. Another major effort has gone into the attempt to determine the age of limestones from the intensity of their natural thermoluminescence.

The laboratory researches have emphasized studies on the mechanism and use of thermoluminescence, the crystal damage produced by alpha, beta and gamma radiation and their effect on thermoluminescence and on coloration of the crystals. Attempts have been made to correlate the thermoluminescence glow curves with chemical impurities in the crystals. It has been found that pressure and crystallization can sometimes supply the high energy necessary to dislodge electrons and lead to thermoluminescence without exposure to radioactivity. The use of thermoluminescence measurements for the evaluation of chemical catalysts and for the recording of gamma ray exposure in radiation dosimetry has been explored. The influence of added impurities on the thermoluminescence of calcium carbonate led to a satisfactory explanation of the conditions which give rise to precipitation of calcium carbonate in the two different crystalline forms, calcite and aragonite. These thermoluminescence studies led further to a study of the rates and the kinetics of chemical reactions between crystals of different chemical compounds at elevated temperatures.

One of the most important requirements for effective fundamental research in the universities is the absolute freedom of the investigator to follow his work wherever he desires to carry it. Sometimes the university researches, sponsored by government agencies, have been criticized because they may tend to be restricted to the areas specified in the contracts, and because they may tend to emphasize practical results rather than fundamental theoretical work. The list of researches summarized in this final report show that such a criticism cannot be made against the research program described here. The principal investigator has felt perfectly free to follow the lines of investigation into any field that he felt might be interesting and productive and he has never received suggestions from the administrative staff of the Atomic Energy Commission as to what specific

researches he might or might not be encouraged to undertake. He felt just as free to direct the research program as if it had not been supported financially, in considerable part, by the Atomic Energy Commission. The researches on the extraction of uranium ore in the field took a considerable part of the cost of the total program and did have a practical slant which was a bit foreign to the normal research program of a chemistry department. Nevertheless, the program was undertaken at the initiative and the desire of the research group. It was interesting and challenging, but when it became too large and too expensive in money and administrative time, the program was discontinued. It was carried through only to the point where others better equipped for engineering and large-scale operation could carry on the work if they desired.

II. Recovery of Uranium Ores with Portable Equipment

The purpose of this investigation was to explore the possibility of carrying equipment and chemicals to a uranium mine and extracting the uranium there. Such an operation would eliminate the large cost of transporting the low grade ore, -- one ton of 0.1 per cent uranium is transported for two pounds of uranium recovered. However, the cost of a small-scale operation is of course much greater. Even if such a process is uneconomical in competition with large stationary extraction plants, it might become of importance in a national emergency and it would make possible the utilization of distant and widely scattered deposits of uranium.

Three types of portable units were considered. The first type is a simple "gold panning" operation by a small operator with a minimum capital investment and no charge for his own labor. The second type of recovery involves two men and an investment of around \$50,000 for truck, power equipment, pumps and centrifugal filters. Most of the research effort was devoted to this type of operation. In a still more promising method, the grinding, leaching and extraction equipment is set up at the mine and operated by the same power that operates the mine. The chemicals are brought to the mines and the uranium is taken back on the return trip.

The process as finally developed, with helpful suggestions from the Argonne National Laboratory, consists of the following steps:

- (1) Crushing and grinding the ore (or burning the uraniferous lignite to ash)
- (2) Leaching with 3 molar nitric acid;
- (3) Settling and filtering;
- (4) Solvent extraction of the nitric acid solution with tributyl phosphate and kerosene;
- (5) Rinsing the organic phase and precipitating with ammonia gas from a tank;
- (6) Filtering the flocculent ammonium diuranate;
- (7) Heating to drive off ammonia and leave a solid residue of 65 per cent uranium oxide.

Laboratory measurements were carried out on settling rates, acid consumption, and on leaching and solvent extraction efficiencies.

Pilot plant tests were carried out at the University of Wisconsin over a two-year period, 1954 and 1955, using three different carnotite ores supplied by the Atomic Energy Commission from the Colorado Plateau. Two units were tested. In one, 10 to 20 pounds of powdered ore was used with motor-stirred leaching tanks, centrifugal filters and extraction columns, all made of stainless steel. In the second set of tests, 100 pounds of ore was treated in a batch process with hand-stirring in large settling tanks of stainless steel.

Field tests were carried out with the help of a specially equipped truck. In the summer of 1953, uraniferous lignite was used at a site near Buffalo, So. Dakota, and in the summer of 1954 various carnotite ores were used at Silverton, Colorado.

It was concluded that:

- (1) It is technically feasible to obtain a product of more than 60 per cent uranium with portable equipment.
- (2) The process which was worked out and tested appears to be economically possible for certain types of ores which do not consume excessive amounts of acid.
- (3) The cost of recovery depends on acid consumption, uranium content and on the size of operation. If 5 tons of ore are processed per day and the uranium content is 0.3 per cent and the limestone less than 4 per cent, it was estimated

that the cost would be about \$10 per pound of uranium.

For large-scale, mine-operated plants, a considerable saving in transportation and other costs could be effected by setting up small ammonia oxidation plants to make the nitric acid, and bringing in liquid ammonia in trailer tanks such as are used for agricultural fertilization.

Experiments on special Canadian granite ores with high uranium content which was easily leached by nitric acid indicated excellent results with very low acid consumption and easy filtration.

One of the greatest difficulties in the uranium extraction is the filtration of the ore after leaching out the uranium. After the work was discontinued, a new precipitating agent, Separan 2610, manufactured by the Dow Chemical Company, became available. This was tried out as an aid to rapid settling of the leached ore and it proved to be very effective. The data are given in a supplement to the Final Report of January 1956. When 1 part of Separan was added to 10,000 parts of powdered carnotite ore the settling in 3 M nitric acid was nearly complete in 5 minutes, whereas without the addition of Separan, the settling was less complete even after standing for an hour. Most of the settling was accomplished in two minutes. The estimated cost of recovery, particularly in the batch process should be reduced considerably with this settling agent.

It is realized that uranium is much more abundant now than it was when this project was started, but it is hoped that further tests will be made on a larger scale, particularly under special conditions where the mines are so distant and the reserves are so limited that the large standard, ore recovery plants are not practical.

Complete details of this work are given in "Recovery of Uranium from Ores with Portable Equipment" by Charles W. Pitrat, Leo W. Weisbecker, Edward J. Zeller and Farrington Daniels which is contained in Section XI at the end of this report.

Another research program was carried on for a year by Mr. Dervin Flowers on an attempt to concentrate uranium in powdered granitic ores by dropping the powder through an electrostatic classifier operating at high voltages. The particles which contained the pitchblende should have some adsorbed gas ions produced by the radioactivity of the uranium and its decay products and these particles should be moved more rapidly in an electrostatic field. The work is reported in a master's thesis entitled "Physical Chemical Aspects of Electrostatic Concentration of Uraniferous Material" by Dervin Flowers which was filed in the Library of the University of Wisconsin in 1952.

III. Distribution and Geochemistry of Uranium

Intensive studies were made on the uranium content and the alpha-ray activity of a wide variety of rocks and other materials with the purpose of understanding better the geochemistry of uranium. It was hoped, too, that hypotheses for the geochemical origins of uranium might help in suggesting areas where uranium deposits might be looked for. The development of very sensitive fluorimetric methods for uranium analyses and scintillometer methods for low alpha ray activity is described in Section VII. Several publications resulting from these researches on uranium distribution are abstracted here.

(1) Alpha Radioactivity of Some Rocks and Common Materials by John B.

Ockerman and Farrington Daniels, J. Phys. Chem. 58, 926-7 (1954).

The alpha ray activity of nearly 300 samples of materials are reported. They include granites, limestones, bentonites, building materials, well-water residues and plant liter. The special scintillometer responded to individual alpha particles escaping from a powder of infinite thickness and gave counts which ranged from 0.05 to 12 alpha counts per hour per sq. cm. The apparatus was sensitive only to alpha particles and uncertainties from cosmic rays and gamma rays were eliminated. The published article gives only the counts for the different samples without describing the samples, but a mimeograph sheet is available which describes each sample and gives the location from which it was taken. The

results show that the occurrence of radioactivity of low intensity is widespread. All granites contain some uranium and thorium, but so do limestones, ground water and plants. Bentonite clays with adsorbed uranium and other alpha emitters often give appreciable radioactivity.

- (2) Uranium and Thorium Content of Volcanic Rocks by John A. S. Adams, Chapter 2.2, NUCLEAR GEOLOGY, pages 89-99; Edited by Henry Paul, John Wiley and Sons, Inc., New York (1954).

The obsidians offer an unusually good opportunity for comparing the alpha-ray activity with the uranium and thorium content. In many rocks the daughter elements produced by radioactive decay may be lost by weathering and the gaseous products thoron and radon are likely to escape. But in obsidians, which are volcanic glasses, the original uranium and all its decay elements were sealed off permanently in glass when the volcanic material solidified. Obsidians from many different locations were analyzed for both uranium content and alpha-ray activity.

As expected, a close correlation was found between chemical analysis of uranium and radioactivity.

On the basis of available analyses, the average uranium content of basic lavas is between 0.6 and 1.1 parts per million. Differentiation at Lassen volcano produced dacitic lavas with four times as much uranium as the most basic lava analyzed, and differentiation can be expected to produce acidic volcanic rocks with at least six times as much uranium as the average basic lavas. Some obsidians were found with 15 parts per million of uranium. The data indicate that thorium is about three times more abundant than uranium in unweathered volcanic rocks and that this ratio probably holds constant during differentiation.

- (3) Uranium Geochemistry of Lassen Volcanic National Park, California by John A. S. Adams, *Geochimica and Cosmochimica Acta*, 8, 74-85 (1955)

Thirty-nine samples of different types of rock were collected in Lassen Volcanic Park. These samples included andesite, lava, pumice, dacite, basalt, tuff and clay from mud pots. The alpha-ray activity of these samples ranged from

11 to 51 alpha particles per hour from a thick layer of powder in a dish of 20 square cm. The uranium content varied from 1 to 3.6 parts per million; Na_2O content ranged from 3.26 to 4.30 and the K_2O content from 1.26 to 3.34.

The uranium analyses, obtained fluorimetrically, agreed very closely with the uranium content obtained by others using the radon method and assuming radioactive equilibrium. These checks support the accuracy of the analyses and show that the uranium was in equilibrium with its decay products. Much of the uranium is contained in the glassy potassium-containing materials and in small crystals of zircon. Alpha counts were plotted against uranium content and potassium was also plotted against uranium content. Approximately straight lines were obtained.

It is concluded that during differentiation at Lassen, uranium potassium and probably thorium were concentrated in the residual magmas at almost the same rate. Fractional crystallization is adequate to explain the observations.

(4) The Distribution of Alpha-Radioactivity in Native Vegetation by

J. T. Curtis and Ralph Dix, Botanical Gazette 117, 232-237 (1956).

Chemical elements are "pumped" by growing plants and trees from the subsoil through the roots to the leaves and then deposited on the surface of the soil when the leaves drop. Many of the elements are not leached back to the subsoil and are retained by adsorption or chemical action in the surface layer or humus. An attempt was made to determine the geological and botanical factors which determine the distribution of uranium and alpha ray emitters in the forests of Wisconsin and the Southern Appalachian mountains.

In general, the alpha counts ranged from 0.6 to 7.0 counts per hour per sq. cm. depending on the depth of the humus and soil and the type of vegetation. Data were obtained for eighteen different types of herbs, shrubs and trees.

High alpha ray activities are associated with high soil acidity, low soil calcium, low summer temperatures and coniferous forests. A considerable concentration of alpha emitting elements occurs in the forests with acid humus. The leaves on the trees have relatively low concentrations ranging from 0.6 to 5 counts per hour per sq. cm.

(5) Distribution of Alpha-Radioactivity in Certain Forest Types by

John T. Curtis and Ralph Dix, Science 123, 779-800 (1956).

The number of alpha particles emitted per sq. cm. per hour above an "infinitely thick" layer of ash was determined accurately for eighty stands of hardwood and conifer forest in Wisconsin and in the southern Appalachian region. Alpha counts were obtained for the living leaves of the dominant trees, of the dead and decomposing litter beneath the trees and the top soil and the subsoil. The subsoil was remarkably constant in its alpha radioactivity and the vertical distribution of radioactivity was similar in all cases, but the radioactivity of the decomposing leaf litter, on top of the top soil, varied greatly.

The hardwood forests in the prairie-forest border of southwestern Wisconsin were low (2.6 to 3.4 counts per hour per sq. cm.) in radioactivity while the mixed conifer-or pure conifer forests in northeastern Wisconsin, the Cumberland Mountains and the Great Smoky Mountains were unusually high (5.1 to 9.8, and 20. in one case).

Much of the alpha ray activity was due to radioactive elements other than uranium and the retention of the alpha emitters in the decomposing litter is probably due to the specific nature of the chelating humic acids.

(6) Radioactivity in Ground and Surface Water by Sheldon Judson and

J. Kenneth Osmond, American Journal of Science 253, 104-116 (1955)

Seventy-seven samples of underground and surface waters were collected in Wisconsin, Illinois, Kentucky, Texas, New Mexico, Utah and Colorado. Several liters of water of each sample were collected and evaporated to dryness in the field using large stainless steel trays. The residues were analyzed for traces of uranium and the alpha ray activity was measured with a scintillometer. In many cases the pH and the fluorine content of the waters were determined also.

Although there is a considerable amount of information available on the radioactivity of water, particularly in mineral and thermal springs, there is very

little information as to the fraction of the radioactivity which is due to uranium. One of the purposes of the investigation was to determine whether or not the uranium content of ground and surface water would be helpful in prospecting for uranium.

Waters from the Colorado Plateau in mineralized areas (carnotite aquifers) near the uranium mining district ran high in uranium, from 100 to 460 parts per billion, but in the non-mineralized aquifers the uranium ranged from 2 to 9 parts per billion.

In Wisconsin the samples, which include water from deep wells drilled down to the pre-Cambrian basement, contain only 0.1 to 1.7 parts per billion of uranium. There is some indication that the uranium content decreases as the pH increases. In the shallower Wisconsin wells in sandstone, dolomite and gravel, the uranium content is similar to that in the water of the deep wells but the total radioactivity is lower.

The uranium content of water from the high plains of Texas ranged in five samples from 2 to 10 parts per billion. The source of uranium here is thought to be volcanic ash. The uranium content of water collected in the western Kentucky Fluospar district is low, 0.1 to 0.5 parts per billion and that of surface waters in Wisconsin ranged from 0.4 to 3 parts per billion.

Studies were made on the change of radioactivity of the samples with time. The thoron and radon originally present were of course driven off by boiling in the process of obtaining the sample residues. Attempts were made to correlate the uranium analysis with the value obtained by calculation from the alpha-ray activity.

(7) Uranium Content of the Rivers of Wisconsin by John A. S. Adams,
Forthcoming publication.

One of the most interesting studies in distribution of uranium is that of the uranium content of the waters of Wisconsin. Improvements in the sensitivity and accuracy of the analyses for uranium were made during the course of the

project, so that small traces of uranium in water could be determined accurately. It was found, in general, that the uranium content of the rivers of northern Wisconsin increased in the winter time and that it increased in southern Wisconsin in the summer time. This situation is explained by the fact that in northern Wisconsin, the rivers are frequently in contact with outcrops of granite from which uranium can be leached, and in the winter time much of the precipitation is frozen so that the water volume flowing past the granite is smaller. In the summer time, there is more water from rainfall and the uranium is diluted. In the southern part of the state there is much agricultural land, but very little granite, and the uranium comes from phosphate fertilizer mined in Florida. This phosphate rock from Florida is high in uranium, up to 30 parts per million and higher and when it is placed on the farms in the spring, some of the uranium is leached out by the rains and carried to the streams and rivers.

Another interesting observation was that the uranium content of a small stream flowing into a lake (Lake Mendota, 5 miles in diameter) is considerably higher than that in the stream that flows out of the lake. Much of the uranium which came into the incoming stream from the fertilized farm land, apparently settled out in the lake and went to the bottom either as uranium adsorbed on small clay or soil particles or it precipitated as insoluble inorganic or organic uranium compounds, or it coprecipitated out with calcium carbonate.

(8) Average Uranium Content of Limestones by John A. S. Adams, In press.

All limestones contain small, but easily measured concentrations of uranium. Analyses of several samples of limestone were given earlier in this section (III - (1)).

During the course of this project, samples of limestones were collected from a great many different formations in the United States and elsewhere. They were used chiefly for studies of thermoluminescence. When these measurements were completed it was decided to make a composite sample of many smaller samples for the different significant limestone formations and to run uranium

analyses on these composite samples in an attempt to obtain a good average value for the uranium content.

(9) Uranium Content of Tektites by John A. S. Adams, In press.

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In addition to these published reports on the distribution and geochemistry of uranium, several other researches were carried out which have not yet reached a point where publication is justified. One or two of them may be published at a later date.

The uranium content of volcanic materials at Mt. Lassen, California, was studied in detail and these investigations have already been referred to. A trip was made to Paricutin Volcano in Mexico in 1952 just before it ceased to erupt. Samples of fresh ash fall were collected close to the volcano and at various distances. Volcanic ash was collected at various depths corresponding to the ash fall of the last few years since the volcano started eruptions. Steam and volcanic gases were pumped through water to collect any traces of volatile uranium compounds. An unsuccessful attempt was made, with the help of an improvised balloon, to test the gases in an ash cloud before it settled to the earth. All of these samples were found to be quite low in uranium, -- less than 1 part per million.

Before the contract started, Dr. Edward J. Zeller took a trip to Mt. Aetna and Mt. Vesuvius in the Mediterranean Ocean to collect volcanic material for uranium analyses. This trip was financed by the Research Committee of the University of Wisconsin with funds from the Wisconsin Alumni Research Foundation. Dr. Zeller also collected samples of material from a new volcanic island southwest of California. Samples of volcanic material were obtained also from Hawaii and from the new volcano Hibok-hibok in the Philippine Islands. Dr. Zeller and Dr. Donald F. Saunders collected a considerable number of samples in the

Valle Grande, the large volcanic area, west of Los Alamos, New Mexico. All of these volcanic materials from several different parts of the world contained uranium, but its concentration did not exceed a few parts per million.

As stated earlier, Mr. Kenneth Osmond traced beds of bentonite spread over several states and collected samples for uranium analyses and alpha particle counting. This material came originally from a layer of volcanic ash. The findings are reported in detail in a Ph.D. thesis, under the direction of Professor Sheldon Judson, on the Radioactivity of Bentonites by Dr. Osmond, filed in the Library of the University of Wisconsin in June, 1954. A final report on this work was prepared and circulated. The radioactivity of the bentonite formations was not high, but it was about twice as high as that of the beds which enclose them. Bentonite and other clays have high adsorption for the heavier elements including the alpha emitters, but whereas underclay and kaolin were occasionally radioactive, only bentonite was found to be consistently radioactive. The interpretations are complicated by the early alteration of the volcanic ash and the later weathering to give bentonite, and by the adsorption and desorption of uranium, thorium and their radioactive decay elements.

The uraniferous lignites near Buffalo, South Dakota were studied, and here it seems clear that the uranium has been leached from the clays which overlie the lignite beds. This clay is derived from volcanic ash and it contains uranium which is dissolved by the rain water which soaks through. When this water passes through the lignite beds which underlie the slightly uraniferous clay the leached uranium is adsorbed accumulatively and so the upper part of the uppermost layer of lignite in these formations is much richer in uranium. This volcanic-ash, adsorption hypothesis had been proposed by N. M. Denson, G. O. Bachman and H. D. Zeller of the U. S. Geological Survey Trace Elements Report 175 in 1950. This hypothesis was abundantly supported by the work of the present contract. Many samples of the upper part of the uppermost lignite layer gave uranium as high as 0.1 per cent in the ash, the overlying clays of volcanic

ash were found to contain about 1 part per million of uranium. Water flowing out of the clays in the form of springs contained uranium in parts per billion and in the laboratory it was found that the lignite readily adsorbed uranium from solution at suitable pH values. The success of this hypothesis suggested the importance of checking other cases of uranium enrichment to determine if volcanic ash is the original source of the uranium in sedimentary deposits.

Professor R. C. Emmons of the Geology Department, University of Wisconsin, has shown that in the formation of granites, black lamprophyre dykes are sometimes formed by the transport of iron and magnesium, probably as halides, from a large mass of the granite. These materials then concentrate and deposit under the influence of water in cracks and dykes. The uranium halides are volatile and so it was suggested that uranium too might be collected from a large volume of rock in the granitization process and concentrated in the lamprophyre dykes. Professor Emmons and Professor Daniels sought to test this hypothesis in the uranium mining districts north of Lake Superior, and in the Lake Athabaska area.

Thermodynamic calculations on the volatility of uranium halides were carried out by Harold F. Mason. The results were summarized and distributed as a final report in February 1954,--"The Thermodynamics of Reactions Leading to the Volatilization of Uranium from Volcanic Systems." The calculations included reactions between uranium oxides and halides (chlorine and fluorine), metal halides, hydrogen halides (HCl and HF), at temperatures and pressures prevailing under volcanic conditions. It was shown that volatilization of uranium chloride at pressures greater than 10^{-5} mm is unlikely unless chlorides of iron, aluminum or manganese are present. These calculations were checked by a limited number of laboratory experiments. It was found experimentally also that uranium is not driven out of uraniferous obsidians by heating. The researches indicated that volatilization of uranium compounds in the gas phase is not a significant geological factor in volcanic action.

Professors R. C. Emmons and R. M. Gates took systematic samples of outcrops of granites in the Canadian shield. The samples were ground and separated into fractions by using liquids of different densities and then analyzed for uranium and alpha ray activity. It was hoped that a fair estimate could be made for the uranium content of an "average" granite in this region where the uranium had not been concentrated by geochemical means.

A significant contribution to the geochemistry of uranium and thorium was made by Dr. John A. S. Adams during the course of this project. According to his hypothesis which he has subjected to extensive experimental and field testing, the ratio of thorium to uranium is about 3 to 1 in the igneous rocks where reducing conditions are maintained and both thorium and uranium have a valence of four. This is probably the ratio of uranium and thorium in the original igneous rock material. After the igneous rocks become weathered and oxidized, the uranium is oxidized to a valence of six, but in as much as thorium has only one valence state, four, it cannot be oxidized. At this point the uranium and thorium part company and the dissolved hexavalent uranium compounds react chemically quite differently than the tetravalent thorium compounds. The ratio of thorium to uranium is no longer 3 in the sedimentary rocks which have been formed after the weathering and oxidation. The uranium is dissolved and concentrated in secondary deposits by precipitation and adsorption. By determining the thorium-uranium ratio in secondary deposits of different geological ages, Dr. Adams hopes to obtain information concerning the geological time at which oxygen appeared in the atmosphere and changed the thorium-uranium ratio in the secondary deposits.

IV. Geochemical Studies Based on Thermoluminescence

As already stated, the early impetus for the present research program and the contract AT(11-1)-178 with the Atomic Energy Commission came from the discovery that the natural thermoluminescence of rocks is due to the traces of

uranium which they contain. This thermoluminescence is produced by submitting a crystal to intense radiation such as gamma rays or alpha rays, which release electrons from their normal positions in the crystal. Most of the electrons fall back to a position of lower energy but a few of them become trapped in crystal imperfections caused by physical defects or chemical impurities. When sufficient kinetic energy is supplied by heating the crystal to a higher temperature the electrons escape from their traps and evolve light as they fall to positions of lower energy.

Most of the work of the project has been done on limestones because thermoluminescence is always present and because the glow curves exhibit a great variety of patterns. The intensity of the thermoluminescence, particularly at the lower temperatures, and the number of peaks in the glow curves are greatly increased by exposing the crystals to gamma or X-rays in the laboratory. The thermoluminescence glow curves have been used for studies of stratigraphy, for age determination and for the geology and geochemistry of limestones. Thermoluminescence is helpful also in geochemical studies of fluorites and other minerals.

Abstracts of the published papers are given here and they are followed by a brief discussion of other studies which were not sufficiently far along to warrant publication at the present time.

(1) Thermoluminescence and Surface Correlation of Limestones by

Donald F. Saunders, Bulletin of the American Association of Petroleum Geologists 37, 114-124 (1953).

This is the first work published on the thermoluminescence glow curves of limestones. Fuller details are contained in the Ph.D. thesis of Dr. Saunders filed in the Library of the University of Wisconsin in 1950. Thermoluminescence glow curves, in which light intensity is plotted automatically against the temperature, were determined for a large number of typical limestones and other rocks. It was expected that limestones of different geological origins would give different glow curves with peaks of high light intensity coming in at

different temperatures, but it was hoped that a limestone of given geological origin would give a uniform and characteristic pattern over wide geographical areas. Four different limestones from a section of the Black Hills, South Dakota gave distinctly different patterns. In a quarry of Niagara limestone in Wisconsin samples along a horizontal layer gave identical thermoluminescence patterns for a distance of 2100 feet, whereas the glow curve patterns along a vertical section from different strata gave widely different patterns. Three different limestones, the Pahasapa limestone of the Black Hills, the Madison limestone of Wyoming, and the Redwall limestone of Arizona had been recognized as correlative. Samples were taken from each along a vertical section and all three limestones showed very nearly the same thermoluminescence patterns.

(2) Use of Thermoluminescence of Limestones in Sub-Surface Stratigraphy

by James M. Parks, Jr., Bulletin of the American Association of Petroleum Geologists, 37, 125-142 (1953).

Fuller details are contained in a Ph.D. thesis filed in the Library of the University of Wisconsin in 1951. Through the cooperation of the Illinois State Geological Survey, borings from 5 wells in southern Illinois and Kentucky were made available for these thermoluminescence studies. They were compared with surface outcropping limestones. They included samples through the entire Chesteran series, and some penetration into the Meramecian series. One of the borings gave a continuous core through the Levias limestone, member of the Ste. Genevieve limestone. The summary of conclusions is as follows.

The pattern of variation in intensity of thermoluminescence, coupled with typical glow curve shapes, may serve to identify and characterize a formation.

Where several limestones occur in sequence with no great lithologic breaks, the intensity and glow-curve shape variation may assist in recognizing tops and bottoms of formations.

They may assist also in splitting thick carbonate rock sequences into small units useful in correlation.

Once a typical pattern of variation is recognized for a formation, the absence of parts of that pattern at other localities may indicate erosion or nondeposition.

Within one basin of deposition and one short period of geologic time, it was found that the variation in radioactivity of the limestones is an important factor in the thermoluminescence.

- (3) Surface Correlation of Some Pennsylvanian Limestones in Mid-Continent by Thermoluminescence by Robert E. Bergstrom, Bulletin of the American Association of Petroleum Geologists 40, 918-942, (1956).

Many limestone samples collected from established stratigraphic horizons in outcropping Pennsylvanian rocks of Iowa, Missouri and Kansas have been subjected to thermoluminescence study to evaluate the use of thermoluminescence in correlation.

Although each limestone selected for study is a unit whose lateral continuity has been reasonably well demonstrated by other stratigraphic methods there is wide variation among the limestones in the lateral persistence of specific thermoluminescence properties. Some show fairly persistent thermoluminescence patterns over a township-to-county area, whereas other limestones show wide variations within a square mile.

Thermoluminescence curves from cyclical limestones of the Kansas City and Shawnee groups show cyclical repetitions. A relation between glow-curve shape and lithologic character is suggested for some limestones in the cyclical sequences, but the factors controlling thermoluminescence, such as chemical composition, amount of radioactivity, recrystallization and sedimentation are complex and need further study. More complete details are given in a Ph.D. thesis under the direction of Professor L. M. Cline, filed in the University of Wisconsin Library in 1953.

- (4) Thermoluminescence of Limestones of Mississippian Madison Group in Montana and Utah by C. W. Pitrat, Bulletin of the American Association

of Petroleum Geologists, 40, 943-952 (1956).

It was possible to differentiate the Lodgepole and the Mission Canyon formations of the Madison Limestones on the basis of their glow curves, but further subdivision was not successful. The radioactivity, as measured by the alpha particle counts, was not an important factor in the thermoluminescence glow curves, but the magnesium content of the limestone had a profound effect on the shape of the glow curves. Calcitic limestones tend to have a low temperature peak; whereas magnesian limestones and dolomites have a middle-temperature peak. The distinction between the Lodgepole and Mission Creek formations on the basis of thermoluminescence depends largely on the difference in magnesium content. The Mission Creek limestone has the higher magnesium content.

The limestone samples were ground to powder 100-200° mesh in size, and exposed for 72 hours in a 5 curie, cobalt 60 source. The samples were kept on dry ice until the glow curves were determined.

- (5) Factors in Age Determination of Carbonate Sediments by Thermoluminescence
by Edward J. Zeller, John L. Wray and Farrington Daniels, Bulletin
of the American Association of Petroleum Geologists 41, 121-129 (1957).

The intensity of thermoluminescence obtained by heating a sample of limestone or other rock depends on the chemical impurities and physical properties of the rock and on the amount of radiation the rock has received. If the only radiation comes from the traces of radioactive elements (1 part per million of uranium in limestones) and, if the thermoluminescence effects are accumulative, it should be possible with proper measurements and corrections to determine the age of the limestone since its last crystallization. This possibility seemed so intriguing and so important that attempts to determine geologic age through measurements of thermoluminescence have occupied an appreciable part of the program from its beginning.

In the general dating of rocks by radioactivity, the decay of uranium and the heavy radioelements have been very useful for the very old rocks and results of extraordinary value have been obtained with radioactive carbon, C^{13} , for measurements of organic material up to 50,000 years. But there has been no satisfactory comparable laboratory technique for determining the age of limestones in the range of a hundred thousand years to several hundred million years.

There have been serious difficulties in determining the age of limestones and other rocks by thermoluminescence, but in this paper published in 1957, considerable progress is described and the method seems to be effective within certain limitations.

For a given crystal, the intensity of thermoluminescence light will depend both on the concentration of alpha particle emitters (usually uranium and its radio decay elements) and on the length of time of exposure. The alpha radioactivity of the powdered limestone is determined with the help of a scintillometer and electronic circuit which records each alpha particle as it leaves the surface of the powder. The number is so very small, however, that a considerable error results even when counting is continued over several hours. If there are only 3 counts per hour, an error of one alpha particle will make an error of 30 per cent. Improvements in alpha counting sensitivity and accuracy are needed.

Limestones give prominent peaks in the thermoluminescence curves at roughly 235° and 312° C. and at other temperatures. Limestones exposed to intense gamma rays give a peak at around 110° but this and other low temperature peaks are annealed out at earth temperatures. The trapped electrons which require a temperature of around 375° , however, are not lost, even after standing at earth temperatures for very long periods of time. Accordingly, the measure of natural thermoluminescence is determined by obtaining the area, with a planimeter, under the thermoluminescence glow curve between 250 and 375° , when the sample of limestone is heated. These measurements are made without exposure to gamma radiation in the laboratory.

The presence of varying amounts of different impurities and the previous history of the limestone greatly affect the intensity of thermoluminescence. To correct for these variations, allowance is made for radioactivity sensitivity. The powdered limestone is heated to 400° C. to release all the trapped electrons and destroy all the natural thermoluminescence. It is then divided into four samples and each is given a different exposure to gamma radiation from cobalt 60, ranging from 72,000 to 288,000 roentgens. The planimetered areas of thermoluminescence are plotted against the number of roentgens of exposure and a smooth curve is plotted. With this calibration curve the relative equivalent radiation dosage R_a , required to duplicate the natural radioactivity, is determined. This relative equivalent dosage is then divided by the number of alpha counts to get a number R_a/α which is a measure of the relative age of the limestone. When R_a/α is plotted against geologic time, a reasonably good straight line is obtained from tertiary to pre-Cambrian. Thus with a calibration curve using limestones of known ages, it is possible to estimate the ages of the older limestones.

The younger limestones, however, did not seem to give their proper geological ages when tested by this method. It was found, as will be described presently, that some thermoluminescence can be induced by crystallization alone, without high energy radiation. In other words for the geological dating, some thermoluminescence capacity is introduced when the limestone is first deposited in crystalline form and zero luminescence does not necessarily start with zero time. This discovery introduces a serious handicap into the dating of limestones by thermoluminescence, but a way was found to minimize this difficulty. It was found that the application of a pressure of 50 tons per square inch increases the thermoluminescence in the geologically younger limestones, whereas it gives a smaller increase in the limestones of Lower Tertiary and gives an actual decrease in all Mesozoic and Paleozoic limestones.

The crystallization-induced thermoluminescence is produced at the time of the limestone is crystallized and is not produced again. It is increased by the application of pressure. However, the radiation-induced thermoluminescence is not increased by the application of pressure, but is decreased. The crystallization-induced thermoluminescence gradually decays over geologic time, and in the older rocks, it has disappeared, and all of the observed thermoluminescence is produced by alpha-particle radiation from the uranium present in traces. This accumulated effect is the basis for the age determination. The application of high pressure then permits one to determine whether or not the crystallization-induced thermoluminescence has decayed. Only in case the application of high pressure fails to increase the natural thermoluminescence is it safe to draw conclusions regarding the age of the limestone from the measurements of thermoluminescence intensity and alpha particle counts.

It is important to point out that any age determination by thermoluminescence gives only the age since the last recrystallization when the present crystal lattice and its impurities were formed. This age, of course, may be considerably less than the time since the original bed of limestone was deposited.

(6) Thermoluminescence of Carbonate Sediments by Edward J. Zeller, Nuclear Geology, Edited by Henry Faul, p. 180-188, John Wiley and Sons, Inc., New York (1954).

The estimation of the age of limestones from thermoluminescence measurements is explored. Alpha particles from polonium were used instead of gamma rays from cobalt 60 because this type of activation is more like the type which results from the traces of uranium. However, no advantage was found in the use of polonium. The presence of impurities and their removal through leaching in the weathering process is important. Manganese and strontium in the calcium carbonate crystals serve as activators and increase the thermoluminescence whereas iron decreases the intensity of thermoluminescence. This work was carried out before the crystallization thermoluminescence was discovered and at that time the possibility of

determining age from thermoluminescence seemed less hopeful.

- (7) Radioactivity, Energy Storage and Volcanism by Farrington Daniels, Nuclear Geology, Edited by Henry Faul, p. 188-194, John Wiley and Sons, Inc., New York (1954).

An hypothesis of intermittent heating in geological time is proposed and criticized. Heat is supplied continuously by radioactive elements and a small fraction of it is used in releasing electrons, some of which are trapped. At a later time, the energy of these trapped electrons can be released quickly by heating so as to give more intense energy, as evidenced by thermoluminescence light. If some analogous process could take place in geology, it might be possible to convert a long slow process of low radioactive heat evolution into an intermittent cycle with an occasional large evolution of stored heat.

As a theoretical maximum, it can be calculated that if a rock contained 10 parts per million of uranium and 30 parts per million of thorium, it would evolve 260 calories per gram over a 20 million year period. If all of this heat were stored as potential energy and released suddenly and adiabatically, there would be enough heat to raise the temperature to 1000° C. and melt the rock. Obviously, it is not possible to approach this theoretical limit because only a very small fraction of the radioactivity energy can be converted into potential energy and stored. Metamict minerals are known, however, which have had their crystal structures altered greatly by radioactivity damage and in one of these minerals, described later, heat storage of 65 calories per gram was found. By heating the mineral to a moderate temperature, this heat is released suddenly so that a large and rapid rise in temperature is obtained.

The amount of energy stored in thermoluminescent crystals was measured and found to be extremely small. Metamict minerals have a very complex structure and are rarely found. They apparently have such complex lattices that the atomic displacements due to radioactivity energy do not anneal out at room temperature. Minerals which contain large amounts of uranium and thorium, and have simple

lattice structures, do not store the energy produced by radioactive disintegration because the displacements of atoms in the crystal lattice are quickly restored by annealing at Earth temperature. This hypothesis for storage and intermittent heat release does not seem adequate to account for geological heating under normal conditions, but researches should be ^{carried} out to determine if the fraction of heat stored in disordered lattices of rocks can be much increased by the application of very high pressures such as exist at depths under the Earth's crust.

- (8) Physical Chemistry in Geology by Farrington Daniels, Journal of Physical Chemistry, 60, 705-707 (1956).

The author was asked to organize a symposium on Geochemistry at the national meeting of the American Chemical Society in Minneapolis in 1955. Twenty papers were presented, four of which were published in the Journal of Physical Chemistry as symposium papers. The rest were published elsewhere. In the present introduction to the symposium, the applications of many branches of physical chemistry were pointed out including thermodynamic equilibria of solids, liquids and gases; phase diagrams; oxidation and reduction; pH; solubility; precipitation; crystallization; electrolytic reactions; adsorption; sedimentation; kinetics of rate processes; heat transfer; radioactivity; isotopic tracers; nuclear reactions; radiation damage and thermoluminescence. The factors involved in the movements of solids, liquids, solutions, gases and colloidal material are discussed.

- (9) Thermoluminescence Analysis by Farrington Daniels, Chapter in "Subsurface Geology in Petroleum Exploration", Edited by J. D. Haun and L. W. LeRoy, Colorado School of Mines, Golden, Colorado, (1958).

This chapter discusses the theory of thermoluminescence and the experimental techniques. Examples and curves of thermoluminescence are shown for inorganic crystals, limestones and other minerals. Applications of thermoluminescence to problems of stratigraphy and age determination are discussed with the help of illustrations.

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The published researches on geology and geochemistry related to thermoluminescence have been summarized in this section. Additional researches have been carried out which have not yet reached the stage of publication.

The fluorites give bright thermoluminescence which has been measured by Dr. D. F. Saunders and Dr. J. M. Parks on samples collected from several different locations. Thermoluminescence glow curves were obtained on large crystals of calcium fluoride containing impurities of rare earth elements and other elements.

Now that the influence of pressure and crystallization-induced thermoluminescence is understood, the geological significance of the thermoluminescence of fluorites should be re-examined.

After the contract was terminated, an investigation was carried out by W. F. Ammentorp on the thermoluminescence of calcium sulfate and the anhydrites. Many samples of cores were obtained from drilling operations carried out by the petroleum companies. The thermoluminescence glow curves of the anhydrites are quite simple and the variations are not great enough to give much help in problems of stratigraphy.

Thermoluminescence measurements were made on stalactites, and variations were found in the different rings of the stalactites indicating that impurity ions from the seepage water varied from year to year, depending somewhat on the rainfall. The temperature in these caves is extremely constant and so the temperature of formation can be ruled out as a factor in changing the nature of the thermoluminescence glow curves.

Core drillings from Bikini Island in the Pacific Ocean were made available for thermoluminescence studies by Dr. Harry S. Ladd of the U. S. Geological Survey. These samples extended down to the underlying igneous rock and it was hoped to test the method of estimating geological age through thermoluminescence. There have been no lateral pressures or upheavals in these coral deposits, and the depth at which the limestone samples was taken is an indication of the age. It was found that samples taken near the surface, and at the surface, showed some

thermoluminescence even though they were too young to have accumulated a detectable amount of displaced and trapped electrons for producing thermoluminescence. Tests showed that radioactivity from atomic bomb tests was not responsible for the abnormally intense thermoluminescence. These measurements by Dr. E. J. Zeller led to the discovery that young limestones and fresh precipitates of calcium carbonate are rendered thermoluminescent by the process of crystallization even without any exposure to radioactivity.

Exploratory calculations were carried out by Professor Norris F. Hall for a short time on the possibility of estimating geological age from a change in the concentration of an isotope which is formed by the absorption of a neutron.

Most age determinations by nuclear disintegrations depend on the ratio of the radio-decay elements to the original element. Two different elements are involved and these will have different rates of oxidation and solution. Accordingly, long weathering will tend to affect the ratio, due to the different chemical properties of the two elements.

If a new isotope of the same element can be made by the absorption of naturally occurring neutrons, then weathering and chemical action will not be able to affect the isotopic ratio, because the chemical properties of the isotopes are the same. In some minerals there is a natural, low flux of neutrons liberated by spontaneous fission, by the action of alpha particles on beryllium, or by other nuclear reactions. This neutron flux can be measured and the absorption cross-section of the elements are known so that it should be possible to determine the rate of new isotope production. The ratio of the isotopes of the same element can be determined by mass spectrometry and from these data it is theoretically possible to tell how long the new isotope has been accumulating and how old the mineral is. Gadolinium 138 produced from neutron absorption by gadolinium 137 appears to be one of the best possibilities for this type of age estimation, but the present mass spectrometers do not give the gadolinium 138-gadolinium 137 ratio with sufficiently high accuracy. It is hoped that with

improved apparatus and perhaps with other elements, such as boron or cadmium, this method may sometime become useful.

V. Thermoluminescence

The study of thermoluminescence is interesting in many ways, in addition to its applications in geology. It was an obscure phenomenon which had not received much attention when this research program was started. Part of the work under this contract and that of the preceding contract was concerned with fundamental knowledge of thermoluminescence and with possible applications of this phenomenon.

- (1) Thermoluminescence as a Research Tool by Farrington Daniels, Charles A. Boyd and Donald F. Saunders, *Science* 117, 343-349 (1953).

The phenomenon of thermoluminescence and apparatus for measuring it are described and applications are suggested in the identification of solid chemicals and minerals, in dosimetry, catalysis, radiation damage, mineralogy, stratigraphy and geological age.

- (2) Thermoluminescence of Fourteen Alkali Halide Crystals by Louis F. Heckelsberg and Farrington Daniels, *Journal of Physical Chemistry* 61, 414-418 (1957).

The alkali halides were chosen for the first studies because they all exhibit thermoluminescence after previous exposure to gamma rays or x-rays and because they have simple crystalline structures. Large fused crystals of LiF, NaCl, KCl and KBr were obtained from the Harshaw Chemical Company and the crystals of LiCl, LiBr, NaF, NaBr, NaI, KF, KI, RbCl, RbBr and RbI were crystallized in the laboratory from the molten state. The thermoluminescence glow curves were determined from liquid air temperatures up to red heat. The data are presented as relative, composite glow curves with a supplementary table. The coloration of the crystal, produced by the gamma ray exposure, disappears when the crystal is heated at the temperature of the high temperature

glow curve peak. This fact was well known and explained by the trapping of an electron in a negative ion vacancy. A comparison of the glow curves for the many alkali halides brought out the new relationship that the temperature of this glow curve/^{peak} drops to lower temperatures as the diameter of the negative ion increases from fluoride to iodide.

The influence on the glow curves of increasing exposure to radiation from 10 to 400,000 roentgens was studied in LiF and NaCl. Many new peaks were formed and there is a tendency for continued radiation to shift the relative intensity of the peak to higher temperatures. For a study of the influence of the crystal on the thermoluminescence, the minimum amount of radiation should be used in activating the crystal so as to obtain a characteristic glow curve uninfluenced by the radiation itself.

Crystals prepared from mixtures of NaCl and NaBr gave considerably brighter thermoluminescence for a given exposure to gamma rays than either salt alone. Glow curves were obtained with NaCl, and one mole per cent additions of other sodium halides. The addition of a smaller size halogen ion increases the crystal's ability to thermoluminesce and the addition of a larger halogen ion decreases it.

The addition of foreign alkali or halogen ions affected greatly the intensity of the thermoluminescence, but did not affect the maximum temperatures of the peaks. It is concluded from this observation that the minor glow-curve peaks, if related to impurities, are due to impurities other than the alkali or halogen family.

(3) Thermoluminescence of Some Inorganic Crystals and Glasses by

James K. Rieke, Journal of Physical Chemistry 61, 633-635 (1957).

Over fifty inorganic compounds and glasses have been examined for γ -ray induced thermoluminescence. A specially constructed thermoluminescence apparatus was used. Nearly half of the crystals, picked at random, exhibited no thermoluminescence, even after exposure to 100,000 roentgens. The maximum temperature

and areas of the different glow curve peaks are recorded for twenty inorganic crystals including oxides, carbonates and halides. In view of the common thermoluminescence of the alkali halides and of many minerals studied in this laboratory, it is somewhat surprising to find so many inorganic compounds which exhibit no thermoluminescence. Probably many of these crystals would show thermoluminescence if irradiated at temperatures much below that of the room. Impurities are a large factor in thermoluminescence, and their concentration may be so low as to be undetectable by many standard methods of analysis.

A rough tentative classification of thermoluminescence intensities was attempted.

High intensity	F^- , Cl^- , $CO_3^{=}$, $SiO_2^{=}$, $O^{=}$; Li^+ , Na^+ , K^+ , Mg^{++} , Ca^{++} , Sr^{++} , Al^{+++}
Intermediate intensity	$HPO_4^{=}$, Br^- , I^- , $PO_4^{=}$; Pb^{++} , Cd^{++} , Ba^{++}
Low intensity	$CrO_4^{=}$, $Cr_2O_7^{=}$, $S_2O_8^{=}$; Ag^+ , Hg^{++} , NH_4^+ $Fe(CN_6)^{=}$, HSO_4^- , MnO_4^- , NO_3^-

About twenty glasses of different composition were studied and most of them showed thermoluminescence after exposure to 300,000 roentgens, but failed to show it after an exposure of 5000 roentgens. Increasing iron content in a sodium, calcium, silicate glass gave a decrease in the thermoluminescence.

(4) Thermoluminescence of Sodium Sulfate and Lead Sulfate and Miscellaneous Sulfates, Carbonates and Oxides by Louise E. Moore, Journal of Physical Chemistry 61, 636-639 (1957)

This investigation was undertaken to explore the usefulness of thermoluminescence as an analytical tool and to study the influence of impurities on glow curves in a few selected inorganic salts.

Sodium sulfate was chosen because it is easily purified by recrystallization. It is complicated by the fact that it contains water of crystallization which is driven off by heating with the formation of vacancies in the crystal lattice.

There is always a prominent peak at 110° and there are other peaks which appear to depend on the temperature and the rate of dehydration. The addition of lead sulfate in 75 to 150 parts per million produced another peak coming in at a temperature somewhat above 200° .

Lead sulfate was studied because it is free from the complication of water of crystallization. Pure PbSO_4 is not thermoluminescent, but it is rendered thermoluminescent by the addition of several different impurity ions.

Other sulfates, including those of Li, Na, Mg, Sr, Ca and Ba; carbonates of Li, Na, Tl, Ca and Ba; and oxides of Be, Mg, Al and Th were studied also and the relative thermoluminescence was recorded graphically at the several different peak temperatures exhibited in the glow curves. Most of these measurements were made on "Spec pure" materials which had been highly purified and analyzed spectrographically. Over twenty of the oxides and carbonates showed no thermoluminescence even after exposure to 145,000 roentgens of gamma radiation.

The effects on thermoluminescence of impurities at different concentrations are very complicated. In order to affect thermoluminescence, the impurities present in the solution must be taken up into the crystal structure to give special types of imperfections. Thermoluminescence glow curves might be used as a control for uniformity in certain types of crystallization operations.

(5) Thermoluminescence Studies of Aluminum Oxide by James K. Rieke and

Farrington Daniels, Journal of Physical Chemistry 61, 629-633 (1957).

The thermoluminescence behavior of thirty samples of aluminum oxide was studied in an attempt to supply information of significance on the nature of the crystalline material and on the possible catalytic behavior. The samples, representing various crystal phases, degrees of hydration and chemical impurity were prepared and characterized by Dr. Allen S. Russell of the Aluminum Company of America. They were ground to give 100-200 mesh powder.

Typical glow curves are given and a summary of the maximum temperatures and areas under each peak is given for each of the samples. The quantity of thermoluminescence light increases as the removal of water increases. It is largest in

synthetic sapphire which is crystalline α - Al_2O_3 without water.

The curves can be resolved into four peaks at approximately 103° , 123° , 164° and 236° . The peak at 123° is the most characteristic peak for aluminum oxides, hydrates and partial hydrates. It is found in almost all samples until a high degree of calcination has been reached; and then with further removal of water it disappears abruptly. To a limited extent, the area under the curve at this peak can be correlated with the several different crystal phases.

The 103° peak and the 164° peak appear at intermediate stages in the calcination which removes water from the crystal. The 164° peak appears first when the alumina has been heated to 600° . No correlation with impurities was found.

The 236° peak occurs only in samples which have been calcined above 1000°C . Its area increases nearly linearly with the sodium concentration and it must be due to the presence of an impurity of sodium ion. The synthetic sapphire shows an additional peak at 300° .

In this investigation it was found that with some of the samples, thermoluminescence can be induced by visible light without any activation by gamma rays or X-rays. This phenomenon is found in the partially hydrated samples and the fact that it is quickly quenched by adsorbed water suggests that the trapping centers are surface sites and that H_2O must be chemically bound. The color of this thermoluminescence light is pale blue. It is likely that the emission centers occur in surface regions where OH radicals or ions exist.

- (6) Thermoluminescence Induced by Pressure and by Crystallization by Edward J. Zeller, John L. Wray and Farrington Daniels, Journal of Chemical Physics 23, 2187 (1955).

Until the light-induced thermoluminescence of aluminum oxide was discovered as described in the preceding abstract it was assumed that exposure of a crystal to ionizing radiation such as gamma radiation is necessary to obtain thermoluminescence. Certainly in the interior of crystals, energies of 10 volts or so must be required to liberate electrons to permit thermoluminescence light. Then it was observed that coral deposits and very young limestones have abnormal thermoluminescence.

This observation led to the discovery that calcium carbonate precipitated in the laboratory from calcium nitrate and sodium carbonate exhibits thermoluminescence in the range 250 to 450° even without any exposure to gamma rays or high energy radiation.

This thermoluminescence is increased markedly after subjecting the powder to a pressure of 50 tons per square inch.

To explain this pressure-induced thermoluminescence, it is suggested that the pressure applied to a mass of crystals creates by friction and point-contact effects, high electrostatic voltages in local areas which are greater than the voltage necessary to release electrons in the crystal lattice. Triboluminescence is a well-known phenomenon in which visible light is produced by crushing crystals. The number of electrons liberated is much greater than the small number which are trapped in lattice imperfections, but the trapped electrons are accumulated and released suddenly with a burst of light. Accordingly thermoluminescence is probably a more sensitive test than triboluminescence for the liberation of electrons in a crystal.

These experiments indicate, too, that in the crystallization process, high voltages are created also, possibly by a frictional force somewhat analogous to that generated in the high pressure experiments.

The pressure-induced and crystallization-induced thermoluminescence are very weak and could easily have escaped detection in earlier work with less sensitive equipment. It is estimated that in these experiments only one electron is released and trapped among 10^9 atoms.

(7) Thermoluminescence Dosimetry by William P. Riemen and Farrington Daniels,
Forthcoming publication.

The thermoluminescence of lithium fluoride, and several other crystals, was found to be nearly proportional to the number of roentgens of gamma radiation to which it was exposed. Accordingly, a considerable effort was made to use thermoluminescent crystals as radiation dosimeters. Part of this program was supported

by the Atomic Energy Commission, but the major part of the work was sponsored by the Chemical Corps of the army.

Clear crystals about 1 cm. square and 3 mm. thick were exposed to gamma rays from cobalt-60 for given intervals of time and the total area under the thermoluminescence glow curve was measured. Several checks were made and in one series of experiments the gamma radiation was obtained inside a cancer patient who had been given radioactive salts, by Dr. Marshall Brucer of the Oak Ridge Hospital. The patient swallowed the insoluble lithium fluoride crystal and it was recovered later for thermoluminescence measurements.

It was found, however, that the large crystals of lithium fluoride were not sufficiently uniform and that different samples gave different amounts of thermoluminescence per Roentgen of gamma radiation. Accordingly, the crystals were ground to coarse powder and thoroughly mixed so as to give uniformity of thermoluminescence. It was soon discovered, however, that the process of grinding the lithium fluoride crystals introduced an additional thermoluminescence, after exposure to gamma radiation, which exhibited a peak at about 110° . This new thermoluminescence tended to anneal out at room temperature after a few weeks and so the dosimeter was unreliable because its reading would depend in part on the time which elapsed between radioactive exposure and thermoluminescence reading.

The problem was eventually solved by using a powder prepared by grinding fused aluminum oxide. This material is less bright in its thermoluminescence, but it is uniform and it does not show the low-temperature thermoluminescence. Greater sensitivity was obtained by heating the aluminum oxide powder to 400° for an hour. This annealed aluminum oxide powder was then cemented to small cups 1 cm in diameter and 1 mm high made of thin silver. Many of these dosimeters were tested in the laboratory and in the field near atomic bomb tests.

A portable thermoluminescence indicator was developed in which dosimeter discs were heated in a light-tight box by a hot plate operated from a storage battery. The photomultiplier tube was operated on dry batteries. An electronic circuit with

capacity, an amplifier, and a micro ammeter measured the accumulated thermoluminescence. The conversion to roentgens was accomplished by reference to a standard luminous button of a tritium phosphor, and by calibration with dosimeter discs exposed to known gamma ray intensities.

VI. Crystals - Radiation Damage, Polymorphous Crystals and Kinetics of Solid Reactions between Crystals

The experiments on the thermoluminescence of crystals led to a study of the influence of continued radiation on thermoluminescence and to a broader study of radiation damage. The studies on age determination and the thermoluminescence of limestones led to further investigations of the polymorphous forms of crystalline calcium carbonate - calcite, aragonite and vaterite. The thermoluminescence studies of crystals containing chemical impurities, which were heated to high temperature, led to a study of the kinetics of chemical reactions between mixed powders of different crystalline salts. These three different studies are grouped together here in one section.

- (1) Storage of Radiation Energy in Crystalline Lithium Fluoride and Metamict Minerals by Frederick F. Morehead and Farrington Daniels, Journal of Physical Chemistry 56, 546-548 (1952).

Quantitative measurements were made on the fraction of the high-energy radioactive radiation which can be stored in a crystal. Crystals of lithium fluoride were exposed to a measured quantity of gamma radiation from cobalt-60 and the total amount of thermoluminescence light emitted was then determined with a photomultiplier cell as determined from the area under a glow curve graph. The glow-curve graph areas were then calibrated with light from a mercury vapor lamp placed at a considerable distance from the photomultiplier tube. The mercury lamp in turn was calibrated with the help of a thermopile placed closer to the lamp, and a standard carbon filament lamp certified by the U. S. Bureau of Standards. The thermopile was much less sensitive to the ultraviolet lamp than the photomultiplier tube and the inverse square law was used in calculating the radiant energy at the different distances.

It was found that the number of ergs of light emitted in thermoluminescence was only about 0.005 per cent of the number of ergs of gamma radiation absorbed by the crystal. This small value indicates that only a very small fraction of the electrons released in the crystal by the gamma radiation become trapped in imperfections and released later with the production of light, when heated.

A search for greater storage of energy by radiation damage led to studies of metamict minerals. These minerals are unique in that they have a complex crystallographic structure containing columbium or other rare-earth elements, and uranium and thorium. They have suffered so much radioactive damage over geological ages that their crystal lattice is completely displaced and they show no diffraction of an X-ray beam. When these metamict minerals are heated sufficiently, the normal crystal lattice is re-established with the evolution of heat and the crystals then refract X-rays.

A simple, differential thermal analysis apparatus was used to determine the heat released when the temperature was raised. A thermocouple was used, and each junction was placed in a small hole bored in an iron cylinder which was heated at a uniform rate. The powder of metamict mineral was placed around one junction, and a reference powder, which had no stored energy, was placed in the other. The magnitude of the area under the peak obtained by plotting temperature against time was a measure of the heat evolved, and it was calibrated by melting, under the same conditions, metals and salts which have melting points in the same range and for which the heats of fusion are known.

It was found in one of these metamict crystals that the energy stored in lattice displacement, and released on heating, amounted to 25 calories per gram.

(2) Storage of Energy in Metamict Minerals by Sheldon F. Kurath, American Mineralogist 42, 91-99 (1957).

The storage of energy in metamict minerals as described in the preceding abstract was so interesting that an improved differential thermal analysis apparatus was built possessing greater accuracy and capable of going up to 700°. A table is

shown which gives the heat evolved in calories per gram at each of several temperatures which correspond to peaks in the differential thermal analysis curves. The alpha particle counts per minute per square cm are given also. Measurements are given for the following metamict minerals, Ellsworthite, Fergusonite, Sammaraskite, Euxenite and Exchynite-priorite. The total heat evolved ranged from 22 to 65 calories per gram.

Several highly radioactive minerals were measured with the differential thermal analysis and found to have no stored energy. It seems clear that in minerals which have simple ionic crystal structures, the displacement of atoms by alpha particles and recoil atoms is not permanent. The displacements are restored by long standing at earth temperature. Only in very complex crystal forms will the energy required to restore the displaced atoms to their normal positions be so great that the displacements will continue for long periods of time at earth temperature.

In this work and in that described in the preceding work, it was necessary to work in an atmosphere of nitrogen to prevent the production of heat caused by chemical energy and assure that the only heat effects were those due to displacements of units in the crystal lattice.

A calculation is given for the minimum age of a sample of fergusonite. These calculations involve the number of alpha particles emitted from the surface, the number absorbed within the crystal, the estimated fraction of the energy of alpha particles and recoil atoms which can go into lattice displacements and the heat evolved when these displacements are destroyed by heating. It is calculated that 1.1×10^{11} alpha particles are emitted per year per gram and that the heat stored amounts to 2.9×10^{-4} cal. per gram per year. The laboratory measurements showed that a total of 57.2 calories of heat was stored and evolved when the normal lattice was restored by heating. These data show that at least 198,000 years would be required to produce the 57.2 calories of heat. There are many uncertainties involved which would make the age greater than this.

(3) Differential Thermal Analysis of Inorganic Hydrates by Hans J. Borchardt and Farrington Daniels, *Journal of Physical Chemistry* 61, 917-921 (1957).

The differential thermal analysis apparatus used in the preceding research was improved and used for studying endothermic chemical changes. The equipment had been perfected for studies of stored energy from radioactivity and was available for other applications. The hydrates of inorganic salts were selected for measurement, including $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$. The different lower hydrates produced by the removal of water were characterized by their X-ray diffraction patterns.

The two thermocouple junctions were centered in small holes, one of which held a 50 per cent mixture of the salt hydrate and calcined alumina powder, while the other held pure alumina powder. The block containing these samples was heated at the rate of 10° per minute and the difference in temperature was amplified and recorded with a potentiometer. The heating unit was surrounded by an evacuated jacket to minimize heat losses.

The investigation brought out the fact that anomalous peaks in the curve, obtained by plotting temperature differences against time, may be observed and that caution is necessary in interpreting some of the differential thermal analysis data. One anomaly is produced by the condensation and subsequent vaporization of liquid water especially under conditions of high humidity and a suitable rate of heating. The other type of anomalous peak is due to the sudden increase in the thermal conductivity of a sample when the solid starts to melt and the spaces are filled with liquid. A "false" peak of this type appears to be exothermic and if it occurs while an endothermic reaction is taking place, an impression of two endothermic peaks is obtained. Examples of each type of anomaly are given.

The measurements on $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at high temperatures showed that CuSO_4 breaks down to CuO and a compound $\text{CuSO}_4 \cdot \text{CuO}$. Evidence was clear also for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$. $\text{CuSO}_4 \cdot 4\text{H}_2\text{O}$ has been reported by others, but the peak

corresponding to this composition did not always appear, and no change in X-ray diffraction pattern could be obtained. Only when liquid was formed by condensing out the water vapor from the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was there an indication of heat absorption between compositions corresponding to $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$. It was proved that there is no $\text{CuSO}_4 \cdot 4\text{H}_2\text{O}$ and that the absorption of heat is due to the evaporation of the condensed water. The observed phenomena are easily interpreted with the help of a phase diagram. Similar anomalies were obtained with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$.

(4) Thermoluminescence and Coloration of Lithium Fluoride Produced by Alpha Particles, Electrons, Gamma Rays and Neutrons by Frederick F. Morehead and Farrington Daniels, J. Chem. Phys. 25, December (1957).

The coloration and thermoluminescence produced by 2 mev alpha particles, 2 mev electrons, 1 mev gamma rays from Co^{60} and thermal neutrons are described. The energy initially required to produce F-centers is about 2000 ev for the alpha particles, 140 ev for the electron beam, 30 ev for the gamma rays, and 500 ev for thermal neutrons.

The amount of thermoluminescence light produced and the number of thermoluminescence peaks increases with the length of exposure, in each of these radiations. The larger the radiation dosage, the greater is the fraction of thermoluminescence emitted at the higher temperatures. Much of the thermoluminescence is related to the emptying of F-centers but only one photon is emitted as visible thermoluminescence for every 10^9 electrons removed from F-centers. The mathematical relations and the mechanism of optical and thermal decolorization are discussed. The ionizing radiation produces absorption in the ultraviolet at 2500 Å. It is due to F-centers, -electrons trapped at the sites of missing anions. With more radiation other absorption bands appear, of which the most important is at 4500 Å.

Thermoluminescence glow curves, absorption spectra and other measurements were made on LiF after exposure to varying amounts of the four types of radiation. Wherever possible, mathematical relations were developed. It is hoped that the

information obtained in this investigation will increase our knowledge of the nature of the action of these ionizing radiations on crystals and contribute to our understanding of radiation damage.

- (5) Factors Influencing the Precipitation of Calcium Carbonate by E. J. Zeller and J. L. Wray, Bulletin of the American Association of Petroleum Geologists, 40, 140-152 (1956).

The attempts to determine the age of limestones from measurements of thermoluminescence and alpha particle counts required a more fundamental knowledge of the factors which determine whether a precipitate of calcium carbonate will crystallize as calcite, aragonite or vaterite. Many precipitations of calcium carbonate were carried out in the laboratory under a wide variety of conditions including temperature, pH and concentration of impurity ions. The precipitations were made by adding 20 ml of 1.0 molar sodium carbonate solution to one liter of 0.1 molar calcium nitrate solution containing inherent or added impurities. The temperature was held constant and the solutions were kept surrounded with an atmosphere of nitrogen. The solutions were vigorously stirred during mixing and for 24 hours afterward, and then filtered after taking the pH of the solution with a glass electrode. The solution was filtered, the precipitate was dried in the air and another 20 ml of sodium carbonate was added to the filtrate. Further precipitations were carried out in a similar manner. The precipitates were examined for the ratio of calcite, aragonite and vaterite using X-ray analysis and microscopic examination. The experiments were repeated with solutions of calcium nitrate containing larger quantities of added Fe, Mn, Sr, Ba and Mg.

Spectrographic analyses for these elements were carried out on the precipitates and on typical limestones collected from different parts of the world. A table of solubilities of the hydroxides and carbonates of Fe, Mn, Sr, Ba and Mg is given and used for comparing the theoretically predicted concentrations in the precipitates with the concentrations actually found. If the metals precipitate as carbonates they can be incorporated into the crystal lattice of CaCO_3 , but if they

precipitate as hydroxides, they probably do not enter the lattice as impurities.

When the larger ions such as strontium are incorporated into the calcium carbonate crystal structure, the tendency is to form aragonite which has a larger volume than the calcite. When manganese carbonate is precipitated with the calcium carbonate, it has a smaller ion diameter and the precipitation of the more dense and stable calcite is formed.

The pH of the solution at the time of precipitation is very important in determining the impurities present and establishing the crystal form as calcite or aragonite. Almost all the iron is removed in the first precipitate at a pH of 6.9. Only about half of the manganese was brought down and almost no barium, strontium and magnesium. Continuing the precipitation at a pH of 7.1 the second precipitate had only a trace of iron and the manganese was decreasing. By the time successive additions of sodium carbonate brought the pH up to 8.1, there was only 0.08 per cent of manganese and the crystals of calcium carbonate were otherwise quite pure and they were low in thermoluminescence. In the fifth precipitate at pH 8.6, strontium showed a slight increase, while in the sixth precipitate at a pH of 10.9, the strontium was 2.5 per cent, the barium 2 per cent, and the magnesium, 1.2 per cent. Temperature and rate of recrystallization were found to be important factors in determining whether the calcite or the aragonite form predominates.

It has been stated frequently in the literature that the impurity uptake by calcium carbonate precipitation is determined by the crystal form, -- aragonite taking up strontium for example. This statement appears to involve a confusion of cause and effect. The impurities which are coprecipitated with the calcium carbonate determine the crystal form, and as already stated, the presence of strontium leads to the formation of aragonite.

The geological significance of these experiments is discussed. In all the measurements made in this work, those limestones which had the aragonite crystal form were high in strontium. The temperature of the ocean water at the time of

precipitation of the limestone is a factor in determining whether calcite or aragonite will be formed. The present research suggests that temperature is important in a rather indirect way, -- at the higher temperatures carbon dioxide is driven out of solution, the pH of the water is increased and the strontium and barium are precipitated, thus tending to form the aragonite which is the less dense form. Conditions of high pH might be expected in shallow marine waters and basins with restricted circulations and here the strontium, barium and magnesium would be expected to precipitate out with the calcium carbonate and tend to produce aragonite.

(6) Precipitation of Calcite and Aragonite by John L. Wray and Farrington Daniels, *Journal of the American Chemical Society* 79, 2031-2034 (1957).

The researches described in the preceding section seemed so important in explaining the conditions necessary for the formation of aragonite or calcite that the investigation was carried further. There may be applications in chemistry as well as implications in geology. For example, the ratio of calcite to aragonite is a factor in determining the efficiency of certain CaCO_3 powders for chromatographic adsorption in laboratory operations.

At room temperature and atmospheric pressure, calcite is the thermodynamically stable form and yet it was found possible to obtain either aragonite or calcite depending on the controlled conditions of temperature, concentration and aging. The time factor is important and the ratio of the two polymorphs of CaCO_3 is a matter of kinetics of metastable forms rather than a matter of equilibrium conditions.

In these experiments, 20 ml of 1.0 M $\text{Ca}(\text{NO}_3)_2$ was added to 200 ml of 0.1 M Na_2CO_3 with vigorous stirring over a four-minute period. Again 20 ml of 1.0 M Na_2CO_3 was added to 200 ml of 0.1 M $\text{Ca}(\text{NO}_3)_2$. The temperature was varied from 30° to 70° and the period of aging was varied from 6 minutes to 18 hours. The per cent of calcite, aragonite and vaterite was determined by X-ray analysis and by microscopic examination with an error of ± 15 per cent. The crystal grain-size ranged from 5 to 20 μ .

The results show that the temperature is critical over a small range. At 40° the calcium carbonate precipitate is nearly pure calcite. At 45° it is 30 per cent calcite and 70 per cent aragonite, but changes during two hour's digestion to more than 90 per cent calcite. At 50° the precipitate is mostly aragonite.

At temperatures between 45° and 50° with suitable periods of digestion, one can obtain practically any ratio of calcite to aragonite. Although the precipitate suspended in solution may go rather rapidly to the more stable calcite, this change is stopped by filtering and drying the material. The rate of change in the dry state is indefinitely slow in the laboratory.

Calcite is the stable crystal form, but the less dense aragonite is formed if larger ions such as strontium, lead and barium are present in the solution and are incorporated into the crystal lattice. The pH of the solution is an important factor in determining whether or not these impurities are incorporated. They are co-precipitated at high pH, but not at low pH.

The aging process which converts aragonite into calcite involves first a rapid precipitation as a colloid, then a conversion into the crystalline form and finally a recrystallization. This recrystallization extending over minutes, hours or days determines the fraction of aragonite that is converted to calcite. If there is sufficient time after precipitation and before crystallization and recrystallization, the strontium ions will diffuse away, with the result that the calcite lattice is formed.

At the higher temperatures, the rate of crystallization is more rapid and the strontium ions do not have time to escape and thus they are incorporated into the CaCO_3 lattice giving aragonite.

When the aragonite crystals stand for longer periods of time in contact with water, they recrystallize and permit the loss of strontium ions, and the aragonite is thus converted into calcite. This hypothesis was tested by allowing the precipitated aragonite to stand in solution containing a high concentration of added strontium ions. There was no conversion to calcite after 20 hours, whereas

under the same conditions, but without the added strontium, half of the aragonite had changed to calcite.

- (7) Kinetics of Solid State Reactions of Silver Sulfate with Calcium and Strontium Oxides by William P. Riemen and Farrington Daniels, Journal of Physical Chemistry 61, 802-805 (1957).

Most researches in chemical kinetics have been concerned with reactions in solution or in the gas phase. Progress in solid state physics suggests interesting studies in solid state chemistry. Reactions of solids to give solids would be exceedingly slow except for imperfections which act as centers for the diffusion of materials through the crystal structure. Reactions between solids are significant in geological phenomena, where long periods of time have been available. They are important also in preparation of crystals of high purity and in the production of catalysts and other materials which involve specified impurities. It is not easy to find suitable solid-solid reactions which can be followed by simple chemical methods, but the reaction

is one which can be followed either by the loss of weight, due to the escape of gaseous oxygen, or by the decrease in water-soluble silver sulfate. The two methods agreed within 5 per cent. The two solids were ground to powder, sieved and thoroughly mixed and then heated to temperatures from 500 to 570° for periods of five minutes to nine hundred minutes. Similar measurements were made on the reaction of silver sulfate with strontium oxide.

It was found that these reactions proceed by diffusion through different product layers and that the formula

$$1 - X = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 kt}$$

applies where x is the fraction of the reaction completed at time t and $k = \frac{\pi^2 D}{a^2}$ where D is the diffusivity and a is the "radius" of the particles.

"X" is determined from chemical analysis and the corresponding value of kt is obtained from mathematical tables. Then kt is plotted against time. After an

initial period, the resulting lines are straight lines. During an initial period of less than 100 minutes, the reaction proceeds abnormally fast and it is probable that during this time a faster surface reaction is taking place. After this initial reaction at the surface is complete, the dominant mechanism then is volume diffusion. Microscopic examination of large crystals of silver sulfate surrounded by calcium oxide powder and heated for a while gave a grayish-black surface. Thin sections viewed under the microscope showed that during the preliminary reaction, the silver was deposited only on the surface. Inward diffusion was not observed until after a longer reaction period.

(8) Kinetics of the Reaction between Silver and Sulfur in the Solid State
by William P. Riemen, Journal of Physical Chemistry 61, 813 (1957).

Another solid-solid reaction was studied because its rate can be followed so easily. Sulfur and silver powders were thoroughly mixed and allowed to stand at 25° for periods up to 50 days. Black silver sulfide Ag_2S is formed by diffusion and the amount of sulfur remaining unreacted after a given time interval was determined by dissolving it out with carbon disulfide and weighing the remaining mixture of silver and silver sulfide. The rates of the reaction were found to fit very well the diffusion-controlled reaction formula given in the preceding abstract.

Particles of different size were used and the value of k , determined experimentally gave a straight line when plotted against the reciprocal of the square of the radius, -- in agreement with the theoretical derivation.

In addition to the work described in these eight publications, several other experiments were carried out. The influence of pressure on the thermoluminescence of crystals was studied, but additional work is necessary to distinguish between "brittle" pressure of a dry powder in a cylinder, and "volume" squeezing in which the crystals are subjected to hydraulic pressure in paraffine or other fluid.

Triboluminescence was found to be quite a common phenomenon in salt crystals taken from laboratory bottles. Mr. Donald Pryor ground up, in the dark, crystals

of a large number of different chemicals and noted the emission of light in many of them. Apparently when a crystal is pulverized, high voltages are produced, probably from forces of friction, and these voltage differences are sufficiently high to drive electrons from their positions in the crystal lattice. As the displaced electrons fall to positions of lower energy, they emit light.

For a time it was thought alpha bombardment of lithium fluoride crystals produced a condition in the interior of the crystal which led to thermoluminescence. This observation of thermoluminescence beyond the range of the alpha particles, was recorded by James Rieke in one of the annual reports. Before publication, however, Mr. W. P. Riemen proved that the effect was due to the reflection of alpha particles by air around the edge of the crystal.

Another misinterpretation of observations was recorded in one of the annual reports. Mr. Sheldon Kurath measured with a very sensitive calorimeter the heat evolved when alpha particles struck the surface of certain solids and produced heat. It was hoped to get evidence for the storage of some of the energy of the alpha particles .

Some materials appeared to evolve less heat (up to 3 per cent less) than others under bombardment by alpha particles from polonium. Mr. Hans Borchardt, however, proved that this effect was not due to conversion of alpha particle energy into stored lattice energy, but that it was due to different thermal conductance at the contact between the material and the thermocouple.

VII. Experimental Techniques

In both the thermoluminescence researches and the geochemical studies, it was necessary to develop accurate instruments capable of measuring very small quantities. thermoluminescence
The/measurements required a reliable electrically-heated plate of silver which could be heated from room temperature to red heat in 10 minutes, and a photo-multiplier tube included in a stable electronic circuit with an amplifier. This in turn is connected to a standard recording potentiometer. Two curves are drawn, -- one for the intensity of the light and one for the temperature of the

sample as given by a thermocouple. The details of construction are given in the published researches (VI (1) (2) (3)). In one investigation (VI (2)) some of the irradiations were carried out at liquid air temperatures. The temperature regulation was carried out manually to give a uniform rise in temperature. A device was developed to give automatic temperature control and to permit cooling of the samples below room temperature, but it was not used extensively.

Apparatus for more rapid measurements of thermoluminescence was developed and a detailed description will be published after further experience with it. A strip of nichrome sheet, 1 inch wide, is heated to red heat within 10 seconds by means of a heavy-current step-down transformer. The photomultiplier tube is connected to an amplifier and Sanborn recorder which has a very fast response. All of the thermoluminescence can be produced within ten seconds and since more photons are released per second, the sensitivity is greater and the operations are much faster.

Accurate measurement of the very low alpha particle activity of limestones and other rocks was an important part of the geochemical section of the present research program. A considerable effort was devoted to the development of suitable apparatus. A brief description of one of these instruments is given in one of the publications (IV (1)).

It is necessary to count accurately the number of alpha particles escaping from a thick layer of the powdered sample even though there is less than 1 alpha particle per square centimeter per hour. A larger dish, having an area of 20 square cm. is used to give a greater effect. The alpha particles hit a phosphor placed directly above the sample, and above the phosphor is placed a photomultiplier tube connected to an amplifying circuit and counter. Cosmic rays and beta rays do not generate enough light to actuate the counter, but every alpha particle that hits the powdered phosphor produces a flash of light sufficient to be recorded by the mechanical counter. After a few days of operation the phosphor is apt to become contaminated with radon and lead to an erroneously large number of counts. This difficulty was solved by using a wide strip of scotch tape with powdered phosphor

adhering to the sticky side, as previously described in the literature. The alpha particles hit the phosphor adhering to the under side of the transparent tape and the light produced passes through to the photomultiplier tube. When contamination becomes serious, the tape with adhering phosphor is removed and replaced by a fresh one.

Other techniques were developed, or were taken from the literature, or from the laboratories of the U. S. Geological Survey, and adapted to the purposes of this investigation. A few of these have been published and are abstracted here.

- (1) A Convenient Source of Gamma Radiation by Donald F. Saunders, Frederick F. Morehead and Farrington Daniels, Journal of the American Chemical Society 75, 3096 (1953).

A hollow cylinder of metallic cobalt powder was prepared by filling the space between two concentric cylindrical aluminum cans having an outside diameter of 3 cms, an inside diameter of 2 cms and a length of 13 cms. This was exposed to neutrons in the Oak Ridge reactor and a three-curie source which was reasonably easy to handle gave a radiation within the hollow cylinder of 6000 roentgens per hour. Calculations and thermoluminescence tests with a stack of crystals showed that the radiation was quite uniform throughout most of this volume. The cobalt source was set into a lead cylinder, placed in a basement floor and covered with a removable lead cover. The cobalt powder is subject to the hazard of leakage if the aluminum container becomes corroded and a machined cobalt cylinder, which is now available, would be better.

- (2) Fluorimetric and Colorimetric Microdetermination of Uranium in Rocks and Minerals, by J. A. S. Adams and William J. Maeck, Analytical Chemistry 26, 1653 (1954).

Many thousand samples of rocks were analyzed routinely in which the uranium ranged from 0.1 to 10 parts per million. The samples are dissolved with nitric acid and hydrofluoric acid. Iron and other interfering elements, which quench the fluorescence of uranium, are removed by extraction with ethyl acetate and aluminum nitrate solution, which has been treated to remove all traces of uranium. The

solution is evaporated with radiant heat to dryness in a gold dish, and a mixture of highly purified sodium fluoride mixed with sodium and potassium carbonate is fused in the dish. After cooling the discs of flux are removed and exposed to ultraviolet light in a dark box. The fluorescent light from the uranium is measured with a photomultiplier cell. The intensity of fluorescent light is calibrated in terms of parts per million of uranium by using flux containing measured traces of uranium from a stock solution.

- (3) A Spectrographic Method for Thorium by Frederick J. Lindstrom, Report AECU-2851, Technical Information Service, A. E. C., Oak Ridge, Tennessee.

A spark is used with silver electrodes, one of which is a slowly rotating disc dipping into an aqueous solution of thorium chloride containing an internal standard of chromium chloride. An exposure of 50 seconds is used with a 1.5 meter grating spectrograph, comparator and densitometer.

The logarithms of the ratios of the intensity of the Th 2837A line to that of the Cr 2835 line are plotted against the logarithm of the micrograms of thorium per milliliter. The smooth calibration curve is then used for the analysis of unknown solutions of thorium.

- (4) Alpha Particle Autoradiography with Liquid Emulsion by John Guilbert and John A. S. Adams, Nucleonics 13, No. 7, page 43 (1955).

The location of alpha ray emitting centers in thin sections of Wisconsin granites is determined by photo-micrograph-autoradiograph. Liquid Kodak NTA emulsion is poured over the surface of a thin section of rock and protected with an emulsion binder of gelatine and allowed to stand in the dark at 5° for 20 days. After development and fixing of the emulsion the photo-microphotographs are taken with a magnification of 250 fold. The straight tracks of alpha particles are clearly evident, emanating from localized spots in the granite.

VIII. Continuation of Researches

Although it was decided not to request a renewal of Contract AT(11-1)-178 beyond June 30, 1956, some of the work is being actively continued. In 1956-57 a research was completed on the thermoluminescence of calcium sulfate and the anhydrites. Also studies were made of the relative radiation damage induced by high energy gamma rays and by X-rays. In 1957-58 studies are being carried out on the effect of impurities on the thermoluminescence of sodium chloride and other alkali halides. It is important to try to determine whether the persistent peaks in the thermoluminescence curves are determined by the dimensions of the ions in the crystal lattice and the physical treatment ^{of} crystals or whether they depend primarily on the presence of impurity ions which are incorporated into the crystals.

Studies will be made on thermoluminescence effect of "brittle" pressure on crystalline powders and of hydraulic squeezing in a non-crystalline medium, such as paraffine. The interesting phenomenon of pressure-induced and crystallization-induced thermoluminescence will be studied further, together with investigation of triboluminescence.

Professor Edward J. Zeller is continuing an active program in the Department of Geology at the University of Kansas on the thermoluminescence and geochemistry of calcium carbonate in relation to radioactive impurity content. He will continue research on the determination of the age of limestones and other rocks through measurements of thermoluminescence. He is constructing improved apparatus for thermoluminescence and alpha particle counting for this work.

Professor John A. S. Adams is continuing research on the geochemistry of uranium and thorium in the Department of Geology at Rice Institute. He is continuing also the analysis for traces of uranium in inland waters and in rocks.

Dr. John L. Wray is continuing work on thermoluminescence of limestones in the laboratory of the Ohio Oil Company.

Geological applications of thermoluminescence have recently been reported from other laboratories, -- by Dr. Donald Lewis at the Shell Development Company

in Houston, Texas, by Professor Houtermans in Switzerland and by the U. S. Geological Survey laboratories in Denver and in Washington.

IX. Acknowledgements

This program has been generously supported by the Atomic Energy Commission. We are deeply appreciative of this help and desire to thank particularly Dr. Daniel R. Miller of the Research Division in Washington, and Mr. Joseph Trocino and Mr. Milton Klein of the Chicago Operations office of the Atomic Energy Commission. We are indebted to Dr. Joseph Katz and Dr. Donald Peppard of the Argonne National Laboratory for help in the research program on the recovery of uranium from ore.

Three Associate Directors of the uranium project, described here, have contributed greatly to its success. They are Dr. Donald F. Saunders, Dr. Edward J. Zeller and Dr. John A. S. Adams.

Thirty-five other research assistants, project associates and a few faculty members in Chemistry, Geology and Botany have helped at various times in the research program. Most of these are co-authors of papers listed here, or are mentioned in the abstracts.

Mrs. Pat Johnson deserves great credit for efficient secretarial work throughout the whole contract. Miss Patricia A. Smith gave valuable administrative help and Mrs. Joyce Bauer Muckenfuss and Miss Marjory Miller helped effectively with the uranium analyses and alpha particle counting. Mr. Harold Schimming was very helpful in ordering supplies and equipment.

The Department of Mining and Metallurgy generously gave laboratory space for one phase of the uranium recovery research.

X. Summary

The recovery of uranium at the mine with portable equipment has been shown to be technologically feasible. A process was developed which involves grinding the ore, leaching with nitric acid, extracting with tributyl phosphate and kerosene, and precipitation with ammonia gas. A pilot plant was operated at the University of Wisconsin and field tests were carried out in Colorado. A hand operation with settling tanks was explored. Data were obtained for a more elaborate operation with pumps and centrifuges powered by the engine of the truck. Cost estimates, of course, are higher than for stationary large scale recovery plants, but the process might be useful in case of an emergency. Savings can be made in the transportation of ore from difficultly accessible regions.

The distribution of uranium has been studied in various geographical regions and in several different materials including limestones, granites, clays, rivers and underground water, lignites, and volcanic ash and lavas. A tentative hypothesis for intermittent geological heating, based on radioactivity, has been explored. The hypothesis was not proved, but many interesting facts were found concerning the uranium content of secondary deposits.

Geochemical studies, based on thermoluminescence include stratigraphy, age determination of limestones and aragonite-calcite relations in calcium carbonate.

Considerable effort was devoted to the study of thermoluminescence of crystals, a theory for the phenomenon, and attempts to find practical uses. Among the crystals studied for thermoluminescence were lithium fluoride, the alkali halides, aluminum oxides, sulfates and many inorganic salts and minerals.

These researches led to studies of radiation damage in lithium fluoride and metamict minerals and to the development of apparatus for differential thermal analysis. The factors which influence the production of aragonite instead of calcite were studied in the crystallization of calcium carbonate. The rates of reaction between crystalline reactants were measured and described in terms of kinetic equations based on diffusion.

In order to carry out these researches, it was necessary to develop new apparatus of improved accuracy and greater sensitivity. This included apparatus for measuring thermoluminescence of crystals which had been exposed to gamma radiation, scintillometers for measuring alpha particle activity in limestones and other materials which contained only traces of uranium. The program required also the development of very sensitive fluorimetric methods for analyzing for traces of uranium amounting to less than 1 part per million.

Several interesting by-products and unfinished problems, related to the main research have been mentioned.

Publications

AEC Contract Number AT(11-1)-178

I. (History of the Project)

II. Recovery of Uranium Ores with Portable Equipment

- (1) Final Report. Recovery of Uranium from Ores with Portable Equipment, by Charles W. Pitrat, Leo W. Weisbecker, Edward J. Zeller and Farrington Daniels, (59 mimeographed pages, to be condensed for publication in a chemical engineering journal) (1956).

III. Distribution and Geochemistry of Uranium

- (1) Alpha Radioactivity of Some Rocks and Common Materials by John B. Ockerman and Farrington Daniels, J. Phys. Chem. 58, 926-7 (1954).
- (2) Uranium and Thorium Content of Volcanic Rocks by John A. S. Adams, Chapter 2.2, NUCLEAR GEOLOGY, pages 89-99; Edited by Henry Faul, John Wiley and Sons, Inc., New York (1954).
- (3) Uranium Geochemistry of Lassen Volcanic National Park, California by John A. S. Adams, Geochimica and Cosmochimica Acta, 8, 74-85 (1955).
- (4) The Distribution of Alpha-Radioactivity in Native Vegetation by J. T. Curtis and Ralph Dix, Botanical Gazette 117, 232-237 (1956).
- (5) Distribution of Alpha-Radioactivity in Certain Forest Types by John T. Curtis and Ralph Dix, Science 123, 779-800 (1956).
- (6) Radioactivity in Ground and Surface Water by Sheldon Judson and J. Kenneth Osmond, American Journal of Science 253, 104-116 (1955).
- (7) Uranium Content of the Rivers of Wisconsin by John A. S. Adams, Forthcoming publication.
- (8) Average Uranium Content of Limestones, by John A. S. Adams, In press.
- (9) Uranium Content of Tektites by John A. S. Adams, In press.

Publications (Con't)

IV. Geochemical Studies Based on Thermoluminescence

- (1) Thermoluminescence and Surface Correlation of Limestones by Donald F. Saunders, Bulletin of the American Association of Petroleum Geologists 37, 114-124 (1953).
- (2) Use of Thermoluminescence of Limestones in Sub-Surface Stratigraphy by James M. Parks, Jr., Bulletin of the American Association of Petroleum Geologists, 37, 125-142 (1953).
- (3) Surface Correlation of Some Pennsylvanian Limestones in Mid-Continent by Thermoluminescence by Robert E. Bergstrom, Bulletin of the American Association of Petroleum Geologists 40, 918-942 (1956).
- (4) Thermoluminescence of Limestones of Mississippian Madison Group in Montana and Utah by C. W. Pitrat, Bulletin of the American Association of Petroleum Geologists, 40, 943-952 (1956).
- (5) Factors in Age Determination of Carbonate Sediments by Thermoluminescence by Edward J. Zeller, John L. Wray and Farrington Daniels, Bulletin of the American Association of Petroleum Geologists 41, 121-129 (1957).
- (6) Thermoluminescence of Carbonate Sediments by Edward J. Zeller, Nuclear Geology, Edited by Henry Faul, p. 180-188, John Wiley and Sons, Inc., New York (1954).
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II. Recovery of Uranium Ore with Portable Equipment

Final Report

Recovery of Uranium from Ores with Portable Equipment

U. S. A.E.C. Contract Number AT(11-1)-178

by

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May 1952 to Dec. 1955

Final Report

RECOVERY OF URANIUM FROM ORES WITH PORTABLE EQUIPMENT

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Abstract

The transportation of low grade uranium ore from the mine to the processing plant is expensive. Would it be better to carry equipment and chemicals to the mine for the recovery of uranium? Even if only of questionable economic advantage such a method would have value for quick expansion in case of a national emergency and it would make possible the development of scattered deposits and deposits which are located too far from a processing plant.

The possibilities of extraction of uranium with portable equipment has been under investigation for three and a half years and the work is now completed. It included laboratory experiments, the operation of stationary pilot plants to obtain optimum working conditions, and the experience of field trips in the summers of 1953 and 1954.

The process which was developed, consists of the following steps: a) crushing and grinding the ore (or burning the uraniferous lignite for ash), b) leaching with dilute nitric acid, c) settling and filtering, d) solvent extraction of nitric acid solution with kerosene and tributyl phosphate, e) rinsing the organic phase and precipitating with ammonia gas, f) filtering the flocculent ammonium diuranate, g) heating, to drive off ammonia leaving a solid residue of 65 per cent uranium oxide. The process is efficient, and with some carnotite ores from the Colorado Plateau, over 90 per cent of the uranium is easily recovered.

For the field operations a 6 ton truck was specially equipped for rough field use and provided with ore crushing and grinding machinery. A gasoline power unit generated electricity for operating the pumps and the centrifugal filters. Attempts were made to carry out the operations with settling tanks instead of centrifugal filters. The field trips gave operating experience and supplied material for estimating cost data. The chief technical problem is the filtration of the leached ore. Centrifugal filters are satisfactory but expensive. Further research with coagulating agents is recommended. The chief economical problem is the consumption of nitric acid by limestone and other material in the ore.

It is concluded that:

- a) It is technically feasible to obtain a product of more than 60 per cent uranium with portable equipment.
- b) The process described here appears to be economically feasible for certain types of ores which do not consume excessive amounts of acid.
- c) A cost of recovery of about \$10 per pound of uranium is indicated for certain ores if 5 tons are processed per day. The cost depends greatly on acid consumption, on the uranium content of the ore and on the scale of operations.
- d) Further investigation is recommended for operation on a larger scale of about 10 tons per day, taking advantage of technical knowledge which is presumably available on the handling of uranium ores and the deflocculation of precipitates.

Introduction

The purpose of this investigation is to study the practicality of obtaining uranium from its ores with portable equipment. The uranium content of many ores ranges from 0.1 to 0.4 per cent or 2 to 8 pounds per ton. A great saving could be effected by transporting the few pounds of uranium rather than the ton of ore. This saving is particularly important when the distance from mine to the chemical processing plant is great and the roads are poor.

If the chemical recovery can be made sufficiently simple, the cost of operation and the cost of transportation of the equipment and chemicals might, in some cases, be less than the cost of transporting the raw ore. As a general rule, however, small scale operations of this type are much more expensive than the operation of a permanent plant with its large tonnages and low labor requirements.

Some uranium deposits are located so far from a processing plant that it does not pay to mine the ore even though its uranium content is higher. The reserves in that location may not be large enough to justify the construction of a permanent chemical recovery plant. In such locations a portable unit or a

semi-portable unit might be successful. A mobile processing plant may move continuously around a circuit of several mines using up the accumulated stock pile at each small mine.

There is another argument for studying portable processing units. In case of a national emergency, such as might be produced by the blocking of the ocean routes to South Africa or the bombing of present chemical processing plants, sub-marginal uranium mines would become worth operating. It would be expensive to build a large processing plant in such an area and hold it in stand-by condition. It would be cheaper to have designs and plans ready for the rapid mass production of portable equipment in small units. Such a plan would be in accord with a policy of decentralization. Information obtained through the operation of the proposed portable unit may be helpful also in the larger problem of utilizing low grade deposits not only of uranium but of other metals too, as our high grade ores become more scarce.

Three types of uranium recovery with portable equipment are envisioned. First is the "gold panning" type of operation in which two men with a minimum of capital investment and without charging for their own labor are able to obtain uranium oxide even though they waste an appreciable fraction of the uranium content of the ore. The second type of recovery involves two men and an investment of \$50,000 or so with power equipment, pumps and centrifugal filters. It aims for a recovery of 90 per cent or more of the potential uranium. This is the type which has been studied most thoroughly in the present investigation. In the third type of recovery, which is perhaps the most promising, the grinding and leaching equipment is set up at the mine and operated with the same source of power that is used for the mining. The nitric acid and ammonia are brought to the mine for processing and the solvent extraction equipment may be portable or it may be permanently connected to the mine facilities.

The present investigation has involved three different approaches extending

from 1952 through 1955¹.

1. Research Progress Reports, U. S. Atomic Energy Commission Contract Number AT(11-1)-178. The Geochemistry of Uranium and the Recovery from Low Grade Ores by Farrington Daniels, Donald F. Saunders and Sheldon Kurath II-1 (1952); by Farrington Daniels, C. W. Pitrat, E. J. Zeller and L. W. Weisbecker IV-1 - IV-2 (1953); by F. Daniels, C. W. Pitrat, E. J. Zeller and L. W. Weisbecker P. 15-16 (1954); by F. Daniels and L. W. Weisbecker (1955); Report on Mobile Leaching Operation, Summer 1953 by F. Daniels, C. W. Pitrat, E. J. Zeller, J. A. S. Adams, G. Sanderson and R. J. Goll: "An Investigation of the Extraction of Uranium Ores with Application to Portable Equipment", by L. W. Weisbecker, M. S. Thesis, University of Wisconsin, Madison, Wis., 1955.

Laboratory measurements were carried out on settling rates and acid consumption and on leaching and solvent extraction efficiencies.

Pilot plant operations were carried out at the University of Wisconsin in the Mining and Metallurgy Building in 1953-54. We are grateful to Professor E. R. Shorey and the Mining and Metallurgy Department for the use of these facilities. In 1954-55 the pilot plant operations were carried out in a shelter built in a corner of the courtyard of the Chemistry Building.

Field tests were carried out in the summer of 1953 at Buffalo, S. D. on uraniferous lignite; and in the summer of 1954 at Silverton, Colo. on carnotite ores kindly provided by the Raw Materials Division of the U. S. Atomic Energy Commission.

This process for obtaining uranium from its ores was developed primarily for carnotite ores of the Colorado plateau, emphasizing simplicity of operation and portability of equipment. In this development valuable advice was obtained from Dr. Joseph Katz and Dr. D. F. Peppard of the Argonne National Laboratory. Many of the steps had been worked out before and some of them have been summarized and

published².

2. Reprocessing Reactor Fuels, by H. A. Ohlgren, J. G. Lewis and M. Weech, Nucleonics, Vol. 13, No. 3, 18-22 (1955).

The process as finally developed consists first in grinding the ore enough to separate the sandstone grains but not enough to crush all the grains. The ore of mesh size is then leached with 3M nitric acid preferably while contained on a centrifugal filter. The ore is then rinsed and the clear, acid filtrate is extracted with a 1 to 1 mixture of tributyl phosphate and kerosene, using either a batch process with stirring or a continuous extraction column. The organic phase rises to the top. It is scrubbed with water to remove the excess of nitric acid which it contains, and then ammonia gas is bubbled through. Ammonium diuranate is precipitated as a flocculent precipitate which is removed in a centrifugal basket filter. It is scraped out and heated to give a residue of about 60 per cent U_3O_8 .

The solvent extraction method with tributyl phosphate and kerosene was recommended by Dr. J. Katz and Dr. D. F. Peppard of Argonne National Laboratory. It was chosen instead of other solvents because of its specificity for uranium, its low cost and its small fire hazard. The nitric acid was chosen as the leaching medium because the uranyl nitrate formed is readily extracted by tributyl phosphate from nitric acid solution. The ammonia precipitation was developed to give a simple and complete removal of the uranium dissolved in the organic solvent.

The process is simple, continuous and easily operated. It uses relatively light equipment except for the grinding equipment and it is economical in the use of water. In normal climates it requires no heating nor cooling equipment.

Laboratory Experiments

Ores Tested. Most of the work described in this report was done on carnotite ores of the Colorado Plateau including the following: a) Edgemont ore from Edgemont, South Dakota; b) Slickrock ore from Monticello, Utah; c) Lukachukai ore from stock pile 16 and d) Uraninite Utex ore, stock pile 33 from Grand Junction, Colorado. These ores were kindly supplied by the Raw Materials Division of the Atomic Energy Commission.

Schroekingerite ore was obtained from the Red Desert deposit near Wamsutter, Wyoming.

Uraniferous lignite ash was obtained by burning lignite from Slim Butte near Buffalo, South Dakota.

A few special tests were made with granites and other rocks.

Chemical Analysis.

The success of this research project required the accurate and rapid analysis of uranium. The samples were fused with a flux and excited by ultraviolet light. The fluorescence intensity was read with the aid of a photomultiplier tube and calibrated with standard samples. Details were worked out by Adams and Maeck³. All

3. J. A. S. Adams and W. Maeck, Analytical Chemistry 26, 1635 (1954).

the analytical work was done in a dust free, air-conditioned room. The analytical work was supervised by Dr. J. A. S. Adams until September 1954. The analyses were made by Miss Marjory Miller and Mrs. Joyce Muckenfuss to whom we express appreciation.

Grinding Ores. Laboratory experiments were carried out

to determine the optimum grinding conditions for effective leaching of the ore. The principle ores in this work were carnotite ores, in which the uranium is frequently found in the mineral-cementing material that holds the sandstone grains together. Frequently the siliceous grains contain very little uranium. With ores of this type it is important to grind sufficiently to loosen all the material which surrounds the grains, but it is undesirable to grind the ore too much because of the extra cost. Moreover, the excess of fine material dilutes the uraniferous parts of the ore and makes filtering still more difficult and it exposes additional material which may consume the acid needlessly. Sieve analysis and leaching tests are helpful in determining the most favorable conditions.

A sample of carnotite ore from Edgemont, South Dakota was subjected to successive grindings and the particle size distributions determined by sieve analysis with a "rotatap" machine. The results are shown in Table I.

Table I

GRINDING EXPERIMENTS

Sample of Edgemont Carnotite (0.189% U)

Sieve Analysis, weight per cent	Extra Coarse	Coarse	Medium	Fine
Retain on 80	94.7	88.0	77.1	76.4
Retain on 100	2.5	2.6	3.6	0.9
Retain on 200	1.5	5.9	12.6	12.9
Pass 200	1.0	3.5	6.7	9.8

Uranium Analysis, parts per million

Retain on 80	1850	2120	1442	1490
Retain on 100	1980	3160	2860	3540
Retain on 200	3470	5300	4750	2760
Pass 200	16500	2980	0600	5830

Table I (cont)

	Extra Coarse	Coarse	Medium	Fine
Per cent of Total Uranium in Fraction				
Retain on 80	86.7	68.8	44.1	54.3
Retain on 100	2.5	3.0	4.1	1.5
Retain on 200	2.6	11.5	23.7	17.0
Pass 200	8.2	16.7	28.1	27.2

Sample of Schroekingerite (0.120% U)

Retain on 80	55.2
Retain on 100	5.2
Retain on 200	14.2
Pass 200	25.3

The various samples were leached with 0.25 M nitric acid for 5 minutes using 3 parts of acid per 1 part by weight of ore. The results are given in Table II.

Table II

LEACHING OF GROUND ORE (Edgemont Carnotite)

Coarseness of Ore	Leach Uranium Concentration gm per ml x 10 ⁶
Fine	550
Medium	550
Coarse	525
Extra Coarse	37

It is evident from these tables that the "extra coarse" grinding of these particular ores is unsatisfactory because the coarse particles are not properly leached and only the fine particles give up most of their uranium. However, the efficiency of uranium extraction is nearly as good with the "coarse" grinding as with the medium and fine grinding.

Leaching. In finding the optimum conditions for leaching, several variables were studied including contact time, acid concentration and the ratio of the weight of acid to the weight of ore. The temperature was in the neighborhood of 25° C. The efficiency of uranium recovery was studied, but it must be realized that for practical considerations the acid consumption and the filterability of the leached ore are very important also.

The carnotite ores contain not only uranium, in concentrations of about 0.2 per cent, but they contain also limestone and other materials which react with the nitric acid. Accordingly, when the powdered ore is placed in an insufficient amount of nitric acid, the acid becomes depleted and some of the uranium precipitates out at the resulting higher pH. A concentration of 1 to 3 M nitric acid, a ratio of 2 or 4 parts of nitric acid by weight to one part of ore, of 1 to 10 minutes were found to be favorable. When the concentration falls too low, the proper amount of concentrated acid is added. It was usually possible to leach out rather quickly more than 90 per cent of the uranium contained in the ore.

Unsuccessful attempts were made to change acid concentrations and contact times in such a way as to dissolve the uranium out before the limestone was completely consumed. Apparently it is necessary to assume that sufficient acid must be added to react with the uranium minerals and all the other acid-consuming materials present in the ore.

Extraction. The optimum conditions were studied for extracting the uranium from the nitric acid solution into the organic phase which consisted of tributyl phosphate. The variables studied include the nitric acid concentration, the uranium concentration, the ratio of the volume of organic phase to the volume of aqueous phase, and finally the concentration of tributyl phosphate in the organic phase, i.e. the dilution of tributyl phosphate with kerosene.

It is desired to have the distribution ratio such that there is a high concentration of uranyl nitrate and a low concentration of nitric acid in the organic phase. The nitric acid, however, can be extracted from the organic phase, by scrubbing with water.

Figure 1 shows the effect of concentration on the nitric acid distribution coefficient, calculated as the weight of the nitric acid in the organic phase to that in the aqueous phase. Fig. 2 shows the influence of nitric acid concentration on the uranyl nitrate distribution coefficient, calculated as weight of uranium in the organic phase to that in the aqueous phase. The higher the acid concentration of the leach solution, the more effective is the removal of uranium into the organic phase. The nitric acid loss into the organic phase is greater too, although the distribution coefficient decreases slightly at the higher concentrations of nitric acid. As expected these distribution coefficients did not change appreciably when the volume ratios of tributyl phosphate to 1 M nitric acid were varied from 1/10 to 1.

Dilution of the tributyl phosphate with an inert solvent such as kerosene increases the volume ratio of organic phase to aqueous phase and aids in the extraction of uranium. Extraction experiments with a solution containing 650×10^{-6} grams of uranium per milliliter of an ore leach are given in Figures 3 and 4. They show that the higher the concentration of acid the greater is the efficiency of uranium extraction. They show also that with concentrated solutions of acid a 20 per cent solution of tributyl phosphate in kerosene is practically as effective as more concentrated solutions. With 0.25 M nitric acid a 50-50 solution of tributyl phosphate in kerosene is desirable. Although the uranium extraction is quite effective in a single equilibrium stage, still better results can be obtained with counter-current, multistage operations as indicated in shaking

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FIGURE 1. EFFECT OF ACID STRENGTH ON NITRIC ACID DISTRIBUTION BETWEEN EQUAL VOLUMES OF TBP AND ACID

FIGURE 2. EFFECT OF ACID STRENGTH ON URANIUM DISTRIBUTION BETWEEN EQUAL VOLUMES OF TBP AND ACID

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FIGURE 3. SINGLE STAGE EXTRACTION WITH TBP-KEROSINE SOLVENT OF LEACH MADE WITH EDMONT CARNOTITE ORE USING 3M NITRIC ACID

FIGURE 4. SINGLE STAGE EXTRACTION WITH TBP-KEROSINE SOLVENT OF LEACH MADE WITH EDMONT CARNOTITE ORE USING 0.25 M. NITRIC ACID

experiments summarized in Figure 5. In 3 M nitric acid, however, the gain is not significant.

In another experiment, Dr. J. A. S. Adams shook 25 ml of 3 M HNO_3 solution containing 25 milligrams of uranium as uranyl nitrate for two minutes with 25 ml of a mixture of equal volumes of tributyl phosphate and kerosene. The efficiency of extraction into the organic phase was 98 per cent. Again 98 per cent of the remaining uranyl nitrate was extracted into a second 25 ml volume of tributyl phosphate and kerosene. When the 25 ml of tributyl phosphate and kerosene contained 186 mg. of uranium, the extraction from a 25 ml solution of uranium in 3 M HNO_3 was 88 per cent effective.

No quantitative laboratory experiments were carried out on the efficiency of scrubbing out nitric acid from the organic phase with pure water nor on the efficiency of the precipitation of the uranium with ammonia gas bubbled through the tributyl phosphate and kerosene. It was found in the pilot plant tests, to be described shortly, that these operations were very effective. The ammonia gas removes practically all the uranium from the organic phase as ammonium diuranate, and the organic phase does not absorb any excess of ammonia.

Recovery Process for Uranium

Flow Sheet. A flow diagram for the proposed recovery plant is shown in Fig. 6 where the numbers refer to the various plant streams as described in the following paragraphs. The full lines give the circuits of the aqueous phase containing uranyl nitrate and nitric acid and the dotted lines give the circuits of organic phase containing tributyl phosphate and kerosene.

1. The ground uranium ore with particle size distribution similar to that given in Tables I and III is fed from a hopper into the leaching tank.

FIGURE 5. MULTISTAGE COUNTERCURRENT EXTRACTION OF LEACH FROM EDGEMONT CARNOTITE ORE WITH TBP-KEROSENE SOLVENT

FIGURE 29.6 URANIUM EXTRACTION PLANT FLOW DIAGRAM

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2. After the ore has been leached, it is discarded, but any solution clinging to it will waste both uranium and nitric acid. Furthermore, the acid solution containing the uranium must be clear in order to permit effective extraction with the organic phase. It is desirable, therefore, to pass the ore through a centrifugal filter before discharging it at 2. The use of a filter press or the separation by repeated settling and washing by decantation are other possibilities. With an effective filter the solution loss should not be more than 10 per cent of the weight of the ore. The losses of this 10% of solution can be recovered in part by rinsing the ore on the filter. If this filter cake is rinsed with water, equivalent to the solution held by it, the loss of uranium and nitric acid will be only half as great. It is not possible to use much water, however, because it will dilute the acid more than can be offset by the make-up acid added in the form of concentrated nitric acid. The filter cake is rinsed with the scrubbing water which has been used to recover nitric acid from the organic phase at a later stage and thus much of the uranium is saved; but, there is some acid loss.

3. The clear nitric acid leach containing the dissolved uranium and other nitric acid soluble elements is pumped to the solvent extraction vessel for the removal of the uranium. This vessel may be either a continuous-flow, packed column or a mixing vessel with motor-driven stirrer giving a batch process.

4. In the solvent extraction, an organic liquid is chosen which will have a high solubility for uranyl nitrate and very little solubility for the other nitrates which are present. Equal volumes of tributyl phosphate and kerosene were chosen for this investigation. The leach solution after the extraction of uranium is returned to the ore leaching vessel. If a little uranium escapes solvent extraction it will not be lost because it is returned to the leaching

vessel for the next pass. The only loss of uranium comes from incomplete leaching of the ore and from the loss of solution which adheres to the discarded filter cake.

5. Some of the acid is consumed by limestone and other materials in the ore, some is extracted into the tributyl phosphate along with the uranyl nitrate and some is lost by precipitation of the product with ammonia. Accordingly it is necessary to add makeup acid in such quantity and concentration as to maintain the acidity of leaching solution at a fixed value - 3 molar in most of the work described here.

6. Water is lost when the filter cake of spent ore is discarded and so it is necessary to add an equivalent amount. The water added should not exceed that which is lost for then the nitric acid inventory would be continuously diluted. The water is added at this point in order to recover the nitric acid which has been extracted into the organic phase along with the uranyl nitrate. It is possible to re-extract most of the nitric acid without re-extracting appreciable quantities of uranium. The small amounts of uranium taken into the water phase are not lost; they are returned to the leach solution for the next pass. In some cases it will be desirable to use the make-up water for rinsing the filter cake of spent ore before it is added to the organic phase at 6. In this way the losses of nitric acid and uranium on the filter cake are reduced but the operation is complicated by the necessity for keeping the wash product separated from the filtrate.

7. The water containing the nitric acid, scrubbed from the organic phase is returned to the leaching solution. It is used first for rinsing the filter cake, thereby reducing the filter cake loss of uranium and reducing some of the filter cake loss of nitric acid. Under ideal conditions the amount of acid recovered from the tributyl phosphate solution would equal the amount of leach acid lost to the organic phase in the uranium extraction and the total volume of this stream would equal the volume of liquid lost to the filter cake.

8. The remaining steps in the flow diagram indicated by dotted lines, are concerned with the organic phase which in most of the present work was a mixture of equal volumes of tributyl phosphate and kerosene. This solvent is introduced at the

bottom of the uranium extraction vessel which is either a solvent-extraction column in a continuous process or a motor-stirred liquid in a batch process.

9. After the uranium and some of the nitric acid is removed from the aqueous solution the organic phase is pumped to the water-scrubbing tower where most of the acid is removed.

10. The organic phase containing the uranium and some nitric acid next goes to a tank where the uranium is precipitated with ammonia. The pure organic solvent is then returned through 8 to be used again. The loss of tributyl phosphate clinging to the precipitate of uranium is small and very little make-up of organic phase is required.

11. Ammonia gas from a pressure tank is bubbled through the tributyl phosphate in a deep open tank. White ammonium nitrate is precipitated as soon as the pH reaches 4, and continues until the pH reaches 5, when the uranium starts to precipitate. This precipitation of ammonium diuranate continues rapidly, depending on the rate of bubbling of ammonia. When the pH rises to about 7 the precipitation of uranium is complete and the odor of ammonia becomes strong. So little ammonia remains in solution in the organic phase that it is not necessary to blow out the ammonia with air before returning the pure organic phase through 8 to the uranium extraction vessel.

12. The flocculent precipitate of ammonium diuranate accumulates in the tank. Eventually it is allowed to settle and is separated in a centrifugal filter. The filter cake of ammonium diuranate is heated to drive off adhering organic phase and then heated to red heat to convert the uranyl nitrate into the final product containing about 65 percent U_3O_8 . It may be purified by solution in nitric acid and re-precipitation with ammonia.

Pilot Plant Data on Leaching

The pilot plant to test the practicality of acid leaching of the ores was set up in the courtyard of the Chemistry Building of the University of Wisconsin as shown in Figs. 7, 8 and 9 and Table III.

FIGURE 7. LEACHING PILOT PLANT FLOW DIAGRAM

FIGURE 8 PERFORATE BASKET CENTRIFUGE

FIGURE 9 IMPERFORATE BASKET CENTRIFUGE

Table III

EQUIPMENT NUMBERS ON LEACHING PILOT PLANT FLOW DIAGRAM

1. 12 inch diameter perforate basket, centrifugal filter
2. Receiver tank
3. Pump
4. Leach run tank
5. Mixer
6. Pump
7. 12 inch diameter imperforate basket centrifuge
8. Receiver tank
9. Pump
10. Rotameter flow indicator
11. Acid run tank

The numbers of Fig. 7 and Table III for the leaching experiments have no relation to the numbers used in Fig. 6 and the preceding section to describe the steps in the flow diagram of the overall process. All the tanks, pumps, valves and stirrers were made of stainless steel to withstand nitric acid. Connecting tubes were made of polyethylene plastic. Sometimes the tanks too were made from polyethylene fabricated with hot air welding techniques. Five motors, designated by M, were used for the two centrifuges and the three pumps.

A 10 to 20 pound charge of dry ground ore was put into the filter bag of the centrifugal filter 1 shown in Fig. 8. The filter bags were made of "vincel" style V-1902 by the National Filter Media of Salt Lake, Utah. They were very satisfactory. Filter bags of canvas do not last long in the nitric acid solutions. The centrifuge was then run up to speed and a charge of nitric acid run into the centrifuge through a spray nozzle from the acid reservoir 11. The leach solution containing nitric acid and the dissolved uranyl nitrate and other soluble salts was run out into the receiver tank 2. The leach was conducted by pump 3 into the centrifugal filter

until the desired time was up, and then it was run into the leach run tank 4. In this way the acid was cycled through the ore many times resulting in an adequate and measurable contact time and insuring efficient filtration. The contents of the receiver tank 2 were kept uniform by mixing with the larger quantity of solution in the leach run tank 4. The leach in tank 4 was cloudy, due to fine particles which passed the filter bag, so it was sent through pump 6 to a second centrifugal filter with a 12 inch imperforate basket shown in Fig. 9. The clear leach was discharged into the receiver tank 8, and discharged by pump 9 through a rotameter flow indicator 10. When operating for the recovery of uranium this clear solution from 10 was sent to the uranium extraction tank for removal of uranium by the organic liquid which is immiscible with water. In the work described in this section the pilot plant was used for studying the optimum conditions for ore leaching and so the clear acid from 10 was usually pumped back into the acid reservoir 11 as shown in Fig. 7.

Some of the filtrate from the second centrifugal was returned through a stand-pipe arrangement back into the leach run tank 4 for recycling through the second centrifuge. In this way the removal of the last small particles was facilitated and a constant hydrostatic pressure was provided for the operation of the rotameter flow indicator.

The pilot plant leaching experiments were made with the following ores - Slick Rock; Lakachukai Stockpile 16; Uraninite Utex pile 33; and lignite ash. The particle size distribution is given in Table IV.

TABLE IV

ORE CHARACTERISTICS

Ore Sample	Slick Rock	Lukachukai, Stockpile 16	Uraninite Utex, Pile 33
Sieve Analysis, weight percent			
Retain on 28	27.9	20.5	34.6
Retain on 48	8.1	13.7	18.0
Retain on 100	24.3	32.7	12.6
Retain on 150	14.2	14.4	3.9
Retain on 200	7.6	5.7	2.7
Pass 200	17.9	13.1	28.3
Uranium Concentration,			
	2960 ppm	1650 ppm	1840 ppm
	0.296 percent	0.165 percent	0.184 percent

The experiments started with a fixed quantity of nitric acid. This acid was contacted with the ore at a certain rate and at a certain acid-to-ore ratio. The leach was then recycled back into the acid. Thus the acid was depleted, and the uranium concentration of the leach increased. The volume of leach decreased by the amount of liquid lost to the filter cake. Samples of the leach and the spent ore were taken every hour. The leach was analyzed for uranium and acid content and the spent ore (filter cake) was analyzed for uranium and moisture. In this way complete material balances were obtained on the system. From these data, the acid consumption per pound of uranium and the percent uranium recovery were calculated. All these data are plotted as a function of the total pounds of ore leached in Figures 10 through 21. In all the figures the number of pounds of ore leached is plotted horizontally. The pounds of nitric acid are plotted vertically as in Fig. 10 where the lower line with white circles gives the nitric acid consumed by chemical reaction with the ore and the upper line with black circles gives the total amount of acid consumed for any total quantity of ore treated. The difference between the two lines is the amount lost to the filter cake.

The pounds of uranium are plotted vertically against the accumulated pounds of ore leached as shown in Figure 11, where the lowest line indicated by white circles indicates the uranium contained in the acid leach. The difference between the

FIGURE 10. CUMULATIVE NITRIC ACID CONSUMPTION IN LEACHING SLICK ROCK ORE

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FIGURE II. CUMULATIVE URANIUM MATERIAL BALANCE IN LEACHING SLICK ROCK ORE

lowest line of white circles and the center line of black circles gives the pounds of uranium that are lost to the filter cake; and the difference between the center line of black circles and the uppermost line indicated by half-shaded circles represents the pounds of uranium that are not leached from the ore. The uppermost line represents the total amount of uranium in the ore as determined by analysis of the original ore. An ordinate for the lowest line divided by the corresponding ordinate for the uppermost line gives the percent of the total uranium which is recovered in the leaching solution.

The leaching conditions are given in Table V.

Table V

LEACHING CONDITIONS

Ore Sample	Slick Rock	Lukachukai	Uraninite Utex
Contact time with acid leach (minutes)	10	10	10
Acid/ore ratio	2.8	2.4	2.4
Initial acid molarity	4.43	3.46	4.08
Final acid molarity	2.79	1.00	1.98
Final uranium concentration g/ml x 10 ⁶	3850	1350	1000
Percent moisture in filter cake	11.7	11.8	10.5
Percent of uranium leached from ore	88.1	89.1	(112.9)

Slick Rock Data. The data obtained with Slick Rock ore are given in Figs. 10-13.

It is evident from these figures that the recovery of uranium from Slick Rock ore is very good and that the acid consumption is relatively low. The leaching efficiency as shown in Fig. 13 is quite constant at 90 percent recovery of the uranium. The consumption of nitric acid as shown in Fig. 12 drops at first and then levels off at a value of 40 pounds of nitric acid (calculated as 100 percent HNO₃) per pound of uranium recovered. Neither the decrease in acid concentration during the continued leaching nor the build up of calcium and other elements seems to decrease the efficiency of leaching in the case of Slick Rock ore as indicated in Fig. 13. In large scale operations of course the nitric acid will be replenished as needed by adding concentrated acid, and at intervals the leaching solution will have to be discarded when it has accumulated too much foreign material.

FIGURE 12. CUMULATIVE HNO₃ CONSUMED PER URANIUM RECOVERED RATIO IN LEACHING SLICK ROCK ORE

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FIGURE 13. CUMULATIVE URANIUM RECOVERY IN LEACHING SLICK ROCK ORE

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Lukachukai Data. The leaching data for Lukachukai ore are shown in Figures 14-17.

The nitric acid consumption per pound of uranium recovered is higher for Lukachukai ore than for Slick Rock ore, and keeps on increasing. The efficiency of uranium leaching reaches about 84 percent and then decreases as the acid concentration decreases. Toward the last of this leaching experiment the high alkaline content of the ore is responsible for reducing the nitric acid concentration to 1 molar at which concentration the leaching of this ore is apparently inefficient in a contact time of ten minutes. Higher efficiencies of leaching could be obtained by adding make-up concentrated nitric acid to maintain a high concentration (3M).

Uraninite Utex Data. The leaching data for Uraninite Utex ore are given in Figures 18-21.

The recovery of uranium from this ore is worse than that from the Lukachukai ore and much worse than that of Slick Rock. The consumption of nitric acid is less than in the case of the Lukachukai ore but the recovery of uranium is quite low. Although the acid concentration is maintained fairly well there is a marked failure to extract all the uranium in the ore. The uranium in this uraninite ore apparently dissolves so slowly that a 10-minute leach time is not sufficient. It is expected that longer contact time between ore and acid leach solution would give better extraction.

FIGURE 14. CUMULATIVE NITRIC ACID CONSUMPTION IN LEACHING LUKACHUKAI ORE, STOCKPILE 16

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FIGURE 15. CUMULATIVE URANIUM MATERIAL BALANCE IN LEACHING LUKACHUKAI ORE, STOCKPILE 16

FIGURE 16. CUMULATIVE HNO_3 CONSUMED PER URANIUM RECOVERED RATIO IN LEACHING LUKACHUKAI ORE, STOCKPILE 16

FIGURE 17. CUMULATIVE URANIUM RECOVERY IN LEACHING LUKACHUKAI ORE, STOCKPILE 16

FIGURE 18. CUMULATIVE NITRIC ACID CONSUMPTION IN LEACHING URANINITE UTEX ORE, PILE 33

FIGURE 19. CUMULATIVE HNO_3 CONSUMED PER URANIUM RECOVERED RATIO IN LEACHING URANINITE UTEX ORE, PILE 33

6
10

FIGURE 20. CUMULATIVE URANIUM MATERIAL BALANCE IN LEACHING URANINITE UTEX ORE, PILE 33

FIGURE 21. CUMULATIVE URANIUM RECOVERY IN LEACHING URANINITE UTEX ORE,
PILE 33

Lignite Ash Data. A leaching experiment was carried out with lignite ash from Slim Butte, Buffalo, S.D., under the conditions described for the preceding three ores. The second experiment used the leach from the first experiment. The results are summarized in Table VI.

Table VI

LEACHING OF LIGNITE ASH		I.	II.
Uranium content parts per million		1280	1280
Original molarity of HNO_3		3.73	3.61
Pounds of ore leached		18.5	37.0
Acid strength, molarity		3.61	3.50
Acid ore ratio		7.65	7.67
Uranium concentration of leach gm/ml x 10^6		31	53
Percent moisture of filter cake		32 (approx.)	32 (approx.)
Pounds of HNO_3 consumed by chemical reaction		0.54	0.62
Pounds of HNO_3 lost to filter cake		1.36	2.68
Pounds of HNO_3 lost Total		1.90	3.30
Pounds of uranium in leach		0.0071	0.0119
Pounds of uranium lost to filter cake		0.00053	0.00123
Pounds of uranium not leached from ore		0.0072	0.0253
Cumulative pounds of HNO_3 consumed per pound of uranium recovered assuming leach lost to filter cake is not recovered		268	277
Cumulative HNO_3 consumed per pound of uranium recovered assuming leach lost to filter cake is recovered		71	47
Percent uranium recovered without recovery from filter cake		47.7	30.9
Percent uranium recovered with recovery from filter cake		51.3	34.2

The lignite ash is very light and fine. It does not filter as effectively as the other types of ores and the filter cake is not readily drained. The acid consumption per pound of uranium recovered is not excessive assuming that most of the liquid lost to the filter cake could be recovered; however, the leaching efficiency is not good. The leaching efficiency is of the same order as that of the Uraninite Ute ore and much less than that of the carnotite type of ores. Stronger nitric acid and longer contact time would probably improve the leaching efficiency.

Solvent Extraction and Precipitation. The purpose of the work just described was to study the leaching efficiency of a few typical ores and to find optimum working conditions on a pilot plant scale. The efficiency of solvent extraction by tributyl phosphate and kerosene had been established by the laboratory experiments and by work done in other laboratories.⁴ The high efficiency of the precipitation with

4. Argonne National Laboratory and Oak Ridge National Laboratory and others. Some references are cited in reference 3.

ammonia had been established also in this laboratory. Nevertheless a few experiments were carried out with the solution from the leaching of the Slick Rock ore. Approximately 10 gallons of leach solution containing 3850×10^{-6} gram of uranium per liter was stirred up for 10 minutes with 10 gallons of the tributyl phosphate and kerosene. The concentration of uranium remaining in the aqueous leach solution was only 150×10^{-6} gram of uranium indicating a 96.1 percent recovery. Three other spot checks showed 96.2, 94.3 and 95.5 percent extraction from the water phase into the organic phase.

The efficiency of precipitation was determined also in these four spot checks. The concentration of uranium in the organic phase was determined before and after precipitation with ammonia and it was found that practically all the uranium had been removed. The efficiencies of removal were 100, 100, 100 and 99.8 percent.

The calcined uranium diuranate analyzed 47.0 percent uranium or 55.5 percent U_3O_8 . An arc spectrographic analysis gave the impurities shown in Table VII.

Table VII

ARC SPECTROGRAPH ANALYSIS

Compound, percent	CaO	MgO	Fe	MnO	TiO ₂	Al ₂ O ₃	SiO ₂	V	U
Original leach	30	0.5	2.7	0.35	0.11	0.1	0.1	high	high
Extracted leach	25	0.5	2.2	0.25	0.05	0.1	0.1	high	--
Product	1	0.1	0.1	0.1	--	--	--	--	high

Although it is difficult to determine the extent of the solvent extraction of vanadium and uranium by spectrographic means the extraction and precipitation appear to be quite selective for uranium.

The success of the process described here appears to depend largely on the efficiency of the acid leach in dissolving most of the uranium from the ore without at the same time consuming too much nitric acid. Longer contact times and counter current leaching would help to lower the costs of extracting marginal ores. In counter-current leaching the solution lost with the filter cake is that of the original acid solution rather than that of the leach solution which contains the uranium.

A Primitive Batch Process

The investment in pumps, centrifugal filters and chemical engineering equipment is fairly high if standard procedures are followed such as indicated in Figs. 6 and 7 and later in Fig. 25. Studies were undertaken to explore the possibility of obtaining uranium directly from the ore with very little capital investment. The equivalent of a lone miner's "gold-panning" operation was sought which is cheap but inefficient. A great saving in initial cost can be achieved if the ore can be separated by settling and decantation rather than by power-driven centrifugal filters. Laboratory tests and one primitive pilot plant operation were carried out in an attempt to determine efficiencies and quantities of ore which might be handled.

Laboratory Experiments. Experimental measurements were made on the rate of settling of Slick Rock ore, such as shown in Fig. 22. Two hundred and fifty grams of the pulverized ore with a sieve analysis similar to that given in Table IV was added to a large graduated measuring cylinder which was then filled with acid

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FIG. 22. RATE OF SETTING OF SLICK ROCK ORE.
250 GRAMS IN 1.5 M HNO_3 TO GIVE 1000 ML.

solution up to the 1000 ml mark. After thorough agitation the cylinder was allowed to stand. The larger sand particles settled very quickly and the fine "mud" particles more slowly, leaving a clear, bluish solution on top. As seen in Fig. 22 half of the volume has cleared in 7 minutes and three-quarters in 30 minutes. Very little further separation is accomplished after standing longer than an hour. These data are fairly typical for several different carnotite ores, both coarsely and finely ground, and for concentrated and, dilute acid and water. In these experiments with an acid/ore ratio of approximately 4 to 1, 75 percent cleared in an hour and with a 2 to 1 ratio 60 percent cleared in an hour.

These laboratory data suggest that a 4-1 acid/ore ratio be used with 1.5M nitric acid and that after thorough agitation the ore and leach solution be allowed to stand for an hour. The supernatant solution on top (75 percent) is then drawn off and the remaining 1/4 volume with the spent ore is washed twice more with 1000 ml of water, using a settling time of ten minutes each. This washing permits the removal of about half of the dissolved uranium each time. In principle this procedure should give a $75 + 12.5 + 6.2$ percent recovery of uranium, i.e., over 90 percent.

In a typical washing experiment of this type with Slick Rock ore it was found that the first clear solution with 1.5M nitric acid contained 810×10^{-6} grams of uranium per ml, the first wash 200, the second wash 69 and the third wash 33×10^{-6} grams of uranium per ml. The original ore contained 2960 parts per million of uranium and the spent ore 24 ppm. There are serious technical difficulties in extending these experiments to field operations. There is a large loss of nitric acid in the muddy, discarded solutions and there is a mounting inventory of water which dilutes the nitric acid too much. This difficulty can be made less serious by using the same acidified wash water over again and extracting the uranium with tributyl phosphate after each washing.

Pilot Plant Test. This primitive method of recovering uranium from the ore was tested with 100 pound batches in the courtyard of the Chemistry Building at the University of Wisconsin on November 28, 1954. The only electrical devices were one

motor-driven stainless steel pump and a solid-basket centrifugal filter for recovery of the ammonium diuranate product. The ore from Monument Valley was of the carnotite tyuyaminite type in a sandstone gauge. It assayed 0.25% U_3O_8 .

The leaching took place in two galvanized iron stock watering tanks (\$14) 2 feet wide, 2 ft. high and 4 ft. long. They were coated with acid-resistant paint for this temporary test. One hundred and seventy-five pounds of 1.5M nitric acid was placed in each of the tanks and 50 pounds of the finely ground ore added. The resulting mixture was stirred for about 15 minutes and allowed to settle. The effervescence from the action of the nitric acid on carbonate in the ore persisted for a long time in the hand-stirred slurry and prevented the rapid settling of the muddy layer. Accordingly after partial settling, the leach from both tanks containing the fine particles was pumped into a large tank and allowed to clarify by settling. The inlet to the pump was moved down in this operation until it nearly contacted the coarse sand at the bottom of the leaching tanks.

Each of two tanks was then filled with 175 pounds of 7 volumes of tributyl phosphate and 10 volumes of kerosene. The clear supernatant acid solution containing the uranium was then pumped in through a nozzle giving a fine spray which settled down to give two layers. The organic phase was then separated and rinsed with water introduced through the spray nozzle. After decantation ammonia gas from a pressure tank was bubbled through the organic liquid and ammonium diuranate was precipitated as a flocculent precipitate which was centrifuged and heated to give U_3O_8 .

The results of the first larger scale experiment were not very satisfactory. Two men worked hard for 9 hours and treated 400 pounds of ore. The hand stirring of the slurry was not adequate and there was a 41 percent loss of uranium not leached from the ore. The extraction into the organic phase was only 75 percent efficient. The precipitation and recovery was 94 percent efficient but the unexpected high losses in leaching and extraction resulted in a final product which contained only 29 percent of the original uranium in the ore.

This experiment showed that it is necessary to have more efficient stirring of

the slurry in the leaching and also more thorough stirring in the extraction by the tributyl phosphate. A motor-driven, stainless steel stirrer is necessary in both of these operations. The recovery of uranium then might be more nearly equivalent to that expected on the basis of the laboratory experiments.

There are other difficulties, however. There is a loss of nitric acid and uranium in the coarse sand and in the muddy layer in the settling tank which is discarded. The settling process does not leave a sparkling clear supernatant solution, such as can be obtained with a centrifugal filter, and the unsettled fine particles lead to the formation of a scum and a tendency to form an emulsion of tributyl phosphate and leach solution which cannot readily be broken down.

Experiments should be tried with much larger settling tanks and with longer settling times. An organic extraction liquid may possibly be developed which will sink in the leach solution instead of floating on it. In this way the formation of scum and emulsions may perhaps be reduced.

Field Test on Uraniferous Lignite at Buffalo, S.D., in 1953

To test the practicality of a portable recovery process, it was decided to fit out a truck with processing equipment and go into the field. The Colorado Plateau area was to be avoided and accordingly the tests were made on uraniferous lignite in Harding County in northwest South Dakota. The lignite lies in the Ludlow member of the Fort Union geological formation. The equipment was set up at the Wammen ranch near Slim Butte, a few miles from Buffalo, S. D. at location SW 1/4, SE 1/4, Sec. 8 T1 7N R8E. We are much indebted to Mr. and Mrs. William Wammen for the use of their property and for hospitable cooperation. We are indebted also to Mr. Norman Denson and Mr. James Gill of the U. S. Geological Survey. Details of the work of the summer of 1953 at this location have been reported¹. Lignite ores were obtained from the Wammen ranch, from the Mendenhall Mine and from a lignite bed in the Custer Forest Reserve. The Wammen lignite contained 0.039% uranium in the ash, the Mendenhall lignite 0.071 and

the Custer Forest lignite 0.20 per cent.

The origin of the uraniferous lignite is well understood. The lignite seams, ranging from a few inches to a few feet in thickness, underly deep deposits of volcanic ash, which is now weathered to clay. Rain water leaches out traces of uranium from this clay and as the water settles down through the lignite bed, the uranium is taken up by the lignite as in chromatographic adsorption. The uranium is found only in the uppermost part of the highest lignite seam.

A core sample from drilling in the Custer Forest Reserve by the Geological Survey gave a uranium analysis of 0.35 per cent, at a depth of 20 ft. The overlying earth was removed with a bull dozer and the top of the lignite seam exposed over a 15 x 30 ft. area. Samples from the top of this exposure going around the rectangle at intervals of a few feet gave 0.44, 0.50, 0.40, 0.19, 0.33, 0.35, 0.48 and 0.34 per cent uranium in the lignite ash. This finding is important in showing that a high uranium concentration in the drill-core is not confined to a small, accidental sample, but that it is characteristic of a reasonably large area at a given stratum.

The mining operations were carried out with the help of bulldozers and several hundred pounds of lignite from each of the three locations was bagged and carried to the recovery site a few miles away.

The lignite was burned over a shallow pit 16 feet long, 8 ft. wide. Expanded metal lath was placed over the pit and supported by angle iron on concrete blocks. The lignite was shovelled onto the metal lath and the fire started with gasoline. Effective under-draft ventilation was produced with a small portable blower operated with a gasoline engine. A fine screen over the top prevented the escape of sparks. As the lignite burned the ash fell through the metal lath and into the shallow pit from which it was removed at intervals.

Fresh lignite was added as needed. The rate of burning was regulated

by the air blower so that the fire would not become not enough to sinter the ash and imprison the uranium in glazed material from which it could not easily be leached.

Equipment. Some of the equipment is shown in Fig. 23, page 43. A 4-600 Ford truck with a stake body was obtained for \$2500. It was provided with a 4-wheel drive and a winch and cable welded to the front of the truck. An iron frame was also welded to the truck. An hydraulic lift was attached at the tail gate. The total cost of the truck and all the accessories was \$7,736. Of these accessories, it turned out that only the winch and the tail gate lift would be indispensable in future operations. With the winch, the expensive 4-wheel drive became unnecessary.

The ore dressing equipment consisted of a 3 1/4" x 4 1/2" Denver Type H jaw crusher at \$550, a 6 inch Masco "Gy-roll" reduction crusher at \$548 and a 9 1/2 K Denver McCool pulverizer "Gy-roll" at \$587. This equipment was mounted on the truck immediately back of the drivers seat and operated by the truck engine with a power take-off. It was quite satisfactory except that the reduction crusher and pulverizer required dry ore.

A 5-KW generator driven by a gasoline engine costing \$725 operated the pumps, stirrers, and lights. Additional equipment included stainless steel stirrers, pumps, valves and pipes, stainless steel tanks for leaching, extracting and settling, flowmeters, and a 250 gallon water tank. A water pump and gasoline engine cost \$117. Other accessories included plastic tubing and buckets, a pH meter, a fire extinguisher, scales and a wheelborrow.

The nitric acid came in large stainless steel drums, the tri-butyl phosphate and kerosene in iron cans and the ammonia in pressure tanks. The gasoline cost for operations and travel including travel from Madison and return was \$400.

FIG. 23

FIELD RECOVERY TESTS ON URANIFEROUS
LIGNITE SLIM BUTTE, BUFFALO, S.D.. GRINDING
MACHINERY IS ON TRUCK. SUMMER 1953.

Results. Heavy rains interfered with operations during the first part of the 2 1/2 months field program. The mining and burning of the lignite were eventually quite satisfactory. The chemical results were unsatisfactory but much valuable information on operation and cost data were obtained. The filter was not delivered until the summer was over and so the work was carried out with settling and decantation. The settling of lignite ash is very slow and the fine particles remaining in the water phase together with hydrolysis products of the tributyl phosphate led to the formation of troublesome emulsions. This difficulty can be lessened some what by washing the tributyl phosphate occasionally with sodium carbonate solution to remove hydrolysis products. The emulsions were carried over to the final product and this extra inert material resulted in a low uranium concentration.

When the lignite ash proved to be unsatisfactory, experiments were carried out with carnotite ore obtained from Edgemont, S. D. through the courtesy of the Raw Materials Division of the Atomic Energy Commission. Even with this material analyzing 0.25 per cent uranium the final product did not analyze better than 5.5 per cent.

It was learned in this work that the nitric acid was too dilute, that the ratio of tributyl phosphate to kerosene was too low and that improvements in the chemical engineering operations were needed.

Several hundred pounds of the lignite ash were carried back to Madison for further testing. Even with improved conditions, it was found that the ash was not very effectively separated by settling and that in the filtering operation the filter cake retained a high concentration of moisture which resulted in a considerable loss of uranium and nitric acid in the leach.

More serious still is the fact/^{that} only about half of the uranium was leached out from the lignite ash under pilot plant conditions as

indicated in Table VI. Time did not permit finding if this leaching failure could be corrected by longer leaching. It is not known whether the temperature of lignite burning was high enough to glaze over some of the ash and render subsequent leaching more difficult. Earlier experiments had led to the belief that the acid leach is effective in taking out the uranium from the ash.

The consumption of nitric acid by the lignite ash was low, at least in some of the samples. The general conclusion, however, is that although uraniferous lignite can be easily mined and ashed, it is not satisfactory for effective recovery with the acid leach and with the portable equipment developed in this research program.

Field Test on Carnotite Ores at Silverton, Colorado in 1954

After the field test at Buffalo, S. D., improvements were made in the process. A rotary vacuum filter was tried, but it proved to be unable to handle the carnotite ore with its high percentage of sand grains. Two centrifugal filters were obtained as described in the pilot operations and shown in Figures 8 and 9 and these were quite satisfactory for laboratory and pilot plant but their capacity was too small for field production.

For the field tests in the summer of 1954, Silverton, Colorado was chosen because it was far enough removed from any uranium mining operations on the Colorado plateau and yet it was close enough to truck in different types of ore from the buying stations. Several tons of Slick Rock ore was obtained from the Atomic Energy Commission station in Monticello, Utah and brought by the truck to Silverton for processing. The ore was of a type and grade fairly representative of the ores being mined on the Colorado plateau. The ore was of the carnotite-tyuyaminitite type in a gangue of slightly calcareous sandstone. The ore assayed 0.3% U_3O_8 and 4% lime.

Some of the uranium recovery equipment is shown in Fig. 24. An isolated site was picked by an abandoned mine and a stream of water about a mile from Silverton. Arrangements were made to occupy the site for the summer for a small rental fee (paid for privately). We are indebted to several people of Silverton who helped us get necessary equipment and supplies. We wish to thank particularly a mining engineer, H. P. Ehrlanger, who gave us valuable advice.

The dry ore was crushed in a jaw crusher and reduced to sand-sized particles in a pulverizer as described for the Buffalo, South Dakota test. This equipment was mounted on the Ford-600 truck and operated with a power take-off from the engine. The truck and grinding equipment was located 100 feet away from the equipment, shown in Fig. 24, page 47.

The equipment included a multiple stage extraction tower made from plastic with hot air welding. This extraction column was not used later in the summer because a single batch operation with a stirrer gave such excellent results and handled a larger quantity of material. Moreover, the basket centrifuge could take only a few pounds at a time and the total operation was slow.

Accordingly, for much of the summer's work, the leaching was performed batchwise in a large cast iron ore bucket which was protected against serious acid corrosion with a coating of paraffin and tar.

The ore was leached in 500 lb. batches with 3.5N nitric acid in a ratio of 2 lbs. of acid per pound of ore. Mixing of acid and ore was accomplished by a combination of hand stirring and a small motor-driven, stainless steel stirrer. All the pumps and stirrers were operated by the 5KW gasoline driven dynamo.

No filtration was employed, separation of liquid from solids being accomplished by settling and decantation. After effervescence

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FIG. 24

FIELD RECOVERY TESTS ON CARNOTITE ORES,
SILVERTON, COLO.. GRINDING MACHINERY AND
TRUCK NOT SHOWN. SUMMER 1954.

had stopped, the leach was allowed to settle for about two hours. In this period of time all but the finest particles had settled to the bottom, and fairly clean leach could be obtained by siphoning off the supernatant liquid which was then stored in stainless steel acid drums until the processing could be completed. Actually, such storage allowed a second period of settling which ranged from 1 to 15 hours depending upon the state of the remainder of the processing.

Extraction was carried out in a large cylindrical tank which held 20 gallons of leach and 20 gallons of the organic solvent, consisting of 50% kerosene and 50% tri-butyl phosphate. Mixing of the two phases was accomplished by a 1/3 H.P. electric stirrer operating for 15 minutes. After the two phases had separated, the leach was discarded, and the organic phase was pumped through an acid drum containing water in such a way that it was broken up into droplets passing upward through the water. This procedure removed most of the nitric acid which had been dissolved in the organic phase.

Next the organic phase was pumped into an open cylindrical tank of 20 gallon capacity for precipitation. Ammonia from a pressure tank was introduced as a stream of small bubbles into the organic phase through a porous outlet. Shortly after the first introduction of ammonia, a white precipitate began to come down; this precipitate was the ammonium nitrate formed by the reaction of the residual nitric acid and the ammonia. During the first part of the precipitation, the pH rose very slowly. However, at about pH 3, most of the nitric acid had been neutralized and at that point the pH began to rise rapidly. At about pH 4 the uranium began to precipitate as ammonium diuranate. Most of the precipitation appears to take place between pH 4 and 5, but the ammonia addition was continued until pH 7.5 was attained and the sharp odor of ammonia was apparent. Since the pH rises very rapidly in this range, the

additional consumption of ammonia was of no great consequence. The organic liquid was returned to storage or used at once for another extraction. Two batches were in operation, so that extraction and precipitation could go on simultaneously.

The precipitated ammonium diuranate did not settle readily, and for that reason it was necessary to resort to a solid basket centrifugal to recover the product, a procedure which worked very efficiently. As a final step, the product was heated over an open fire to drive off any adhering liquid and decompose the ammonium nitrate.

The chemical efficiency of leaching averaged approximately 90%. Laboratory data suggest that an efficiency of better than 95% should be expected under the conditions. The discrepancy between 90 and 95 per cent removal of the uranium can be blamed on faulty contacting of leach and ore. A considerable amount of uranium, perhaps 40 per cent, was lost in the leach solution which did not clear sufficiently to permit extraction with tributyl phosphate and kerosene. In these particular experiments the centrifugal filtration in small batches was too slow and the uranium was not recovered from the muddy solution at the bottom.

The efficiency of extraction in this single stage batch process averaged 95 per cent as computed by comparing analyses of fresh and extracted leach.

The efficiency of precipitation as determined by comparing the uranium analyses before and after precipitation and removal of the ammonium diuranate was very high. Only a trace of uranium remained in the organic phase. The efficiency of removal averaged 99.9 per cent. The leaching, extraction, precipitation and recovery were all very simple and efficient. The large loss came in the decantation process in which large quantities of the leach solution were discarded along with the spent ore, because the lower solution was too

muddy for the organic extraction. Filtration equipment capable of handling large quantities of ore is necessary to supplement the partial separation by settling.

The filtered and dried ammonium diuranate gave 15.2 per cent of U_3O_8 , and the product after heating to drive out the ammonium nitrate contained 59 per cent U_3O_8 .

With this method and the simple equipment described here a maximum of about 1500 pounds of ore could probably be processed in a day. Three men were working, one primarily on grinding, one primarily on leaching, and one on the chemical operations.

The consumption of acid by the ore amounted to 112 pounds of HNO_3 per ton whereas the calculated amount for 4 per cent $CaCO_3$ in the ore is 98.5 pounds of HNO_3 per ton.

Cost Estimates for Larger Units

Very rough cost estimates will be attempted for processing uranium ore on a more practical scale. Four different types of equipment will be described --

1. A simple settling type involving the minimum of capital investment;
2. A 1/4-ton-per-day batch process based on the Silverton experience;
3. A 5-ton-per-day continuous process based on the pilot plant data; and
4. A larger stationary unit located at the mine.

It must be emphasized that these cost data are very tentative. Important opportunities for cutting costs are obvious, but on the other hand, there are unknowns such as emulsion formation which may increase costs considerably. An ore which is high in carbonate cannot be considered for practical recovery in any of these methods.

(1) Settling-tank Method. The decantation method described on page 38, is ineffective and wasteful, but it could perhaps be operated more effectively with very large settling tanks of thin stainless steel, with sloping sides, nested for transportation. In a permanent installation, large concrete tanks with acid proof paint could be used. A flocculating agent may already be known which will give rapid and more complete settling of the leached ore. This method requires very little cost for equipment, but the loss of uranium is excessive and the emulsification of the organic solvent may be serious.

(2) Batch Process with Stirrers. (A) Leaching takes place in open cylindrical polyethylene tanks 1 ft. in diameter and 2 ft. deep. The tanks are easily fabricated with a hot-air welding unit. Nested cylinders of stainless steel are better, but more expensive. This size allows 50-pound batches of ores. The leach tank is fitted with a removable, coarse "tea bag" fitting closely inside the cylinder and supported by a wooden frame and plastic screen. The 1.5M or 3.0M acid and the 50 pounds of ground ore are stirred with a 1/3 HP Lightning stirrer. (B) The filtration is accomplished in two steps-- (1) Most of the solids are removed when the tea bag is lifted (2) The solids remaining in the solution are removed by the Tolhurst centrifugal filter shown in Fig. 3. The tea bag and filter cake are rinsed with a little water. The tea bag holds back the large amount of sand and the centrifugal filter removes the mud. (C) The single stage extraction is accomplished in a tank of the same dimensions as the leaching tank. Equal volumes of the leach solution and the organic phase are stirred with a 1/3 h.p. Lightning stirrer and allowed to settle. The organic phase consists of equal volumes of tributyl phosphate and kerosene. The leach solution is drawn off and returned for leaching more ore. (D) The organic phase is scrubbed with an equal

volume of water in the same vessel to remove nitric acid using the stirrer. After settling, the water solution is added to the leach solution. (E) Ammonia gas is bubbled through the organic phase. (F) The precipitate of ammonium diuranate is filtered with the Fletcher centrifugal filter shown in Fig. 2.

It is estimated that one man can handle over 50 pounds an hour, or about 1/4 ton per day. No pumps are used and the liquids are siphoned or transferred in plastic buckets. The power for the two centrifuges and two stirrers is provided with a gasoline-powered generator. If the ore is not already ground it is necessary to have grinding equipment operated by the truck engine. The empty acid drums of stainless steel are used for storage of liquids. The cost of equipment might be around \$3000 to \$5000 in addition to the truck. The cost of chemicals per ton are given in the next section.

(3) A 5-ton-per-day Unit. A portable unit capable of handling 5 tons of ore per day is diagramed in Fig. 25.

The cost of such a processing unit is estimated in Table VIII.

TABLE VIII. Rough Cost Estimate of Equipment for Processing 5 Tons of Ore Per Day

Truck	\$6,000
Living Supplies	1,000
Acid Trailer	1,000
Water Trailer	1,000
Ore Bin	400
Rotary Ore Feeder	1,000
Centrifugal Filter	15,000
Mixer	300
Uranium Extraction Column	300
Acid Extraction Column	300
Ammonia Tanks	300
Product Centrifugal Filter	1,500
8 Pumps	3,200
Gas Regulator	200
6 Tanks	1,200
Tributyl Phosphate and Kerosene (tributyl phosphate	
Initial cost (Losses unknown) 53 cents per pound)	500
Piping and Installation	5,000
Generator and Auxiliaries	5,000
Flow controllers and accessories	2,000
Total	\$45,200

M. MOTOR.

FC. VALVE FLOW CONTROLLER.

— WATER OR NITRIC ACID SOLUTIONS.

----- IMMISCIBLE ORGANIC LIQUIDS.

FIGURE 25. FLOW DIAGRAM FOR PORTABLE PLANT EQUIPMENT

At a cost of less than \$50,000, the investment amounts to less than \$10,000 for a ton a day capacity.

In Table IX, the cost of processing a ton of ore is estimated on the basis of a 5 ton per day operation.

TABLE IX. Rough Cost Estimate for Processing One Ton of Slick Rock Ore (5 tons per day)

<u>Chemical Expense</u>	Cost per Ton (5 ton per day operation)
HNO ₃ 272 lbs. per ton of 67% HNO ₃ \$0.0755/lb. in returnable stainless steel drums	\$ 20.52
Ammonia 0.94 lbs. at \$0.18/lb. in returnable pressure cylinders	.17
Shipping of chemicals at \$0.06 per ton-mile and 500 miles	4.50
Labor - 2 men at \$3 per hour. Capacity of plant 5 tons in 8 hours	9.60
Cost of plant estimated at \$10,000 per ton daily capacity, amortized over a 3 year period. (900 days)	11.11
Reserve for repairs at 60% of plant cost	3.00
Power cost (estimated)	<u>1.60</u>
Total Chemical Processing cost	\$50.50
Cost of grinding ore (estimated)	<u>5.00</u>
Total cost (excluding purchase of ore)	\$55.50

* Total of 25 horsepower including 15 h.p. for centrifugal filter, 8 pumps at 1 h.p. each, rotary feeder at 1 h.p. and mixer and product centrifuge at 1/2 h.p. each. Assume 4 gallons of gasoline per hour or \$8 per day.

The cost of processing a ton of ore depends greatly on the amount of acid-consuming material such as limestone which it contains. For each 1 per cent of CaCO₃ in the ore, 28 pounds of HNO₃ are consumed per ton of ore. In the slick rock ore analyzing 4% CaCO₃, 112 pounds of nitric acid would be the expected HNO₃ consumption in the leaching

operation. In addition to the acid consumed in neutralizing the ore, a further amount is lost in the discarded filter cake. Allowing for the total acid requirements and expressing in terms of 67 per cent nitric acid, it is estimated that a ton of Slick Rock ore will require 272 pounds of the 67 per cent acid.

The cost of obtaining a pound of uranium from the ore is given in:

Table X. Rough Cost Estimate of Obtaining 1 pound of Uranium
as U_3O_8

Slick Rock ore contains 0.30 per cent uranium
90 per cent recovery = 0.27 per cent = 5.4 pounds uranium
Cost of producing uranium (in the form of U_3O_8)
= $\$55.50 / 5.4$ pounds = $\$10.38$ per pound.

Lukachukai ore contains 0.165 per cent uranium
90 per cent recovery = 0.15 per cent = 3 pounds uranium
If other costs remain the same as indicated in Table VIII,
the cost of uranium (in the form of U_3O_8) is $\$55.50 / 3 =$
 $\$18.50$ per pound.

Monument Valley ore contains 0.40 per cent uranium
90 per cent recovery = 0.36 per cent = 7.2 pounds uranium.
The acid consumption is only 172 pounds of nitric acid
costing \$13.00 instead of \$20.52 as in Slick Rock ore.
The processing cost is \$48 per ton. Cost of producing
uranium (in the form of U_3O_8), is $\$48.00 / 7.2 =$ $\$6.66$ per lb.

These capital costs given in Table VIII and operating costs given in Table IX can be taken merely as approximate guesses. They are given only so that some estimate of the economic possibilities can be considered. A change in the acid consumption of the ore, a change in filterability of the leached ore or a difficulty with emulsion formations could change the costs considerably. It is believed, however, that the estimates of Tables VIII and IX are conservatively estimated and that very likely a considerable reduction in actual practice may be expected.

It is interesting to consider further the economic possibilities in operating a 5-ton-per-day recovery plant with ore equivalent to Slick Rock ore. In a hypothetical situation, it is assumed that there

is a deposit of 5000 tons of ore similar to Slick Rock ore containing 0.30 per cent uranium. It will take a little over three years to process the 5,000 tons at the rate of 5 tons per day and 300 days per year.

In this hypothetical example, it is assumed that the 5,000-ton deposit of 0.3 per cent ore is located in southern Arizona. The mine is reasonably close to an Atomic Energy Commission mill, but the ore is of a type which cannot be handled by the mill. The mill officials do not believe that the reserves in this deposit are large enough to warrant modifying the mill to take the ore. Furthermore, the mine operators, being short of capital and unwilling to borrow large amounts, have decided to work their deposit on a small scale, thus avoiding large capital outlays. This fact means that the ore would arrive at the mill in small lots, and further strengthens the decision of the mill operators not to alter the circuits.

Some 500 miles to the north another mill is set up in such a way that it could process the ore from this deposit without changes in the circuit. However, transporting the ore 500 miles would reduce the mine-owners profit too much.

The mine owners decide to mill the ore on the premises using the process outlined in this report. They could construct their own mill, but because they know very little about ore processing, they decide to call in one of the companies which has been building and operating small plants for mine-owners in similar situations.

The mine owners pay the company nothing for the mill to be built on their property; they simply sign an agreement that they will supply the mill with a certain quantity of ore per day, for which they will receive the current Atomic Energy Commission price, which is dependent upon grade of the ore. The mine owners also agree to handle ore grinding and the disposal of tailings.

At the end of three years the operating unit will have produced 5000 x 5.4 pounds or 27,000 pounds of uranium in the form of U_3O_8 at a cost of \$277,500. The initial capital investment of \$50,000 is absorbed into the operating costs over the three-year period.

Stationary Unit at the Mine. The emphasis in this research has been on cheap portable equipment for the recovery of uranium. Much better economy can be obtained, of course, with larger units. There are situations where the portable units process is too expensive, but the size of the uranium deposit is too small to justify the erection of a large, standard recovery plant and the distance to an already-operating recovery plant is too great. Under these conditions a stationary plant at the mine based on the process described here may well be considered. The mine would have to be large enough to have power equipment and electricity.

The processing of 10 tons per day and more (100 tons?) becomes possible. The grinding of the ore is easily handled. Large settling tanks and a large centrifuge are used. The labor costs per ton become much lower. The capital investment can be reduced below \$10,000 per ton and the operating cost can be greatly reduced. The process still is unsatisfactory for ores that have too much alkaline material.

A considerable saving can be effected in a larger plant by making nitric acid directly from ammonia. Liquid ammonia in large trailer tank trucks is readily available for fertilizer purposes and ammonia can be transported easily to the mine. An interesting article by G. B. Knecht^{*} describes a 1-ton-a-day nitric acid

^{*} G. B. Knecht, "The Case for a Small Nitric Acid Plant, Chemical Industries, March p. 357 (1950)

production plant which has been built and operated. The capital cost is \$50,000 and 60 per cent nitric acid can be produced for about 3 1/2 cents per pound as against the 7 1/2 cents per pound when bought in drums as described in this report. The plant operated in 1949 is described in this article. It occupies a space 20 x 15 ft. and uses the oxidation of ammonia with a platinum catalyst. Not only could there perhaps be a saving of about 50 per cent in acid cost, but the

transportation weight for ammonia would be less than one fifth as much as that of the nitric acid. The cost and weight of the stainless steel drums could be eliminated also.

As given earlier, the cost of 67 per cent nitric acid at \$7.50 per hundred pounds is the largest item in the process described here.

In the Slick Rock ore it amounted to over one third of the cost. Another advantage in the ammonia oxidation system lies in the fact that the nitrogen oxides can be absorbed directly in the wash water from the spent ore. In this way the water inventory can be kept down even with much more efficient washing. The decantation method becomes more attractive under these conditions.

Conclusions

The uranium recovery process involving nitric acid leach, solvent extraction with tributyl phosphate and precipitation with ammonia gas is simple and satisfactory. Portable equipment for this process has been built and tested.

Small-scale operations for a quarter of a ton a day are quite possible and they do not involve large capital investments but they are inefficient and expensive.

A five-ton-a-day portable plant appears possible at a cost of about \$10 per ton of ore with suitable characteristics such as 0.3 per cent uranium, less than 4 per cent limestone and normal filtering characteristics.

Large-scale operations with small stationary equipment at a mine appear attractive for certain types of ores in certain locations. Such a mine already has Diesel engine power, or other power, and a supply of water. The costs can be greatly reduced in such a situation with a ten-ton-a-day production or more--particularly if the nitric acid is produced by the oxidation of ammonia at the mine. Such a process may well be considered for geographically isolated deposits, or for special types of ores, or for mines with reserves of over 10,000 tons, but without sufficient reserves to justify construction of a standard, full-sized plant.

Certain types of ores are particularly suitable for the process described here. A granite type of ore with acid-soluble pitchblende of high uranium content could give excellent results without consuming much acid and without causing filtration problems. Laboratory experiments on two such ores from Ontario and Lake Athabaska, Canada gave complete leaching of the uranium and practically no consumption of nitric acid. Under these conditions, small portable leaching units might prove to be quite economical, particularly in isolated areas.

Recommendations

It is recommended that the program described here be continued on a larger scale. A group of workers already familiar with the processing of ores and the use of deflocculating agents may well be able to simplify the operations and expand the scale effectively. Some commercial organizations already operating or yet to be formed may be interested in processing uranium ore as a private enterprise or on contract.

It is suggested that the various ores known to the Atomic Energy Commission be studied to determine if there are locations and low-acid consuming ores where this process could well be used economically even without extensive additional research.

Acknowledgements

The authors of this report are indebted to many people who have assisted them in this project. Dr. Donald F. Saunders and Dr. John A. S. Adams were associated with the early part of the work and Dr. Adams assisted with the analyses and field trips. Miss Patricia A. Smith gave clerical, secretarial and laboratory help. Mrs. Patricia Johnson gave secretarial assistance. Mr. Dallas Pagel gave valuable help in the laboratory, pilot plant and field tests. Mr. Bruce Ringey assisted with the pilot plant tests. Miss Marjory Miller and Mrs. Joyce Muckenfuss carried out the chemical analyses. Mr. John L. Wray, Mr. George Sanderson and Mr. Robert J. Goll took part in the field trips. Mr. Harold A. Schimming has been helpful in handling orders and supplies and Mr. Henry A. Kroening has been helpful with administration problems.

We are greatly indebted to the Atomic Energy Commission for the continued support of this project and particularly to Dr. Daniel R. Miller of the Research Division in Washington and to Mr. Joseph L. Trocino and Mr. W. E. Unbehauen of the Chicago Operations Office at Argonne National Laboratory.

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January 14, 1956

Appendix

to Final Report of December 1955 on RECOVERY OF URANIUM FROM ORES WITH PORTABLE EQUIPMENT

Contract Number AT (11-1) - 178

by

Farrington Daniels
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September, 1957

Tests of a primitive batch process are described on pages 37-40. Possibilities of extraction were explored in which large settling tanks were used to avoid the large investment and heavy weight of centrifuges. Figure 22 on page 37a shows the time required for finely ground Slickrock ore to settle. At least half an hour was required and then the separation was not satisfactory. On page 58 under recommendations, it is stated that "Workers familiar with the use of deflocculating agents may well be able to simplify the operations and expand the scale effectively."

The program was discontinued at the end of 1955, but in 1956 samples of an excellent deflocculating agent, Separan No. 2610, were obtained through the courtesy of the Dow Chemical Company. Measurements were made with this material similar to those described on page 37a. The settling rates of the same Slickrock ore with Separan are shown in Figs. 1 and 2. It is evident that the time required for settling is cut from over half an hour to about 3 minutes and that only 10 to 20 milligrams of Separan are required per 250 grams of ore, a ratio of less than 1 to 10,000. On this basis, a ton of ore would require $1/5$ to $1/10$ of a pound of Separan.

The time of settling is so greatly shortened and the clarity of the supernatant nitric acid solution so improved that the primitive batch process should be re-examined for use under special conditions. In marginal economic operations the elimination of filters and centrifuge and the use of smaller settling tanks would be of great help in reducing the capital investment. The cost of the plant,

Appendix (Con't)

amortized over a three-year period, the repairs and the power are summarized on Page 53. They amount to nearly one-third of the total cost of processing the ore. A part of this cost might be saved by the use of settling tanks with Separan.

Fig. 2 Influence of Separan
on settling rate of
250 g carnotite ore

III. Distribution and Geochemistry of Uranium

[Reprinted from the Journal of Physical Chemistry, 58, 926 (1954).]

Alpha-Radioactivity of Some Rocks and Common Materials

By John B. Ockerman and Farrington Daniels

α -RADIOACTIVITY OF SOME ROCKS AND COMMON MATERIALS

BY JOHN B. OCKERMAN AND FARRINGTON DANIELS

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin

Received April 23, 1954

The α -ray activity of nearly three hundred samples of material are reported here. They include granites, limestones, bentonites, building materials, well water residues and plant litter. Measurements were made with a scintillometer and range from 0.05 to 12 α -counts per hour per sq. cm. from a powder layer of infinite thickness.

During the course of an extended study of the geochemistry of uranium, approximately two thousand determinations of relative α -activity were carried out on specimens collected from many localities in North America. Scintillation counters were employed for these measurements on thick sources of pulverized sample. The greatest amount of study was devoted to granite, limestone, bentonite, water residues, plant ashes and various types of building brick and tile. This paper summarizes the data accumulated by presenting the average α -activity (counts per hour per sq. cm.—c.p.h./cm.²) found for each class of material together with the range of variation encountered.

Apparatus.—Scintillation counters were selected for measurement of α -radioactivity because of low background and high efficiency of counting. The type of instrument employed has been described by Reed.¹ Two such counters were purchased from the R-C Scientific Instrument Co. and a third was built from components consisting of a photomultiplier tube (RCA 5819), a mounting and light-tight housing for the tube, phosphor screen and sample holder, and a Nuclear Instrument and Chemical Co. Model 162 scaler which also served as the high voltage supply.

The detector unit of each counter was a 5819 photomultiplier tube and a phosphor screen 2.25 in. in diameter below which was placed a tray to hold the sample in a reproducible position directly below the screen. The screen was prepared by stretching acetate-base Scotch tape, 3 inches wide, across the hole in an aluminum-screen frame and sprinkling silver-activated zinc sulfide phosphor over the sticky surface. A uniform, reproducible layer is obtained when the excess phosphor is removed by inverting the frame and tapping lightly. This technique is described by Reed.¹ The Type D ZnS-Ag phosphor was obtained from E. I. du Pont de Nemours Co., Photo Products Department, Towanda, Pa. The screen was replaced between the powdered sample and the photomultiplier tube with the phosphor side down and only 4 mm. above the powder. When the α -particles were ejected from the sample, they hit the phosphor and emitted a bright light which was transmitted through the transparent tape and into the photomultiplier tube where it was counted. The sample tray was an aluminum plate having a circular depression in the center in which a 2 in. diameter lucite sample dish was placed. An amplifier and scaler unit with a stabilized high voltage supply and register made up the balance of the counter. The voltage of the a.c. power input to each counter was regulated by a constant-voltage transformer.

Calibration and Technique.—At a fixed amplifier and discriminator setting and with a monoenergetic source of α -particles, the scintillation counters used in this study may exhibit a long plateau (100–200 volts) in the counting-rate vs. voltage curve between 800 and 1000 volts. The amount of amplification and the discriminator adjustment, which fixes the minimum pulse voltage required to produce a count in the scaling circuit, will affect the nature of the plateau as will the use of a source emitting α -particles of mixed energy such as a thick source of uranium ore. In the calibration, curves of counting-rate were plotted against voltage for several amplifier and discriminator settings using a polonium source. The best plateau thus obtained was further investigated by making counts of a standard pitchblende sample at voltages along the lower two-thirds of the plateau until the previously determined counting rate of

the standard sample was consistently reproduced by the counter. It then remained to check the background counting rate at the voltage setting thus established. It was usually advisable to prepare a new phosphor screen before measuring this background rate to avoid the effects of contamination. Contamination with radon required frequent replacement. The background should not exceed 0.1 to 0.2 count per hour per sq. cm. for these instruments when the sample tray is inserted with the depression empty, or filled with mineral oil.

The counters were calibrated in this way in order to have confidence in the relative comparisons of many samples. Standard pitchblende samples were used as an aid in interpreting counting rates in terms of uranium content when certain types of materials were studied but generally the possible presence of members of the thorium family and the uncertainty regarding radioactive equilibrium makes such estimation of a specific emitter very doubtful.

Samples for counting were prepared by grinding to pass 100 mesh and then were stored 2 to 4 weeks to allow gaseous disintegration products to approach equilibrium. For counting, the sample was packed lightly and leveled off in a clean lucite dish 2 in. in diameter and 1.5 mm. deep. Such sources have been tested and found to be infinitely thick, i.e., any natural α -particle directed upward from the bottom of the sample will be absorbed before reaching the top surface of the sample.

The samples on which this article is based were counted to a statistical precision of $\pm 20\%$ at the 90% confidence level which required the accumulation of at least 70 counts above background. Duplicate counts were made on many samples. Background counts were ordinarily made overnight and the screen replaced when background exceeded 0.2 to 0.25 counts per hour per sq. cm.

Results²

1. **Standard Ore Samples.**—Tabulated below are the counting rates of standard samples which were the basis of calibration of the counters. The rates given were established when the standards became available by making several counts of each sample in one of the counters. The other instruments were then referred to these counts for calibration. The variation encountered in the original determinations is shown as a percentage of the average rate. Secular equilibrium was assumed to exist in these samples in which short-lived daughter products are in equilibrium with a parent of long life and are decaying at the same rate as the parent.

A. Pitchblende standards, Department of Mines and Technical Surveys, Canada			c.p.h./cm. ²
R-T-1-1	220 p.p.m. U		70 $\pm$ 8%
R-T-1-3	2540 p.p.m. U		763 $\pm$ 2%
B. Thorium ore standards, U.S. National Bureau of Standards			
A	10 p.p.m. Th + 0.4 p.p.m. U		1.7 $\pm$ 12%
B	100 p.p.m. Th + 4.0 p.p.m. U		9.1 $\pm$ 12%
C	200 p.p.m. Th + 8.0 p.p.m. U		17.8 $\pm$ 13%
D	500 p.p.m. Th + 20.0 p.p.m. U		45.4 $\pm$ 10%
E	1000 p.p.m. Th + 40.0 p.p.m. U		82.0 $\pm$ 6%

These infinitely thick pitchblende samples indi-

(2) More detailed descriptions of these samples may be obtained from the American Documentation Institute or from the authors.

(1) C. W. Reed, *Nucleonics*, 7, no. 6, 56 (1950).

cate that 1 part per million of uranium in equilibrium gives roughly 0.31 c.p.h./cm.². This ratio was found in a large number of materials containing uranium in radioactive equilibrium.

2. α -Activity of Rocks, Water Residues, Plant Ashes and Miscellaneous Building Materials.—

The following results are reported first as the average counting rate of all the samples tested together with the maximum and minimum values obtained. In addition, the individual results in each series are tabulated in order of increasing activity. All values are given in c.p.h./cm.².

a. Granite—40 samples

Av. activity, 3.2

Max. activity, 9.6

Min. activity, 0.2

Individual measurements: 0.2, 0.4, 0.4, 0.6, 0.6, 0.7, 0.8, 0.8, 1.0, 1.0, 1.1, 1.2, 1.3, 1.4, 1.6, 1.7, 1.7, 1.7, 1.8, 2.0, 2.4, 2.5, 3.3, 3.4, 3.5, 3.6, 3.8, 4.1, 4.4, 4.6, 5.1, 5.3, 5.7, 6.1, 6.4, 6.6, 8.1, 8.2, 8.6, 9.6

b. Limestone—82 samples

Av. activity, 0.4

Max. activity, 1.7

Min. activity, 0.05

Individual measurements: 0.05, 0.05, 0.06, 0.06, 0.06, 0.08, 0.08, 0.09, 0.10, 0.12, 0.12, 0.13, 0.13, 0.13, 0.15, 0.15, 0.15, 0.15, 0.18, 0.18, 0.20, 0.20, 0.20, 0.20, 0.20, 0.25, 0.25, 0.25, 0.25, 0.25, 0.25, 0.25, 0.25, 0.25, 0.30, 0.30, 0.30, 0.30, 0.30, 0.30, 0.30, 0.30, 0.33, 0.36, 0.36, 0.36, 0.36, 0.37, 0.38, 0.41, 0.43, 0.43, 0.43, 0.43, 0.46, 0.51, 0.51, 0.51, 0.51, 0.51, 0.51, 0.55, 0.56, 0.56, 0.61, 0.61, 0.61, 0.66, 0.66, 0.66, 0.71, 0.71, 0.71, 0.76, 0.82, 0.86, 0.87, 0.97, 1.02, 1.07, 1.12, 1.73

c. Bentonite (Ordovician)—36 samples

Av. activity, 4.1

Max. activity, 10.3

Min. activity, 1.0

Individual measurements: 1.0, 1.2, 1.8, 2.1, 2.4, 2.4, 2.6, 2.6, 2.6, 3.0, 3.0, 3.2, 3.4, 3.5, 3.5, 3.6, 3.9, 4.0, 4.0, 4.1, 4.3, 4.3, 4.3, 4.6, 4.7, 4.7, 4.7, 4.8, 4.8, 5.2, 5.4, 6.1, 6.6, 6.7, 6.9, 10.3

d. Wisconsin well water residues—41 samples

These results were obtained by making counts on the solid material remaining after evaporation of the water samples.

Av. activity, 3.7

Max. activity, 11.7

Min. activity, 0.1

Individual measurements: 0.1, 0.2, 0.2, 0.3, 0.3, 0.4, 0.4, 0.4, 0.5, 0.5, 0.6, 0.7, 1.0, 1.1, 1.5, 1.8, 2.1, 2.1, 2.4, 2.5, 3.0, 3.3, 3.3, 4.0, 4.0, 4.5, 5.5, 5.5, 5.6, 6.1, 6.5, 6.6, 7.1, 7.1, 7.6, 7.6, 7.8, 8.6, 9.2, 9.8, 11.7

e. Ashes from plant litter

The α -activity of plant material ash collected throughout Wisconsin is presented below. Litter from several types of trees is included as well as that from

prairies. With each litter sample an additional sample was collected from the soil just below.

Plant Litter—34 samples

Av. activity, 3.6

Max. activity, 10.2

Min. activity, 1.0

Individual measurements: 1.0, 1.6, 1.7, 2.1, 2.2, 2.3, 2.5, 2.5, 2.7, 2.7, 2.8, 2.8, 2.9, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.4, 3.8, 3.8, 3.9, 3.9, 4.0, 4.1, 4.1, 4.2, 4.3, 4.3, 5.5, 6.3, 9.1, 10.2

Soil below plant litter—33 samples

Av. activity, 2.2

Max. activity, 6.8

Min. activity, 1.0

Individual measurements: 1.0, 1.1, 1.2, 1.5, 1.5, 1.6, 1.6, 1.6, 1.7, 1.7, 1.7, 1.7, 1.7, 1.7, 1.8, 1.8, 1.8, 1.8, 1.8, 1.8, 1.9, 2.1, 2.2, 2.3, 2.7, 2.9, 3.1, 3.4, 3.7, 4.8, 6.8

f. Miscellaneous building materials (brick and tile)—25 samples

Av. activity, 2.4

Max. activity, 3.4

Min. activity, 1.5

Individual measurements: 1.5, 1.8, 1.8, 1.9, 2.0, 2.0, 2.1, 2.1, 2.2, 2.2, 2.2, 2.2, 2.3, 2.4, 2.4, 2.6, 2.6, 2.7, 2.8, 2.8, 2.9, 2.9, 3.0, 3.3, 3.4

Conclusions

These results show that the occurrence of radioactivity is widespread. It has been generally known that granites contain traces of uranium and thorium and their decay products but the fact that other common materials also contain them has perhaps not been so well recognized. Bentonite clays with adsorbed uranium and other α -emitters are somewhat more active than granites. Clay materials used for building carry along with them traces of radioactive materials.

Most of the findings here will be described in other reports from this Laboratory. They have been made in connection with studies on the geochemistry of uranium. Emphasis has been placed on the possible role of volcanism in supplying uranium in small amounts which is then leached and concentrated. The radiation damage caused by these α -particles over geological ages, particularly in limestones, has been the object of extensive study in this Laboratory with emphasis on measurements of thermoluminescence. This investigation has been made possible by financial support from the Atomic Energy Commission, for which the authors are grateful.

The samples have been contributed by Drs. J. A. S. Adams, J. T. Curtis, Sheldon Judson, J. K. Osmond, D. F. Saunders, and E. J. Zeller. Mrs. Joyce B. Muckenfuss assisted with some of the measurements.

LIMESTONE
Detailed Data on Alpha Ray Activity
J. Phys. Chem. 58, pp.926-27, Oct.1954

Sample Number	net cph	cph/cm ²	Description
Z-1-2-1	12	0.61	Timpas Ls - Canon City, Colo.
Z-1-2-3	14	0.71	" " " " "
Z-1-3-2	15	0.76	Greenhorn Ls - Canon City, Colo.
Z-8-1-8	6	0.30	Triassic Ls - Augusto Mt., Sonoma Range, Nev.
Z-8-2-1	8.4	0.43	Silurian Ls - Ponomint Range
Z-8-4-1	10	0.51	Jurassic Ls - Sunrise formation
Z-8-6-1	10	0.51	Pliocene Ls - Carrizo Creek, Imperial Valley, Cal.
Z-9-1-4	12	0.61	Ls - Dun Glen formation, Sonoma Range, Nev.
Z-10-1-2	8.4	0.43	Hossellkus Ls - Brock Mt. Shasta National Forest
Z-10-1-3	10	0.51	" " " " " " "
Z-11-1-1	1.2	0.06	Burrows Ls - Cherry Creek Canyon, Eagan Range, Nev.
Z-11-1-2	5	0.25	Swasey Ls - " " " " "
Z-15-1-1	8.4	0.43	Sierra Blanca Ls - Los Padres Nat. Forest
Z-15-1-3	13	0.66	" " " " " " "
Z-17-1-1	1.2	0.06	Dunderberg Ls - Adams Hill, Nev.
Z-17-1-4	2.4	0.12	" " " " "
Z-21-1-4	7.2	0.37	Pogonip Ls - East Confusion Range, Utah
Z-25-2-3	10	0.51	Siyeh Ls - Glacier National Park
Z-30-1-3	1.8	0.09	Lithographic Ls - Kentland Quarry, Kentland, Ind.
Z-30-1-8	6	0.30	" " " " " "
Z-31-2-5	10.8	0.55	Stonehenge Ls - Nittany Valley, Pa
Z-34-1-1	6	0.30	Manlius Ls - Indian Ladder Area, N. Y.
Z-36-2-1	1.2	0.06	Shoreham Ls - Glen Falls, N. Y.
Z-37-1-1	5	0.25	Richmond Ls - Camden, Ohio
Z-45-2-2	8.4	0.43	Crown Point Ls - Plattsburg, N. Y.
Z-47-4-1	2.4	0.12	Shelburne Marble - Brandon, Vt.
Z-50-1-2	17	0.86	Fernvale Ls - Cape Girardeau, Mo.
Z-50-2-1	3.6	0.18	Girardeau Ls - Cape Girardeau, Mo.
Z-1-3-1	6	0.30	Greenhorn Ls - Canon City, Col.
Z-2-1-1	4	0.20	Calcite and Ls - North Granite Mt., Utah
Z-3-1-1	10	0.51	Meekaceras Ls - Confusion Range, Utah
Z-4-1-3	14	0.71	Stalagmite - Lehman Caves, Nev.
Z-5-1-2	5	0.25	Notch Peak Ls - House Range, Nev.
Z-6-1-1	6	0.30	Guilemette Ls - Utah
Z-6-1-4	3.5	0.18	Guilemette Ls - Utah
Z-7-1-1	1.5	0.08	Calcite - House Range, Utah
Z-8-1-1	4	0.20	Moenkopi Ls - Logan Wash, Nev.
Z-12-1-1	4	0.20	Guadalupian Ls - Pequop Range, Nev.
Z-12-2-1	6	0.30	Triassic Ls - " " " "
Z-15-1-2	7	0.36	Sierra Blanca Ls - Los Padres National Forest
Z-16-1-5	10	0.51	Highland Peak Ls - Panaca, Nev.
Z-18-1-1	7	0.36	Archaeocythus Ls - Silver Peak, Nev.
Z-20-1-1	21	1.07	Wedding Cake Ls - Conger Spring, Utah
Z-20-1-2	17	0.87	" " " " " "
Z-21-1-5	4	0.20	Pogonip Ls - East Confusion Range, Utah
Z-25-1-2	14	0.71	Siyeh Ls - Glacier National Park (algal Ls)
Z-25-1-3	7	0.36	" " " " " (oolitic Ls)
Z-25-3-2	20	1.02	" " " " " "
Z-25-3-6	2.5	0.13	" " " " " "
Z-25-3-7	16	0.82	" " " " " "

LIMESTONE
continued

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Sample Number	net cph	cph/cm ²	Description
Z-25-4-2	6	0.30	Altyn Ls - Clacier National Park
Z-25-5-1	11	0.56	Marble " " "
Z-26-1-1	19	0.97	Twin Creek Ls - Swift Creek Canyon, Afton, Wyo.
Z-26-1-2	6.5	0.33	" " " " " " " "
Z-27-1-1	34	1.73	Sundance Ls - Devils Tower, Wyo.
Z-30-1-4	1.5	0.08	Ls - Kentland Quarry, Kentland, Ind.
Z-31-2-1	13	0.66	Bellefonte dolomite, Nittany Valley, Pa.
Z-31-2-3	5	0.25	Nittany dolomite - Nittany Valley, Pa.
Z-31-2-4	12	0.61	" " " " " "
Z-32-1-1	6	0.30	Schodack Ls - Schodack Landing, N. Y.
Z-33-1-1	3	0.15	Grenville Marble - Minerva N. Y.
Z-34-2-2	7.5	0.38	Coeymans Ls - Indian Ladder Area, N. Y.
Z-36-1-2	1	0.05	Isle Matte Ls - Glens Falls, N. Y.
Z-36-1-5	3	0.15	Amsterdam Ls - " " "
Z-40-1-1	6	0.30	Onondaga Ls - Union Springs, N. Y.
Z-41-1-1	2.5	0.13	Ls - Rockland formation, Dexter, N. Y.
Z-42-1-1	5	0.25	Little Falls dolomite - Middleville, N. Y.
Z-42-2-1	5	0.25	Tribes Hill Ls - Middleville, N. Y.
Z-47-5-1	4	0.20	Bascom Marble - Brooksville, Vt.
Z-50-1-1	9	0.46	Kimmswick Ls - Cape Girardeau, Mo.
Z-50-3-1	5	0.25	
Z-53-1-1	5	0.25	Ls - Shellrock formation, Iowa
Z-53-2-1	3	0.15	Owen Ls - Iowa
Z-53-2-2	2	0.10	" " "
Z-53-3-1	1	0.05	Cedar Valley Ls - Iowa
Z-54-1-1	3	0.15	Ste. Genevieve Ls - Ste. Genevieve, Mo.
Z-54-2-1	2.5	0.13	St. Louis Ls - " " "
Z-57-1-1	22	1.12	Kinkaid Ls -
Z-58-1-1	7	0.36	Pennsylvania Ls - Idaho
Z-58-1-2	13	0.66	Permian Ls - Idaho
Z-59-1-1	11	0.56	Lonsdale Ls - Cramer, Ill.
Z-60-1-1	8	0.41	Leonardian Permian Ls - Salt Lake Desert, Utah

MISCELLANEOUS BUILDING

MATERIAL

Detailed Data on Alpha ray Activity

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Sample Number	net cph	cph/cm ²	Description
M-7	58	3.0	Fire clay brick - mfd in Great Bend, Kansas
M-8	44	2.2	Brick - mfd in Nebraska City, Neb.
M-9	64	3.3	Brick - mfd in Arkansas
M-10	35	1.8	Drain tile - mfd in Indiana
M-11	44	2.2	Sewer tile - mfd in Whatcheer, Iowa
M-12	29	1.5	Brick - mfd in Waupaca, Wis.
M-13	66	3.4	Building tile - mfd in Straitsville, Ohio
M-14	42	2.1	Brick - mfd in Chicago area
M-15	54	2.8	Tile - mfd in Logan, Ohio
M-17	56	2.9	Brick - mfd in Arkansas
M-18	38	2.0	Brick - mfd in Hastings, Neb.
M-19	46	2.3	Building tile - mfd in Sheffield, Ill.
M-20	43	2.2	Brick - mfd in Summitville, Ohio
M-23	43	2.2	Sewer pipe - origin unknown
M-24	48	2.4	Brick - mfd in Des Moines, Iowa
M-25	36	1.8	Brick - mfd in Streator, Ill.
M-26	42	2.1	Brick - mfd in Shale City, Ill.
M-27	52	2.6	Brick - mfd in Cook, Kansas
M-28	55	2.8	Flue lining - mfd in Bloomington, Ill.
M-29	48	2.4	Sewer tile - mfd in Uhlrichsville, Ohio
M-31	53	2.7	Brick - mfd in Crawfordsville, Ind.
M-32	52	2.6	Brick - mfd in Brazil, Ind.
M-33	56	2.9	Brick - mfd in Steubenville, Ohio
M-34	40	2.0	Tile - mfd in Whatcheer, Iowa
M-35	37	1.9	Tile - mfd in Streator, Ill.

GRANITE
Detailed Data on Alpha ray Activity
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Sample Number	net cph	cph/cm ²	Description
D-301	100	5.1	Granite - Black River Falls, Wis.
D-302	95	4.6	" " " " "
D-380	8	0.4	Granite - Kakabeka Falls, Ontario, Canada
D-409	129	6.6	Granite - 21 mi. W. jct. 17-17A - Ontario, Can.
D-411	159	8.1	Granite - " " " " " " "
D-445	168	8.6	Granite - 30 mi. N Port Arthur Hy. 17, Canada
D-502	70	3.6	Granite - 15 mi. E. Geraldton, Ontario (Hy 11) Can.
D-508	13	0.7	Granite - 50 " " " " " " "
D-511	15	0.8	Granite - 56 " " " " " " "
D-522	5	0.2	Granite - Smooth Rock Falls, Ontario, Canada
D-532B	15	0.8	Granite - Kenogami Lake, Ontario, Canada
D-569A	40	2.0	Granite - 25 mi. S Cobalt, Ont. (Hy 11) Canada
D-570	23	1.2	Granite - 1/2 mi. S D-569A on Hy. 11
D-582	64	3.3	Granite - 21 mi. E Coniston, Ont. (Hy 17) Canada
D-602A	12	0.6	Granite - 1 mi. E. Sprague, Ont. (Hy 17) Canada
D-620A	188	9.6	Granite - 16 mi. E Iron Bridge, Ontario, Canada
D-620B	25	1.3	Granite - Same location on Hy 17 as D-620A
D-644	125	6.4	Granite - 30 mi. N Sault Ste. Marie, Ont. (Hy 17) Can
D-649B	7	0.4	Granite - 28 mi. N of D-644 on Hy 17, Canada
D-708	120	6.1	Granite - Peavy Falls, Wis.
D-757	33	1.7	Granite - origin unknown
D-1359	12	0.6	Granite - 2 mi. N Nederland, Col. on Hy 160
D-1370	160	8.2	Granite - 6 mi. S Raymond, Col. on Hy 160
D-1386	105	5.3	Granite - 4 mi. S Estes Park, Col. on Hy 160
D-1389	75	3.8	Granite - Estes Park, Colorado
D-1390	86	4.4	Granite - near Estes Park, Col. on Hy 34
D-1396	81	4.1	Granite - dump, west end of Moffat Tunnel, Col.
D-1398	36	1.8	Granite - " " " " " " "
D-1399	34	1.7	Granite - " " " " " " "
D-1401	20	1.0	Granite - " " " " " " "
D-1482	48	2.4	Granite - processing plant, St. Cloud, Minn.
F-1-G	22	1.1	Granite - collected in Brazil
F-2-G	32	1.6	" " " "
F-3-G	112	5.7	" " " "
F-4-G	34	1.7	" " " "
F-5-G	68	3.5	" " " "
F-6-G	67	3.4	" " " "
F-7-G	50	2.5	" " " "
F-8-G	20	1.0	" " " "
F-10-G	27	1.4	" " " "

ORDOVICIAN BENTONITE
Detailed Data on Alpha ray Activity
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Sample Number	net cph	cph/cm ²	Description
J-12-0-1	59	3.0	High Bridge bentonite - Kentucky
J-12-1-2	93	4.7	Little Platte bentonite - Platteville, Wis.
J-12-2-3	132	6.7	McGregor bentonite - McGregor, Iowa
J-12-2-7	50	2.6	" " " "
J-12-2-18	76	3.9	" " " "
J-12-3-5	66	3.4	Guttenberg bentonite - Guttenberg, Iowa
J-12-3-16	90	4.6	" " " "
J-12-4-3c	119	6.1	" " " "
J-12-4-9	78	4.0	" " " "
J-12-4-27	105	5.4	" " " "
J-12-5-6	47	2.4	Mount Ida bentonite - Mount Ida, Wisconsin
J-12-5-23	51	2.6	" " " " " "
J-12-5-28	71	3.6	" " " " " "
J-12-6-4	95	4.8	Lancaster bentonite - Lancaster, Wisconsin
J-12-7-10a	94	4.8	Livingston Bentonite - Livingston, Wisconsin
J-12-7-10b	84	4.3	" " " "
J-12-8-13	78	4.0	Platteville bentonite - Platteville, Wisconsin
J-12-9-5	85	4.3	Spechts Ferry bentonite - Spechts Ferry Sta., Ia.
J-12-9-7	68	3.5	" " " " " "
J-12-9-24	92	4.7	" " " " " "
J-12-10-4	59	3.0	Fever River bentonite - Benton, Wisconsin
J-12-10-8	36	1.8	" " " " "
J-12-11-5	81	4.1	Galena bentonite - Galena, Illinois
J-12-12-4	102	5.2	Mineral Point bentonite - Mineral Point, Wis.
J-12-13-2	19	1.0	Calamine bentonite - Calamine, Wisconsin
J-12-13-4	23	1.2	" " " "
J-12-14-4	68	3.5	Turk Church bentonite - Wisconsin
J-12-14-5	41	2.1	" " " "
J-12-14-6	62	3.2	" " " "
J-12-15-2	47	2.4	Janesville bentonite, Janesville, Wisconsin
J-12-18-3	92	4.7	Oil Rock bentonite - Lancaster, Wisconsin
J-12-19-5	84	4.3	Glenwood " " "
J-12-20-1	136	6.9	Weaver bentonite - Oak Hall, Pennsylvania
J-12-20-2	130	6.6	" " " "
J-12-22-1	202	10.3	Tennyson bentonite - Tennyson, Wisconsin
J-12-23-2	50	2.6	bentonite - Galena, Illinois

WELL WATER RESIDUES
Detailed Data on Alpha ray Activity
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Sample Number	net cph	cph/cm ²	Description
J-10-2-1	64	3.3	Well water residue - Wisconsin
J-10-3-1	10	0.5	same
J-10-4-1	2	0.1	same
J-10-5-1	11	0.6	same
J-10-6-1	48	2.4	same
J-10-7-1	41	2.1	same
J-10-8-1	130	6.6	same
J-10-9-1	79	4.0	same
J-10-10-1	110	5.6	same
J-10-11-1	49	2.5	same
J-10-12-1	6	0.3	same
J-10-13-1	89	4.5	same
J-10-14-1	59	3.0	same
J-10-15-1	64	3.3	same
J-10-16-1	22	1.1	same
J-10-17-1	150	7.6	same
J-10-18-1	193	9.8	same
J-10-19-1	180	9.2	same
J-10-20-1	140	7.1	same
J-10-21-1	229	11.7	same
J-10-22-1	150	7.6	same
J-10-23-1	154	7.8	same
J-10-24-1	169	8.6	same
J-10-25-1	41	2.1	same
J-10-26-1	109	5.5	same
J-10-27-1	140	7.1	same
J-10-29-1	120	6.1	same
J-10-30-1	107	5.5	same
J-10-31-1	128	6.5	same
J-10-32-1	79	4.0	same
J-10-35-1	6	0.3	same
J-10-36-1	8	0.4	same
J-10-37-1	7	0.4	same
J-10-38-1	7	0.4	same
J-10-39-1	19	1.0	same
J-10-40-1	4	0.2	same
J-10-42-1	29	1.5	same
J-10-43-1	10	0.5	same
J-10-45-1	13	0.7	same
J-10-46-1	35	1.8	same
J-10-47-1	5	0.2	same

PLANT LITTER
Detailed Data on Alpha ray Activity
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Sample Number	net cph	cph/cm ²	Description
1A ₀	76	3.9	Wet Prairie - Waukesha County, Wis.
1A ₁	66	3.4	
2A ₀	50	2.5	Hardwood Forest (Basswood) - Green County, Wis.
2A ₁	52	2.7	
3A ₀	60	3.1	Hardwood Forest (Hickory) Green County, Wis.
3A ₁	61	3.1	
4A ₀	201	10.2	Hardwood Forest (Beech) - Door County, Wis.
4A ₁	32	1.6	
5A ₀	124	6.3	White Cedar Swamp - Door County, Wis.
5A ₁	133	6.8	
6A ₀	77	3.9	Wet Prairie - Jefferson County, Wis.
6A ₁	45	2.3	
7A ₀	45	2.3	Oak-maple woods - Jefferson County, Wis.
7A ₁	33	1.7	
8A ₀	34	1.7	Sugar maple woods - Jefferson County, Wis.
8A ₁	33	1.7	
9A ₀	75	3.8	White oak woods - Dane County, Wis.
9A ₁	56	2.9	
10A ₀	80	4.1	Bitternut Hickory - Dane County, Wis.
10A ₁	43	2.2	
11A ₀	41	2.1	Dry prairie - Dane County, Wis.
11A ₁	29	1.5	
12A ₀	52	2.7	Red oak woods - Green County, Wis.
12A ₁	35	1.8	
13A ₀	53	2.7	Red oak woods - Green County, Wis.
13A ₁	31	1.6	
14A ₀	67	3.4	Dry prairie - Green County, Wis.
14A ₁	41	2.1	
15A ₀	75	3.8	Black and white oak - Kettle Moraine State Park, Wisconsin
15A ₁	22	1.1	
16A ₀	64	3.3	Low Prairie - Kettle Moraine State Park, Wis.
16A ₁	34	1.7	
17A ₀	84	4.3	Low prairie - Scuppernong ditch, Waukesha Co., Wisconsin
17A ₁	35	1.8	

PLANT LITTER

continued

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Sample Number	net cph	cph/cm ²	Description
18A ₀	56	2.9	Shagbark hickory - Pieper's Woods, Wisconsin
18A ₁	34	1.7	
19A ₀	62	3.2	Yellowbark hickory - Pieper's Woods, Wis.
19A ₁	35	1.8	
20A ₀	107	5.5	High prairie - Black Earth, Wisconsin
20A ₁	32	1.6	
21A ₀	82	4.2	Basswood - Brodhead, Wisconsin
21A ₁	35	1.8	
22A ₀	56	2.9	Black Walnut - Brodhead, Wisconsin
22A ₁	38	1.9	
23A ₀	58	3.0	Sugar maple - Spring Green, Wisconsin
23A ₁	32	1.6	
25A ₀	66	3.4	Sugar maple - Freedom, Wisconsin
25A ₁	35	1.8	
28A ₀	54	2.8	Mesic prairie - Sylvania, Wisconsin
28A ₁	33	1.7	
30A ₀	179	9.1	Hemlock - Sawyer, Wisconsin
30A ₁	34	1.7	
31A ₀	81	4.1	White Cedar - Bowler, Wisconsin
31A ₁	95	4.8	
44A ₀	78	4.0	Red and White pine - Wis. Dells, Wisconsin
44A ₁	20	1.0	
45A ₀	48	2.5	White pine - Augusta, Wisconsin
45A ₁	33	1.7	
48A ₀	84	4.3	Fir - Port Whing, Wisconsin
48A ₁	23	1.2	
54A ₀	54	2.8	Dry lime prairie - Grant County, Wis.
54A ₁	30	1.5	
58A ₀	32	1.6	Beech - Denmark, Wisconsin
58A ₁	72	3.7	
61A ₀	44	2.2	Black oak - Urne, Wisconsin
61A ₁	35	1.8	
62A ₀	20	1.0	Aspen leaves - Urne, Wisconsin

Reprint from Nuclear Geology

Edited by Henry Faul

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CHAPTER 2

RADIATION DAMAGE AND ENERGY STORAGE

2.2 Uranium and Thorium Contents of Volcanic Rocks

By

J. A. S. Adams

2.2 URANIUM AND THORIUM CONTENTS OF VOLCANIC ROCKS *

J. A. S. ADAMS †

The average uranium and thorium content of volcanic rocks has been of special interest in several studies: (1) the relation of radio-

*The author is indebted to the Atomic Energy Commission, Research Division, for its support of a research program of which this work is part.

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activity to volcanism, (2) the hypothetical volatilization of uranium from volcanoes, and (3) the possible leaching of uranium from tuffs. For these and other studies, the average and range of thorium and uranium concentrations in these rocks are of fundamental importance.

2.2.a Sampling of volcanic rocks

The sampling of all common rocks is complicated by their very large weight-to-sample ratio, already discussed in Section 2.1.a. Furthermore the possible existence of volcanic uraniferous provinces must be taken into account in any sampling procedure. It is difficult to estimate the relative abundances of the various volcanic rock types. The great volume of the basic lavas and tuffs makes them the most important single factor in calculating an average uranium content for volcanic rocks. Published analyses give values from 0.6 to 1.1 ppm for the average uranium content of basic rocks (Evans and Goodman, 1941; Davis and Hess, 1949; Paneth, 1953). Thus ordinary basic lavas can be expected to have an uranium content somewhat less than 1 ppm. The less abundant acidic volcanics have long been known to have higher uranium concentrations than the basic ones. In order to see how much higher the uranium content of acidic volcanics can range, it is useful to discuss a suite from Lassen Volcanic National Park, California, and a collection of unweathered obsidians and other volcanic glasses from widely separated localities.

2.2.b Analytical errors

The alkali analyses in Tables 2.2.1 and 2.2.2 were done with a flame photometer. One National Bureau of Standards standard sample is included for evaluation of the technique. The average error in the alkali analyses is believed to be less than ± 4 percent of the amount present in these samples. The uranium analyses were done fluorimetrically, using procedures essentially the same as those described by Grimaldi et al. (1952). Cross-checks with other laboratories using the fluorimetric technique gave agreement to within 5 to 10 percent of the amount present in granites, phosphate rocks, and low-grade carnotites. Cross-checks between the fluorimetric and other methods of uranium analysis in the range of a few parts per million are rare. The obsidian from Obsidian Cliff in Yellowstone National Park (see Table 2.2.1) was analyzed by Evans and Goodman (1941), using the radon technique (see Section 1.14). Their value for uranium in this obsidian was 3.9 ± 0.8 ppm as compared with 6.2 ± 0.4 ppm (9 determinations) by the fluorimetric method in this laboratory. The two

Table 2.2.1 Analyses of volcanic glasses from various localities

Locality	% Na ₂ O	% K ₂ O	Relative Alpha Counts Hour	Average U (ppm)	Number of U Analyses
Lepari, Italy	4.40	5.04	138	15.4	6
Vulcano Island, Italy	4.35	4.82	122	14.1	6
Rocky Mt. Park, Colorado	3.08	5.10	125	10.9	3
Corbits, Germany	3.32	3.17	81	7.9	5
Grants, New Mexico	5.27	4.28	76	7.9	6
Silverton, Colorado	4.15	5.00	79	7.7	5
Lake County, California	3.94	4.75	77	7.6	5
Frijoles Canyon, New Mexico	4.35	4.42	74	6.9	8
Mt. Taylor, New Mexico	4.78	4.52	60	6.3	9
Yellowstone Pk., Wyoming	4.03	4.90	78	6.3	4
Yellowstone Pk., Wyoming	3.67	5.31	81	6.3	5
McKinley Park, Alaska	3.15	4.36	46	6.0	4
Mono Craters, California	4.16	4.66	52	5.9	4
Götterfelsen, Meissen, Germany	4.40	3.15	61	5.3	7
Tokaj, Hungary	4.19	4.70	59	5.0	5
Ascension Island	1.18	4.50	40	4.9	3
Boulder City, Nevada	3.49	5.27	66	4.9	3
Magdalena, Mexico	4.72	4.91	44	4.6	3
Newberry Crater, Oregon	5.59	4.05	38	4.5	4
Valle Grande, New Mexico	3.81	4.30	47	4.1	5
New Zealand	5.90	3.45	35	3.9	4
La Piedad, Mexico	4.61	4.15	30	3.2	3
Stromboli, Italy	2.40	2.00	56	3.1	3
Glass Buttes, Oregon	4.17	4.38	27	2.9	6
San Benedicto Is., Mexico	3.51	5.30	36	2.4	3
Amshitska Is., Alaska	4.32	3.50	26	2.3	4
Kanaga Island, Alaska	4.03	3.09	19	2.0	3
Parícutin, Mexico	3.11	3.74	16	1.7	3
Little Sitkin Is., Alaska	4.52	2.09	12	1.0	3
Shirayama Pref., Japan	4.55	1.86	8	0.80	4
Bur. of Standards stand- ard 91 opal glass					
flame photometer	8.72	3.23			
accepted value	8.48	3.25			

methods were used on different samplings, and at least part of the discrepancy may be due to a real difference in various parts of Obsidian Cliff. However, two samples from different parts of the cliff gave the same value fluorimetrically for U, but different alkali analyses (see Table 2.2.1). Dalton et al. (1953) placed more reliance on

Table 2.2.2 Analyses of volcanic rocks from Lassen Volcanic National Park, California

Rock Description	% Na ₂ O	% K ₂ O	Relative Alpha Counts Hour	Average U (ppm)	Number of U Analyses
Raker Peak pyroxene andesite	3.26	1.26	11	1.0	2
Andesite	3.83	1.76	16	1.3	3
Twin Lakes andesite	4.13	1.44	16	1.4	3
Basalt	4.36	1.89	23	1.6	4
Flat iron andesite	3.88	1.93	20	1.7	3
Pilot Mt. rhyolite	3.70	1.95	18	1.8	3
Table Mt. basalt	3.81	2.05	23	1.9	3
Raker Peak dacite	3.80	2.15	26	2.0	4
1915 Lava dacite	4.29	2.39	28	2.1	4
1915 Mud flow	4.27	2.52	34	2.1	4
Raker Peak dacite	4.29	2.16	31	2.2	4
Chaos Jumbles dacite	4.32	2.53	32	2.2	3
Dacite tuff	4.53	2.80	39	2.5	4
Raker Peak dacite	4.80	2.65	40	2.6	2
Chaos Crags dacite	4.54	2.99	42	3.0	4
Manzanita dacite	4.73	2.91	49	3.1	2
Dacite pumice	4.43	3.11	40	3.2	3
Pre-Lassen dacite	4.58	2.95	47	3.2	3
Raker Peak dacite	4.30	3.34	51	3.6	4

their fluorimetric determinations of uranium than on their radon determinations. Preliminary results on the one granite sample available show agreement to within 10 per cent between the fluorimetric and isotope dilution methods of uranium analysis for the 3 ppm present. The average error is believed to be within ± 15 per cent of the uranium present for the values from this laboratory given in Tables 2.2.1 and 2.2.2. The alpha activities given are relative to one of the samples selected as arbitrary standard. Thick-source alpha scintillation counters were used (see Section 1.12) with a sample area 20.3 cm². Counting on each sample was continued long enough to give a statistical precision of at least ± 20 percent at the 90 percent confidence level.

2.2.c Uranium content

The uranium analyses in Table 2.2.1 give an average of 5.6 ppm for volcanic glasses, including obsidians, giving each locality equal weight. Omission of the low-uranium, low-alkali glasses from the

list would not change the average figure much, since nearly two-thirds of the samples are within the range 4.1 to 7.9 ppm, and most obsidians could be expected to fall within that range. The localities have a wide geographical distribution, and the figure is fairly representative. The relative abundance of obsidians is quite small, and, even if the rhyolites were grouped with them, it would be difficult to estimate what weight should be attached to the uranium content of obsidians in the calculation of the average abundance of uranium in volcanics. The average of 5.6 ppm probably does represent a fair upper limit for the average uranium contents of acidic volcanics.

On the assumption that differentiation of the Bowen reaction series type is the dominant process in enriching obsidians in uranium, it is interesting to see how much the differentiation can vary the uranium content of a series of lavas. The uranium and alkali analyses of the Lassen suite are useful in this connection (see Table 2.2.2, Figures 2.2 and 2.3). Williams (1932) has published a variation diagram for

Figure 2.2 Variation of soda and potash content with silica content of the rocks in the Lassen Peak region, California. After Williams (1932).

Lassen, and Figure 2.2 is based upon his diagram. Nockolds and Allen (1953) have studied the trace-element distribution in the Lassen suite. Potassium increases systematically during differentiation, whereas sodium passes through a low maximum. A plot of uranium parts per million versus potassium oxide in weight percent is surprisingly linear (Figure 2.3) and indicates that both uranium and potassium were systematically concentrated in the liquid phase as differentiation (crystal fractionation) proceeded. Evans and Williams (1935) found a correlation between potassium and radium in the Lassen suite. Their data is independent substantiation for linearity in Figure 2.3. The linearity in Figure 2.3 can be explained on the

basis of the exclusion of these two elements from the common minerals formed during the crystallization of the Lassen magmas. The different space requirements of potassium and uranium, as represented by their ionic radii and coordination numbers with respect to oxygen, do not permit them to substitute readily for other common ions. The slope of a trend line in Figure 2.3 is about 0.75, indicating that ura-

Figure 2.3 Relation between potash and uranium content of rocks in the Lassen Peak region, California (see Table 2.2.2).

num was concentrated faster than potassium, probably because the latter entered the crystalline phases to some extent.

The data from Lassen show that the differentiation produced a four-fold enrichment of uranium in the most acidic Lassen lavas. Differentiation at Lassen is not very extreme; the most acidic lava is dacitic. Where more acidic lavas are formed, a larger enrichment factor may be attained.

Assuming that crystal fractionation is primarily responsible for concentrating uranium in acidic volcanics and taking 1 ppm for the average uranium content of basaltic parent magma, we find that the average volcanic glass is enriched about 6 times in uranium. The Lipari samples would then be enriched 15 times. However, the possibility should not be excluded that at Lipari other enrichment mechanisms are operative or that Lipari and Vulcano, but not Stromboli,

are in a volcanic uraniferous province. It should be noted that the Lipari uranium value is based on 3 different samples from two independent collections, whereas the other values are based on replicate determinations on a single hand specimen.

The differentiation mechanisms just described for potassium and uranium would require that other ions with uncommon space requirements be concentrated along with the uranium. One such ion is tetravalent thorium, which has the same space requirements as tetravalent uranium. Analytical difficulties greatly restrict the number of trace thorium analyses available. A plot of total relative alpha activity versus uranium (Figures 2.4 and 2.5) can give some indirect evi-

Figure 2.4. Relative alpha activity (in counts per hour) plotted as a function of the uranium content of volcanic glasses from various localities (see Table 2.2.1). 'Y' denotes samples from Obsidian Cliff, Yellowstone National Park, Wyoming.

dence of what is happening to thorium during differentiation. Neglecting uranium²³⁵, the total alpha activity can be divided into 4 terms:

$$\text{Alpha activity} = U + \text{Daughters}_U + \text{Th} + \text{Daughters}_{\text{Th}} \quad (1)$$

At radioactive equilibrium, there is a fixed relationship between parents and their daughters and equation 1 can become:

$$\text{Alpha activity} = U + 7U + \frac{\text{Th}}{K} + \frac{5\text{Th}}{K} \quad (2)$$

where K is a constant correcting for the difference between the decay constants and concentrations of thorium and uranium. The decay constant of uranium is about three times that of thorium, and the total relative activity of thorium and thorium daughters will be three times less on this account. Therefore, assuming equal amounts of uranium²³⁸ and thorium²³², equation 2 becomes:

$$\text{Alpha activity} = U + 7U + \frac{\text{Th}}{3} + \frac{5\text{Th}}{3} \quad (3)$$

The energies of the alpha particles from the two series under discussion are about equal, and thus their likelihood of being counted in a scintillation instrument is almost equal, as a first approximation. The average thorium:uranium ratio in the accessible part of the earth and in meteorites is about 3 according to Keevil (1944) and Paneth (1953), and, using that figure in equation 3, it is reduced back to equation 2 with K equal to 1. These approximate relations show that if radioactive equilibrium exists and all of the three-times-more-abundant thorium is removed with its daughters, the total alpha activity would be decreased by only about 43 percent. A counting uncertainty of 15 percent would prevent the determination of a one-third reduction in the relative amount of thorium and its daughters.

2.2.d Thorium:uranium ratio

Figure 2.4 is a plot of relative alpha activity versus uranium in parts per million for the obsidians and other volcanic glasses listed in Table 2.2.1. The curve is almost linear, indicating that the thorium:uranium ratio does not vary greatly. Some of the deviations may be due to a lack of radioactive equilibrium. Assuming that Keevil's average thorium:uranium ratio of 3 holds for most of these samples, it is interesting to note that the obsidian from Yellowstone either has a higher-than-average thorium:uranium ratio or is not in radioactive equilibrium. Evans and Goodman (1941) give a value of 5.4 for the thorium:uranium ratio in this obsidian. The precision of the alpha counts and the uranium analyses (about ± 15 percent) does not justify more exact calculations. Figure 2.5 is a plot of relative alpha activity versus uranium for the Lassen volcanics listed in Table 2.2.2. The main deviations are in partially weathered samples, which are almost certainly not in radioactive equilibrium. These data indicate no large shift in the thorium:uranium ratio during differentiation at Lassen. They do provide independent analytical substantiation for earlier

conclusions in the literature, based on many fewer samples, that the thorium:uranium ratio in volcanics is fairly constant. Exact and rapid analytical techniques to determine thorium in parts per million concentrations are needed. Several possible methods based upon nuclear track techniques are under study at the U. S. Geological Survey (Senffle et al., in press), the University of Wisconsin, and in France (Coppens and Vernois, 1953).

Figure 2.5 Relative alpha activity (in counts per hour) plotted as a function of the uranium content of volcanic rocks from Lassen National Park, California (see Table 2.22). The plot suggests that the thorium:uranium ratio is roughly constant in these rocks.

By detailed studies of the thorium:uranium ratio, one may obtain insight into the volcanic and general geochemistry of these two elements. First of all, the fair constancy of thorium:uranium ratios in the volcanics so far studied points to an average thorium abundance that is about 3 times the average uranium abundance. Second, this constancy during differentiation locally as at Lassen (Figure 2.5) and after differentiation in 30 localities (Figure 2.4) shows that uranium and thorium are separated little, if at all, during differentiation. This lack of separation indicates that uranium is probably tetravalent during magmatic volcanic processes. The similarity of the oxidizing po-

tentials of bivalent iron and tetravalent uranium and the high bivalent:trivalent iron ratio in fresh volcanics also make the tetravalent the most likely state for the uranium in fresh volcanics.

Mason (unpublished thesis, Univ. of Wis., 1954) made a thermodynamic and experimental study of the formation of uranium hexafluoride and other volatile uranium compounds under molten volcanic conditions. The results were negative. The formation and removal of this gaseous fluoride or its chloride analogs would have greatly changed the thorium:uranium ratio. Finally, the thorium:uranium ratios may be very useful in discriminating between those volcanic and plutonic rocks derived in part from sediments and those volcanics containing iron and uranium that have never been oxidized. The oxidation of tetravalent uranium to the hexavalent uranyl ion gives it an entirely different chemistry from that of thorium, since thorium does not form an analog to the uranyl ion. Uranium in the uranyl state is leached out of rocks during weathering (see Section 2.3) but tetravalent thorium is left behind. Thus, one might expect the thorium:uranium ratios in oxidized sediments to be much higher than the same ratios in rocks that have never been oxidized. However the present state of the art of thorium analysis does not permit a test of this hypothesis.

2.2.e Conclusions

On the basis of available analyses, the average uranium content of basic lavas is between 0.6 and 1.1 ppm. At Lassen differentiation produced dacitic lavas with 4 times as much uranium as the most basic lava analyzed, and differentiation can be expected to produce acidic volcanic rocks with at least 6 times as much uranium as the average basic lavas. Obsidians with 15 ppm are known, and extreme differentiates may have even higher concentrations of uranium. Present data indicate that thorium is about 3 times more abundant than uranium in unweathered volcanic rocks and that this ratio probably holds constant during differentiation.

The uranium geochemistry of Lassen Volcanic National Park, California

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(Received 18 May 1955)

ABSTRACT

The uranium contents and relative alpha-particle activities have been determined on thirty-nine samples from Lassen Volcanic National Park. Sodium and potassium were also determined on nineteen of the samples. Secular radioactive equilibrium to within sampling and analytical error was found between the uranium values and the radium values of other workers. The K_2O/U ratio was found to be constant over a fourfold variation in uranium. The relative alpha-particle activity to uranium ratio was also found to be constant in the main Lassen sequence. There is some evidence that zircon crystals contain a proportion of the uranium in the Lassen volcanic rocks.

INTRODUCTION

It has long been known that the more silicic rocks are more radioactive and more uraniferous than the less silicic rocks (STRUTT, 1905). This generalization was firmly established by many later researches, particularly by the work of EVANS and GOODMAN (1941), who also summarized and evaluated earlier radiometric data on rocks. Still more recent studies (SEFTLE and KEEVIL, 1947; DAVIS and HESS, 1949; and others) added more confirmation. Most of the recent studies used the technique of direct-fusion for releasing radon from the rock sample. The alpha-particle activity of the radon was then measured, and that quantity was used to calculate the equilibrium amounts of radium and uranium. The details of technique, the assumptions, and the estimated errors of the direct-fusion method can be found in the papers just cited.

The work presented in this paper was undertaken to gain a more detailed insight into the uranium geochemistry of volcanoes. The hypothetical volatilization of uranium halides from volcanoes (MASON, 1954) was one geochemical mechanism of interest. The possible leaching of uranium from volcanic tuffs was another mobilization mechanism of interest. This study differs from previous work on the volcanic geochemistry of uranium in several respects: (1) the uranium concentrations were determined fluorimetrically; (2) a more detailed study of a single differentiation series was made; (3) strong experimental evidence for secular radioactive equilibrium was found; (4) an attempt was made to follow uranium through a solfataric alteration of the lavas.

Lassen Volcanic National Park, California, was selected for this detailed study because of the large amount of petrographic and chemical data available (WILLIAMS, 1932; DAY and ALLEN, 1925; and NOCKOLDS and ALLEN, 1953; in particular). The accessibility of the area, the presence of fluorite, and the opportunity to compare the fluorimetric uranium analyses with earlier radon analyses (EVANS and WILLIAMS, 1935) were additional reasons for selecting Lassen.

SAMPLING

After conferring with Professor H. WILLIAMS, the author and Dr. D. F. SAUNDERS collected the samples listed in Tables 2 and 3. The rock nomenclature of WILLIAMS (1932) is followed. The sample localities are shown on the accompanying index map, Fig. 1. Hand specimens of the freshest available outcrops were taken in each case with the exceptions of samples 2 and 38, Table 3. Sample 2 was an aggregate of small samples picked up around the mudpots at the Sulfur Works (Sapan's

Fig. 1. Index map of California and Lassen Volcanic National Park.

Springs, which is excellently photographed by DAY and ALLEN, 1925). Sample 38 was collected by submerging a gallon polyethylene bottle in one of the mudpots at the Devil's Kitchen. For some of their stay in June, 1952, the collectors were accompanied in the field by Park Ranger P. E. SCHULTZ; the author would like to acknowledge here a debt to him and to the director and staff of Lassen Volcanic National Park for their kind assistance.

Fifty to one hundred grams of each fresh sample were crushed in a steel mortar and ground in a mullite mortar to pass completely through 100-mesh silk bolting cloth. Duplicate samples were ground in several cases, and these demonstrated that the sampling and grinding techniques gave reproducible results. Cases of microuranium contamination have been observed in this and other laboratories, and great care was taken to avoid contamination. The sequence in which the samples were ground and analyzed was always noted, so that possible contamination from unexpectedly high uranium concentrations could be checked.

METHOD OF URANIUM DETERMINATION

About 1.0 gram of the well-mixed sample was used for each uranium determination. The fluorimetric uranium procedure followed was basically that described by GRIMALDI *et al.* (1954). The exact procedure and the results of inter-laboratory

cross-checks are given elsewhere (ADAMS and MAECK, 1954). The estimated error of the uranium determinations given below is less than ± 15 per cent of the amount present. It should be noted that repeated cross-checks with an isotope dilution uranium determination on the Uncompahgre Granite by Dr. GEORGE TILTON agree to within 10 per cent of the 3.4 parts per million uranium found.

METHOD OF POTASSIUM AND SODIUM DETERMINATION

The potassium and sodium determinations given in Table 2 were obtained with a Perkin-Elmer Flame Photometer, Model 52C, using lithium as internal standard. Hydrofluoric and nitric acid treatments were used to open the sample. With this procedure, analysis of National Bureau of Standards Standard Samples Numbers 70, 80, 91, and 99 gave values within ± 4 per cent of the assigned values where more than 0.5 per cent of K_2O or Na_2O was present. The Standard Samples were glasses, clays, and feldspars. The average of duplicate potash and soda determinations is given in Table 2. One of the uranium determinations on each sample in Table 2 was made on an aliquot from the solution used for the alkali determinations.

METHOD OF MEASURING RELATIVE ALPHA ACTIVITIES

At least one month after grinding, the relative alpha-particle activity of each powdered (-100 mesh) sample was measured with an alpha scintillation counter (see CURRAN, 1953, for general principles of this instrument, and KULP, HOLLAND, and VOLCHOK, 1952, for the applications to minerals). The instrument used was a Scintillscaler, Model CX14, manufactured by Reed and Curtis, Pasadena, California. The prototype of this instrument is described by REED (1950). The procedure followed was that devised by OCKERMAN (1954). Counting was continued until a statistical error of less than ± 20 per cent at the 90 per cent confidence level was obtained. The counts were made with the sample in a 2.00-in. diameter dish, giving a sample area of 3.14 sq in. or 20.2 cm². The powdered sample was several millimetres thick,

Table 1. Replicate net alpha counts on sample 10, Raker Peak dacite

Date	Net alpha counts per hour	Total time of counting
		hours
December 8, 1953	31	17.0
December 18, 1953	35	2.5
December 21, 1953	31	2.0
December 23, 1953	31	2.0
December 28, 1953	27	4.0
December 29, 1953	31	8.0
January 2, 1954	33	4.0
January 5, 1954	33	20.0
January 9, 1954	30	3.3
January 14, 1954	28	4.0
January 28, 1954	26	17.0
February 1, 1954	29	4.0
February 23, 1954	27	18.5
March 8, 1954	29	5.0

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giving essentially an infinitely thick alpha source. There was a 2-mm air gap between the surface of the sample and the 2.25-in. diameter ZnS screen. Background counts were taken with the sample dish full of mineral oil, since this substance was found to have a very low intrinsic alpha-particle activity. The background count was measured at least every ten counts, though long experience demonstrated that the background changes very little during the counting of such low alpha activities. In counting the samples listed in Tables, 1, 2, and 3, the background was found to be between one and two alpha counts per hour in every case.

Table 2. Analyses of rocks from Lassen Volcanic National Park, California

Sample number	Rock description	%Na ₂ O*	%K ₂ O*	Net relative alpha counts/hour*	Average U in p.p.m.*	Number of U determinations
36	Raker Peak pyroxene andesite	3.26	1.26	11	1.0	2
35	Andesite	3.83	1.76	16	1.3	3
37	Twin Lakes andesite	4.13	1.44	16	1.4	3
7	1915 lava with pumice	4.36	1.89	23	1.6	4
17	Flatiron andesite	3.88	1.93	20	1.7	3
18	Pilot Mountain andesite	3.70	1.95	18	1.8	3
15	Table Mountain basalt	3.81	2.05	23	1.9	3
8	Raker Peak dacite	3.80	2.15	26	2.0	4
12	1915 dacite	4.29	2.39	28	2.1	4
13	1915 mud flow	4.27	2.52	34	2.1	4
10	Raker Peak dacite	4.29	2.16	31	2.2	4
16	Chaos Jumbles dacite	4.32	2.53	32	2.2	3
34	Dacite tuff	4.53	2.80	39	2.5	4
11	Raker Peak dacite	4.80	2.65	40	2.6	2
14	Chaos Crags dacite	4.54	2.99	42	3.0	4
5	Manzanita dacite	4.73	2.91	49	3.1	2
33	Dacite pumice	4.43	3.11	46	3.2	3
6	Pre-Lassen dacite	4.58	2.95	47	3.2	3
9	Raker Peak dacite	4.30	3.34	51	3.6	4

* See text for estimation of analytical errors.

In order to check the stability of the Scintillscaler and the precision of replicate loadings of the sample dish, a sample of intermediate alpha activity was selected as an arbitrary standard (Sample 10, Raker Peak Dacite, Table 2). This sample was recounted at short intervals during, and after, the measurements on the Lassen suite (see Table 1). The arithmetic mean of the fourteen determinations in Table 1 is slightly under thirty net alpha counts per hour.

The extreme values are 35 and 26, corresponding to extreme deviations of about 17 per cent from the mean. The standard deviation was 2.5 alpha counts per hour. In the three-month period covered in Table 1, there seems to be a small systematic decline in the net alpha count of Sample 10. This decline could be due to a slight decrease in instrument sensitivity, or to a real decrease in the activity of the sample because of slower radon leakage or some other phenomena. This apparent decline was small compared to the statistical error and the experimental standard

deviation. A value of thirty-one net alpha counts per hour is given for sample 10 in Table 2, because the other Lassen samples were all counted in the first six weeks, covered in Table 1. These data show that the net alpha counts per hour given here are at least as reproducible as the fluorimetric uranium determinations (± 15 per cent).

Relative net alpha counts are used in this study because they are quite sufficient to detect significant differences between samples. Furthermore, there were no inter-laboratory standards of comparable rock type and low alpha flux available. The detailed and, at times, sad history of radon measurements (EVANS and GOODMAN, 1941; and DAVIS and HESS, 1949) and of chemical analysis of rocks in general (FAIRBAIRN *et al.*, 1953) demonstrate that absolute inter-laboratory comparisons can only be made on thoroughly homogenized and carefully analyzed standards. To facilitate later comparisons, National Bureau of Standards Sample 787, the monomineralic Carthage limestone was counted with the Lassen samples. A relative net count of 3.5 alphas per hour was obtained.

Table 3. Additional uranium analyses and relative alpha activities

Sample number	Sample description	Relative alpha counts per hour*	Uranium in parts per million	Number of replicate uranium determinations
34	Dacite tuff, Crescent Crater	41	3.1	2
40	Clay from Mudpot, Devil's Kitchen	36	3.0	4
25	Andesite, Painted Dunes	25	3.0	2
28	Quartz basalt, Old post-Cinder flow	22	2.5	3
38	Clay and water from Mudpot, Devil's Kitchen	23	2.3	4
2	Aggregate sample from Devil's Kitchen	33	2.2	4
27	Volcanic ash, Cinder Cone	26	2.1	3
30	1915 Lava with pumice	22	2.1	4
26	Volcanic ash, Painted Dunes	24	2.0	3
39	Quartz basalt bomb, Cinder Cone	16	2.0	2
4	Brokeoff Andesite Unaltered	24	2.0	4
29	Diatomaceous Earth, near Butte Lake	11	1.8	3
23	Andesite, 1851 flow, altered (?), Cinder Cone	21	1.7	2
24	Vesicular basalt, Cinder Cone	19	1.7	2
39	Flatiron andesite (altered) Devil's Kitchen	18	1.7	3
19	Ash, Cinder Cone	18	1.7	4
22	Quartz basalt, source of 1851 flow, Cinder Cone	18	1.6	2
20	Ash, Cinder Cone	28	1.4	3
31	Eastern basalt, Butte Lake	8	0.86	3
32	Pahoehoe Lava, Subway Cave (outside Lassen Park)	2	0.36	4

* See text for estimation of analytical errors.

Experiments indicate an effective geometry of about 32 per cent for the instrument used (REED, 1950; and this laboratory). The relative net counts per hour given in Tables 2 and 3 can be converted to estimated total alpha particles/square centimetre/hour by dividing by 12. The figure obtained would represent the number of counted alpha particles coming off the surface of the sample, not the total alpha flux in a given volume of the sample. The total alpha flux would depend upon a number of factors (see NOGAMI and HURLEY, 1948), including the distribution of the alpha emitters and the absorption of the sample. NOGAMI and HURLEY also discuss the merits of thick- versus thin-source alpha counting. The Lassen samples are well suited to thick-source alpha counting, because they are fine grained and, as is shown below, their alpha-particle activity is largely concentrated in the glassy phase.

DISCUSSION

Relationship of Radium and Uranium

The radon concentrations of the Lassen suite were determined by EVANS and WILLIAMS (1935). From their radon measurements they calculated the radium concentrations in twelve Lassen rocks. These values ranged from 0.28×10^{-12} gram/gram in basic lavas to 1.14×10^{-12} gram/gram in the more silicic lavas, with an observational uncertainty of 0.02×10^{-12} gram/gram. The equilibrium amounts of uranium would then range from 0.79 to 3.20 parts per million (10^{-6} gram/gram). The fluorimetric uranium analyses, which were made on an entirely independent sampling of the Lassen suite, range from 0.85 to 3.6 parts per million (see Tables 2 and 3), with an estimated uncertainty of less than ± 15 per cent of the amount present. A comparison of the equilibrium uranium values calculated from the radium values of EVANS and WILLIAMS (1932) and the fluorimetric uranium values is given in Table 4. Four of EVANS and WILLIAMS's samples are not listed, because comparable samples were not collected and analyzed fluorimetrically.

Table 4 indicates excellent overall agreement between the two methods of uranium determination. The largest difference, 0.79 versus 2.0 p.p.m., is in the Brokeoff andesite, Sample 4. This large difference may represent a real difference in the sample similar to the difference EVANS and WILLIAMS found in the Chaos Crags dacite and to the difference found in the Raker Peak dacite (see Table 4). However, the Brokeoff andesite values differ by 250 per cent of the lower value, whereas the difference in the Raker Peak dacite values is only 80 per cent of the lowest value. Any contamination after sampling would have to be of a very special type, since Sample 4 has the same relative alpha-particle activity to uranium ratio as the other Lassen samples (see below). This ratio, and the fact that the Brokeoff andesite is one of the older flows, suggest that radon and uranium are probably in equilibrium, and the difference is not due to a loss of radon. Examination of Table 4 will show that 2.0 p.p.m. uranium cannot be considered an unusually high value for a Lassen andesite. A petrographic examination of a thin section of Sample 4 showed no radical difference from the description given by EVANS and WILLIAMS. It is believed that Sample 4 may be from one of the more

dacitic parts of the Brokeoff andesite as described by WILLIAMS (1932) and that EVANS and WILLIAMS determined radon on a less dacitic part.

Aside from the Brokeoff andesite, the other seven examples show good agreement between the fluorimetric and calculated uranium determinations, although the two analyses were made on different samplings. The comparisons in Table 4

Table 4. Comparison of direct-fusion and fluorimetric uranium determinations

<i>Fluorimetric</i>			<i>Direct-fusion</i> (EVANS and WILLIAMS)		
<i>Sample No.</i>	<i>Rock description</i>	<i>U in p.p.m.</i>	<i>Sample No.</i>	<i>Rock description</i>	<i>U in p.p.m.</i>
31	Eastern basalt, Butte Lake	0.86	2	Basalt, NE Butte Lake	0.98
36	Raker Peak andesite	1.0	5	Andesite, Raker Peak	1.01
17	Flatiron andesite, Pilot Mountain	1.7	9	Andesite, Crystal Lake	1.96
4	Brokeoff andesite	2.0	6	Andesite, Brokeoff Volcano	0.79
12	1915 dacite	2.1			
13	1915 mud flow	2.1	11	Dacite (1915) Lassen Peak	1.96
7	1915 dacite + pumice	1.6			
30	1915 dacite + pumice	2.1			
16	Chaos Crags dacite	2.2	13	Dacite, Chaos Crags	1.97 2.64
33	Dacite pumice, Lassen Peak	3.2	8	Dacite pumice, Lassen Peak	2.24
8	Raker Peak dacite	2.0	14	Dacite, Raker Peak	3.20
10	Raker peak dacite	2.2			
11	Raker Peak dacite	2.6			
9	Raker Peak dacite	3.6			

are made on samples taken from a few yards to nearly four miles apart. Except for the Brokeoff andesite, all differences between the two sets of values can be easily accounted for on the basis of analytical errors and variations within the rock. Each set of data has an example of variation within a rock unit, and the Raker Peak case is particularly convincing because the variation in uranium content is paralleled by a variation in potassium content as is discussed below.

The data in Table 4 indicate that the relationship between uranium and radium in the Lassen suite is one of secular equilibrium to within analytical error. These data also independently confirm the direct-fusion method of uranium determination in samples of this type.

Relationship of Uranium and Potassium

EVANS and WILLIAMS (1935) found a positive correlation between radium and potassium in the Lassen suite. In the Chaos Crags dacite they found most of the radium concentrated in the potassium-rich glass phase first described and analyzed by HAGUE and IDINGS in 1883. A very definite positive correlation between

potassium and uranium is found in the samples listed in Table 2 (see Fig. 2). Allowing for a ± 10 per cent error in the uranium determination, a straight line can be made to pass through all nineteen points in Fig. 2. This linearity is preserved in the four samples of the Raker Peak dacite (Samples 8, 9, 10, and 11). The glassy phase then is the main carrier of potassium, radium, uranium, and

Fig. 2. Uranium versus potash.

probably thorium. These data do not exclude the possibility that the uranium is contained in very small crystals, e.g., zircons, within the glass (see below). This very linear relationship between potassium and uranium can be interpreted in terms of fractional crystallization with the exclusion of these elements from the crystalline phases formed and separated from the magma. The ionic size and co-ordination number with respect to oxygen of potassium and uranium are consistent with such an interpretation. The slope of a trend line in Fig. 2 is about 0.75 (K_2O in percent, U in p.p.m.), indicating that uranium was excluded more effectively than potassium from the crystalline phases precipitated from the magma. The correlation between potassium and uranium is another general form of expressing the correlation between silica and uranium, since both silica and potassium increase in the residual magma during the first stages of magmatic differentiation. It seems unlikely that there was any loss of uranium to a gaseous phase at Lassen, for a loss of uranium would deplete uranium relative to potassium in the later differentiates. The actual case is that uranium was concentrated relative to potassium in the later stages by the removal of some potassium into the

crystalline phases. These last observations agree with the conclusions of MASON (1954) regarding the unlikelihood of uranium halides forming under volcanic conditions where the rocks are molten.

If the "original magma" had a uranium content similar to the least uraniferous Lassen basalt (about 0.8 p.p.m.), and if fractional crystallization was the

Fig. 3. Uranium versus relative net alpha activities.

dominant mechanism, the Raker Peak dacite represents about 25 per cent of the volume of magma from which its uranium was derived. This figure of 25 per cent is similar to the figures obtained in analogous calculations made by WAGER and MITCHELL (1953) on the basis of trace element analysis of Hawaiian lavas. If the pahoe-hoe lava from Subway Cave, a few miles outside Lassen Park, is representative of the uranium content of the "original magma," the Raker Peak dacite represents only about 10 per cent of the volume of magma from which its uranium was derived.

Relation of Thorium, Uranium, and Relative Alpha Activity

A plot of the net relative alpha-particle activity versus uranium content of each sample is shown in Fig. 3. The solid circles represent the unaltered Lassen volcanics, and the open circles represent altered Lassen volcanics, including mud-pot clays. The open squares represent the Cinder Cone lavas and tuffs and the pahoe-hoe lava from Subway Cave. Pairs of values from these three groups fell

on the same point in a few cases. The main Lassen sequence (solid circles) shows a strong positive correlation between uranium content and relative alpha activity. The relative alpha activity is a measure of a complex of phenomena involving over twenty different alpha-emitting nuclides in the U^{238} , U^{235} , and Th^{232} decay series. Many of these nuclides contribute so little to the total alpha-particle activity that they may be omitted from this discussion. Thus, the entire U^{235} series may be neglected because it contributes only about 4 per cent of the total alpha activity from both uranium series, and about 2 per cent of the total activity from the U^{238} , U^{235} , and Th^{232} series at radioactive equilibrium, assuming a Th/U ratio of 3.

The interpretation of the relative alpha-particle counts is further simplified if radioactive equilibrium exists. Radioactive equilibrium probably exists in the Lassen samples, because U^{238} and Rn^{222} are in close equilibrium where they have been measured (see above and Table 4). This equilibrium could only exist if all intermediate members of the series are in equilibrium. If the U^{238} series is in equilibrium through Rn^{222} , the rest of the series requires only a hundred years or so to come to equilibrium. The entire Th^{232} series requires less than a hundred years to come to equilibrium.

Assuming for these samples that radioactive equilibrium exists in the U^{238} and Th^{232} series, it follows from the decay scheme that for each alpha particle emitted from U^{238} , seven alpha particles are emitted from the other members of the series on the average. Similarly, for each alpha particle emitted from Th^{232} , five alpha particles will be emitted from the other members of that series on the average. Since the specific activity of Th^{232} is about one-third that of U^{238} , we may write as a first approximation:

$$\frac{\text{number of alpha particles emitted}}{\text{}} = s_U + \frac{K 6_{Th}}{3} \quad (1)$$

where $K = Th/U$. K is equal to about 3 in most types of rocks and meteorites. From equation (1) it follows that at equilibrium change of the Th/U ratio from 3 to 2 would reduce the number of alpha particles emitted by about 14 per cent. Thus, the total alpha particles emitted to uranium ratio is a rather insensitive measure of Th/U ratios.

Another point to be considered is the relation between the total number of alpha particles emitted, and the relative alpha count measured. The alpha particles from the U^{238} and Th^{232} series do not have the same energies, and thus their likelihood of being counted is not the same (see NOGAMI and HURLEY, 1948). No correction for this difference in energies is made here, because the precision of the data does not justify it. If a Th/U ratio of 3 is assumed in the average Lassen sample, it is unlikely that the Th/U ratio has been shifted to less than 2 or to more than 4 during differentiation. KIRSH and HECHT (1938) believed that differentiation finally separates thorium and uranium, but the data presented here give no indication that this separation has begun to take place at Lassen.

The Cinder Cone samples in Fig. 3 (open squares) show the widest deviations from the main trend. This may have been caused by selective leaching of uranium from some of the weathered samples. Their deviating from the main Lassen sequence is not inconsistent with the view of FINCH and ANDERSON (1930) that

these are contaminated rocks. Some of the open circles in Fig. 3 are well off the main trend, and these are weathered Lassen lavas; selective leaching of uranium is probably the cause. The open circles in Fig. 3, that are on the main Lassen sequence, are samples of mud-pot clay. This would indicate that the mud-pot clays had about the same Th/U ratio and degree of radioactive equilibrium as the main Lassen sequence, which is surprising considering the extreme weathering taking place in the hot, acid mud-pots. It was hypothesized that zircons in the mud-pot clays were responsible for much of the observed uranium concentration and alpha particle activity. The autoradiographic work of PICCIOTTO (1950) on European igneous rocks showed that much of the uranium in these rocks was contained in zircons, as well as sphene and apatite. EVANS and WILLIAMS (1935) reported zircons in some of the Lassen mud pots, and HAGUE and IDDIGS found zircons and apatites in the Lassen dacite.

Zircons were separated by means of carbon tetrabromide from mud-pot clay Samples 38 and 40 in Table 3. The zircons separated were single crystals 10 to 30 microns parallel to the *c*-axis and 5 to 10 microns perpendicular to the *c*-axis. It was not difficult to locate zircon specimens in the heavy mineral separate. Most examples had the common prismatic and pyramidal forms, though some appeared corroded. Most of the zircons observed were quite transparent, but one liquid inclusion and some mineral inclusions, perhaps thorite, were noted. Quantitative attempts were made to separate the high-density minerals from the mud-pot clay. The alpha activity of the low density fraction and the uranium content of the tiny, heavy mineral separate could then be determined. Both sodium-hydroxide size segregation (PENNINGTON and JACKSON, 1947) and carbon-tetrabromide methods were tried with inconclusive results. With the best separation achieved, the relative alpha activity of the light-clay fraction was decreased about 50 per cent.

The zircons, together with similar resistant minerals and rock fragments, are believed to contain the uranium found in the mud-pot clays. These materials would also be capable of retaining the uranium daughters and the thorium series, so that the material would have a uranium to alpha-activity ratio characteristic of the Lassen suite (Fig. 3).

CONCLUSIONS

The main conclusions of this study are:

- (1) The direct fusion and fluorimetric methods of uranium determination agree closely on the uranium content of the Lassen suite of rocks.
- (2) This agreement is both a result and a proof of secular radioactive equilibrium between radon and uranium. This equilibrium implies that there is radioactive equilibrium throughout the thorium and uranium series in these rocks.
- (3) During differentiation at Lassen, uranium, potassium, and probably thorium were concentrated in the residual magmas at almost the same rate. Fractional crystallization is adequate to explain the observations.
- (4) Some of the uranium of the Lassen lavas is present in small zircon crystals.

Acknowledgements—This research was done at the University of Wisconsin, Madison, Wisconsin, under Atomic Energy Commission Research Contract At(11-1)-178, Professor FARRINGTON DANIELS, Director. The author would like to thank his

colleagues, particularly Dr. DONALD F. SAUNDERS, for their assistance in this work. The many courtesies of the Director and staff of Lassen Volcanic National Park, California, provided indispensable aid.

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III-4

THE DISTRIBUTION OF ALPHA-RADIOACTIVITY IN
NATIVE VEGETATION¹

J. T. CURTIS AND RALPH DIX²

Introduction

In the phenomenon of "solute pumping" by vegetation, various elements are removed from the subsoil by the deep roots of trees and herbaceous plants, moved to the aerial leaves, and then de-

posited on the surface of the soil when those leaves drop. Many of the elements are not leached back down to the subsoil but are held in the surface layer, thus effecting an enrichment or accumulation at the top and a depletion below. The actual rate of this "pumping" differs among species and might be quite unlike in different forest types, depending upon the proportionate species composition of the dominant tree layer (7).

¹ This work was supported in part by funds from U.S. Atomic Energy Commission Contract no. AT (11-1)-178.

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This process may be accounted for solely by normal movement of elements along diffusion gradients from the soil to the root, with upward movement in the tree and deposition in the leaves owing to transpirational processes. In many instances, however, plants have the ability to take up certain elements against a concentration gradient. A well-known case of accumulation is that of rare earths by hickory trees (*Carya* sp.). Soils in the Appalachian Mountains with a concentration of 0.02% of rare earths on a dry-weight basis supported hickory trees whose leaves contained up to 2.5% of their ash in these elements, with yttrium making up 38% of the total (13). Eleven different rare earths were recorded for hickory. More recently, BRAUCHLI (2) in the same area has shown that germanium may be present in relatively high concentrations in the humus layer (A_0) of the forest soils.

Cobalt, copper, manganese, and zinc were shown by BEESON *et al.* (1) to be differentially accumulated in various species of woody plants on the Atlantic Coastal Plain. Swamp blackgum (*Nyssa sylvatica*), for example, contained a maximum of 118 p.p.m. of cobalt on a dry-weight basis.

Leaf analysis, in which living leaves or other plant parts from the dominant vegetation of a particular site are analyzed for commercially valuable metals, has long been used as a technique of geobotanical prospecting (9). The method has been used for lead, zinc, copper, gold, silver, and other metals of commercial importance. CANNON (4) reported on the distribution of uranium in certain desert plants and its use in the discovery of uranium deposits. When the physiological process involved is simple diffusion, the leaf-analysis method may give valuable results; but, if absorption by the

plant against a concentration gradient is involved, then leaf analyses may be misleading. The classic case was reported by MILLER and BYERS (10), who found, on a dry-weight basis, 1250 p.p.m. of selenium in *Astragalus bisulcatus* and only 3 p.p.m. in *A. missouriensis*, both growing in soil with 2 p.p.m.

The present paper presents a study of the distribution of alpha-emitting radioactive substances and other rare elements in several types of native vegetation.

Material and methods

A number of native stands were used that had been examined previously in a study of Wisconsin vegetation (3, 5, 6). They were undisturbed remnants and as such presumably represented a balance among plants, climate, and geology. An effort was made to distribute the stands so that each major vegetation type was represented over its entire range in Wisconsin. In addition, all the types in each of several regions were examined. This rather crude stratification method of sampling was employed so that effects resulting from possible regional differences in climate and geology might be separated from vegetational effects.

In Wisconsin there is a shift from a mixture of prairie and hardwood forest in the southwestern part of the state to a mixture of conifer forest and hardwood forest in the northeastern section. This transition is accompanied by a distinct difference in climate, but it also is correlated with changes from sedimentary rocks of dolomite and calcareous sandstone to igneous rocks of granitic nature, from driftless topography to a heavy covering of glacial drift, and from a deep loess blanket to no loess cover. The stratified sampling enabled these correlated factors to be separated in part but could

not effectively differentiate between the bedrock geology and the loess cap, especially in the region of the coniferous forest types. Further attempts to separate vegetational from geological effects were made by studying a series of stands in the Cumberland Mountains of Kentucky and the Great Smoky Mountains of Tennessee, where the hardwood-to-conifer forest transition could be found on loess-free soils over uniform bedrock on an altitudinal basis.

Within each forest stand, collections were made beneath mature individuals of the tree species which was the leading dominant. In every case, samples were collected from the humus (A_0) and topsoil (A_1) layers separately. In addition, samples from the subsoil (C) layer and samples of living leaves from the tree were collected in many stands. In the case of grassland, samples were collected from the A_0 and A_1 only. The A_0 layer was interpreted to include the litter, fermentation, and humus layers (12) where these were present. The A_0 samples were collected from a measured area of the soil surface and their dry weights determined. In this way, analytical results could be reported on both an area and a weight basis. Aliquots of the mineral soil samples (A_1 and C layers) were analyzed for calcium content and for pH value.

For further tests, the A_0 , A_1 , and C layer samples were burned in open crucibles. The crude ash was then further heated in an electric muffle furnace at 600° C. for 8 hours. The ash was analyzed for several heavy metals and rare earths by spectrographic methods. Uranium was determined colorimetrically. Alpha-emitters were determined by a scintillometer (11), with results presented as the average number of alpha counts per square centimeter of test sample per hour (alpha cph/sq cm) from the surface

of an "infinitely thick" layer. These alpha counts give a direct measure of intensity and a relative measure of concentration but cannot be interpreted directly in terms of total amounts of active elements present. Some indications of the quantity factor under natural community conditions were obtained by multiplying the alpha-count value by the ash weight in pounds per square foot of the original soil area, thus arriving at a relative indication of the total quantity per unit area of soil. No determinations of the chemical nature of all the substances responsible for the alpha-radioactivity were made. It is probable that radium and uranium are the main active agents, since radon gases would be driven off in the ashing process, but it cannot be assumed that these two were always present or in the same proportions.

The final data were recorded on a specially prepared form with blanks for the several measured variables, one form for each stand. Then the forms were sorted in decreasing order for any one variable and separated into appropriate size classes. Following this, the average value was calculated for each of the other variables for each size class of the first. This very simple statistical correlation was employed in place of more rigorous tests because of the relatively small number of samples available. The results, therefore, must be interpreted as preliminary or exploratory in nature.

Results and discussion

In a series of tests in eleven stands in the major vegetation types, the vertical distribution of alpha-emitting substances from the subsoil to the living leaves was found to be remarkably similar in Wisconsin and the southern Appalachians. In both areas the source region in the C layer of the soil is very low in alpha-

radioactivity, with values ranging only from 0.50 to 1.81 cph/sq cm and averaging 1.04 cph. Activity in ash of the living leaves is appreciably higher, averaging 2.06 cph/sq cm, with a range of 1.03 to 4.85. The A_0 layer is highest of all, with an average count of 9.19 and a range from 4.15 to 14.60 cph/sq cm.

These profile studies showed that there is a very considerable apparent accumu-

lation of alpha-emitting substances in the A_0 layer of a number of widely divergent plant communities in contrast to a uniformly low concentration of such materials in the subsoil. This implies some activity of the plants themselves, and therefore a difference among different plants might be expected. When the Wisconsin samples were averaged according to major vegetation type, it was

found that the degree of apparent accumulation of alpha-emitters varied with different vegetations, but the nature of the relationship was not clear, since geographically adjacent but ecologically unrelated communities were more similar than distant but related communities. A further analysis of the samples in regard to a variety of geological and climatic variables is shown in table 1. The bedrock, glacial covering, depth of loess, and temperature are independent variables not affected by the vegetation, while the soil calcium and soil pH are, in part at least, the result of vegetational activities. The alpha-radioactivity of plant litter is inversely proportional to depth of loess, amount of available soil calcium, soil pH, glacial age of the soil, and average July temperature. Unfortunately, all these factors tend to vary concomitantly from southwestern Wisconsin to northeastern Wisconsin, with the two regions separated by a tension zone (6) in which pronounced changes in vegetation are correlated with steep climatic gradients. On either side of this tension zone, conditions of geology and climate within each region are relatively uniform. Separation of the influence of vegetation from that of physical environment on the results reported might be possible within one of the regions, although not in the state as a whole. A further check on the role of vegetation in affecting the concentration of alpha-emitting substances was made by the series of samples from the southern Appalachians, where a number of plant communities similar in floristic composition to those of Wisconsin are found.

The average conditions for all stations in the two portions of Wisconsin and in the Appalachian region are summarized in table 2. The resemblances between northeastern Wisconsin and the

TABLE 1

CORRELATION OF ALPHA-RADIOACTIVITY IN
THE A_0 LAYER AND ENVIRONMENTAL
FACTORS IN WISCONSIN

	Average alpha cph/sq cm
Bedrock	
Dolomite.....	4.32
Sandstone.....	4.33
Igneous.....	7.90
Glacial covering	
Driftless.....	2.66
Illinoian.....	3.30
Wisconsin (Cary).....	5.44
Wisconsin (Mankato).....	6.01
Loess covering (depth)	
0- $\frac{1}{2}$ ft.....	6.81
$\frac{1}{2}$ -2 ft.....	4.35
2 ft. plus.....	3.27
Soil calcium (lb/acre)	
0-2000.....	6.40
2000-4000.....	4.57
4000-6000.....	3.97
Soil pH (A_1 layer).....	
4.0-4.9.....	7.23
5.0-5.9.....	6.04
6.0-6.9.....	4.13
7.0-7.9.....	3.92
8.0-8.9.....	3.41
July temperature ($^{\circ}$ F.)	
64-65.....	9.43
66-67.....	7.06
68-69.....	5.48
70-71.....	3.64
72-73.....	3.21

lation of alpha-emitting substances in the A_0 layer of a number of widely divergent plant communities in contrast to a uniformly low concentration of such materials in the subsoil. This implies some activity of the plants themselves, and therefore a difference among different plants might be expected. When the Wisconsin samples were averaged according to major vegetation type, it was

Appalachian region are much greater than between the northeast and the southwest of Wisconsin. This resemblance is also present in the vegetation itself, since maple-beech-hemlock forests and other conifer-hardwood forests are found in the two similar regions but are lacking in the prairie-forest region in Wisconsin.

Within southwestern Wisconsin three different communities had essentially the same intensity of alpha-radioactivity in the ash of their A₀ layers—maple-basswood forests with an average of 3.27 cph, oak-hickory forests with 3.36 cph, and

forest region. Plant communities in the Appalachian Mountains which are floristically related to those of northeastern Wisconsin had intensities or quantities which closely resembled those of their Wisconsin counterparts. Thus, the beech-hemlock forests had an average alpha count in the A₀ layer of 10.71 and a quantity factor of 0.87, while the spruce-fir forests averaged 20.70 cph but had a quantity factor of 0.88 because of a lesser amount of litter per unit area. On the other hand, the mixed-mesophytic hardwood forests of the Appalachians averaged 6.82 cph with a quantity factor of

TABLE 2
COMPARISON OF SOUTHWESTERN WISCONSIN, NORTHEASTERN WISCONSIN, AND THE SOUTHERN APPALACHIAN MOUNTAINS

Character	Southwestern Wisconsin	Northeastern Wisconsin	Southern Appalachians
Number of stations.....	41	28	8
Alpha cph, A ₀ layer.....	3.39± 0.15	7.25± 0.69	11.86± 1.05
Alpha cph, A ₁ layer.....	1.86± 0.73	2.72± 0.42	3.38± 0.39
Soil pH, A ₁ layer.....	6.8	5.4	4.7
Depth of loess (ft.).....	3.14	0.47	0
July temperature, ° F.....	72.4	67.0	66.2
Dry weight of A ₀ layer (lb/sq ft)...	0.189	0.390	0.575
Ash weight of A ₀ layer (lb/sq ft)...	0.034	0.078	0.065
Ash weight X alpha cph, A ₀	0.11	0.56	0.77

tall-grass prairies with 3.47 cph. Since the amount of litter and its ash content were also similar, the quantity factor (alpha count times ash weight in pounds per square foot) was likewise uniform in the three communities, with averages varying only from 0.11 to 0.12. In northeastern Wisconsin, however, the three major communities present there differed considerably in the A₀ layer both in alpha-radioactivity and in the quantity factor. The forests dominated by pine trees averaged 6.11 cph, with a quantity factor of 0.19; the maple-beech-hemlock forests averaged 7.93 cph and 0.50; and the spruce-fir forests averaged 6.70 cph and 0.89. All these values are much higher than equivalent figures in the prairie-

0.34, which is in line with their closer vegetational relationship to the maple-basswood forests of southwestern Wisconsin. Thus it appears that the general level of alpha-radioactivity in the A₀ layer of the native plant communities is related to the geology and climate of the region where the communities are located but that, at least within the environment which will support mixed coniferous forests, there may be a differential activity correlated with the species of dominant plants. In both Wisconsin and the Appalachians, hemlock (*Tsuga canadensis*) produces humus with the greatest intensity of alpha emission of any species, averaging 9.14 cph in Wisconsin and 9.87

cph in the Appalachians. This behavior of hemlock is not correlated with a physiological ability of the species to accumulate alpha-emitting substances in the leaves, since the radioactivity in the leaves differs but little in the various tree species in any one region. Table 3 shows the alpha cph for the ash from living leaves for all species tested in the present study. The sample of herbs is too small

TABLE 3
AVERAGE ALPHA-RADIOACTIVITY FOR ASH OF
LIVING LEAVES OF ALL SPECIES

	Alpha cph/sq cm
Herbs	
<i>Astragalus canadensis</i> (Wis.).....	0.6
<i>Thermopsis rhombifolia</i> (S. Dak.).....	1.1
Coniferous trees	
<i>Abies balsamea</i> (Wis.).....	2.0
<i>Picea mariana</i> (Wis.).....	1.3
<i>Tsuga canadensis</i> (Wis.).....	2.0
<i>T. canadensis</i> (Appal.).....	3.1
Deciduous trees	
<i>Acer saccharum</i> (Wis.).....	2.4
<i>A. saccharum</i> (Appal.).....	2.3
<i>Carya cordiformis</i> (Appal.).....	2.1
<i>Fagus grandifolia</i> (Wis.).....	2.3
<i>Populus tremuloides</i> (Wis.).....	1.2
<i>Quercus rubra</i> (Wis.).....	1.7
Ericaceous shrubs	
<i>Andromeda glaucophylla</i> (Wis.).....	4.5
<i>Chamaedaphne calyculata</i> (Wis.).....	3.2
<i>Kalmia polifolia</i> (Wis.).....	3.1
<i>Ledum groenlandicum</i> (Wis.).....	3.4
<i>Rhododendron maximum</i> (Appal.).....	4.9
<i>Vaccinium angustifolium</i> (Wis.).....	3.1

to warrant any firm conclusion, but the ericaceous shrub average is based on fifteen different samples of six species and clearly indicates that this family is effective in the physiological accumulation of alpha-emitting substances.

Since the high values for humus under the hemlocks and in conifer forests in general are not due to high concentrations in the living tree leaves, they must be dependent upon some property of the A_0 layer itself. The most obvious correlation is with the quantity of the layer per unit area. When the A_0 weights for all stations are grouped into three size

classes (0-0.3, 0.3-0.6, and 0.6-0.9 pounds per square foot) and the alpha counts are averaged for each class, the resulting values increase from 4.35 to 6.15 to 8.46. The high A_0 weights are associated with a mor type of humus, while low weights are found in mull humus. The latter type of humus tends to decompose rather quickly, often disappearing in the summer following the shedding of the leaves, while the mor humus is much more resistant to decay and may require 3 or more years for any given annual crop of leaves to decompose. The mor humus is characteristically produced by acid leaves, such as conifer needles, and is typically found in cool regions of high humidity with a soil low in bases.

High alpha-radioactivities are thus associated with high soil acidity, low soil calcium, low summer temperatures, and coniferous trees. This is a typical multiple-factor relationship, in that no one factor can be separated easily from the rest as being the cause or even the most important cause. The climate and the soils combine to favor the growth of coniferous forests, and all three result in mor humus which has the ability to retain high concentrations of alpha-emitting substances.

Certain other rare elements are similarly accumulated in the same medium. This is shown in table 4, where the average concentration of a number of elements in the A_0 layer is correlated with the alpha cph of the same samples in three size classes. Boron, copper, gallium, lead, silver, and zirconium increase with increasing alpha count and hence are most abundant in the mor humus type. On the other hand, lanthanum, nickel, vanadium, and yttrium are present in high concentrations in the mull humus types. It is probable that the chelatin

systems (8) or other adsorbing mechanisms differ in the two kinds of humus. Further investigations of the specific nature and activity of these systems would appear to hold great interest. The relatively high concentrations of many of the rare elements, both radioactive and non-radioactive, in the humus layers of native plant communities may be of considerable importance in the life history of humus-dwelling plants. The tree species whose seeds germinate directly in the A₀ layer, and the numerous forest herbs whose roots and crowns are imbedded within the layer, may be subjected to concentrations of unusual elements far higher than those normally experienced by crop plants or other plants which are rooted in mineral soil. It is possible that the well-known failure of many tree seeds to germinate in the humus may be related to this condition.

Summary

1. Analysis of the soil and of the plants in a variety of plant communities in Wisconsin and the southern Appalachian Mountains for alpha-emitting substances showed that a considerable concentration occurred in the A₀ soil layer. This concentration was greatest in coniferous forests growing on loess-free, igneous soils in cool climates. Such forests had an acid, mor humus, and the apparent accumulation was correlated with certain unknown properties of the humus, since the tree species showed uniform and relatively low concentrations in their living leaves. The humus beneath

hemlock trees showed the greatest alpha-radioactivity.

2. A number of other rare elements were similarly concentrated in the mor humus of coniferous forests, including copper, gallium, lead, and zirconium. The high concentrations reached by these elements and the radioactive substances, indicate that the immediate soil

TABLE 4
CORRELATION OF ALPHA-RADIOACTIVITY AND
RARE ELEMENTS IN A₀ LAYER. AVER-
AGES OF ALL SAMPLES

CHARACTER OF A ₀ LAYER	ALPHA CPH/SQ CM OF A ₀ LAYER		
	0-5	5-10	10+
Dry wt/sq ft (lb.)...	0.24	0.32	0.63
Ash wt/sq ft (lb.)...	0.04	0.04	0.13
Elements present in ash (p.p.m.)			
Boron.....	155	200	200
Cobalt.....	28	17	36
Copper.....	132	141	155
Gallium.....	8	16	20
Lanthanum.....	75	0.4	0
Lead.....	157	254	295
Nickel.....	86	76	72
Silver.....	1.8	2.0	5.0
Uranium.....	1.6	2.0	2.0
Vanadium.....	75	60	55
Yttrium.....	16	12	12
Zirconium.....	87	97	169

environment of tree seedlings and many forest herbs may be very different from that expected from ordinary soil analyses in the region.

✓ We gratefully acknowledge the aid of Drs. FARRINGTON DANIELS, JOHN ADAMS, GRANT COTTAM, and RICHARD WARD, all of the University of Wisconsin, in various phases of the work.

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Distribution of Alpha-Radioactivity in Certain Forest Types

It is known that various types of forests accumulate calcium and other bases in the organic matter layer at the surface of their soils (1). In the current study, a similar accumulation was found for alpha-emitting radioactive substances.

Table 1. Vertical distribution of alpha-radioactivity. Units are counts per hour, per square centimeter.

Vertical position in forest	Average	
	Wis.	S. Appalachians
Living leaves of dominant tree	1.74 ± 0.21	4.63 ± 0.51
A ₀ layer beneath dominant tree	8.28 ± 0.79	12.68 ± 1.13
A ₁ layer of soil	4.32 ± 0.68	3.31 ± 0.39
C layer of soil	1.11 ± 0.10	0.85 ± 0.08

Eighty stands of hardwood and conifer forest in Wisconsin and in the southern Appalachian region were examined in 1953 and 1954 for alpha-radioactivity by the scintillometer method of Ockerman and Daniels (2).

Analyses were made of leaves of the dominant trees, of the dead and decomposing litter (A₀ layer) beneath those trees, and of the topsoil (A₁ layer) and subsoil (C layer). All samples were ashed at 600°C for 8 hours, ground to pass 100 mesh, and stored for 2 to 4 weeks before testing. The results are presented

as counts per hour, per square centimeter of the test surface in an "infinitely thick" layer (3). The results for individual samples are the averages of duplicate tests, each of which was counted to a statistical precision of ± 20 percent at the 90-percent confidence level by the accumulation of at least 70 counts above background. The background counts themselves did not exceed 0.1 to 0.2 counts/hr cm². The variations shown in Table 1 are standard errors.

The vertical distribution of alpha-radioactivity from subsoil to living leaves was similar in all forest types that were examined in both geographic regions, as shown by the average values in Table 1. The subsoil values were remarkably constant in all stands, but the intensity of the maximum activity in the A₀ layer varied greatly in different forest types. Hardwood forests in the prairie-forest border region of southwestern Wisconsin (4), which were dominated by species of *Quercus*, *Carya*, *Tilia*, or *Acer*, were uniformly low in alpha-radioactivity, while mixed conifer-hardwood or pure conifer forests in northeastern Wisconsin, the Cumberland Mountains, and the Great Smoky Mountains were usually high in activity (Table 2). The highest values in the A₀ layer were found in forests that were dominated by species of *Abies*, *Picea*, *Tsuga*, and *Fagus*. All such forests examined were characterized by a relatively low July temperature (67°F or less), a soil acidity of pH 5.5 or less, and an A₀ layer of the mor humus type (1)

Table 2. Alpha-radioactivity of the A₀ layer in different forest types. Units are counts per hour, per square centimeter.

Species dominant in forest	Average		
	S.W. Wis.	N.E. Wis.	S. Appalachians
<i>Acer saccharum</i>	2.63	6.77	8.35
<i>Tilia americana</i>	3.30		
<i>Quercus</i> sp.	3.28		
<i>Carya</i> sp.	3.42		8.46
<i>Pinus</i> sp.		5.11	
<i>Fagus grandifolia</i>		6.61	8.75
<i>Tsuga canadensis</i>		9.14	9.87
<i>Abies</i> sp.		6.70	20.70

which weighed 1.5 kg or more per square meter. The retention of the alpha-emitting substances in the mor humus may be related to the specific nature of its chelating humic acids (5). Further work on this relationship is in progress.

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17 October 1955

III-6

RADIOACTIVITY IN GROUND AND SURFACE WATER

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ABSTRACT. Values for the uranium content and total radioactivity of some underground and surface waters are presented for samples from 77 localities, largely in the United States. The uranium content for these samples ranges between 0.02ppb and 460ppb. The uranium content and total radioactivity of water from carnotite-bearing beds in the Grand Junction, Colorado area are spectacularly high when contrasted with values for water from non-mineralized beds.

Uranium content and total radioactivity was determined from residues obtained by evaporation of water samples. The total radioactivity of these residues is shown to change through time. (auth)

INTRODUCTION

General statement.—A portion of the geochemical cycle of uranium includes the transportation of the element by water, both on and beneath the surface. Little, however, is present in the literature on the uranium content of such natural waters. For instance Kuroda (1953) in a compilation of data on the radioactivity of natural waters lists uranium values for one locality in Japan and two in Portugal. Furthermore, most references to the radioactivity of natural waters emphasize sea water, and mineral and thermal springs. For these waters values for radium, radon, thoron, and total activity expressed in radium equivalent are most common. As an exception to this, however, Adams (1954) has listed the uranium content of some surface waters in Wisconsin.

The investigations here reported are primarily concerned with the uranium carried in ground water and secondarily with that in surface water. Brief consideration is given to the nature of other radioactive elements found in these waters.

Purpose of investigation.—This study was begun to determine the amount of uranium carried in underground waters and, if possible, the nature of additional radioactive elements. The investigations were also pursued to establish whether or not the radioactivity of ground water might be useful in prospecting for radioactive deposits.

The investigation has produced some values for the uranium content of underground and surface waters from various environments, and some rudimentary speculations on other radio elements in these same waters. Furthermore it seems feasible to use the radioactivity of water in geochemical prospecting under certain conditions.

Acknowledgments.—This study is part of a general program supported by funds granted by the U. S. Atomic Energy Commission to the University of Wisconsin under University contract No. AT (11-1)-178. The project since its inception in 1951 has been under the general direction of Professor Farrington Daniels, Chairman of the Department of Chemistry, University of Wisconsin. Uranium analyses in this report were made in the analytic section of the project under the supervision of Dr. J. A. S. Adams, now of the Department of Geology, Rice Institute. Dr. Adams has also criticized this report in manuscript form. The bulk of the alpha count measurements were made in the Department of Chemistry at Wisconsin by Mr. John Ockerman, now of the Ray-O-Vac Co., Madison, Wisconsin. A few of the alpha counts were

made by Miss Joyce Bauer, also of the Wisconsin Chemistry Department. Dr. M. Starr Nichols, Assistant Director of the Wisconsin State Laboratory of Hygiene at Madison kindly provided analyses of the fluorine content of certain waters.

The writers are indebted for assistance in the collection of samples to Mr. William A. Oesterling, Alcoa Mining Company, and Mr. E. A. Brecke, Ozark-Mahoning Co., both of Roseclaire, Illinois, to Dr. Henry Faul, and Mr. David Phoenix, both of the U. S. Geological Survey.

METHOD OF INVESTIGATION

Collection of samples.—Samples were collected by the authors from various underground and surface localities in Wisconsin, Illinois, Kentucky, Texas, New Mexico, and the Colorado Plateau states of Utah and Colorado.

A total of 77 water samples from various underground and surface localities are reported on in this paper. Their general distribution is given in table 1. Of these 68 were 7.6-liter (2-gallon samples), 5 were 8-liter samples and 2 were 7-liter samples. The sample was evaporated to dryness in a steel pan and the residue, usually amounting to a few grams, was removed by scraping. It is estimated that more than 95 percent of the residue obtained from each sample was recovered. In all cases evaporation was carried on within a few days of the collection of the sample, and in many instances only a few hours elapsed between collection of the sample and evaporation. The residues were later analyzed in the laboratory.

TABLE 1
General Distribution of Water Samples Discussed in this Report

Location	No. of Samples
Wisconsin	50
Southern Illinois-Western Kentucky	8
Colorado Plateau in vicinity of Grand Junction, Colorado	8
Texas Panhandle	6
Canada	3
Others	2
Total	77

At the time of collection the approximate pH of the water was determined with a colorimetric field test using phenyl red. Samples which appeared turbid were filtered before evaporation.

Alpha counts.—The radioactivity of the residues was measured in terms of alpha counts per hour using scintillation counters.¹

A circular sample dish 2 inches (5.08 cm) in diameter contains a "thick source" of the sample. The distance between the counting surface of the sample and the phosphor screen is 0.78 cm. The counting geometry has been estimated by Ockerman as about 33 percent.

The alpha scintillation counters used were of the type described by Reed (1950). Some of the counters were constructed by Mr. John Ockerman at the Department of Chemistry, University of Wisconsin. Others were commercially manufactured units purchased from the Nuclear Instruments and Chemical Corp., Berkeley, California.

Samples were counted long enough to obtain a standard deviation of less than 10 percent. Most of the alpha counts reported in tables 1-4 were obtained on residues from 6 to 9 months after evaporation of the water.

The number of alpha counts per hour of a sample is a measure of the radioactivity of the residue only at the time of counting. As discussed later the radioactivity of the sample changes with time, and it is therefore impossible to obtain a check of the alpha counts of any one sample by later counting (table 2). Furthermore, because the sample counted was a residue obtained by evaporation, any radioactive gases such as thoron or radon which may have been present in the original water sample would not be present in the residue at any time, being driven off by the process of evaporation. Despite these facts the total alpha counts give at least a relative measure of the intensity of radioactivity in the residue and hence in the water from which it was derived.

TABLE 2
Change of Total Radioactivity of Water Residue with Time

Sample No. 5-5-25. Eagle Hutson mine sump, Salem, Ky.			
U p.p.b. (water) = 0.5 p.p.b. Wt. residue = 2.7 g.			
Time (months)	1/2	9	29
U-eq. p.p.b.	34	13	15
U/U-eq. (%)	1 1/2	4	3
Sample No. 9-3-1. Cactus Rat Mine seep, Colorado Plateau			
U p.p.b. (water) = 100 p.p.b. Wt. residue = 11.4 g.			
Time (months)	2	6	23
U-eq. p.p.b.	370	520	380
U/U-eq. (%)	27	19	26

Uranium content of the residue.—The uranium content of the individual samples of residue was determined under the supervision of Dr. Adams using the fluorimetric method described by Grimaldi, May and Fletcher (1952). Repeated analyses were found to fall within the range of a standard error originally estimated to be between 10 and 15 percent.

Uranium content of the water.—The uranium content of the original water sample was obtained by the following formula:

$$\frac{\text{Uppb}}{\text{(water)}} = \frac{\text{Uppm}}{\text{(residue)}} \times \frac{\text{gms. residue}}{\text{gms. water evaporated}} \times 10^3$$

Total radioactivity of the water.—Uranium accounts for only a portion of the radioactivity of the original water. An attempt was made to determine the total radioactivity of the water in terms of uranium equivalent using the following formula:

$$\frac{\text{U-equiv. ppb}}{\text{(water)}} = \frac{\text{alpha cph}}{\text{(residue)}} \times 2 \times \frac{\text{gms. residue}}{\text{gms. water evaporated}} \times 10^3$$

The factor of "2" was determined empirically in the laboratory where it was found that standard water samples gave one alpha cph for 2 ppm of uranium.

The values of uranium-equivalent, however, are at best an approximation of the total radioactivity of the original water. In addition to the errors

inherent in residue recovery in alpha counting and in uranium recovery other considerations limit the precision of the final figures of uranium-equivalent. Thus radioactivity of the residue changes through time as already mentioned, and thus the alpha counts represent only a measure of the radioactivity of the residue at time of counting. Secondly, radioactive gases in the original water would be lost in evaporation and cannot be represented in the resulting residue.

Therefore the values of uranium-equivalent given for the original water sample are approximations only. The same is true of the percentage of the radioactivity of the original water due to uranium. This value is obtained by dividing the uranium content of the water by the uranium equivalent of the radioactivity of the water in ppb and multiplying by 100. Nevertheless the figures probably have a qualitative value although their degree of precision is difficult to judge.

Procedural checks and conclusions.—Procedural checks were made in the laboratory with standard and "spiked" water samples to determine (1) the proportion of residue recovered after evaporation of the water, (2) the proportion of the uranium recovered from the residue, and (3) the alpha counts produced by a given quantity of uranium in the residue. These checks showed (1) that at least 95 percent of the residue is recovered by scraping, (2) that at least 70 percent of the uranium is recovered from the residue sample, and (3) that 2 ppm of uranium yields one alpha count per hour.

On the basis of these facts and in view of the fair consistency of the values for the uranium content for different samples of waters of the same general type, it is felt that the uranium content of residue and original water as given in the tables to follow have quantitative significance. The validity of these values is further emphasized by the fact that Adams (1954) obtained values for the uranium content of Wisconsin surface waters similar to those reported in table 9. Adams obtained his data by the fluorimetric analysis of water samples rather than by the analysis of residues as in this study.

The values in uranium equivalent for total radioactivity of the original water and the values for the percentage of uranium of total radioactivity in the original water are approximations only, as previously indicated. Despite this these values are probably of the correct order of magnitude.

The data in the following sections are reported with the full appreciation of the limitation imposed by the method of the investigation here reported.

URANIUM CONTENT AND RADIOACTIVITY OF WATER

Data for 73 of the 77 water samples collected are listed in tables 3 through 9. The four samples not tabulated are discussed in the text.

Ground water from the Colorado Plateau.—Table 3 lists data on waters from aquifers in the uranium mining district of the Colorado Plateau in the vicinity of Grand Junction, Colorado. Five samples were collected from mineralized (carnotite) aquifers and three from non-mineralized aquifers. The table clearly shows that the waters from the mineralized areas are more radioactive than those from the non-mineralized aquifers. In uranium content waters from mineralized aquifers range from 100 to 460 ppb, whereas

TABLE 3
Data on Samples from Localities
on the Colorado Plateau in Colorado and Utah

Sam- ple No.	Location	Source	Aquifer	pH	Residue				Water		
					Weight	Uranium ppm	Alpha cph	Time elapsed to count (months)	Uranium ppb	Uranium equiv. ppb	U/U-eq. (%)
Mineralized Aquifer											
9-3-1	Cactus Rat Mine, Thompson, Utah	mine seep	Morrison fm.	8.3	11.4	66	173	6	100	520	19
9-4-1	Yellow Cat Camp, Thompson, Utah	spring	Morrison fm.	>8.4	4.1	468	664	6	250	720	35
9-5-1	Yellow Circle Camp, Moab, Utah	spring	Morrison fm.	>8.4	2.5	640	454	6	200	300	67
9-8-1	45-90 Mine, Uravan, Colorado	mine seep	Morrison fm.	>8.4	3.7	950	627	6	460	610	75
9-9-1	Henry Clay mine, Uravan, Colorado	mine sump	Morrison fm.	>8.4	2.0	1040	1767	6	270	930	29
Non-mineralized Aquifer											
9-6-1	Joe Davis Canyon, Egnar, Colorado	spring	Morrison fm.	>8.4	7.4	2.1	9	6	2.0	17	12
9-7-1	Gypsum Gap, Naturita, Colorado	spring	Dakota fm.	>8.4	9.4	7.2	25	6	9.0	62	15
9-10-1	Dolores River Canyon, Gateway, Colorado	spring	Wingate fm.	>8.4	1.9	10.9	19	6	2.7	10	27

in non-mineralized aquifers the range is from 2 to 9 ppb. The total radioactivity and the percentage of radioactivity due to uranium are also significantly higher in the mineralized than in the non-mineralized zones. All waters were alkaline having pH values of 8.3 or more.

Ground water from northeastern Wisconsin.—Ground-water samples from Cambrian sandstone in northeastern Wisconsin are listed in table 4, and water from Ordovician, Silurian and late Pleistocene aquifers of the same area are listed in table 5.

The waters from the Cambrian sandstone were obtained from wells which were drilled far into the aquifer and which, in some cases, reached to the Precambrian basement. The Paleozoic rocks of the area dip to the southeast off the Wisconsin arch or dome of Precambrian rocks. Therefore the wells increase in depth toward the southeast and bottom between 200 feet and 1000 feet beneath the surface.

Compared with the Colorado Plateau waters, particularly those from mineralized aquifers, these Wisconsin waters are much lower in uranium content, ranging from 0.1 to 1.7 ppb. The total radioactivity expressed as uranium-equivalent is much lower than that of the water from the carnotite-bearing beds of the Colorado Plateau but is similar to the total radioactivity

TABLE 4

Data on Samples from Deep Wells in Northeastern Wisconsin

Aquifer in all instances, Cambrian sandstone.

Well depths range between 200 and 1000 feet and average about 800 feet.

Sample No.	Location	Well	pH	Fluorine	Residue				Water		
					Weight	Uranium ppm	Alpha cph	Time elapsed to count (months)	Uranium ppb	Uranium equiv. ppb	U/U-eq. (%)
10-1-1	Appleton	Outagamie Asylum	7.6	0.5	2.06	1.6	39	6	0.4	20	2
10-2-1	Kaukauna	City Well #4	7.4	2.0	7.90	1.6	54	6	1.7	112	1½
10-3-1	Wrightstown	Fox River Dairy	7.6	2.6	8.44	1.0	9	6	1.1	20	5
10-8-1	Point Sauble	Village Well	7.8	2.6	4.93	0.13	108	6	0.1	140	0
10-9-1	Pulaski	City Well	7.8	0.4	2.14	1.2	67	6	0.3	32	1
10-10-1	Suamico	Suamico Dairy	7.8	1.7	1.81	21.0	93	6	5.0	44	9
10-13-1	Bonduel	City Well	8.0	0.1	1.80	1.1	75	6	0.3	36	1
10-14-1	Seymour	City Well #2	7.8	0.4	2.29	1.6	46	6	0.5	33	1½
10-17-1	De Pere	East Bank Well	7.8	2.2	2.13	1.2	126	6	0.3	71	½
10-18-1	De Pere	Armour & Co.	7.8	2.2	1.79	1.5	162	6	0.4	76	½
10-19-1	Green Bay	Ashwaubenon Sanitary District	7.8	2.6	1.82	2.1	151	6	0.5	72	½
10-20-1	Green Bay	Gray Street Well	8.0	2.0	1.97	0.8	118	6	0.2	61	½
10-21-1	Green Bay	Boland Road Well	7.6	2.0	1.91	4.2	192	6	1.1	50	2
10-22-1	Preble	Deckner Ave. Well	7.8	2.8	2.69	2.4	126	6	0.9	89	1
10-23-1	Preble	Town Well #2	7.8	2.4	5.54	1.7	130	6	1.2	190	½
10-24-1	Green Bay	Northern Paper Mills	7.8	2.3	2.89	1.7	143	6	0.7	110	½
10-25-1	Hortonville	City Well	7.4	0.1	2.38	3.7	36	6	1.2	23	5
10-26-1	Marinette	Marinette Paper Mills	7.6	1.2	5.44	1.7	93	6	1.2	132	1
10-27-1	Peshtigo	Peshtigo Paper Mills	8.2	0.7	1.43	0.9	119	6	0.2	42	½
10-29-1	Lena	Village Well	7.8	0.1	1.43	1.7	102	6	0.3	38	1
10-30-1	Oconto Falls	City Well #3	8.0	0.1	1.44	1.8	91	6	0.3	34	1
10-31-1	Oconto	City Well #6	8.0	1.6	1.67	1.2	109	6	0.3	48	½
10-32-1	Coleman	Village Well	7.6	0.1	2.00	2.5	67	6	0.7	35	2

of water from non-mineralized beds of that area. The total radioactivity of the water due to uranium is low when compared to Colorado Plateau waters from both mineralized and non-mineralized aquifers.

The pH of the waters from the Wisconsin Cambrian rocks ranges between 7.4 and 8.2. There is some indication that the total amount of uranium carried in these waters decreases with increasing pH. In this regard we may note that Phair and Levine (1953) report that uranium in the form of UO_3 is preferentially leached in H_2SO_4 solutions at the expense of UO_2 , Ra and Pb and further that increasing concentration of H_2SO_4 increases the proportion of UO_3 leached.

The ground water in northeastern Wisconsin is relatively high in fluorine ranging from 0.1 ppm to 2.8 ppm. The correlation between uranium and

TABLE 5
Data on Samples from Wells of Intermediate Depth in
Northeastern Wisconsin. Aquifers as Indicated

Sample No.	Location	Well	pH	Residue				Water		
				Weight	Uranium ppm	Alpha cph	Time elapsed to count (months)	Uranium ppb	Uranium equiv. ppb	U/U-eq. (%)
Aquifer: Ordovician ss.				Depth: 200 to 1300 feet; Average, 500 feet						
10-4-1	Denmark	Chi. & N.W. RR Depot	8.4	8.14	4.3	4	6	4.6	9	50
10-5-1	Brillion	City Well	7.6	2.15	1.8	10	6	0.5	6	8
10-6-1	Algoma	City Well #2	7.4	3.82	2.4	41	6	1.2	41	3
10-11-1	Suamico	Carl Jenkins	8.2	1.66	9.0	42	6	2.0	18	11
10-12-1	Mill Center	Walter Kimbs	8.4	0.87	0.3	6	6	0.3	1½	2
10-15-1	Kaukauna	Rapid Crocke Powerhouse	7.6	6.30	0.8	54	6	0.7	90	1
10-16-1	Little Rapids	Brown Co. Sanitarium	8.0	2.80	0.5	18	6	0.2	14	1½
Aquifer: Ordovician limestone.				Depth: 30 to 150 feet.						
10-37-1	De Pere	Harry Liebergen	8.4	1.68	0.4	6	6	0.1	2½	4
10-38-1	Little Rapids	Roy Wellmer	8.2	3.19	0.8	6	6	0.3	5	6
10-47-1	Seymour	George Sieserman	7.4	2.36	0.6	4	6	0.2	2½	8
Aquifer: Silurian ls.				Depth: 70 to 106 feet.						
10-7-1	Casco Junction	Green Bay and Western RR Well	7.4	2.56	4.6	35	6	1.6	24	6
10-35-1	Algoma	Louis Manly	7.8	2.56	1.5	6	6	0.5	4	13
10-36-1	Dykesville	John Collin	7.8	1.90	1.5	7	6	0.4	3½	11
10-39-1	Shirley	George Trembl	7.6	7.98	1.5	16	6	1.6	33	5
Aquifer: Glacial Drift.				Depth: 50 to 100 feet.						
10-40-1	Green Bay	Clarence Greatens	8.2	3.06	0.1	3	6	0.05	2½	2
10-42-1	Pound	Leo Cudnoski	8.4	1.59	6.5	24	6	1.4	10	14
10-43-1	Oconto Falls	Walter Birr	7.6	2.09	0.6	8	6	0.2	4½	4
10-45-1	Embarrass	Anthony Anton	8.4	0.75	0.4	11	6	0.05	2	2
Aquifer: fractured granite and glacial drift.				Depth: 350 feet.						
10-46-1	Embarrass	Wedig Krubsach	8.0	1.42	10.0	29	6	1.9	11	17

fluorine is not marked, but in general the total radioactivity of the water in uranium-equivalent increases with an increase in the fluorine content of the water. The fluorine concentration is greatest in the deeper wells down the dip of the Cambrian sandstone with the highest values recorded along the Fox River Valley between Lake Winnebago and Green Bay.

The results of water measurements from shallower and stratigraphically higher aquifers than the Cambrian in northeastern Wisconsin are given in table 5. The aquifers are Ordovician sandstone and dolomite, Silurian dolo-

mite, and Pleistocene (Wisconsin) gravel. The waters from these aquifers are similar in uranium content to that from the Cambrian, but their total radioactivity is not so great. The proportion of radioactivity due to uranium is variable but averages about 5 or 10 percent.

Ground water from the Texas High Plains.—Table 6 lists the data on five water samples from the Ogallala formation (Pliocene) of the High Plains of Texas. Their uranium content, 2 to 10 ppb, is intermediate between that of the Wisconsin waters and the waters from mineralized waters of the Colorado Plateau. They are similar in uranium content to the waters from the non-mineralized aquifers of the Colorado Plateau. Their total radioactivity is small but the percentage of activity due to uranium is between 25 and 63, similar to the water from the carnotite-bearing aquifers of Colorado and Utah. The source of uranium in these samples is thought to be volcanic ash which occurs in Pleistocene beds above the Ogallala and probably in the Ogallala itself. Ground-water recharge of the Ogallala is local.

TABLE 6
Data on Samples from the Texas Panhandle
Aquifer: Ogallala fm. (Pliocene)

Sample No.	Location	Source	ph	Residue				Water		
				Weight	Uranium ppm	Alpha cph	Time elapsed to count (months)	Uranium ppb	Uranium equiv. ppb	U/U-eq. (%)
8-3-3	Exell, Texas	Stock well	—	1.06	19	36	8	2.7	10	27
8-4-1	Exell, Texas	Stock well	8.1	1.11	16	30	8	2.3	9	25
8-7-1	Dawn, Texas	House well	—	2.08	25	44	8	6.8	24	27
8-7-3	Hereford, Texas	Irrigation well	—	1.56	21	20	8	4.3	8	54
8-8-3	Tule Canyon, Texas	House well	—	3.03	25	20	8	10.0	16	63

Ground water from southern Illinois-western Kentucky.—The results for seven water samples from the southern Illinois and western Kentucky Fluospar district are listed in table 7. Six of these samples were collected from mine workings, and one from an artesian spring. The uranium content is uniformly low, having values between 0.13 and 0.5 ppb.

Miscellaneous ground water samples.—A sample from the warm spring at Pagosa Springs, Colorado, and a sample from an artesian well at Newkirk, New Mexico, were collected. The results are given in table 8.

Surface waters.—Waters from surface streams were collected at nine localities, seven of them in Wisconsin. Data on these waters are given in table 9. The uranium content is generally low as is the total radioactivity in terms of uranium equivalent. The percentage of radioactivity due to uranium tends to be high.

Waters not tabulated.—The data for four additional samples are not included in tabular form. One of these was collected from a spring at the

TABLE 7
Data on Samples from Southern Illinois and Western Kentucky
Aquifer: Mississippian Limestone

Sample No.	Location	Source	ph	Residue				Water		
				Weight	Uranium ppm	Alpha cph	Time elapsed to count (months)	Uranium ppb	Uranium equiv. ppb	U/U-eq. (%)
5-3-2	Rosiclare, Ill.	Rosiclare Fluor-spar Mine	7.8	1.61	1.2	10	9	0.25	4	6
5-6-9	Cave-in-Rock, Ill.	W. Green Fluor-spar Mine	7.2*	12.55*	1.1	4	9	0.18	13	1
5-7-1	Cave-in-Rock, Ill.	Deardorf Fluor-spar Mine	8.2	2.84*	1.1	10	9	0.4	8	5
5-8-1	Rosiclare, Ill.	Alcoa Fluor-spar Mine	8.3	2.81	1.9	13	9	0.7	10	7
5-5-25	Salem, Kentucky	Eagle Hutson Zinc Mine	8.1	2.70*	1.4	19	9	0.5	14	4
5-4-1	Cave-in-Rock, Ill.	"Rd. Spring" (artesian)	7.4	3.38*	1.4	68	9	0.6	58	1

* 8 liter sample.

Fission Mines, Wilberforce, Ontario; another from a pond in a pegmatite quarry, Madawaska, Ontario. The third, an 8-liter sample, was supplied by Mr. Alan Gregory from Beaverlodge Lake in the Lake Athabaska Area, Saskatchewan. Each of the samples was chosen because of proximity to a uraniferous source. In each instance, however, the amount of residue recovered was so small that the analytical results were not judged to be reliable. A fourth sample of water from Cambrian sandstone at Madison, Wisconsin is referred to later.

TABLE 8
Data on Miscellaneous Samples

Sample No.	Location	Source	ph	Residue				Water		
				Weight	Uranium ppm	Alpha cph	Time elapsed to count (months)	Uranium ppb	Uranium equiv. ppb	U/U-eq. (%)
8-9-1	Newkirk, N. M.	Housewell—	>8.4	9.88	1.7	4	8	2.2	10	22
9-1-1	Pagosa Springs, Colo.	(Triassic ss) Warm Spring	7.0	19.10	1.7	33	8	4.6	180	3

Conclusions.—On the basis of the data presented above the following conclusions can be drawn:

1. Both underground water and surface water carry uranium in measurable amounts. It cannot be said whether all of this uranium is in solution or whether it is in suspension associated in some way with colloidal-size particles.

2. Where underground waters pass through an aquifer containing carnotite, the total radioactivity and uranium content are high when compared with water from similar but non-mineralized aquifers. It cannot be said on the basis of the data collected whether the same relationships would hold for aquifers containing uranium-bearing minerals other than carnotite. On the other hand, the relatively high uranium content and radioactivity of waters from carnotite-contaminated beds suggests that geochemical methods might well be devised for prospecting for uraniferous deposits.

3. The residue technique used in this study appears to be practical only for those waters which carry much material in solution and thus produce a relatively large residue sample, say 1 gram per 2-gallon water sample.

4. The relation between pH and total uranium carried is not clear from the data at hand. Waters from Cambrian rocks in northeastern Wisconsin, however, decrease in uranium content as the pH increases from 7.4 to 8.0.

5. Incomplete data obtained from water in Cambrian rocks of northeastern Wisconsin also suggest that in these waters fluorine increases with increasing radioactivity but not necessarily with uranium.

CHANGES IN RADIOACTIVITY WITH TIME

It has already been stated that the alpha counts per hour for any one residue sample change with time. The effect of this change on the calculations of total radioactivity of the water in uranium-equivalent and of the percentage of radioactivity due to uranium has been illustrated in table 2. Successive

Fig. 1. Decrease in radioactivity with time thought to be due to thorium X (radium 224 in thorium series). Sample is a residue of water from the Cambrian sandstone at Madison, Wisconsin, taken at the main station well. The sample counted at successive intervals. Large scatter of points due largely to short counting periods.

recounts of a single sample showed that the change of radioactivity was greatest and least predictable in the first few months after evaporation. Samples counted 20 or more months after evaporation were found to be changing at a slower rate.

An excellent example of decreasing radioactivity in terms of alpha counts per hour is provided by a sample of residue obtained from the evaporation of water from a deep well in Cambrian sandstone at Madison, Wisconsin. The sample was counted repeatedly during the three-week period immediately following evaporation of the water. The activity decreased by one-half during this interval as shown in figure 1.

Table 10 lists 25 water samples for which the residue of each was counted two or more times at varying intervals. The data are not complete enough to warrant any definite conclusions or generalizations except (1) that the changes are real, (2) the radioactivity in terms of alpha counts may either increase or decrease with time, and (3) the direction of change appears to reverse itself in some instances.

Members of the $4n + 1$ series cannot be cited as responsible for the change because they are not known to occur in nature. The actinium series is exceedingly rare in nature so must be excluded from consideration. This leaves members of the uranium and thorium series. Of these, elements with long half lives such as Uranium 238 and 234 and Thorium 232 and 230 disintegrate at too slow a rate to be reflected over the short time span of a few weeks, or months, or at most something over two years during which

TABLE 9
Data on Surface Waters

Sample No.	Location	Source	pH	Residue				Water		
				Weight	Uranium ppm	Alpha cph	Time elapsed to count (months)	Uranium ppb	Uranium equiv. ppb	U/U-eq. (%)
5-7-3	Cave-in-Rock, Ill.	Deardorf Creek	7.2	3.09	0.2	4	9	0.13	3	4
5-2-4	Rosiclare, Ill.	Ohio River	7.8	2.65	1.1	9	9	0.5	6	9
8-6-1	N. of Amarillo, Texas	Canadian River	>8.4	4.67	5.7	11	0	3.5	14	25
10-28-1	Middle Inlet, Wis.	Granite Quarry Seep*	>8.4	1.50	4.3	8	6	0.85	3	28
10-33-1	Mountain, Wis.	Oconto River	>8.4	2.62	3.8	6	6	1.3	4	33
10-34-1	Clintonville, Wis.	Pigeon River	>8.4	1.41	16.0	16	6	3.0	6	50
10-44-1	Shawano, Wis.	Wolf River	>8.4	2.64	1.2	2	6	0.4	1½	27
10-41-1	Green Bay, Wis.	Fox River	7.8	1.22	2.9	5	6	0.5	1½	33
10-48-1	Appleton, Wis.	Fox River	>8.4	1.06	3.7	4	6	0.5	1	50
10-49-1	Madison, Wis.	Lake Mendota	>8.4	2.86	1.1	1	1	0.4	¾	50

* Water passes through calcareous drift of Wisconsin age before seeping through granite.

TABLE 10
Change in Radioactivity of Water Residue with Time in Terms
of Alpha Counts per Hour

Sample No.	Location	Time elapsed to count (months)	Alpha cph	Time elapsed to count (months)	Alpha cph	Time elapsed to count (months)	Alpha cph	Time elapsed to count (months)	Alpha cph
5-3-2	Rosiclare, Ill.			7	10	9	10		
5-4-1	Cave-in-Rock, Ill.			7	121	9	68	18	48
5-5-25	Salem, Ky.	½	51			9	19	29	22
5-6-9	Cave-in-Rock, Ill.	½	5			9	4		
5-7-1	Cave-in-Rock, Ill.	½	20			9	10		
5-8-1	Rosiclare, Ill.			7	18	9	13		
8-3-3	Exell, Texas	0	98	8	36				
8-4-1	Exell, Texas	0	56	8	30			23	20
8-7-1	Dawn, Texas	0	50	8	44				
8-7-3	Hereford, Texas			8	20	27	25	29	26
8-8-3	Tule Canyon, Texas			8	20			29	32
8-9-1	Newkirk, N. M.			8	5	17	5		
9-1-1	Pagosa Springs, Colo.			8	33	17	31	29	44
9-3-1	Thompson, Utah	2	123	6	173			23	126
9-4-1	Thompson, Utah	2	638	6	664				
9-5-1	Moab, Utah	2	340	6	454			23	390
9-8-1	Uravan, Colo.	2	571	6	627				
9-9-1	Uravan, Colo.	2	1729	6	1767				
9-6-1	Egnar, Colo.	2	4	6	9				
9-7-1	Naturita, Colo.	2	18	6	25				
9-10-1	Gateway, Colo.	2	14	6	19				
10-10-1	Suamico, Wis.			7	108			23	41
10-14-1	Seymour, Wis.			7	50			23	44
10-18-1	De Pere, Wis.			7	162	15	168		
10-21-1	Green Bay, Wis.			7	192	15	147		

successive counts were made. The cause of the change then must lie among the members of the uranium and thorium series with shorter half lives. These would include those elements with half lives of Thorium X (radium 224) or less, but exclusive of radon and thoron which were not present in the original residue sample. Furthermore, we may exclude those elements of half lives less than three or four days because of the impracticability of measuring them by the alpha count method.

A series of activity curves for members of the uranium and thorium series was constructed. Theoretically the comparison of these curves with the changes in alpha activity of the water residues through time should permit speculations concerning the relative importance of some of the daughter elements of uranium and thorium. Unfortunately, data are insufficient for most samples to allow any precise plotting of the nature of the change of alpha activity through time. Only in the case of a sample obtained from waters in the Cambrian sandstone at Madison, Wisconsin are enough alpha determinations available to sketch the change in alpha activity through time. This

sample was counted at successive intervals over a three-week period and the results given in figure 1. It is presumed that the rapid decrease in activity during the first two weeks was due primarily to the presence of thorium X (radium 224 in the thorium series).

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III - 7

III - 8

III - 9

(7) Uranium Content of the Rivers of Wisconsin

By

John A. S. Adams (Forthcoming Publication)

(8) Average Uranium Content of Limestones

By

John A. S. Adams (In Press)

(9) Uranium Content of Tektites

By

John A. S. Adams (In Press)

IV. Geochemical Studies Based on Thermoluminescence

THERMOLUMINESCENCE AND SURFACE CORRELATION OF LIMESTONES

BY
DONALD F. SAUNDERS

Reprinted for private circulation from
THE BULLETIN OF THE AMERICAN ASSOCIATION OF PETROLEUM GEOLOGISTS
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THERMOLUMINESCENCE AND SURFACE CORRELATION OF LIMESTONES¹

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ABSTRACT

Nearly all limestones emit light when heated to a temperature below that of incandescence. This thermoluminescence is a natural property of the calcium and magnesium carbonate minerals in the rock. It can also be induced artificially by irradiating specimens with gamma rays or X-rays. The natural thermoluminescence has been produced by radiation from radioactive impurities in the rock.

The light emission is measured by a photomultiplier tube circuit as the temperature of the specimen is increased. Both of these variables are recorded simultaneously by means of a two-point potentiometer recorder. A plot of the light intensity as a function of temperature is termed the "glow curve." This shows a series of light-intensity maxima which depend on the amount of radiation that the minerals have received, their impurity content, and their crystallization history.

The glow curves of the artificially induced thermoluminescence of many different limestones have been measured, and the shapes of these curves have been found to be characteristic of the limestone stratum from which the specimens were obtained.

Preliminary tests of the use of this property as a tool in surface correlation of limestones have shown it to be applicable under closely controlled sampling in thick limestones. It has also been indicated that certain well known Pennsylvanian limestones can be differentiated over a county-wide area by the amounts of thermoluminescence as measured from their glow curves.

INTRODUCTION

For many years it has been known that certain minerals possess the property of emitting light when heated to temperatures below that of incandescence. This light is called "thermoluminescence." A specimen exhibits this phenomenon only once, and a second heating does not produce light unless the specimen has been exposed to X-rays or gamma rays after the first heating.

Boyle observed the thermoluminescence of a blue diamond as early as 1663, according to Pringsheim (1949), but during the next 250 years this property was considered to be only a mineralogical curiosity. Although many observations of this phenomenon were recorded, lack of quantitative techniques of measurement made a thorough investigation of this property impossible. These techniques have been developed in the field of phosphor research during the last 20-30 years.

Kohler and Leitmeier (1934), Calaját y Leon (1908), Royer (1937), Saurin (1939), and Northrup (1940) are some of those who have reported on the visual

¹ Taken in part from a Ph.D. dissertation, University of Wisconsin (1950). Read before the Society of Economic Paleontologists and Mineralogists, at St. Louis, April 26, 1951. Manuscript received, January 19, 1952.

² Department of Chemistry, University of Wisconsin. The research reported herein is part of a larger program which has consisted mainly of the application of these new methods to the investigation of the thermoluminescence of minerals in an attempt to develop this mineralogical curiosity into a practical tool in geological research (Daniels, Boyd, and Saunders). This work has been done under the direction of Prof. Farrington Daniels of the University of Wisconsin and has been supported financially by the United States Atomic Energy Commission.

Thanks are extended to Prof. Daniels for many helpful suggestions and to Prof. L. M. Cline for valuable assistance in planning the field work.

The specimens used in this study were collected by J. M. Parks, E. J. Zeller, and the writer in the Milwaukee, Wisconsin, area; by G. Risley and D. Erickson in the Black Hills, Wind River Mountains, and the Grand Canyon; and by R. E. Bergstrom in the Iowa-Missouri area.

observation of the thermoluminescence of many different mineral species. Spectral studies have been made by Iimori (1933) on the thermoluminescent light emitted by certain calcites. The spectra of fluorites have been described by Iwase (1933, 1934) and Steinmetz (1935); potash feldspars by Iimori and Iwase (1935); and quartzes by Futagami (1938). In all cases, with the exception of certain fluorites, the spectra were found to consist of a series of bands. Both Iwase and Steinmetz attributed the line and band spectra in certain fluorites to rare earth impurities. In most cases where the natural and gamma-activated thermoluminescence was studied for a given specimen the same bands were found in both spectra.

Pierce (1908), Steinmetz (1934), and Wick (1927) made the first measurements of intensity of thermoluminescence by matching the intensity of the light emitted with that of a standard light source.

Ellsworth (1932), Kohler (1934), and Alt and Steinmetz (1940) have suggested that the cause of the natural thermoluminescence of minerals is the associated radioactive material. It has also been suggested by Alt and Steinmetz, and Dérivé (1938) that the impurity content of the crystal is a factor in determining the character of the thermoluminescence.

Excellent summaries of the present state of knowledge in the general field of luminescence research are found in several recently published volumes: Pringsheim (1949); Mott and Gurney (1940); Garlick (1949); Leverenz (1950); Kroger (1948); Fonda and Seitz (1948).

PRELIMINARY OBSERVATIONS

As a preliminary survey about 1,500 specimens of common rocks were checked visually for natural thermoluminescence by observing their reaction when placed on a plate heated to a temperature just below red heat. It was found that about 75 per cent of the rocks tested were thermoluminescent and that nearly all the emitted light could be attributed to the calcium and magnesium carbonate minerals which emit a yellow to orange light and the sodium and potassium feldspars which emit in the blue. Both limestones and granites were found to be almost universally thermoluminescent.

EXPERIMENTAL MEASUREMENTS

The method which has been used for the measurement of thermoluminescence was developed originally by Urbach (1930) and later modified by Randall and Wilkins (1945). A description giving the details of this technique has been reported by Boyd (1948, 1949). A diagrammatic representation of the equipment is shown in Figure 1.

Samples were prepared by using a diamond cutting wheel to slice the specimen into pieces 1 centimeter square and 2 millimeters thick. The small electric furnace was used to raise the temperature of the sample from about 25° to 500° C. at a linear rate of 1° per second. The light emitted during this process was

measured by the photomultiplier tube and the temperature of the specimen was determined by a chromel-p-alumel thermocouple. The outputs of these two devices were recorded simultaneously by a Brown potentiometer recorder. A plot of the intensity of thermoluminescence as a function of the temperature is referred to as the glow curve and it is this curve that has been used as a quantitative

ARRANGEMENT OF APPARATUS

FURNACE

GLOW CURVE APPARATUS

FIGURE 1

FIG. 1.—Glow-curve apparatus.

measure of thermoluminescence. Some examples of this type of curve may be seen in Figure 2. Curves for the same material under the same conditions have been found to be reproducible within about 10 per cent.

SOURCES OF GAMMA RADIATION

Laboratory activation of the thermoluminescence of limestones has been done by using the gamma radiation from radioactive cobalt. All glow curves reported herein have been measured for specimens given a standard gamma exposure of 140,000 roentgens. The radiation sources used and the method of calibration have been described in detail by Saunders, Morehead, and Daniels (1952). Briefly, each consists of two concentric aluminum cans with the annular space

between them filled with cobalt metal powder. Specimens to be irradiated are placed in the inner can.

Both a one-curie and a four-curie source were prepared by irradiation of the cobalt with neutrons through the cooperation of the Argonne and Oak Ridge National laboratories of the United States Atomic Energy Commission. The

FIG. 2.—Typical gamma-activated glow curves for section in Black Hills. Vertical coordinates represent relative thermoluminescence intensity.

radio-cobalt (Co^{60}) thus produced has a half life of 5.3 years and emits 1.1 and 1.3 million electron-volt gamma rays. Both the relative and absolute gamma-ray intensity distributions in the sources have been measured experimentally and checked by independent calculations based on geometrical considerations. About 40 specimens 1 cm. square and 2 mm. thick can be irradiated simultaneously and uniformly in each of these sources.

THEORY OF THERMOLUMINESCENCE

The theoretical interpretation of the thermoluminescence process can best be made in terms of the band theory of solids. Johnson (1939) and Boyd (1949) as well as the several general references (referred to previously) give detailed descriptions of this approach.

The first suggestion of the currently accepted theory of thermoluminescence was made by Meyer and Przibram (1916) who studied the coloration and luminescence produced in many different artificial materials by high energy radiations. Their theory was accepted by Lind and Bardwell (1923)-as the explanation of the thermoluminescence and coloration observed in minerals which had been exposed to radium. Lind and Bardwell have translated Meyer and Przibram from the original article as follows.

Certain groups of electrons are displaced by radiation from their normal positions and take up new metastable positions among the atoms.

The coloration produced in these crystals by the radiation was attributed to the absorption of light by the displaced electrons; and as the mineral was heated, the loss of color and the associated thermoluminescence were attributed to the return of the electrons to their normal positions in the crystal.

All real crystals have a certain number of imperfections such as missing ions, interstitial ions, or impurities. Electrons which have been knocked out of their normal positions in the crystal lattice by high energy radiation such as X-rays or gamma rays may become trapped at these imperfections. They can not escape from these traps unless they are supplied with enough energy to penetrate the force fields around the traps. Thermal agitation of the crystal ions may provide the necessary energy to accomplish this. When the electrons return to their normal positions in the lattice some of the excess energy which they possessed while in the traps may be released in the form of light which can be observed as thermoluminescence. Since the energy required to free electrons from each type of trap is different, the temperature required for thermoluminescence in the glow-curve experiment differs for the various types of traps and a series of maxima in the light-intensity curve is observed. Each of these maxima represents a particular variety of electron trapping center.

The natural thermoluminescence of minerals is due to electrons which have been driven into traps by the radiation from radioactive impurities in the crystals.

Many of these electron traps are thought to be of the missing-ion type caused by the dislocation of lattice ions from their normal positions due to alpha-particle bombardment from radioactive impurities. Although the natural rate of production of these dislocations is very small because of the low concentrations of radioactivity, the great lengths of time available are sufficient to produce large enough numbers of imperfections to account for the observed thermoluminescence. Information on the production of lattice dislocations by alpha irradiation of various materials is given by Burton (1950), and the application of thermolumines-

cence to the measurement of radiation damage and geologic ages of limestones is discussed by Zeller (1952).

As shown in Figure 2, the shapes of the gamma-activated glow curves of several different limestones from one outcrop locality are different as are the amounts of thermoluminescence as shown by the heights of the maxima. The relative differences in the sizes of the maxima are interpreted to indicate differences in the

FIG. 3.—Niagara limestone. Vertical section of quarry, with typical gamma-activated glow curves. Vertical coordinates represent relative thermoluminescence intensity.

electron trap distribution in the calcite crystal lattices. Since it is known that alpha rays from radioactive elements are capable of producing displaced ions in various types of crystals (Burton, 1950) and since both the missing ion sites and the interstitial ions can act as electron traps it is not surprising that the electron trap distribution reflects the amount of radioactive impurity present and the time of exposure to the rays from these impurities (age of the limestone). In addition to traps which have been produced by ionic dislocation, other impurities may contribute traps which cause certain of the other peaks in the glow curve.

Although the exact nature of the particular traps which form the several peaks

of the calcite glow curve are not known, one may hypothesize that in general the type of glow curve observed for a limestone reflects the composition and crystallization history of the calcite contained therein. Under normal conditions of limestone formation the conditions which control these variables might be expected to be constant over relatively wide areas of one stratigraphic horizon and would vary according to the position in the geologic section. If this is true then it should be possible to apply the glow-curve characteristics as a tool in identifying a certain limestone stratum or sequences of strata in different outcrop localities.

GLOW-CURVE VARIATION OVER SHORT DISTANCES

A large quarry in Niagaran limestone near Milwaukee, Wisconsin, was chosen for a preliminary investigation of glow-curve variation, both over a short vertical section and along a single bed over a distance of about $\frac{1}{2}$ mile. The relatively rapid change of amount of thermoluminescence and glow-curve shape from top to bottom of a 25-foot section is shown in Figure 3. The bed labeled "key

FIG. 4.—Niagara limestone. Lateral section of quarry, with typical gamma-activated glow curves. Vertical coordinates represent relative thermoluminescence intensity.

bed" was chosen for measurement of the lateral variation. The glow curves in Figure 4 show the constancy of shape and amount of thermoluminescence found over the $\frac{1}{2}$ mile of lateral exposure in a 6-inch interval at the base of the bed above a prominent bedding plane.

These results support the hypothesis that the glow curves reflect the conditions of deposition of the limestone and indicate the possibility of applying these curves as a stratigraphic tool over short distances.

LONG-DISTANCE CORRELATION BY GLOW-CURVE SHAPE

The variation of glow curves of several different limestones and dolomites in an outcrop section near the Black Hills is shown in Figure 2. These results indi-

FIG. 5.—Typical shapes for gamma-ray-activated curves. Vertical coordinates represent relative thermoluminescence intensity.

cate that it is possible to differentiate these formations on the basis of type of thermoluminescence. The Pahasapa limestone of this section has long been recognized as being correlative with the Madison limestone of the Wind River Mountains area in Wyoming, and with the Redwall limestone of the Grand Canyon area in Arizona (Weller *et al.*, 1948). Glow curves were determined for specimens collected for every 3 feet of an exposed section of each of these limestones in the area mentioned. In each case the shape of the glow curves showed similar trends, as illustrated in Figure 5. The glow curves shown are typical of the sections and have been corrected to a unit size for the middle peak so that the shapes could be compared easily. The curves are arranged in the figure according to the position of the specimens in the sections. In general there is a variation from shape "A" to shape "D" in each section as one proceeds from the base upward. In the Redwall limestone only the "B" and "C" types were found, but in this case only the middle two-thirds of the section was sampled.

On the basis of this shape variation a tentative correlation of these limestones has been made, as shown in Figure 6. The limits of the various glow-curve shapes

are given by the dotted lines. The sections shown are not complete since only the exposed parts which were sampled are included.

These results may be taken as a substantiation of the correlation of these three limestones, and as an indication that glow-curve shape can be applied as a correlative tool in thick limestones of this type where relatively long and undisturbed periods of deposition were involved and where conditions of deposition varied widely for the other limestones in the section.

FIG. 6.—Tentative correlation of limestones by shape of gamma-ray-activated glow curve.

CORRELATION BY AMOUNT OF THERMOLUMINESCENCE

Investigation of the possible use of thermoluminescence as a tool in correlating the limestones of the Pennsylvanian formations is now in progress. Preliminary results of this study show that it is difficult to differentiate the thin closely spaced limestones by the shapes of their glow curves. Typical curves for three limestones closely spaced in the Desmoinesian series are given in Figure 7. It can be seen that the shapes of the curves are similar but that the amounts of thermoluminescence are different. At the left in Figure 7 the average height of the lowest temperature peak in the glow curve of each limestone is plotted for several outcrop localities. In a single limestone the amount of thermoluminescence varies from place to place but the amounts in several limestones are comparable relative to each other. It is thought that these results indicate that correlation may be possible in thin cyclical limestones by means of the relative amounts of thermoluminescence of several consecutive formations in each locality.

FIG. 7.—Thermoluminescence of three Pennsylvanian limestones activated by gamma radiation.

CONCLUSIONS

The results of these preliminary tests of the application of thermoluminescence measurements as a stratigraphic tool are in agreement with known correlations based on paleontological and other evidence. It is believed that further work on this problem will indicate that both glow-curve shape and amount of thermoluminescence may be used for correlation. Since nearly all limestones are thermoluminescent, this method may become very valuable in identifying strata in which fossils are rare or other methods are difficult to apply.

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IV-2

USE OF THERMOLUMINESCENCE OF LIMESTONES IN SUB-SURFACE STRATIGRAPHY¹

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ABSTRACT

The thermoluminescence of the limestones of the Meramecian and Chesteran series (middle and upper Mississippian) of the Illinois basin was studied in an attempt to develop the thermoluminescence of limestones into a useful research tool in subsurface geology.

A powder method of sample preparation is described which makes accurate quantitative measurement of thermoluminescence possible. The apparatus used in measuring and recording thermoluminescence is described briefly.

The analysis of patterns of variation in intensity of thermoluminescence and in glow-curve shapes vertically through a formation appears to have some usefulness in subsurface stratigraphy in (a) identifying and characterizing a formation, (b) assisting in recognizing tops and bottoms of limestone formations where lithologic breaks are not present, (c) splitting thick carbonate rock sequences into small units useful in correlation, and (d) recognizing erosion or non-deposition of zones by the absence of parts of the typical pattern of variation.

Within certain limitations, the variations in radioactivity of the limestones appear to be the dominant factor in the cause of variations in thermoluminescence.

INTRODUCTION

Limestone formations of similar lithologic character and containing similar faunal assemblages are difficult to differentiate and correlate in surface outcrops, and are especially difficult to differentiate in subsurface work. Thick limestone sequences are difficult to split into smaller useful units using standard subsurface techniques such as microscopic examination of well cuttings, insoluble residues, and dolomite tests. All of these difficulties also pertain to dolomite formations and mixtures of the two rock types.

One solution to these problems is the spectrochemical sample-logging method proposed by Sloss and Cooke (1946) in which variations in trace element percentages are used to zone and correlate thick carbonate rock sequences. This method is now in limited use in the petroleum industry.

¹ Taken from a thesis for the degree of Doctor of Philosophy, University of Wisconsin (1951). The research described was supported financially by the Wisconsin Alumni Research Foundation and was carried out in close cooperation with the Atomic Energy Commission Project No. AT(11-1)-27.

Read before the Society of Economic Paleontologists and Mineralogists, at St. Louis, April 26, 1951. Manuscript received, January 19, 1952.

² Department of Geology, University of Wisconsin. The well samples used in this work were obtained from the Illinois State Geological Survey, with the assistance of L. E. Workman, Elwood Atherton, Donald Saxby, and Wayne Meets. Doris and Edward Zeller assisted in locating the type areas of some of the Chesteran limestones in southern Illinois.

The University of Wisconsin Department of Chemistry assisted materially in this study. Farrington Daniels initiated the present program of the study of thermoluminescence. Donald Saunders did much of the basic research into the thermoluminescence of limestones. The gamma-ray irradiations in the cobalt 60 source were made with the cooperation of Donald Saunders. John Ockerman made the alpha scintillation counts.

This project was supported in part by a research grant from the Wisconsin Alumni Research Foundation, under the sponsorship of L. R. Laudon and M. L. Thompson.

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Another possible method of approach to these problems is the use of the phenomenon of thermoluminescence of limestones. Saunders (1950, 1953), working with surface outcropping limestones, found that the shapes of thermoluminescence glow curves were characteristic for individual formations; that glow-curve shapes were different for successive formations; and that the characteristic glow-curve shape was fairly uniform both vertically and laterally within the formations investigated.

With this basis, the writer proposed to study the usefulness of thermoluminescence of limestones in subsurface stratigraphy. The Meramecian and Chesteran series of the Illinois basin were chosen for this study for several reasons: the Chesteran series includes eight limestone formations, some of which are difficult to differentiate both in surface outcrop and in the subsurface; the Meramecian series consists of a sequence of thick limestone formations with little or no lithologic change at the boundaries between the formations; the type sections of the limestones were readily available for positive identification; the area had been adequately drilled in petroleum exploration so that well samples would be readily available; and a survey had indicated that the limestones were sufficiently thermoluminescent for this type of study.

A brief survey of the thermoluminescence of the Chesteran limestones, performed on outcrop samples for the most part from type localities, indicated that there were sufficient differences in glow-curve shapes to permit identification and differentiation of the limestones. However, when subsurface samples were used, it became strikingly apparent that mere shapes of glow curves would not be an adequate basis for differentiation of the limestones. The variations in glow-curve shapes within any one formation in the subsurface included many of the variations apparently characterizing different formations at the surface. This was due in part to the limited vertical extent of many type-locality outcrops, and also to the more complete development and thicker section of the formation in the subsurface nearer the center of the Illinois basin.

After further work, it became apparent that the pattern of variation in glow-curve shapes vertically within a limestone formation would be sufficient basis to differentiate that formation from other formations and could be used as a basis for correlation. These patterns of variation have been plotted in a form similar to electric logs to permit easy visual comparison and correlation.

The location of outcrops and wells used in this study is shown in Figure 1. Wells 1-4 are cable-tool wells through the entire Chesteran series, and well No. 1 also penetrates the Meramecian series. Well No. 5 is a continuous core through the Levis limestone member of the Ste. Genevieve limestone.

PROCEDURE AND APPARATUS

Preparation of samples.—In previous work with outcropping limestones (Saunders, 1950, 1953) solid samples were used—small tablets sawed from the hand sample, approximately 1 centimeter square and 2 millimeters thick. In this subsurface study, cable-tool well samples were used almost exclusively, and the small size of chips in these cuttings

made a new sample technique necessary. A powder method was devised, which eventually became more quantitatively accurate than the solid-sample method.

The method of collecting cable-tool well samples imposes certain limitations on a study of this type. In normal drilling operations, these cuttings are collected at intervals varying from 3 to more than 15 feet, and considerable mixing of material from beds within this interval and from adjacent beds can be expected. Rotary-well cuttings were avoided as presenting too many possibilities for contamination. The sets of well samples used in this study were collected with a different purpose in mind, and sampling was erratic, with many samples missing.

The cable-tool well cuttings were examined under a binocular microscope, washed if

FIG. 1.—Sketch map showing location of outcrops and wells. 1. Tunnel Hill Oil Co's. Boner 1, Sec. 30, T. 11 S., R. 3 E., Johnson Co., Ill. 2. Kingwood Oil Co's. Oliver 1, Sec. 11, T. 10 S., R. 6 E., Saline Co., Ill. 3. Mitchell Oil Co's. Fly 1, Sec. 9, T. 11 S., R. 10 E., Union Co., Ky. 4. Ryan and Aetna Oil Co's. Jenkins 1, 18-L-19 (Carter coordinates), Crittendon Co., Ky. 5. Superior Oil Co's. Hawkins 1, Sec. 23, T. 1 N., R. 5 E., Wayne Co., Ill.

necessary, and carefully examined for limestone fragments. Individual limestone fragments deviating from the majority in lithologic character were avoided. Some cuttings were too fine to permit selection of fragments, and that fact was noted on the sample envelope to be taken into account in interpreting the results. Shale and sandstone were found to be principally diluting factors, since their thermoluminescence was smaller by several orders of magnitude.

The limestone fragments were crushed in a porcelain mortar and sized through screens. The minus 100, plus 200 size was used in this project. Every reasonable precaution was observed to prevent contamination from successive use of mortars and screens. Outcrop and core samples were treated in a similar manner.

The limestone powder was placed in gelatin capsules and subjected to gamma radiation in the cobalt 60 source for a standard length of time, 15 hours in the 5 curie source. After irradiation, the samples were stored under refrigeration until ready for use, in order to minimize the draining of the lower temperature peaks.

A small quantity of this powder was placed on a clean circular micro-cover glass, and

a drop of water containing a little wetting agent was added. The mixture was spread evenly over the surface of the cover glass and allowed to dry. Apparently a small amount of calcite is dissolved and recrystallizes against the glass, holding the sample to the glass firmly enough to allow routine handling.

A high order of reproducibility and quantitative accuracy can be achieved by weighing these samples. Weighing the solid samples will not get the same results because the sample is too thick and opaque to allow all the thermoluminescence to be transmitted. In this project, semi-quantitative results were obtained by measuring the amount of powder used in each preparation by a volume method rather than by a weight method, in order to save time. The maximum error was only 7.5 per cent with the volume method, as determined by running duplicate weighed samples. Approximately 25 milligrams of limestone powder was used in preparing each sample.

THERMOLUMINESCENCE EQUIPMENT

The apparatus used for quantitative measurement of thermoluminescence of limestones consists of the following components: a furnace for heating the samples; a multiplier phototube to convert the light energy to electric current and to multiply that current; a light-tight box enclosing the multiplier phototube and the furnace; a power supply for the multiplier phototube; a thermocouple for measuring the temperature of the sample as it is heated; a pre-amplifier; and a two-point recording potentiometer. Figure 2 is a block diagram of the apparatus for measuring and recording thermoluminescence.

The furnace is a specially constructed small hot plate, designed to allow easy control of its heating rate. The heating rate of the furnace is controlled by a manually operated variable transformer. The samples were heated at a linear rate of approximately 1°C. per second. Every effort was made to keep this rate as uniform as possible, as variations in heating rate have a large effect on the height of intensity peaks in the glow curve, although not affecting the total quantity of thermoluminescence. The temperature range used in this study was from approximately 0°C. to 450°C. , at which point the red heat of the furnace begins to interfere with the measurement of light intensities. Between runs, the furnace was cooled with dry ice. A chromel-alumel thermocouple was placed on the furnace plate near the sample for recording of temperature.

The multiplier phototube is an RCA 5819, ten-stage head-on type, providing multiplication of photoelectric current by 150,000 times with 75 volts per stage. The power supply for the multiplier phototube is a battery pack which supplies a steady direct current voltage.

A small $\frac{1}{4}$ -watt neon lamp is used as a standardization lamp, to check the amplification factor at frequent intervals. A dark current trimmer is inserted between the multiplier phototube and the pre-amplifier in order to reduce stray currents.

The pre-amplifier is a micro-micro-ampere direct current amplifier, which amplifies the output of the multiplier phototube to a value high enough to be recorded on the recording potentiometer.

The recording potentiometer is a Leeds & Northrup Speedomax Model G two-point recorder, equipped with a 3-second response. One point records the temperature in millivolts from the chromel-alumel thermocouple, and the other point records the intensity of thermoluminescence as the output of the multiplier phototube and pre-amplifier. By varying the voltage per stage on the multiplier phototube, and by varying the scale multiplier settings on the pre-amplifier, a wide range of amplifications can be obtained.

ALPHA SCINTILLATION COUNTER

The radioactivity of the limestones was determined by making alpha scintillation counts. Alpha particles from the limestone produce scintillations in a suitable phosphor,

which are picked up by a multiplier phototube, converted to electrical impulses, fed into a scaler, and the total count recorded every 15 minutes on a suitable recording device attached to the scaler. Counts as low as one per hour above background were possible with this scintillation counter. However, count rates lower than three per hour were not considered reliable. The alpha scintillation counter was adapted from one described by Holland and Kulp (1950).

FIG. 2.—Block diagram of apparatus for measuring and recording thermoluminescence.

INTERPRETATION OF RESULTS

The thermoluminescence glow curves of the outcrop samples were run first, both as solid samples and as powdered samples. The glow curves of the solid samples of the Meramecian and Chesteran limestones showed considerable variation in shape and wide variation in intensity. Glow curves were run on powder preparations, irradiated as powder, from additional samples from the same outcrops. Comparison of solid-sample glow curves with powder-preparation glow curves from the same outcrops showed no appreciable change in shape of curve, but did show considerable alteration in over-all intensity relationships. The powder preparations eliminated to a considerable extent the factor of differences in transparency between limestones of different color and grain size. The differences were not completely eliminated, but were reduced to a negligible factor for semi-quantitative work.

The differences in glow-curve shapes and over-all intensity relationships between powder preparations from different formations appeared to indicate that identification and correlation of these limestones could be determined on this basis. However, when the glow curves of the subsurface samples were run, it was discovered that within any one formation, the glow-curve shapes and in-

FIG. 3.—Representative gamma-induced thermoluminescence glow curves.

tensities varied through wide limits, including many of the variations apparently characterizing different formations at the outcrop.

Figures 3 and 4 illustrate some of the typical variations in glow-curve shapes of the Chesteran and Meramecian limestone formations from the subsurface. The typical glow curve for the Kinkaid limestone has a high peak number 4 (numbering system for the peaks is indicated in Figure 5), from two to more than four times as high as peaks 1 and 3, which are usually nearly equal. The Clore limestone is typically extremely low in thermoluminescence, and its glow curves have not been illustrated.

The typical glow curve for the Menard limestone is similar in shape to that of the Kinkaid. The only obvious difference is the over-all intensity or height of peak 4: in the Kinkaid limestone peak 4 varies to considerably higher values than observed in the Menard limestone. The Vienna limestone, like the Clore, is almost uniformly low in thermoluminescence.

FIG. 4.—Representative gamma-induced thermoluminescence glow curves.

The glow curves of the Glen Dean limestone are distinctly different from both the Menard and Kinkaid glow curves in having a high first peak, varying from nearly equal to higher than peak 4.

Many of the variations in glow-curve shapes of the Golconda and Paint Creek formations are similar both in shape and intensity, although the Golconda does vary to a higher maximum intensity.

The glow curves of the Renault formation show similarities to those of the Paint Creek and Golconda formations.

The glow curves of the Meramecian formations are in general easily differ-

entiated from those of the Chesteran formations. Almost without exception, the glow curves of the Meramecian formations have high first peaks. Only the Glen Dean curves from the Chesteran formations resemble the typical Meramecian glow curves.

Within the Meramecian series, it is not easy to differentiate the formations on the basis of glow-curve shapes or over-all intensities. All of the formations show considerable variation in both glow-curve shape and intensity.

FIG. 5.—Typical gamma-induced glow curve and resolution of peaks. Vertical component is intensity of thermoluminescence measured in arbitrary units.

ANALYSIS OF PATTERNS OF VARIATION

The wide variations in both glow-curve shape and over-all intensity within a single formation in the thick subsurface sections make identification and correlation of individual limestones and zones difficult from single glow curves or short series of glow curves. An analysis of the pattern of variation through the entire formation, with closely spaced samples, gives promise of producing good results in correlation problems.

For the purpose of analyzing these patterns of variation within separate formations, only peaks 3 and 4 were used. Peak 1, the lowest temperature peak, is too easily affected by room temperature to be used quantitatively without adequate means of refrigeration of samples both during and after irradiation in the cobalt 60 gamma-ray source. Peak 2 is typically so small that it is masked by the first peak. A typical glow curve showing the numbering system for the peaks and the resolution of the curve into its component peaks is shown in Figure 5.

DETAILED ANALYSIS OF LEVIAS CORE SAMPLES

A detailed analysis of the glow-curve variations was made on the continuous core through the Levias member of the Ste. Genevieve limestone (Superior's Hawkins well No. 1). Samples were taken at 1-foot intervals through the 23-foot thickness of the Levias. In this case, the powder preparations were weighed in order to check the accuracy of the volume method used throughout the remainder of this study. The maximum variation between the weighed and unweighed samples was only 7.5 per cent.

In Figure 6, the four left-hand columns show the variations in individual peak heights through the formation. In general, all four peaks are comparatively low in the bottom two-thirds of the formation, and all peaks are relatively higher in the upper third of the formation.

TABLE I.—LITHOLOGIC DESCRIPTION OF LEVIAS MEMBER (SUPERIOR'S HAWKINS NO. 1)

<i>Depth in Well (Feet)</i>	<i>Thick- ness (Feet)</i>	<i>Lithologic Description</i>
2,942-2,944	3	Medium light gray, medium to coarsely crystalline limestone with abundant fossil fragments
-2,947	3	Medium gray, finely crystalline limestone with fossil fragments present
-2,949	2	Medium light gray, coarsely crystalline limestone with abundant fossil fragments
-2,950	1	Medium light gray, finely crystalline limestone with fossil fragments rare
-2,954	4	Light olive-gray, fine-grained limestone with abundant darker oölites and few fossil fragments
-2,962	8	Medium light gray to medium gray finely crystalline limestone with darker oölites and few fossil fragments
-2,965	3	Medium light greenish gray, finely crystalline limestone with darker oölites, and becoming sandy in last foot

The fifth column in Figure 6 shows the variation in insoluble residue percentages through the formation, generally low in the upper half and becoming fairly high in the lower half. The sixth and seventh columns of Figure 6 show the variations in thermoluminescence (TL) for peaks 3 and 4 per milligram of available calcite, corrected for weight of sample and insoluble residue content. From these columns, it is apparent that the differences in amount of thermoluminescence between the upper and lower parts of the formation are real, and not merely a function of the amount of calcite in the sample.

The right-hand column of Figure 6 illustrates the double curve of variation as used in the remainder of this study. The right-hand curve, the A curve, shows variations in intensity or magnitude of thermoluminescence as shown by peak 4. The left-hand curve, the B curve, is an indication of the shape of the glow curve as shown by the ratio between peak 4 and peak 3.

CHESTERAN LIMESTONES

Figures 7 through 11 illustrate the patterns of variation in glow-curve shapes

FIG. 6.—Analysis of gamma-ray induced thermoluminescence glow-curve variations, Levias core, Superior Oil Co's. Hawkins well No. 1.

and intensities for five of the eight Chesteran limestone formations. Two of the formations, the Clore and Vienna limestones, are uniformly too low in thermoluminescence to plot. The very lack of thermoluminescence in these formations may be a characteristic useful in correlation. The third formation not plotted is the Paint Creek formation, in which the samples were too sparse to plot, although they showed strong thermoluminescence.

Kinkaid limestone.—The four plots for the subsurface Kinkaid limestone sections are shown in Figure 7. The locations of these wells can be seen in Figure 1.

FIG. 7.—Kinkaid limestone. Variation patterns of gamma-ray-induced thermoluminescence. Circled letters indicate points of correspondence between curves for different wells.

The bottom of the formation was used as the datum plane. Well depths of top and bottom of the formation are indicated. The extent of the limestone in the formation is shown by the solid line in the center of each pair of curves. The little circles on the curve indicate points at which samples were available and glow curves run.

The patterns of variation in the four wells are not exactly the same, but similarities can be seen. At points marked A, the right-hand curve (A curve), showing intensity of peak 4, rises to the maximum. At points marked B, the intensity curve drops to the minimum, and the shape ratio curve (left-hand, B curve) usually shows a change. At C is another maximum in the intensity curve and the intensity drops to minimum again at D near the bottom of the formation. A

lack of samples may account for many of the dissimilarities. However, the absence of the upper maximum, A, in the right-hand plot (Ryan and Aetna's Jenkins No. 1) is not due merely to missing samples, since the Pennsylvanian shales and sandstones lie directly above the upper limestone bed as shown. This may indicate erosion or non-deposition of that zone at that locality. The patterns of variation for the other Chesteran formations generally show both the top and bottom of formation low in thermoluminescence intensity. The two center plots of the Kinkaid exhibit this characteristic and the absence of this drop in intensity

FIG. 8.—Menard limestone. Variation patterns of gamma-ray-induced thermoluminescence. Circled letters indicate points of correspondence between curves for different wells.

near the top of the formation in the left-hand plot (Tunnel Hill's Boner No. 1) may indicate some erosion at this locality, also.

Menard limestone.—The four variation patterns for the Menard limestone are illustrated in Figure 8. In some of the wells, particularly Mitchell's Fly No. 1, the samples are rather widely spaced, giving poor control. The similarities in pattern are evident. The top and bottom of the formation are low in thermoluminescence, except for the bottom of the Tunnel Hill's Boner Well No. 1, which is high in thermoluminescence intensity. Intensity maxima occur at points marked A and C, and a minimum occurs at points marked B.

Glen Dean limestone.—Figure 9 illustrates the patterns of variation for the Glen Dean limestone in the four wells sampled. Again, the top and bottom of the formation are generally low in intensity, as shown by the right-hand curve in each plot. The typical pattern appears to have two intensity maxima at A and B, with a minimum between, as best shown in the two right-hand plots. The absence of the lower intensity maximum, B, in the two left-hand plots can be ascribed to lack of samples at the critical points.

In order to check one of the possible causes for the characteristic low intensities of thermoluminescence at the top and bottom of the formation, insoluble

residue tests were run on the Glen Dean samples from Ryan and Aetna's Jenkins well No. 1. Insoluble residue percentages varied from less than 1 per cent to 14 per cent, but no correlation was found between the high insolubles and the low thermoluminescence intensities at the top and bottom of the formation.

Golconda formation.—The variation patterns for the four well sections of the

FIG. 9.—Glen Dean limestone. Variation patterns of gamma-ray-induced thermoluminescence. Circled letters indicate points of correspondence between curves for different wells.

FIG. 10.—Golconda formation. Variation patterns of gamma-ray-induced thermoluminescence. Circled letters indicate points of correspondence between curves for different wells.

Golconda formation are illustrated in Figure 10. As observed previously in the other formations, the top and bottom of the Golconda are generally low in thermoluminescence. A double intensity maximum occurs in the upper part of the formation at A. Near the middle of the formation, there is a sharp drop in intensity to the minimum at B. A smaller less persistent maximum occurs at C.

Renault formation.—Only three variation patterns for the Renault formation

are illustrated in Figure 11; not enough samples from the Kingwood's Oliver well No. 1 were obtained to make a satisfactory plot of the variation. The top and bottom of the formation are low in intensity, maxima occur at A and C, and a minimum occurs at B. A third intensity maximum occurs in the middle of the formation in the right-hand plot. In this well, the Renault formation is usually subdivided into the Downeys Bluff limestone above, and the Shetlerville limestone below.

Insoluble residue tests were run on the Renault formation samples from the Tunnel Hill's Boner well No. 1. The percentages of insoluble residue varied from

FIG. 11.—Renault formation. Variation patterns of gamma-ray-induced thermoluminescence. Circled letters indicate points of correspondence between curves for different wells.

FIG. 12.—Levias limestone member (Ste. Genevieve limestone). Variation patterns of gamma-ray-induced thermoluminescence. Circled letters indicate points of correspondence between curves for different wells.

4 per cent to 33 per cent, but again there was no correlation between high insolubles and low thermoluminescence.

Levias limestone member.—The Levias member of the Ste. Genevieve limestone is ordinarily placed in the Meramecian series, but some stratigraphers have thought that it properly belongs in the Chesteran series. Three variation patterns for the Levias member are shown in Figure 12. Two of the cable-tool well sample sets did not contain sufficient samples from the Levias. The middle plot in Figure

12 is from the continuous core through the Levias (Superior's Hawkins No. 1) as shown in Figure 6. It shows more detail because of the one-foot interval samples, with no mixing from adjacent beds. Comparison between these variation plots is difficult. The Levias member of the Ste. Genevieve can not be recognized everywhere in the subsurface, and in some wells the upper beds of the Ste. Genevieve are arbitrarily designated the Levias member. The Levias member is ordinarily fairly thin, in few places more than 25 feet thick, and in cable-tool wells only a few samples are ordinarily taken. A detailed thermoluminescence study, using cores where available, might help to determine the exact relationships of the Levias member.

MERAMECIAN LIMESTONES

One of the wells used in this study (Tunnel Hill's Boner No. 1) penetrated the Meramecian series of the Mississippian system in addition to the Chesteran series. This presented an opportunity to check the variation patterns in a sequence of thick limestones without pronounced lithologic breaks. Unfortunately, as additional sets of samples through the same formations at other localities were not readily available, it is not known how persistent these patterns are laterally.

The variation patterns for the Ste. Genevieve, St. Louis, and the upper part of the Salem limestones are illustrated in Figure 13. The arrows point out major changes in the pattern which might be useful for correlation.

The shape of glow curve, shown by the shape-ratio curve on the left side of the plot, is fairly uniform through the Ste. Genevieve and St. Louis formations, but changes markedly near the St. Louis-Salem boundary.

The intensity of thermoluminescence, shown by the right-hand curve of the plot, varies considerably through the Ste. Genevieve limestone. Some of these variations are distinct enough to be used as marker zones in correlation.

There is no major change in intensity at the Ste. Genevieve-St. Louis boundary, as usually determined in the subsurface from the first occurrence of chert. There are changes in intensity above and below this point. The first occurrence of chert is not everywhere a reliable basis for recognizing the top of the St. Louis limestone; chert may be locally present in the lower part of the Ste. Genevieve, and is absent in some of the upper beds of the St. Louis limestone.

The intensity curve shows larger variations through the St. Louis limestone than through the Ste. Genevieve. There are several intensity zones in the St. Louis distinct enough to be used as markers for correlation.

Near the St. Louis-Salem boundary, there is a sharp change in the shape-ratio curve (left side), and a sharp increase in intensity (right side).

RELATION BETWEEN RADIOACTIVITY AND THERMOLUMINESCENCE

In order to determine the relationship between the radioactivity of a limestone and its thermoluminescence, four samples were chosen which exhibited four distinctly different glow-curve shapes and intensities. Surface outcrop and core

FIG. 13.—Variation patterns for Ste. Genevieve, St. Louis, and upper part of Salem formations.
Arrows indicate major variations which might be useful for correlation.

FIG. 14.—Relation between radioactivity and thermoluminescence.

samples were chosen in order to have enough material for a relative radioactivity determination. The relative radioactivity of each sample was measured in alpha counts per hour above background, as determined by an alpha scintillation counter. The alpha scintillation counter was described briefly in the section on procedure and apparatus. A full description of a similar alpha counter is given by Holland and Kulp (1950).

Figure 14 illustrates the results of this experiment. The four different glow curves are shown, with the peak heights of the three major peaks indicated.

Table II summarizes the characteristics of each limestone.

TABLE II

	<i>Vienna</i>	<i>Paoli</i>	<i>Levias</i>	<i>Kinkaid</i>
Color	Light olive gray	Light yellowish gray	Medium light gray	Olive gray
Texture	Fine-grained	Extremely fine-grained	Finely crystalline	Fine-grained
Insoluble residue	10.5%	0.9%	2.9%	6.0%
Alpha counts per hour	1	6	10	16
Height, peak 1	6	73	102	26
Height, peak 3	5	65	48	22
Height, peak 4	10	45	62	100

The graph in the upper part of Figure 14 shows the height of peak 4, uncorrected for insoluble residues and transparency, plotted against radioactivity in

alpha counts per hour. The four points fall nearly on a straight line. It is obvious that a similar plotting of the peak heights of peaks 1 and 3 would not fall on a straight line, but on curves that rise sharply, and then decrease less sharply. Apparently peaks 1 and 3 reach a saturation level rather early, and further radiation tends to lower the thermoluminescence, perhaps by enlarging or destroying the shallower electron traps.

This evidence, although not sufficiently abundant and detailed to be conclusive, appears to indicate a direct relationship between the radioactivity of a limestone and its thermoluminescence. Within this one basin of deposition and within this relatively short period of geologic time (upper Mississippian), the measurements of thermoluminescence appear to be actually measurements of the relative radioactivity of the limestones. It is highly desirable that this relationship be explored further to determine whether it is real or coincidental.

SUMMARY OF CONCLUSIONS

The preliminary work indicates that thermoluminescence of limestones may have some usefulness in subsurface stratigraphy. Possible applications are outlined as follows.

1. The pattern of variation in intensity of thermoluminescence, coupled with typical glow-curve shapes, may serve to identify and characterize a formation.

2. Where several limestone formations occur in sequence with no great lithologic breaks, the intensity and glow-curve shape variations may assist in recognizing tops and bottoms of formations.

3. The intensity of thermoluminescence and glow-curve shape variations may assist in splitting thick carbonate rock sequences into small units useful in correlation.

4. Once a typical pattern of variation is recognized for a formation, the absence of parts of that pattern at other localities may indicate erosion or non-deposition.

Within one basin of deposition and within one short period of geologic time, the variations in radioactivity of the limestones appear to dominate over variations in activators and variations in lithologic character in the cause of variations in thermoluminescence.

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**Surface Correlation of Some Pennsylvanian Limestones
In Mid-Continent By Thermoluminescence**

By

Robert E. Bergstrom

**Reprinted from THE BULLETIN OF THE AMERICAN ASSOCIATION
OF PETROLEUM GEOLOGISTS, Vol. 40, No. 5, May
(1956)**

THERMOLUMINESCENCE OF LIMESTONES OF
MISSISSIPPIAN MADISON GROUP IN
MONTANA AND UTAH

BY
C. W. PITRAT

Reprinted for private circulation from
THE BULLETIN OF THE AMERICAN ASSOCIATION OF PETROLEUM GEOLOGISTS
Vol. 40, No. 5, May, 1956

THERMOLUMINESCENCE OF LIMESTONES OF MISSISSIPPIAN MADISON GROUP IN MONTANA AND UTAH¹

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ABSTRACT

Glow curves of limestone samples from four sections of the Madison group were run in an effort to determine the extent to which thermoluminescence could be used to subdivide the Madison into smaller stratigraphic units which could be used in correlation. It was found possible to differentiate the Lodgepole and the Mission Canyon formations of the Madison group on the basis of the shapes of their glow curves, but further subdivision of these units was not successful.

Natural radioactivity of the rocks and their impurity content have been considered important factors in determining the intensity of thermoluminescence and the shape of the glow curve. The studies reported here failed to verify the role of radioactivity, but the magnesium content of the limestone was shown to have a profound effect on the shape of the glow curve. Calcitic limestones tend to have a high low-temperature peak in thermoluminescence; whereas magnesian limestones and dolomites have a high middle-temperature peak.

The discrimination between the Lodgepole and Mission Canyon formations of the Madison group was made primarily on the basis of the relative heights of the low- and middle-temperature peaks. This relation depends on the amount of magnesium in the limestone. Thus the distinction between the two formations by thermoluminescence is largely based on the difference in their magnesium content.

INTRODUCTION

Preliminary work by Saunders (1953)³ suggested that changes in thermoluminescence might be used to split the thick sections of lower Mississippian limestones in the Rocky Mountain area into smaller units which could be used in correlation. His examination of the glow curves of limestones from three sections of the lower Mississippian indicated the presence of four thermoluminescence zones. Seemingly the four zones were distinguished mainly on the basis of the intensity of the low-temperature thermoluminescence relative to the middle- and high-temperature thermoluminescence.

Since Saunders' pioneer work new information and techniques, largely the work of Parks (1953), have made advisable a restudy of the efficacy of thermoluminescence in correlating the Mississippian limestones of the Rocky Mountain area. It has been found necessary to refrigerate samples until just prior to the running of the glow curve if the low-temperature thermoluminescence is to be used. Powdered samples have been found to yield more reproducible results than the solid samples used formerly. Finally, methods for graphically expressing the vertical variation in thermoluminescence properties have been developed. These methods eliminate the bias which may sometimes accompany the process

¹ Manuscript received, November 7, 1955.

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The work reported here is part of a continuing research program which has been undertaken at the University of Wisconsin under the direction of Professor Farrington Daniels. It is supported by the Research Division of the United States Atomic Energy Commission under contract No. AT (11-1)-178.

The writer's thanks are extended to Professor Daniels for his many helpful suggestions and to E. J. Zeller, D. E. N. Zeller, and G. A. Sanderson for assistance in the field.

of deciding that a particular glow-curve type is characteristic of a certain stratigraphic interval.

Although radioactivity and impurity ions have been mentioned by most authors as the factors which control the intensity of thermoluminescence in limestones and the shape of the glow curves, very few supporting data have been published. In the present study an attempt has been made to clarify the roles of radioactivity and impurities as activators of thermoluminescence. Until the factors which control thermoluminescence in limestones are thoroughly understood, any stratigraphic conclusions based on thermoluminescence studies must be regarded as tentative.

LABORATORY PROCEDURES

As a first step in preparation, limestone samples were powdered by means of a Braun pulverator. Each powdered sample was screened, the minus 100 plus 200 fraction being retained for the running of the thermoluminescence glow curves.

Samples were irradiated for 72 hours in a 5-curie cobalt 60-gamma-ray source before glow curves were run. Bergstrom (1956) has shown that saturation is achieved under these conditions. Samples were refrigerated immediately after irradiation ceased, and they were kept below 0°F. until just prior to the running of the glow curves. These procedures must be followed if the low-temperature thermoluminescence is to be retained.

Each sample was weighed prior to the running of the glow curve in order that the thermoluminescence per milligram of sample could be computed.

The apparatus used for the running of the glow curves has been described by Saunders (1953), Parks (1953), and Bergstrom (1956), and the description will not be repeated here.

STRATIGRAPHIC SUMMARY

Peale (1893) first assigned definite stratigraphic names to the Upper Paleozoic rocks of western Montana. He gave the name Madison limestone to the Mississippian beds between the Three Forks shale (Devonian) and the Quadrant formation (Pennsylvanian). Peale did not definitely specify a type section for the Madison, but recent workers (Sloss and Hamblin, 1942; Holland, 1952) have concluded that it is located on the Gallatin River at Logan, Montana. To aid in the description of the beds Peale divided the Madison into a lower laminated limestone, a middle massive limestone, and an upper jaspery limestone. Weed (1899) split the Madison into the Paine shale, Woodhurst limestone, and Castle limestone. These names, which were accorded member rank, are approximately equivalent to the descriptive terms of Peale.

Collier and Cathcart (1922) divided the Madison of the Little Rocky Mountains of northern Montana into a lower, thin-bedded Lodgepole limestone and an upper massive Mission Canyon limestone. Sloss and Hamblin (1942) proposed

that the Lodgepole and Mission Canyon be considered formations within the Madison group, and that the Paine and Woodhurst be given the status of members of the Lodgepole. The term Castle limestone, the approximate equivalent of the Mission Canyon, was found to be pre-occupied, and has been dropped. In recent years the terminology of Collier and Cathcart, as modified by Sloss and Hamblin, has found wide acceptance by geologists working throughout the Montana area.

In the subsurface rocks of the Williston basin an evaporite sequence lies between the Mission Canyon limestone and the Kibbey sandstone, the basal formation of the Big Snowy group. These evaporites were given the name Charles formation by Seager (1942), who considered them to be a part of the Big Snowy group. However, recent workers in the area have concluded that the Charles bears closer affinities to the Mission Canyon than to the Big Snowy; accordingly, the Charles is now considered the upper formation of the Madison group.

LOCALITIES

In the present study four sections of the Madison were measured and extensively sampled. Figure 1 shows the approximate location of the sections.

The Three Forks section is located about 4 miles north of Willow Creek, Montana, and about 6 miles west of Three Forks in Secs. 25 and 36, T. 2 N., R. 1 W., Jefferson County, Montana. The exposures occur in a canyon which is reached by a gravel road from the town of Willow Creek. The locality is only 12 miles from the type section of the Madison at Logan, Montana.

The Little Rocky Mountains section was studied in Secs. 4 and 9, T. 25 N., R. 24 E., Blaine County, Montana. The rocks are exposed in the walls of Mission Canyon along the road between St. Pauls and Landusky. Only the Mission Canyon and the upper 100 feet of the Lodgepole were sampled at this locality.

The Little Belt Mountains section is located in Secs. 22, 27, and 34, T. 16 N., R. 7 E., along U. S. Highway 89 just north of Monarch, Cascade County, Montana.

The Bear River Range section was studied in Leatham Hollow, a small canyon about 8 miles southeast of Logan, Cache County, Utah, in Sec. 34, T. 11 N., R. 2 E. Measuring and sampling were begun at the base of the "Chinese Wall" rather than at the base of the Madison as defined by Holland (1952). At this locality the basal Madison beds are shales and sandstones, which are unsuitable for thermoluminescence studies.

MADISON GLOW CURVES

Figure 2 shows a typical gamma-induced glow curve for a sample of limestone from the Madison group. In the illustration there are only three peaks in intensity which appear at 95°, 200°, and 300°C. In some samples additional peaks of lesser magnitude may be detected, but they do not appear to be consistent enough to be useful. The numbering of the peaks in the illustration does not agree with

FIG. 1.—Map showing location of sections.

that used by Parks (1953) or Bergstrom (1956). In their curves an additional peak which they called peak 2 appeared at about 135°C . Peak 1 in this paper is equivalent to peak 1 of Parks and Bergstrom; peaks 2 and 3 are equivalent to their peaks 3 and 4, respectively.

Figure 3 shows representative gamma-induced glow curves of the Madison for each of the sections studied. The upper curve for each of the Montana sections is from the Mission Canyon formation; the lower curves are Lodgepole. The single curve shown for the Bear River Range section is a Lodgepole type. In the Lodge-

FIG. 2.—Gamma-induced glow curve from Madison group, showing peak temperatures and peak numbering system.

pole curves the low-temperature peaks are several times as high as the middle- and high-temperature peaks. The curves from the Mission Canyon of the Little Rocky Mountains and Little Belt Mountains exhibit low- and middle-temperature peaks of approximately equal height; whereas the Mission Canyon of the Three Forks section typically has a middle-temperature peak which is considerably higher than the low-temperature peak. In general, it may be stated that in typical Mission Canyon glow curves the middle-temperature peak is higher relative to the other two peaks than it is in Lodgepole curves.

FIG. 3.—Typical gamma-induced glow curves for Madison group limestones. Curves labeled A are of the Lodgepole type; those marked B are Mission Canyon. Numbers refer to positions of curves in sections.

The consistency of glow curves varies from section to section. In the Three Forks section the Lodgepole and Mission Canyon curves are so consistently distinctive that a single sample would be sufficient to establish which of the two formations was at hand. In the Little Belt Mountains and Little Rocky Mountains sections the picture is not so clear. Occasionally a typical Mission Canyon curve will come from a sample which is clearly from the Lodgepole part of the section. Conversely, some Mission Canyon samples will give Lodgepole curves. Thus in these sections numerous samples must be studied from different horizons before it is possible, from the glow curves, to differentiate Lodgepole from Mission Canyon.

PATTERNS OF VARIATION

It is impractical to illustrate great numbers of glow curves. By the same token it is difficult to visually compare numerous curves. To overcome these difficulties Parks (1953) introduced a method involving the pattern of variation in glow-curve shape through a section. His "double curve of variation" had much the same layout as an electric log with a footage scale in the center and a curve on each side. His "A" curve shows changes in the intensity of peak 4, the high temperature peak, and the "B" curve shows changes in the ratio of peak 4 to peak 3.

Bergstrom (1956) used a different method for analyzing patterns of vertical variation in some of his work. Like Parks, he used two curves to describe the changes in thermoluminescence through the section. One of his curves shows the ratio of the product of peaks 2 and 4 to peak 3. The other curve shows variations in the product of peaks 3 and 4. Thus Bergstrom's first curve is a measure of glow-curve shape; whereas his second curve measures the intensity of thermoluminescence.

In the present study attempts were made to use the methods of Parks and Bergstrom. However, it soon became apparent that in the Madison the low-temperature peak is of considerable stratigraphic importance. No method which failed to consider peak 1 gave any promise of success in subdividing and correlating these strata. It also became evident that glow-curve shape was much more useful than the intensity of thermoluminescence in these stratigraphic studies. The method adopted here to show changes in glow-curve shape through the sections is illustrated in Figure 4. The left-hand curve for each of the sections is a plot of the changes in the ratio of peak 2 to peak 3. The right-hand curve shows the changes in the ratio of peak 1 to peak 2. In both curves values increase to the right. In order to minimize the effects of occasional samples which sharply deviate from the over-all trend a moving average is applied to the data before the final curve is constructed. The Lodgepole-Mission Canyon contact, as it was determined in the field, is shown by an arrow opposite the footage scale on each of the Montana sections. No contact is shown for the Bear River Range section, because the entire section is regarded as Lodgepole.

The figure bears out the difference in glow-curve shape between typical

FIG. 4.—Variation patterns of gamma-induced thermoluminescence. Arrows indicate position of Lodgepole-Mission Canyon contact as determined in field. Depths shown in feet.

Lodgepole and typical Mission Canyon samples. Compared with the Lodgepole, the Mission Canyon is characterized by a low value for the ratio of peak 1 to peak 2 and a high value for the ratio of peak 2 to peak 3. The contact between the two types of glow curves is gradational in each of the sections, just as the changes in bedding and lithologic character are gradational in these sections. The contact between the two formations could probably be determined with about the same degree of precision by using the glow curves as it could by field examinations of outcrop sections.

The curves for the Bear River Range section give little indication of the presence of any Mission Canyon limestone. Near the top of the section the right-hand curve begins to fall rather abruptly, but this fall is not accompanied by the rise in the left-hand curve which is so characteristic of the Mission Canyon in the Montana sections. The writer is inclined to agree with Holland (1952, p. 1731), who states that "no lithologic equivalent of the Mission Canyon limestone of Montana exists within the Madison section in Utah unless the 62 feet of chert-bearing limestones at the top of the Utah Madison represent some part of the upper Madison group."

Although it does seem possible to differentiate Lodgepole from Mission Canyon by the use of thermoluminescence glow curves, the results of this study do

not appear to encourage further subdivision of these units for purposes of correlation over long distances by thermoluminescence. This fact is not at all surprising if one bears in mind the fact that correlation by thermoluminescence is similar to correlation by lithology in the sense that neither method has any intrinsic time value. It seems likely that the thermoluminescence characteristics of a limestone are determined in large part by the conditions attending the deposition of that limestone. Since such conditions change laterally as well as temporally, one need not expect the details of thermoluminescence to persist over long distances.

FACTORS INFLUENCING THERMOLUMINESCENCE OF LIMESTONES

Parks (1953) showed an almost linear relationship between the intensity of the high-temperature thermoluminescence of Chesteran limestones and their

FIG. 5.—Relation of thermoluminescence to magnesium content of limestone.

radioactivity measured in alpha counts per hour. In the present study the writer was unable to detect any such relationship.

Zeller (1954) has reported that impurity ions have a significant effect on thermoluminescence of artificially precipitated calcium carbonate—iron acting as an inhibitor, and manganese and strontium as activators. Recently he has found that magnesium tends to increase middle-temperature thermoluminescence at the expense of low-temperature thermoluminescence in the artificial precipitates (personal communication).

In the present study a number of limestone samples were analyzed spectrochemically in an attempt to discover the relationship, if any, between glow-curve shape and concentrations of impurities in natural limestones. Of the dozen impurities included in the analyses only magnesium appeared to bear any relationship to thermoluminescence. Figure 5 shows the correlation between thermo-

luminescence and magnesium; as the MgO percentage rises, the ratio of peak 1 to peak 2 falls. In other words, magnesian limestones and dolomites tend to have a higher second peak; whereas the more calcitic limestones have a higher first peak. It may well be that the shape of the low-temperature part of the glow curve is controlled by magnesium exclusively.

The reader may recall that in this paper the ratio of peak 1 to peak 2 has been given considerable weight in discriminating between Lodgepole and Mission Canyon. Since the magnesium content seems to control this ratio, the discrimination is based on magnesium to a large extent. Although the magnesium content of the Mission Canyon approaches that of pure dolomite in only one of the sections studied—the Three Forks section—it seems everywhere higher in the Mission Canyon than in the underlying Lodgepole.

Sloss (1952) has interpreted the dolomites high in the Mission Canyon of the Williston basin as part of the lowest evaporite cycle of the Charles formation. If, as seems likely, primary dolomites are indicative of higher than normal salinity conditions, the entire Mission Canyon may be regarded as representing a stage intermediate between the normal marine Lodgepole limestone and the evaporite Charles.

SUMMARY OF CONCLUSIONS

1. It seems possible to differentiate between the Lodgepole and Mission Canyon formations of the Madison group on the basis of thermoluminescence glow curves. In general, the ratio of the low- to the middle-temperature peak is considerably higher in Lodgepole than in Mission Canyon curves. It does not appear feasible to split the Lodgepole or the Mission Canyon into smaller units on the basis of thermoluminescence.

2. In the limestone samples studied there is no clear relationship between the radioactivity of the rocks and their gamma-induced thermoluminescence. If high radioactivity tends to produce an increase in thermoluminescence, the manifestation of this effect is masked by other factors.

3. Impurities are extremely important in determining glow-curve shape. Of the many impurities in the limestones studied only magnesium has so far been demonstrated to affect the glow curves of natural limestones. The magnesium content bears an inverse relation to the ratio of peak 1 to peak 2.

4. The magnesium content of the Mission Canyon is consistently higher than that of the Lodgepole, suggesting that the Mission Canyon represents salinity conditions intermediate to the normal marine Lodgepole and the evaporite Charles.

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FACTORS IN AGE DETERMINATION OF CAR-
BONATE SEDIMENTS BY THERMO-
LUMINESCENCE

BY

EDWARD J. ZELLER, JOHN L. WRAY AND FARRINGTON DANIELS

Reprinted for private circulation from
THE BULLETIN OF THE AMERICAN ASSOCIATION OF PETROLEUM GEOLOGISTS
Vol. 41, No. 1, January, 1957

FACTORS IN AGE DETERMINATION OF CARBONATE SEDIMENTS BY THERMOLUMINESCENCE¹

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ABSTRACT

New data obtained from pressure experiments have shown that at least two genetic types of thermoluminescence exist and have furnished an objective means for the selection of limestone samples for age determination tests. The quantity of gamma radiation necessary to reproduce the natural thermoluminescence of a sample can be determined experimentally. When this value is divided by the natural radiation rate, an index is obtained which bears a linear relationship to geologic age. Possible sources of error have been recognized and their effects are discussed. (auth)

INTRODUCTION

Thermoluminescence methods of geologic age determination have been under study at the University of Wisconsin since 1950. In the earlier studies, it was assumed that all of the light emitted was caused by the thermal release of trapped electrons produced originally by radioactivity due to traces of uranium and other radioactive elements. The results obtained from these experiments presented a complex picture which could not be clearly interpreted. In order to improve understanding of the nature of thermoluminescence, recent experiments have been conducted using both natural limestones and artificially precipitated calcium carbonate. These studies have helped to clear up much of the confusion presented by the earlier results.

The first published report of this work (Zeller, 1954a) described the technique for making thermoluminescence measurements and provided an outline of the theory of this method of age determination. A later paper (Zeller, 1954b) discussed the theory in greater detail and included a description of the effects of impurities and pressure and the errors which these factors might introduce. The theory of the thermoluminescence age determination method was based on the assumption that the thermoluminescence of a rock sample was the result of radiation damage and that the effects of the radiations were cumulative.

Further experimentation with pressure had led to the discovery that geologically young samples and artificially prepared calcium carbonate precipitates show a kind of thermoluminescence which can not be attributed to radiation damage (Zeller, Wray, and Daniels, 1955). These discoveries together with the addition of more extensive data concerning impurities (Lewis, 1956; Pitrat, 1956) and crystal phase changes (Zeller and Wray, 1956) have forced some major

¹ Manuscript received, July 27, 1956.

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This research was done at the Department of Chemistry, University of Wisconsin, Madison. The writers express their appreciation to Harry S. Ladd, U. S. Geological Survey, who provided some of the samples used. They are indebted to the Atomic Energy Commission, Research Division, for its generous support of a research program of which this study is a part.

revisions in the theory of thermoluminescence as it applies to geologic age determination. On the other hand, these discoveries have provided an explanation for some of the heretofore unexplainable and contradictory results which the geologically young samples have shown.

PRESSURE EXPERIMENTS

The newest data from pressure experiments are included here to provide a critical and objective means for the selection of rock samples for geologic age determination. All of the pressure experiments were confined to samples that had *not* been subjected to artificial irradiation.

Pressure was applied to dry powdered samples of limestone and calcium carbonate precipitates in a pelleting mold by a hydraulic press. The pellets were formed in thin-walled silver cups 12 mm. in diameter and were subjected to pressures of approximately 50 tons per square inch for 5 minutes. All of the calcium carbonate precipitates prepared in the laboratory which were subjected to pressure in this manner showed roughly a four-fold increase in the amount of light emitted by the pressed samples as compared with the unpressed material. Further tests were conducted using stalactites, corals, and limestones of Recent

FIG. 1.—Ratio of natural thermoluminescence of pressed to unpressed sample plotted against geologic time.

and Tertiary age. Without exception, it was found that pressure had the effect of increasing the thermoluminescence of the geologically young samples. Lower Tertiary samples showed progressively less increase in thermoluminescence after pressure, and all Mesozoic and Paleozoic limestones showed a reduction in thermoluminescence with pressure. Figure 1 is a curve of the ratio of natural thermoluminescence of a sample of pressed powder to the thermoluminescence of the unpressed sample, plotted against geologic age.

Freshly precipitated calcium carbonate with no radiation, and very young limestone deposits with little exposure to radiation, exhibited some thermolu-

TABLE I. GEOLOGIC FORMATION, LOCALITY, AND GEOLOGIC AGE OF SAMPLES
PLOTTED IN FIGURE 1

Sample	Geologic Formation	Locality	Geologic Age
1	Lab. precip. (CaCO ₃)		
2	Lab. precip. (CaCO ₃)		
3	Lab. precip. (CaCO ₃)		
4	Coral limestone	KDJ 125 Kita-Diato-Jima	Pleistocene?
5	Stalactite	Lehman Caves, Nev.	Pleistocene?
6	Coral limestone	KDJ 690 Kita-Diato-Jima	Pliocene?
7	Fragmental limestone	F-1-4-10 Eniwetok	Miocene
8	Fragmental limestone	F-1-14-26 Eniwetok	Eocene
9	Fragmental limestone	F-1-14-22 Eniwetok	Eocene
10	Sierra Blanca	San Rafael Mtns., Calif.	Eocene
11	Greenhorn	Cañon City, Colo.	Cretaceous
12	Sundance	Devil's Tower area, Wyo.	Jurassic
13	Hosselkus	Brock Mountain, near Redding, Calif.	Triassic
14	Fragmental limestone	Conger Spring, Confusion Range, Utah	Pennsylvanian
15	Ste. Genevieve	Ste. Genevieve, Mo.	Mississippian
16	Onondaga	Union Springs, N. Y.	Devonian
17	Girardeau	Cape Girardeau, Mo.	Silurian
18	Pogonip	E. Confusion Rge., Utah	Ordovician
19	Dunderberg	Adams Hill, near Eureka, Nev.	Cambrian
20	Burrows	Cherry Creek Canyon, Egan Range, Nev.	Cambrian
21	Siyeh	Glacier National Park	Pre-Cambrian

minescence. It is apparent then, that the thermoluminescence of geological samples does not start from zero at the time of deposition as had been previously assumed. It is clear also from these studies that there are at least two genetic types of thermoluminescence shown by calcium carbonate. One type is developed at the time the crystals of the calcium carbonate precipitate are formed, and the other is produced by radiation damage with gamma rays or other high energy radiation. The two types of thermoluminescence are affected differently by the application of pressure, and thus a convenient qualitative means of separating the effects of crystallization from those of radiation is provided. There seems to be little doubt that the thermoluminescence which is produced by crystallization is the result of a process which operates only at the time of crystal formation. Thereafter, an aging process, probably in the form of annealing, causes its gradual

decrease and disappearance. Samples older than Eocene have not been found to show any evidence of crystallization-induced thermoluminescence, as shown by their failure to give increased thermoluminescence after high-pressure treatment. The geologic history of the sample and the natural processes to which it has been subjected undoubtedly have a strong influence upon the length of time through which the initial crystallization-induced thermoluminescence persists.

With the development of a practical method for differentiating between samples which show radiation-induced thermoluminescence and those which show crystallization-induced thermoluminescence, it has become possible to make a critical test of the geologic age determination method. In this test no attempt has yet been made to subtract the effects of crystallization from those of radiation, and all samples showing any evidence of the crystallization effect have been rejected.

AGE DETERMINATION RESULTS

Twenty samples were selected and thermoluminescence age determination tests were made following the technique previously outlined (Zeller, 1954b) but using a modified procedure for obtaining the calibration curves. The natural thermoluminescence of each limestone was measured in the usual way and the area of the high temperature glow-curve peak, arbitrarily chosen between the temperatures of 250°C. and 375°C., was determined by planimetry. Four quantities of the sample, equal in weight to the quantity used to determine the natural thermoluminescence glow-curve, were then heated to 400°C. for 10 minutes in order to remove all of the natural thermoluminescence. The four samples were then subjected respectively to larger dosages of gamma radiation. These dosages ranged from approximately 72,000 roentgens to approximately 288,000 roentgens. The area of the high-temperature peak of each of the artificial glow-curves obtained in this manner was determined by planimetry and the four points thus provided define the calibration curve for the limestone under study. By using the calibration curve, the relative equivalent radiation dosage (R_a) required to duplicate the natural thermoluminescence can be determined. A value directly proportional to geologic age is obtained by dividing the relative equivalent dosage (R_a) by the net alpha count per hour (α) for a 20-square-centimeter area of the sample. The alpha counts give the number of alpha particles emerging from the surface of a thick layer of powder in a dish 2 inches in diameter. Counts per hour per square centimeter may be obtained from these values by dividing by 20. For example, in Figure 2 the relative equivalent dosage (R_a) of a specific sample, obtained by interpolation, is 222×10^3 and the alpha count is 17, as shown in Table II, thus giving a value of 13.1×10^3 on an empirical time scale.

The purpose of the calibration curve with gamma-ray exposure is to make allowance for impurities and other factors which affect the thermoluminescence. The sensitivity of thermoluminescence to a given dosage of radiation will vary greatly with the geologic sample but this sensitivity is established for each sample

FIG. 2.—Sample calculation for thermoluminescence method of age determination.

by the gamma-ray calibration. The slope of the curves may vary considerably from the specific example shown in Figure 2. Figure 3 is a graph showing the values R_0/α of the samples plotted against their relative geologic age as determined by paleontology and stratigraphy.

SOURCES OF ERROR

In evaluating the results shown in Figure 3, it is necessary to consider the possible sources of error and how they may affect the calculated values for the geologic age of the samples. An important source of error is concerned with the chemical and physical nature of the material of which the sample is composed. Even under the most favorable conditions it is not possible to be certain that the crystal lattice of all of the limestone in the initial hand specimen collected in the field is of the same age. In obvious cases, veins or cavity fillings can be observed, but recrystallization of the interstitial cement in detrital limestones might occur without being readily detected even in thin sections. Present knowledge of these recrystallization processes and their effect on the potential thermoluminescence of a limestone sample is very limited.

TABLE II. GEOLOGIC FORMATION, LOCALITY, GEOLOGIC AGE, AND ALPHA COUNT OF SAMPLES PLOTTED IN FIGURE 3

<i>Sample</i>	<i>Geologic Formation</i>	<i>Locality</i>	<i>Geologic Age</i>	<i>Alpha Count (Per Hr. Per 20 cm.² Area)</i>
1-3-1	Greenhorn	Cañon City, Colo.	Mid. Cretac.	6
26-1-2	Sundance	Devil's Tower area, Wyo.	Up. Juras.	6
10-1-3	Hosselkus	Brock Mtn. near Redding, Calif.	Up. Trias.	8
9-1-2	Dun Glen	Sonoma Range, Nev.	Mid. Trias.	5
12-2-1	Meekoceras zone	Pequop Range, Nev.	Low. Trias.	6
12-1-1	Guadalupean ls.	Pequop Range, Nev.	Up. Perm.	4
58-1-2	Wells	Sublett Mtns., Ida.	Low. Perm.	13
58-1-1	Wells	Sublett Mtns., Ida.	Mid. Penn.	7
59-1-1	Lonsdale	Cramer, Ill.	Mid. Penn.	11
20-1-2	Pennsylvanian ls.	Conger Spr., Confusion Range, Utah	Low. Penn.	17
52-1-2	Burlington	Near Milton, Ill.	Mid. Miss.	2
53-1-1	Shellrock	Nora Springs, Iowa	Mid. Devon.	5
40-1-1	Onondaga	Union Spring, N. Y.	Mid. Devon.	6
34-2-2	Coeymans	Countryman Hill, New Salem, N. Y.	Low. Devon.	7
50-2-1	Girardeau	Cape Girardeau, Mo.	Low. Silur.	3
37-1-1	Richmond	Camden, Ohio	Up. Ordov.	4
30-1-8	Platville	Kentland, Ind.	Up. Ordov.	5
21-1-4	Pogonip	South Confusion Range, Utah	Low. Ordov.	6
31-2-2	Axeman	Bellefonte, Penn.	Low. Ordov.	7
17-1-4	Dunderberg	Adam's Hill, near Eureka, Nev.	Up. Camb.	2

In the past, it has been assumed that recrystallization would free all trapped electrons whether it occurred by solution or by heating to high temperatures. There is no doubt that prolonged exposure of limestones to temperatures over 200°C. would drain all of the electrons from their traps and it can probably be assumed that a crystal lattice formed above 400°C. would not be able to hold any electrons which might be freed by the crystallization process. On the other hand, recrystallization occurring by solution and reprecipitation can occur at normal temperatures and any part of the crystal lattice of the sample which has been produced in this manner could show crystallization-induced thermoluminescence.

Probably the largest errors which are introduced into the age calculations come from the uneven distribution and chemical mobility of the radioactive impurities in the limestones. Local concentrations of radioactive elements along grain boundaries might contribute heavily to the alpha count of the sample without adding proportionately to its thermoluminescence. On the other hand, leaching of highly mobile uranium from limestones exposed at the surface would tend to produce a false low alpha count. In such cases, the samples would appear to be older than their true geologic age. A limestone might show high thermoluminescence but low alpha count if the limestone were immediately overlain or underlain by highly radioactive shales. These shales might contribute heavily to the

FIG. 3.— R_a/α of rock samples plotted against geologic time.

natural gamma radiation flux without contributing to the alpha count of the limestone. While alpha particles are much more effective than gammas at freeing electrons in the lattice, a high gamma flux could produce a noticeable effect over a long period of time. The effect in this case would be to cause the sample to appear older than its actual age.

Besides errors introduced by recrystallization and lack of heterogeneity in the distribution of radioactive elements, any change in the general impurity content of the limestone might cause changes in the number of electron traps present in the crystal lattice of the limestone at any one time. If the sensitivity of the thermoluminescence to radiation effects change during the geologic history of a sample, the calibration curve (Fig. 2) will fail to provide a true measure of the radiation intensity necessary to equal the natural thermoluminescence.

In using the calibration curve to determine the value for the relative equivalent radiation dosage (R_a), it is necessary to make the assumption that the curve obtained by high-intensity gamma radiation has the same general form as that resulting from the low intensity of natural radiation rates. Since the values obtained for R_a/α , shown in Figure 3, follow a linear relationship with respect to geologic age it appears that this assumption is justified. Nevertheless, at normal

rock temperatures some electrons even in high-temperature traps may occasionally have enough energy to escape. Thus, an equilibrium might be established between electrons entering traps, due to radiation, and those escaping due to natural thermal stimuli. Presumably, the length of time necessary to reach this equilibrium would be dependent on the natural radioactivity of the sample which affects the rate of filling, and the temperature and trap depth which influence the rate of electron escape. The establishment of such an equilibrium would be possible only if the number of electron traps remained constant. If alpha particles themselves are capable of creating traps as well as filling them, this equilibrium could not be established.

Aside from errors originating within the samples or from the external effects of geological processes, further errors might be introduced in the procedure by which age determinations are made. For example, it is necessary to assume that grinding does not cause a significant reduction or increase in the number of electrons in traps. Experiments with solid and powdered samples of limestones older than Eocene have shown that the effects of grinding are sufficiently small as to be undetectable with our present apparatus; however, there is little doubt that small errors are introduced in this way. It is also necessary to assume that heating samples to 400°C. for 10 minutes prior to irradiating for calibration-curve measurements causes no major changes in their thermoluminescence characteristics. There is no way of deactivating limestone samples other than by heating and the oxidation of iron at higher temperatures could cause significant differences in the transparency and thermoluminescence characteristics of the sample. No completely satisfactory means of evaluating this source of error has been devised.

Finally, the apparatus with which the measurements are made can contribute to inaccuracies in the calculations. The thermoluminescence measurements themselves probably involve errors of less than 10 per cent and repeated runs of the same sample are used to reduce this figure substantially. Alpha counting is certainly the largest source of instrument error. The errors resulting from alpha counting are influenced by factors involving the characteristics of the counter, the length of time the sample is counted, and the background counting rate. In addition, samples which show a net alpha count of only 2 or 3 counts per hour above background always involve a larger margin of error than those with higher counting rates. For example, if there is an alpha count of 3 per hour for a 20-square-centimeter sample, an error of 1 alpha count will make a 30 per cent error in R_a/α and displace the point vertically in Figure 3 by as much as 20 per cent of the full scale. In this particular instance, improved instrumentation will greatly improve the accuracy with which age calculations can be made.

CONCLUSIONS

The results of the tests of the thermoluminescence method of geologic age determination which are reported here are more encouraging than any which

have been obtained during the past six years and they provide evidence to support the theory that thermoluminescence can be used as an actual estimate of geologic age. These tests have pointed out the kinds of errors which might be encountered in future attempts to make practical application of the method. Having recognized these sources of error, it is hoped that means can be found for reducing or eliminating them.

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Reprints from Nuclear Geology

Edited by Henry Paul

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CHAPTER 6

RADIATION DAMAGE AND ENERGY STORAGE

6.2 Thermoluminescence of Carbonate Sediments

By

Edward J. Zeller

6.3 Radioactivity, Energy Storage, and Volcanism

By

Farrington Daniels

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6.2 THERMOLUMINESCENCE OF CARBONATE SEDIMENTS *

EDWARD J. ZELLER †

When heated, many minerals emit visible light. This property is called thermoluminescence and is the result of the release of energy stored as electron displacements in the crystal lattice (Leverenz, 1950). Activation of thermoluminescence in a crystalline substance is believed to occur through the ability of radiations to free electrons from ions which make up the crystal lattice of the substance. These

* The author is indebted to the Atomic Energy Commission, Research Division, for its support of a research program of which this work is part.

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electrons then become trapped in imperfections in the lattice where they are held until the crystal is heated, giving them enough thermal energy to escape from their traps. The actual light emission occurs during the transition from the trap to normal lattice position. In a sense, the imperfections or "holes" are a statistical concept. Electrons which have been dislodged by some electromagnetic force remain as part of a dynamic system but are at an energy level higher than that of their normal state. Thermal effects allow the electrons to return to their former positions, and the energy is released as photons. The exact nature of the electron traps is not known, but impurity inclusions, ion vacancies, and ion dislocations are thought to be the causes of most of the traps.

Since the discovery that carbonate sediments show a general increase in natural thermoluminescence with increasing geologic age, attempts have been made in the laboratories of the University of Wisconsin to produce a usable thermoluminescence age-determination method. Experiments have shown a proportional relationship between the amount of light emitted by a thermoluminescent substance and the amount of radiation to which the substance has been subjected. In theory, the geologic age of a sample could be determined by measuring the alpha radioactivity of the sample and the amount of light released. It is possible to bombard samples with alpha particles and thereby determine the amount of thermoluminescence induced in the sample for each unit of artificial irradiation. We have attempted to determine the degree to which the relationship between thermoluminescence and total irradiation would hold under geologic conditions.

6.2.a Activation of thermoluminescence

In nature, the most likely radiations which could activate thermoluminescence are alpha particles and recoil nuclei which come from the decay of radioactive elements. Radioactive atoms are included as impurities in the crystal lattice of carbonate minerals. All the natural samples that have been studied show a measurable alpha activity, and it appears reasonable to relate thermoluminescence to this activity. Natural gamma radiation undoubtedly accounts for some of the activation but its relative effectiveness is much lower.

In comparing the effects of gamma rays with those of alpha particles, it is essential to consider the basic similarities and differences in processes by which these two types of radiation affect the lattice. Only very rarely is a gamma ray able to impart enough energy to

an ion to actually move it from its lattice position. The ionizing effects of gamma rays are largely confined to the production of primary and secondary electrons through the photoelectric effect and Compton scattering. Alpha particles are able to produce more complex radiation damage effects than gamma rays. Though most of their energy is expended in ionization, they are also capable of dislocating lattice ions by collision.

The effects of gamma radiation are more or less evenly distributed throughout the crystal lattice. On the other hand, the ionic dislocations and the electron displacements produced by alpha-particle radiation are initially confined to the immediate area of the particle's short path through the crystal. Rieke (unpublished thesis, Univ. of Wis., 1954) has shown conclusively that electrons freed by alpha radiation from polonium are capable of slow diffusion throughout the crystal lattice of single large crystals of lithium fluoride. Diffusion effects also occur in single crystals of the carbonate minerals; however, long-range electron diffusion does not occur in carbonate sediments because of the inability of the electrons to cross the crystalline grain boundaries.

Under natural conditions the source of the alpha particles which produce radiation damage lies within the crystal which is affected. Therefore, the alpha particle itself is not the only source of damage because the nucleus from which it is ejected recoils with an equal momentum. The alpha particle, because of its high initial velocity, expends most of its energy in ionization, and it is not until the velocity has been greatly reduced, near the end of its path, that ion dislocations are produced.

The relationship between the initial velocity of the recoil nucleus and that of its alpha particle is the inverse of the proportion of their relative weights, or about $1/55$. Thus the initial velocity of the recoil nucleus will be relatively low, and its ability to cause lattice dislocations will be proportionately large. Even under the most favorable circumstances only a very small proportion of the energy of the alpha particle and its recoil nucleus is expended in the production of lattice dislocations, and these effects become noticeable only after extremely heavy alpha bombardment. Lattice dislocations may influence the thermoluminescence of a substance either through their ability to act as electron trapping centers or more commonly through the destruction of existing electron traps. High degrees of lattice disorder always seem to result in decreased thermoluminescence. Metamict minerals are generally non-thermoluminescent, and calcites

which have been subjected to very large dosages of alpha radiation show a reduction in thermoluminescence intensity.

6.2.b Technique of age determination

Thermoluminescence is measured by means of an apparatus consisting of an electric furnace for heating the sample, a multiplier

Figure 6.3 Thermoluminescence glow curves of a limestone sample in its natural condition and after alpha irradiation. The low-temperature peak is drained under ordinary rock temperatures.

phototube to convert the light emitted into electric current, a pre-amplifier, and a two-point recording potentiometer. The temperature of the electric furnace is recorded simultaneously with the light emitted by the sample. Figure 6.3 shows two glow curves from the same

limestone sample. The curve of natural thermoluminescence is obtained by placing some of the powdered sample directly on the furnace. The alpha-activated glow curve was made by exposing some of the powdered sample to alpha radiation from polonium before placing it on the furnace. The natural glow curve shows two peaks, one at 235° C and the other at 312° C. The alpha-activated glow curve has a third peak at 110° C. This peak is not present in natural glow curves because ordinary rock temperatures are sufficiently

Figure 6.4 Typical calibration curve showing the relationship between thermoluminescence light intensity and the total alpha-radiation dosage received by a sample of limestone.

high to permit the escape of any electrons from the energy level corresponding to the 110° C peak.

To determine the geologic age of a sample it is first necessary to determine the shape of the calibration curve for that particular sample. This curve shows the intensity of thermoluminescence of the 312° C peak plotted against radiation dosage received by the sample. The 312° C peak is always used in these calculations because it is the only one that persists in samples subjected to ordinary rock temperatures. It is necessary to plot the calibration curve for each sample because the shape of the curve varies with the chemical composition.

When the relationship between intensity of thermoluminescence and artificial radiation dosage for a particular sample is known, the amount of radiation necessary to produce the natural thermolumines-

cence can be determined as illustrated in Figure 6.4. In this figure a natural thermoluminescence of 17 arbitrary light units intersects the calibration curve at an alpha-particle radiation exposure of 3.30×10^6 ergs. The amount of artificial radiation damage necessary to produce this amount of thermoluminescence is assumed to be equal to the amount required under natural conditions. The natural alpha radioactivity is measured by means of an alpha scintillation counter (See Section 1.12), and with this value it is possible to calculate the time required for the lattice to receive an equivalent radiation dosage under natural conditions.

In order to apply the results of laboratory studies to geologic specimens, several important assumptions must be made. It must be assumed first that the total quantity of radiation (and not the rate at which it is received) is the significant factor influencing thermoluminescence intensity. Repeated tests have indicated that this assumption is justified when artificial radiation sources of the intensities used in our laboratories (of the order of 1 curie) are dealt with.

In an attempt to compare artificial and natural radiation damage, it is necessary to assume that similar types of radiation produce similar results. Alpha particles from the polonium source used for irradiations in the laboratory do not have the same energy as alpha particles from thorium or uranium. It has been assumed that, when the proportional energies have been taken into account, the results can be expected to be comparable.

Obviously, calculations of this type are valid only if the natural thermoluminescence is truly the cumulative effect of all the natural radiation to which the sample has been subjected. Most of the problems involved in the measurement of the geologic age of carbonate sediments by the thermoluminescence method result from the instability of the crystal lattice of carbonate minerals. Since the number of traps, both filled and unfilled, existing at any time is dependent primarily upon the impurities included in the crystal lattice, each recrystallization is certain to affect the saturation percentage. The number of traps and the number of electrons in each trap may change. Each time a sediment is recrystallized, impurities may be added, removed, or simply redistributed, but each circumstance will have a distinct effect upon the total number of electron traps. If the sediment is heated through geologic processes to a temperature that permits drainage of the traps, refilling would begin again and the age obtained would be that of the return to lower temperature.

6.2.c Effects of impurities

Repeated experiments have shown that several of the commonly occurring impurities in carbonate sediments can influence the shape and magnitude of their glow curves. Manganese and strontium serve as activators, increasing thermoluminescence, whereas iron is an important inhibitor. From the geological point of view, the exact kind or magnitude of effects is less important than the fact that significant changes can be made by addition of small quantities of trace elements to the carbonate lattice. Changes in the chemical makeup of sediments occur during sedimentation and diagenesis and after lithification has taken place. Manganese may be selectively leached or deposited, and both strontium and iron are sufficiently mobile to change their concentrations as impurity ions in the carbonate lattice. The composition of a carbonate sediment undoubtedly reflects its crystal history as well as its source and environment of deposition. Experimental evidence indicates that the glow curve of a carbonate sediment is closely related to the impurities present in the sediment, and the glow-curve shape can be expected to change with chemical changes.

Effective as the common impurities may be in changing the character of the glow curve, the most important trace elements by far are the radioactive elements themselves. Little is known of the extent to which uranium and thorium can be leached or deposited selectively in the carbonate. It seems reasonable to expect these elements to be affected by the same processes that change the concentrations of other elements. Age calculations are based upon the assumption that the rate of irradiation remains essentially constant throughout the geologic history of the sample, with allowance being made for radioactive decay with time. If this is not true, serious inaccuracies will be introduced into the age calculations.

Besides variations in concentration of the trace impurities, the crystal phase conversions, which affect the lattice of calcium carbonate and the inclusion of magnesium to produce dolomite, likewise have marked influences upon the glow curves of the sediment. Each end member of a series may show its own characteristic glow curve which is influenced by any activator or inhibitor ions that have been included in its lattice. Impurities that fit readily into the lattice of one phase may not be accepted into the lattice of another. The relationship of aragonite and calcite and the conditions that bring about their phase conversion are not completely understood, and an equilibrium may exist between the crystal phases. If a sample that shows

the crystal form of calcite retains some groups of cells of aragonite within its lattice (Evans, 1948, p. 256), these areas themselves might act as electron trapping centers.

6.2.d Pressure effects

It has been discovered that pressure has marked effect upon artificially obtained glow curves of both chemically precipitated calcium carbonate and natural carbonate. Figure 6.5 shows the pressure effect upon height of the 110° C and 312° C peaks. The pressure is ap-

Figure 6.5 Effect of compression upon thermoluminescence of otherwise identical samples of alpha-activated calcium carbonate.

plied to dry samples of the precipitate in a pelleting mold in an hydraulic press. After the pellets have been formed, they are all subjected to equivalent radiation dosages and glow curves are run in the normal manner. The height of the 110° C peak decreases markedly with increasing pressure, and the 312° C peak increases. The mechanism by which energy storage is shifted from low- to high-temperature trapping levels is not understood, but its effect in introducing errors into age determinations is obvious since it is the 312° C peak which is always used in age determination.

6.2.e Summary

The thermoluminescence of a sample is definitely a function of the age and the rate of radiation, but it also can be shown to be greatly affected by impurity content, thermal history, and the pressure to which the sample has been subjected. The physical and chemical instability of the crystal lattice of the carbonate minerals is so great that it would appear to render the thermoluminescence method of age determination exceedingly unreliable. This is certainly true unless

extreme care is used in selecting the samples to be used. It is felt that reliable age determinations can be made in some instances. Most of these will be limited to fairly recent sediments or to recent periods of faulting, intrusion, or metamorphism.

Future research in the use of thermoluminescence as an age-determination method might profitably be directed toward the more stable minerals. The carbonates originally appeared the most attractive because of their great abundance and their direct connection with stratigraphic events. Their thermoluminescence is especially sensitive to their physical and chemical history. This sensitivity may greatly restrict the usefulness of the method of age determination, but it may open new fields of investigation which will add to our knowledge of the geological processes that affect the carbonate sediments.

6.3 RADIOACTIVITY, ENERGY STORAGE, AND VOLCANISM *

FARRINGTON DANIELS †

Volcanoes provide us with spectacular evidence that localized areas of the Earth's crust can attain very high temperatures. Metamorphism and hot springs are additional examples, which show that certain areas become heated intermittently at certain times in geologic history.

It is the purpose of this section to inquire into the possibility that occasionally the smooth, continuous evolution of heat from the nuclear disintegration of uranium and thorium and other radioactive elements may be converted into intermittent heating. If part of this energy of radioactivity can be stored for a while and released suddenly at a later time, there may be an occasional heat evolution of unusual magnitude. Such an hypothesis is possible from qualitative considerations, but it becomes less plausible in the light of quantitative measurements.

Experiments thus far indicate that the storage of radioactive energy in displaced crystal lattices under ordinary conditions is too small to be significant; but metamict minerals with considerable amounts

*The author is indebted to the Atomic Energy Commission, Research Division, for its support of a research program of which this work is part.

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of stored energy do exist. Moreover, it is reported in Section 6.2 that the application of high pressure causes electronically stored energy to become less susceptible to thermal release.

Theories for geologic heating are discussed in Chapter 5. Theoretical study of nuclear heating has been handicapped in trying to explain why a given volume of rock has become hot, then cold, and then hot again, as for example, in some granitization processes or volcanic eruptions. It is unlikely that a large mass of radioactive elements would be moved around to give the necessary local and temporary heating. Nuclear energy is produced continuously at very slowly decreasing rates. But the conversion of part of the energy of the radioactivity into dislocations of the surrounding crystal lattice and its storage as potential energy could, theoretically, lead to an increased evolution of heat for a while at a later time.

Most of the energy produced in the nuclear decomposition of uranium and thorium and their daughter elements comes from the alpha particles and the recoil atoms produced by the ejection of the alpha particles. Within a fraction of a second, however, most of this energy is converted into ordinary heat, i.e., kinetic motions of the atoms, and the temperatures rises very slightly. If some mechanism were available to convert part of the kinetic energy into potential energy, the temperature rise would be smaller. If this potential energy could be stored up and eventually released rapidly and adiabatically, we would have a mechanism for intermittent geologic heating.

Energy storage and later release at high temperatures in minerals containing uranium and thorium has been established in thermoluminescent rocks (Section 6.2) and in metamict minerals (Section 6.1). The first of these seems to be too small to be geologically significant, and the second appears to be limited to rather unusual and comparatively rare minerals. The fact that such phenomena do exist is sufficient justification for studying them intensively and exploring other possible relations between radioactivity and volcanism.

6.3.a Thermoluminescence

When certain fluorites, limestones, granites, and other rocks are heated, they emit light, a phenomenon which is called thermoluminescence (Section 6.2). A typical thermoluminescence glow curve for limestone is shown in Figure 6.3. In the glow curve illustrated, no trapped electrons are released, and no light is emitted until the temperature is high enough to supply the necessary kinetic energy, and

then as the temperature is raised still higher more electrons are released and more light is emitted. Finally a maximum is reached (at 235° in the limestone shown in Figure 6.3) beyond which fewer electrons are released because most of the traps have already been emptied. At still higher temperatures, traps of higher energy levels are emptied and new peaks in the glow curves are evident, each one corresponding to a definite type of crystal-lattice defect.

This storage of energy is the type of storage that we are looking for. One can imagine that part of the alpha and recoil-atom energy is first converted into electron and lattice displacements and stored as potential energy but that after a long time the traps become filled with electrons or the lattice displacements are annealed out as rapidly as they are formed. Then there is less opportunity to convert kinetic energy into potential energy, the heat is supplied faster than it can be conducted away, and the temperature rises, eventually reaching such a temperature that the stored energy may be released. The more energy released, the higher is the temperature, and the higher the temperature, the more heat is evolved, thus providing a rapid evolution of heat which can approach adiabatic conditions.

In spite of the attractive features of this hypothesis, it cannot be of geological significance. Morehead and Daniels (1952) have measured the light evolved in thermoluminescence. The energy emitted as light in certain crystals was $\frac{1}{20,000}$ of the energy of the gamma radiation which was absorbed in activating the crystal for thermoluminescence. Measurements of heat are far less sensitive than the measurements of light, but there seems to be no evidence yet that really large fractions of radiation energy can be stored in simple crystal lattices.

6.3.b Maximum possible heat storage

A gram of uranium in equilibrium with all its daughter elements evolves about 0.7 calorie per year. A gram of thorium in equilibrium with its daughters evolves about 0.2 calorie per year. Many rocks contain 1 part per million of uranium and 3 parts per million of thorium, and such a rock will evolve 1.3×10^{-6} calorie of heat per gram per year. If a rock contained 10 parts per million of uranium and 30 parts per million of thorium, it would evolve 260 calories per gram in 20 million years. If there were some mechanism for storing all this potential energy and releasing it suddenly and adiabatically, the temperature of the rock would rise to 1000° C and the rock would melt—assuming a heat capacity of 0.2 and a heat of fusion of 60

calories per gram. Obviously there is no mechanism for storing *all* the energy and releasing it suddenly. Only a small fraction of the energy can be stored, but there are rocks which contain much more than 10 parts per million of uranium and which have remained undisturbed for much more than 20 million years (see Section 2.1).

6.3.c Metamict minerals

Some metamict radioactive minerals (fergusonite, samarskite, zircon, and others) contain reasonably large amounts of stored energy. In some the radiation damage and the displacement of the atoms in the crystal lattice has been so great that a beam of X-rays shows an altered diffraction pattern or none at all, and the density is abnormally low. If these metamict crystals are heated to a sufficiently high temperature, they are annealed and the atoms in the crystal lattice are restored to their normal positions. Most important for the present discussion is the fact that the potential energy is released as heat. Morehead and Daniels (1952) found 20 calories per gram in a polycrase mineral and Kurath (unpublished thesis, Univ. of Wis., 1954) found 65 calories per gram in fergusonite. Many other metamict crystals showed varying amounts of stored energy released on heating. These measurements were made in a differential thermal analyzer. Faessler (1942) has carried out similar experiments which showed up to 89 calories of stored energy per gram in metamict minerals. For reference it may be stated that TNT evolves 1000 calories per gram on detonation. Pabst (1952) has discussed these experiments.

For several reasons differential thermal measurements of this type may not be able to detect all the stored energy of radiation-damaged crystals. The experimental measurements often cannot be carried above 700° C, whereas some energy of lattice deformation is not released until a considerably higher temperature is reached. Kerr and Holland (1951) found that some stored energy in zircons was not released until a temperature of 950° was reached. It is not possible to find evolution of heat by this method unless it occurs within narrow temperature limits. If the heat of crystal damage is released uniformly over a wide temperature range, the differential thermal analysis apparatus will not be sensitive enough to measure it.

6.3.d Measurement of radiant energy storage in crystals

A new method of measuring potential energy stored in a crystal lattice under bombardment by alpha particles has been developed by

Kurath (unpublished thesis, 1954). In these experiments an intense polonium source is placed above a very thin metal cup which is filled with the powder to be subjected to radiation. A similar cup filled with the same material is shielded from the alpha particles. As the alpha particles heat the material in the first cup a slight rise in temperature is produced. If some of the energy of the alpha particle is not converted directly into heat but is stored in the form of potential energy, as in a displaced crystal lattice, the heat evolution will be somewhat less than expected. Kurath was able to detect differences in the amount of energy that is not converted directly into heat.

These measurements do not give information concerning the amount of heat that can be stored for long periods of time. It is likely that the energy from recoil nuclei which are produced in radioactive minerals will contribute considerably more to the atomic displacements than the alpha particles and may permit a greater transformation of energy into stored, potential energy.

Whereas metamict minerals retain considerable amounts of stored energy, uraninite, carnotite, and many other minerals of high uranium or thorium content do not store appreciable amounts of energy even though the bombardment by alpha particles and recoil nuclei is very intense. It is likely that atoms in the crystal lattice of all radioactive minerals are displaced frequently, but usually these displaced atoms return quickly to their normal positions.

Most metamict minerals contain rare-earth elements and all have a complex chemical composition and crystal structure. It may well be that the metamict minerals are unique in storing energy by lattice displacements simply because it is difficult for the displaced atoms to find their normal positions in the crystal lattice. The alpha particles may generate so much localized heat, particularly at the end of their paths, that a small region of the crystal is heated and melted. This localized molten area then cools quickly to a glassy material. If these glassy "thermal spikes" recrystallize only with great difficulty, it may be possible to store the energy. When the glassy material of the thermal spikes can recrystallize rapidly, it is not possible to store the energy and the crystals do not become

metamict. Simple crystals and ionic lattices do not give metamict behavior.

It has been shown that the energy of radioactivity stored in the form of thermoluminescence is quite small.

It is known that the storage of the metamict crystals can be considerable. The question arises whether there are conditions in nature under which it may be possible to store considerable amounts of energy in disordered crystal lattices. It is extremely difficult to carry out calorimetric experiments in the laboratory under high pressures. In some thermoluminescence studies, as described in Section 6.2, the application of pressure increases the energy released as thermoluminescence at high temperatures.

6.3.e Uranium content of volcanic material

If the radioactivity of uranium and thorium supplies some of the heat in some volcanic actions, these elements should be found in volcanic lavas, ashes, and gases. During the course of the investigations in this laboratory many samples of such volcanic material have been collected and analyzed. The most significant are described by Adams in Section 2.2. Lava and ashes, both acidic and basic, from many different volcanoes contain from less than 1 ppm up to 11 ppm of uranium. In most cases the alpha counts are high enough to show that thorium is present also. The amount of radioactive material given off by volcanoes is small, and it varies greatly with the location of the volcano and with the stage of eruption.

The uranium content of lavas and ashes usually increases as the differentiation in the volcano proceeds. At first it was thought that some uranium might be lost in volcanic eruptions in the form of volatile uranium compounds. A search for uranium in the gases evolved from fumaroles at the Parícutin Volcano in Mexico failed to show significant amounts of uranium.

A thorough thermodynamic study of the volatility of uranium halides from rocks has been carried out by Mason (unpublished thesis, Univ. of Wis., 1954). Although the thermodynamic values of free energy, enthalpy, and entropies are not well known at high temperatures for many of the uranium compounds, it has been possible, nevertheless, to make estimates of the vapor pressure of uranium halides in mixtures of various inorganic compounds. These estimates indicate that the escape of uranium in the form of chlorides or fluorides from rocks heated to 1000° C is very unlikely. In the pres-

ence of a large excess of ferrous chloride or aluminum chloride, there may be a chance of some volatility of the uranium halides.

6.3.f Summary

Possibilities of storing some radioactive energy in rocks have been studied in the hope of understanding better the intermittent localized heating of rocks near the Earth's surface. Electron-stored energy as exhibited in thermoluminescence is too small to be significant geologically. Metamict minerals, though rather rare, give definite examples of the storage of energy. Simple lattices containing uranium and thorium do not store the energy produced by radioactive disintegration because the displacements of atoms in the crystal lattice are quickly restored by annealing at Earth temperatures. The metamict minerals have complex lattices in which the atom displacements are not readily annealed, and they point the way to further research designed to find conditions under which radiation damage is not annealed out. Researches should be carried out to determine if the annealing rate of some disordered lattices can be decreased by the application of high pressures such as exist at considerable depths in the Earth's crust.

[Reprinted from the Journal of Physical Chemistry, 60, 705 (1956).]

Physical Chemistry in Geochemistry

By Farrington Daniels

PHYSICAL CHEMISTRY IN GEOCHEMISTRY¹

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Received December 27, 1955

The purpose of this symposium is to call attention to the many interesting problems of geochemistry which can be attacked through physical chemistry, and to point out also unique experiments started long ago in the geological past, which are now available for physical chemical studies. Geochemistry is of interest alike to those who want to find new mineral deposits and to those who merely seek an understanding of the geological processes by which nature has laid down our minerals in their present locations.

Many branches of physical chemistry are involved in geochemistry, including thermodynamic equilibria of solids, liquids and gases, phase diagrams, oxidation and reduction, pH, solubility, precipitation, crystallization, electrolytic reactions, adsorption, sedimentation, kinetics of rate processes, heat transfer, radioactivity, isotopic tracers, nuclear reactions, radiation damage and thermoluminescence. Only a few of these can be illustrated in this symposium but the general principles are applicable to many geological phenomena.

(1) The following 4 papers are based on a Symposium on Geochemistry held on Sept. 12, 1955, at a meeting of the American Chemical Society in Minneapolis. In addition to the papers published here, the symposium included the following: H. C. Urey, "Abundances of the Elements and the Composition of the Earth"; R. M. Garrels, "Environments of Mineral Formation"; H. G. Thode, "The Isotopes of Sulfur in Geochemistry"; G. W. Morey, "Experimental Geology"; E. J. Zeller and J. L. Wray, "Factors Influencing the Precipitation of Calcium Carbonate"; A. M. Pommer, "The Reduction of Vanadium(V) Solutions by Wood or Lignite"; G. C. Kennedy, "Equilibrium Relations in the System $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ and $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ "; J. J. Katz and H. R. Hoekstra, "Chemistry of Uranium and the Genesis of Uranium Minerals"; G. Phair, "Some Aspects of the Geological Cycle of Uranium"; J. R. Arnold, "Age Determination and Other Applications of Cosmic-Ray-Produced Radioactivities"; J. A. S. Adams, "The Log-Normal Distribution of Uranium and Alpha Activity in Obsidians, A Metamorphic Sequence and Wisconsin Water"; P. K. Kuroda, "Some Aspects of the Geochemistry of Radium"; D. R. Carr and J. L. Kulp, "Development and Application of the Potassium-Argon Method of Age Determination"; W. R. Eckelmann and J. L. Kulp, "Some Aspects of Age Determination by the Uranium-Lead Ratio."

In the paragraphs which follow some of the subjects which were discussed at the symposium will be referred to. Four of them are published in detail in this issue of THIS JOURNAL.

The phenomena mentioned above occur both in the igneous or hard rocks and in the sedimentary formations produced by erosion. The primary rocks are formed by the cooling of molten material and efforts have been made to determine what type of material gives an over-all sample of the composition of the earth taken as a whole. Meteorites and the sun apparently are not satisfactory. Geological material may be transported in several different ways as solids, liquids, solutions, gases and colloidal materials. Rivers carry along both dissolved salts and colloidal particles. At high velocities they move large particles and rocks. The glaciers carry large rocks. Volcanic lava and volcanic dust are also important in the movement of material.

Air is a very important geochemical agent and it penetrates to considerable depth below the surface. The oxidation state of an element can tell much concerning the geochemical history of the mineral in which it is found. Combining a knowledge of pH and oxidation-reduction potentials, it is possible to determine the conditions under which a given mineral such as iron oxide or lead sulfide will precipitate. Conversely, when a given mineral is found the conditions of its environment can be accurately ascertained.

The ratio of the sulfur isotopes S^{34} to S^{32} offers a valuable means for studying the geological history. Thode has found that S^{34} is enriched in a fractionating process under oxidizing conditions which give sulfates and that it is depleted under reducing conditions which give sulfides. Native sulfur is in a reduced state and it is depleted in S^{34} . The oxidation history of a mineral deposit or a petroleum deposit may be studied from this isotopic ratio and,

in fact, it may be possible to determine when in the geological past the atmosphere acquired its oxygen.

Water is another geochemical agent of great importance and it must be remembered that the geological temperatures and pressures have frequently been very high. In fact, some of our valuable mineral deposits are best explained on the basis of transportation in highly superheated water.

The study of the crystallization of molten material to give igneous rocks requires an understanding of the phase relations of at least ten metallic oxides. In the crystallization from the molten magma water is an important factor not only in phase relations but in the generation of high steam pressures and the origin of volcanoes.

It is important but difficult to simulate in the laboratory the conditions of very high pressures and temperatures which existed in the geological formation of igneous rocks. Aluminum silicates and aluminum oxides are among the materials which have been studied in water under extreme conditions.

Coprecipitated impurities are often important in setting the crystal pattern as illustrated in the classical and confused interpretation of calcite and aragonite deposits. Impurities such as iron, manganese and strontium affect the crystal form of the CaCO_3 , and they in turn are determined by their solubility products and affected by the pH. The pH in turn is influenced by the temperature and the carbon dioxide content of the solution.

Quantitative high temperature chemistry being developed now on a laboratory scale above 1000° , is finding new implications for geochemistry, specifically in the reactions of volatile hydroxides and nitrides.

The second half of the symposium was concerned with the geochemistry of uranium and nuclear geology, including examples of geological dating. It is well recognized that the Atomic Energy Commission's support of research on isotopes has led to important advances in chemistry, biology and physics. In a similar manner, its support of projects connected with uranium has advanced considerably the development of geology and geochemistry. The perfection of electronic and chemical methods for measuring minute traces of uranium has given this element new importance in geological studies. Uranium has in fact become a tracer for use in geochemical processes. The use of the Geiger counter and scintillometer has been invaluable in rapid field studies.

The chemistry of uranium in its various oxidation states and complex ions is much better established because of recent laboratory studies. From these it is possible to predict the geochemical behavior of uranium. In the crystallization of igneous rocks such as granites the uranium is expected to concentrate in the mother liquor because it does not have an ionic radius suitable for fitting into the minerals which crystallize out first. There are still many unsolved problems in explaining the occurrence of the uranium which is found in some minerals. The deposition in veins from hot aqueous solutions is important.

In igneous rocks tetravalent uranium and thorium occur together because they have about the same ionic radii. However, they part company in sedimentary rocks because the uranium is oxidized to a higher valence with a different ionic radius. The hexavalent uranium in solution is precipitated by other ions or adsorbed on the upper layers of lignite beds or concentrated in various other ways to give deposits of minable value. Even the low concentrations of uranium obtained from the rainwater leaching of volcanic ash are sufficient to account for the formation of some secondary uranium deposits.

Studies of the uranium content of various materials are significant because the analytical methods are so accurate even for very low concentrations. The obsidians are interesting because the uranium and daughter elements are sealed in glass so that the effect of weathering is slight. The uranium content of Wisconsin rivers is interesting because it fluctuates seasonally with the rainwater dilution of uranium dissolved from granites, and with the leaching of uranium-rich phosphate fertilizers used on the agricultural land.

The lead-uranium ratio, the helium-uranium ratio and the argon-potassium ratio are important in age tests, but continuing research is necessary to improve their accuracy. It is necessary for example to be sure that all the gases are removed from the sample and analyzed, and it is necessary to know that none of the elements involved in the ratio have escaped as gas nor leached away by weathering.

Certain elements can be created by natural radioactivity and neutron flux in the earth's crust. If mass spectrometric measurements could be made with greater precision than is now possible gadolinium would be an interesting element for dating purposes. An isotope of gadolinium is formed by neutron bombardment and since both isotopes have the same chemical properties and the same chances of loss, a determination of the isotope ratio and the neutron flux and neutron absorptions would give the age without errors due to weathering.

One of the newest and most powerful methods of dating the younger rocks is based on nuclear transitions brought about by cosmic rays in the upper atmosphere. Tritium for decades, carbon¹⁴ for thousands of years and beryllium¹⁰ for hundreds of thousands of years are finding important uses in geological dating.

Radiation damage to radioactive materials has been examined as an interesting source of stored heat, but evidence has not been obtained to show that it is geologically significant. Metamict minerals of complex lattice are known which contain up to 130 calories of stored energy per gram and which are so badly damaged as to show no X-ray diffraction pattern until the normal lattice is restored by heating.

Thermoluminescence can be produced in the laboratory by heating rocks which have been subject to α -ray bombardment over long periods of time. The α -ray activity comes from traces, about 1 part per million, of uranium or other radioactive elements which are present as an impurity in the rock. The intensity of thermoluminescent light in limestones,

fluorites and certain other rocks can sometimes be used to estimate the age of the rock when the alpha ray activity and the sensitivity of the rock to radiation are also known.

Thermoluminescence Analysis

By

Farrington Daniels

**Edited by J. D. Haun and L. W. LeRoy,
Colorado School of Mines, Golden, Colorado
(1958)**

V. Thermoluminescence

Reprinted from SCIENCE, April 3, 1953, Vol. 117, No. 3040, pages 343-349.

Thermoluminescence as a Research Tool

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Thermoluminescence as a Research Tool

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THERMOLUMINESCENCE IS THE EMISSION OF LIGHT produced by heating a solid to a temperature below that of incandescence. It is exhibited by crystals, such as alkali halides, that have been exposed to x-rays or radioactivity and then heated rapidly. The high-energy radiation dislodges electrons, some of which become trapped in lattice imperfections, and are later driven out with the accompanying emission of light when the temperature is raised to supply the necessary amount of kinetic energy.

Thermoluminescence is a property that is extremely sensitive to changes in the structure of crystals. Changes in minor impurity concentrations, crystallization techniques, and physical treatments all produce profound effects. This structure sensitivity is found in other solid state properties such as catalytic activity, dielectric constant, magnetic susceptibility, light absorption, fluorescence, and phosphorescence. Because of the similarities between thermoluminescence and these other properties it is thought that thermoluminescence measurements may be of value in their interpretation.

The application of thermoluminescence in the analysis of minerals and control of feldspars in the ceramics industry has been described by Deribere (1, 2). It has been used in the interpretation of phosphorescence mechanisms by Garlick and others (3). Further interesting uses of this phenomenon were suggested in preliminary reports (4-6), and it is the purpose of the present communication to outline progress in the application of thermoluminescence to a variety of research problems.

APPARATUS

The technique of measuring thermoluminescence by the so-called glow curves, developed initially by Urbach (7) and modified by Randall (8) and Boyd (9), has been simplified so that many thermoluminescent substances can be studied rapidly and conveniently.

The intensity of light as measured with a multiplier phototube, and the temperature as determined by a thermocouple, are recorded simultaneously, using a recording potentiometer. The specimen is heated at a uniform rate of 1° C per second, producing records such as that shown in Fig. 1. The straight line is a record of the temperature, and the light intensity passes through a series of maxima. The crystalline material is prepared either as a powder or as a plate about 1 cm square and 1.5 mm thick, obtained by

cleaving crystals or cutting rocks with a diamond saw. The powder usually gives a lower light intensity on account of the scattering of the light within the sample, but it is more reproducible because it averages out the heterogeneity of the specimen. It is ground to 100-200 mesh size, and a weighed quantity of about 20 mg is placed on a thin glass plate and moistened with a drop of water containing a trace of detergent. After drying, the powder sticks to the glass well enough to be handled. The electrically heated silver hot plate is adjusted by means of a variac to give a uniform temperature rise as recorded on the graph, more current being allowed to pass as the furnace heats up and the heat losses become greater. The apparatus is enclosed in a light-tight box and, after heating the sample to dull red heat, where thermoluminescence can no longer be detected, the hot plate is removed and cooled quickly with dry ice for the next determination.

Most of the irradiation of crystals has been carried out in two special γ -ray irradiators, each consisting of two concentric aluminum tubes, with cobalt powder filling the annular space between them (10). We are indebted to the Argonne National Laboratory and the Oak Ridge National Laboratory for placing these irradiators in nuclear reactors to produce radioactive cobalt (Co^{60}). In this way a space 2.2 cm in diameter by 8 cm long is available for uniform irradiation with 1.1 and 1.3 mev γ -rays at intensities of 6000 or 1400 roentgens per hour for 4 or 1.3 curies of Co^{60} , respectively.

MECHANISMS

To exhibit thermoluminescence, a substance must have an ordered structure such as is found in crystals, or a semioordered structure as in glasses. In addition, it must be electrically an insulator or semiconductor. The crystal must be exposed to ionizing radiation that will produce a cloud of electrons within the lattice when the radiation is absorbed.

The ability to exhibit thermoluminescence in certain crystals can be produced by a variety of high-energy radiations—hard or soft x-rays, γ -rays, α -particles, and β -rays. An energy of about 10 ev is sufficient to remove electrons from ions in most crystal lattices and to provide them with energy to move around in the crystal, but unless there are traps into which the released electrons can go, there is no mechanism to provide for thermoluminescence. There are several different kinds of possible electron traps: (a) imperfections and vacancies in the crystal lattice produced at the time the crystal is formed, or created later by

¹The authors are pleased to acknowledge the support of this project by grants from the Atomic Energy Commission.

FIG. 1. Typical glow curve recording; γ -activated thermoluminescence of a limestone. 0 = 0°C; 100 = 500°C; 0 = 0 microamp; 100 = 1 microamp. Heating rate = 0.8°C/sec. 115 hr-exposure in γ -source.

mechanical pressure or thermal treatment; (b) statistical imperfections that are due to kinetic motions and that increase in number at higher temperatures; (c) distortions produced by impurity ions of larger or smaller size than those comprising the crystal lattice; and (d) ion dislocations, or "holes," produced by radioactive bombardment.

One of the common types of traps is a negative ion vacancy—for example, a chloride ion missing from a sodium chloride lattice. When such a vacancy is filled with a dislodged electron, it is called an F-center, and it acts as a light-absorbing unit. The color produced by x-radiation in crystals and that found in some fluorites and other minerals containing radioactive impurities are thought to be due to the creation of these F-center and other arrangements of trapped electrons (11, 12). It has long been known that this coloration can be bleached out by heating (13); it is not quite so well known that thermoluminescence usually accompanies the removal of the color.

A crystal may possess many trapped electrons within its lattice and may not produce thermoluminescence when heated unless there is some mechanism for releasing the extra energy of the electrons as visible light. This mechanism is thought to take place in certain emission centers in the lattice, associated with impurities, as is the case in many artificial phosphors and natural fluorites (14–16), or perhaps with displaced lattice ions or other irregularities in the lattice.

The role of impurities in determining the character of thermoluminescence has been discussed by Alt and Steinmetz (17). Our investigation has shown that individual peaks in fluorite glow curves emit different colors of light. This would seem to indicate that these electron traps are intimately associated with particular emission centers, which have been demonstrated to

be rare earth impurities (16). In this case it is thought that the electrons are trapped in distortions produced by the foreign ions.

The production of ion dislocations in various materials by α -particles has been studied by Seitz (18) and Slater (19). Halos of color around radioactive inclusions in minerals are thought to be due to electrons trapped in dislocations produced by α -particles. Certain feldspars exhibit very intense thermoluminescence from such halos, and it is concluded that the electron traps responsible were produced by the α -bombardment. Estermann (20) detected changes in density in KCl crystals exposed to x-rays. These were ascribed to the production of vacancies in the lattice by the radiation. Lithium fluoride has been found to produce increased thermoluminescence on each successive equal exposure to γ -rays from Co^{60} . The increased sensitivity is thought to be the result of the production of additional electron traps by γ -radiation.

Each peak in a glow curve corresponds to a definite energy level of trapped electrons, and low-temperature peaks can be drained out without affecting the high-temperature peaks if the heating is stopped before the high temperatures are reached. The amount of thermoluminescence of a given peak is a result of a balance between the rate at which electrons have been driven into the traps by radiation and their rate of thermal escape at the temperature of irradiation. When the temperature of the irradiated crystal is raised quickly and then maintained constant, the intensity of luminescence decays, with a definite mathematical relation from which the energies of activation (9) of a specified type of trapped electron can be calculated.

The thermoluminescence behavior on continued irradiation has been studied in considerable detail and will be reported elsewhere. In general, saturation oc-

curs at an energy input that varies with the crystal and the type of radiation. Low-temperature peaks are apt to become less prominent with continued irradiation, and new high-temperature peaks are created. The alkali halides and limestones are apt to reach saturation after about 100,000 roentgens of Co^{60} γ -radiation. Continued irradiation may simply give a constant thermoluminescence intensity or it may give a decreasing intensity.

TYPES OF THERMOLUMINESCENT MATERIALS

The alkali halides are all thermoluminescent. In general they have two prominent peaks which shift with the size of the ions, the smaller atoms giving thermoluminescence which comes in at higher temperatures and coloration from F-centers with absorption maxima at shorter wavelengths (21). In lithium fluoride, where both ions are small, the coloration produced by radiation comes in the ultraviolet, and the maxima in the thermoluminescence curves occur at about 220° C and at 320° C.

In addition to the alkali halides, the following give thermoluminescence after irradiation with γ -radiation—calcite, dolomite, fluorite, aluminum oxide, magnesium oxide, gypsum, quartz, glass, certain catalysts, feldspars, feldspathoids, certain dried clays, and ceramics. A large variety of inorganic crystals is being investigated for thermoluminescence, and more sensitive apparatus for testing thermoluminescence is being developed. In general, hard, transparent or translucent crystals of simple crystal structure are most apt to exhibit thermoluminescence after exposure to γ -rays.

Sometimes, of course, the thermoluminescent light emitted probably escapes detection with the present apparatus because it is in the ultraviolet or the infrared. Organic material cannot be studied in air because combustion emits obscuring light, but there is reason to believe that, if certain organic substances are irradiated at liquid air temperatures and then heated to room temperature and above, they, too, will exhibit thermoluminescence. Prominent additional, low-temperature peaks were found in the glow curves when the alkali halides were irradiated at liquid air temperatures (21). These peaks are, of course, registered as fluorescence when irradiated at room temperature, the light being emitted at the time of irradiation.

The presence of impurities is an important factor in thermoluminescence glow curves, and, until theories can be developed to account for the different activation energies of the various energy traps, it is difficult to know whether a given peak is characteristic of a given crystal lattice or of a given impurity, perhaps present in traces.

Preliminary work has been done on the effect of added impurities and mixtures of salts crystallized out together from a given melt (22). When 1 mole per cent of silver chloride is added to fused sodium chloride, for example, the crystallized salt gives 100 times as much intensity of thermoluminescence as the

pure sodium chloride alone. Traces of cupric chloride and manganese chloride, on the other hand, quench the thermoluminescence. When potassium bromide is added to sodium chloride and the two are fused and crystallized, a curve of thermoluminescence intensity plotted against mole fraction gives a maximum at which the intensity of the mixed crystals is considerably greater than that of either sodium chloride or potassium bromide alone. The distortion of the lattice by the introduction of ions of different sizes seems to create holes in which electrons, released by γ -rays, can be trapped.

The color of the thermoluminescence varies at least over the whole visible spectrum with different crystals, and it is quite sensitive to impurities.

DOSIMETRY

Since in many crystals the intensity of thermoluminescence is nearly proportional to the amount of γ -radiation received, a considerable effort has been devoted to developing a practical means of measuring the exposure to γ -radiation (23). Lithium fluoride has been found to be the best crystal for this purpose, and it has been possible to measure exposures of 10–1000 roentgens and more with considerable ease and accuracy (21) by means of a portable photomultiplier tube and microammeter. Measurements of less than 1 roentgen have been made with a nonportable instrument. Lithium fluoride is stable, insoluble, and non-deliquescent, and $\frac{1}{3}$ gram of artificial crystal grown by the Harshaw Chemical Company is sufficient for a measurement. The crystals used originally are about 1 cm², but more recently powdered lithium fluoride has been pressed into pellets, in a thin metal casing. Experiments are still under way to obtain greater uniformity, but successful tests with different laboratory and atomic radiations have been made. The dosimeter crystals, or pellets, are very small and can be placed in experimental apparatus, which is inaccessible to ordinary radioactivity meters. They have been used successfully by Marshall Bruce, of the Hospital of the Oak Ridge Institute of Nuclear Studies, to obtain measurements of internal radiation intensity in cancerous patients injected with radioactive isotopes. The crystals were swallowed by the patients, recovered one or two days later, and the accumulated dosage in roentgens was measured by matching the thermoluminescence intensity with that produced in the crystals by a known roentgen dosage.

IDENTIFICATION

The glow curves are characteristic of specific substances, with definite peaks at definite temperatures, similar in a sense to spectrograms with their lines of light at definite wavelengths. They are typical of crystalline materials that contain specific impurities and that have had definite heat treatments and physical histories. Thermoluminescence measurements are thus not suitable for analysis of chemical compounds, but they may find use in identification and control. For

example, different types of aluminum oxide will give different glow curves depending on impurities and previous heat treatment, but all samples of the same type will give the same glow curve. If one type is desired perhaps it could be selected on the basis of the glow curve. Again, the thermoluminescence glow curve of window glass will vary greatly with the impurities present, chiefly ferric oxide, but if a particular quality of glass is required the thermoluminescence glow curve may become a convenient control test to assure that each batch has the same quality. Limestones, ceramics, and optical crystals are among the materials that may be classified, identified, and controlled.

A collection of about 30 standard clays has been the object of an intensive cooperative research program involving many different measurements, such as viscosity, infrared absorption, and chemical tests. Some, but not all, of these standard clays exhibit characteristic thermoluminescence glow curves which merit further investigation. The nonorganic parts of certain soils should show characteristic glow curves that may be useful in identification and classification of soils.

The color of the light emitted on heating a previously irradiated material is often characteristic. Limestones give a yellow light, and dolomites give an orange light. The orange color may be helpful as a field test in identifying the presence of magnesium carbonate, although it may well be that the color is not related to the magnesium carbonate, but to an impurity associated with it.

CATALYSIS

It was suggested by Boyd and Hirschfelder (22) that thermoluminescence curves might be useful in evaluating the efficiency of surface catalysts. The same strains and lattice imperfections that permit adsorbed molecules to come within optimum distances from each other and bring about chemical reactions might also

provide traps into which electrons could be driven by γ -radiation, and later released by heating. The intensity and nature of the thermoluminescence might be a measure of the catalytic efficiency. At least the thermoluminescence glow curve could be used as a criterion for controlling the preparation of a desired catalyst. A standard, successful catalyst should have a specific type of glow curve.

FIG. 3. Thermoluminescence and catalytic activity.

In the first test a good aluminum oxide catalyst prepared by Homer Adkins was found to give considerably more thermoluminescence than a poor catalyst of the same material. Several commercial catalysts have been examined, three of which are shown in Fig. 2. In this case the areas under the No. 2 peak are correlated with the catalytic efficiency, as shown in Fig. 3. Many catalysts, particularly of the gelatinous type, do not give any thermoluminescence, and in many others there is no apparent correlation, but enough catalysts have been examined to justify the conclusion that thermoluminescence is a new tool in catalyst evaluation and that it may become useful in researches to find new catalysts.

FIG. 2. Glow curves of catalysts.

RADIATION DAMAGE

Most high-energy radiations are effective in producing damage to crystals. The investigation of this phenomenon is of importance in the design of nuclear reactors and in interpreting changes in crystal structure occurring in radioactive minerals over millions of years.

The fraction of γ -radiation energy that can be stored as trapped electrons in crystals is very small. With a photomultiplier tube calibrated with a thermocouple and standard lamp it was found that less than 1/10,000 of the energy of the absorbed γ -radiation was given out as thermoluminescence in lithium fluoride (24).

Thermoluminescence is one means of studying the storage of energy from high-energy bombardment and the crystal damage which can be produced by it. Atom displacements, if they occur, might lead to the storage of greater amounts of energy than that observed in thermoluminescence, but the means for

detecting heat are much less sensitive than the means for detecting light. Thermal analysis has failed thus far to reveal the storage of heat energy in γ -irradiated crystals, but more sensitive methods and greater exposures to radioactivity are now under investigation. In the case of certain metamict crystals containing considerable quantities of uranium the α -ray bombardment for millions of years has caused serious dislocations of the crystal lattice; so much so that x-ray diffraction patterns characteristic of crystals have been obliterated. When these minerals with accumulated radiation damage are raised in temperature, the stored energy is released as heat, and the x-ray diffraction pattern characteristic of a normal lattice is restored. In one case the energy released amounted to as much as 25 calories per gram (24).

THERMOLUMINESCENCE OF ROCKS

Many natural rocks and minerals are thermoluminescent without exposure to x- or γ -rays in the laboratory. Most limestones crushed to millimeter size and dropped onto a faintly red-hot frying pan in a darkroom will emit a bright white or orange light for several seconds. After they are once heated and cooled, no light is emitted if they are heated a second time. However, brief exposure to x- or γ -rays will bring back the property of thermoluminescence, and by proper adjustment of the exposure the same intensity of thermoluminescence can be reproduced. Natural thermoluminescence has been frequently recorded in the geological literature (13, 25, 26) but it has generally been regarded as a curiosity. Some attributed the light to the burning of organic material. It has been repeatedly proved in the course of this investigation that the cause of the thermoluminescence is the presence of traces of uranium, thorium, and other radioactive elements contained in the rocks as impurities (6, 27). These radioactive impurities may be present only to the extent of one part per million or so, but they have been giving off α -, β -, and γ -rays for millions of years, and part of the thermoluminescence effect is cumulative. In fact, natural thermoluminescence of a rock is often a more sensitive means of detecting traces of radioactivity than is a Geiger counter or scintillometer. The relation between radioactivity and thermoluminescence in certain minerals had been earlier pointed out by Ellsworth (25), Kohler (28), and Alt and Steinmetz (17).

Surprisingly many rocks and minerals are naturally thermoluminescent. Over 3000 samples have been studied, mostly limestones and granites, of which about 75 per cent showed visible thermoluminescence, and still more would undoubtedly show thermoluminescence if measured with the most sensitive photomultiplier apparatus. Nearly all limestones and acid igneous rocks are naturally thermoluminescent. Calcium and magnesium carbonates show light-yellow to orange thermoluminescence, and

potassium and sodium feldspars show white to blue-violet. These minerals are responsible for much of the thermoluminescence in the rocks examined, as, for example, in calcareous fossils or inclusions in shales, and in the cementing material between the grains of sandstone. Some fluorites containing uranium give a particularly brilliant thermoluminescence. Quartz, nepheline, topaz, halite, and spodumene react when they contain impurities of uranium, or thorium.

In a Boy Scout collection of 36 minerals over one third gave visible thermoluminescence. Out of 65 rock-forming minerals selected from the mineralogy laboratory's collection at the University of Wisconsin, 34 showed natural thermoluminescence. The intensity of light ranged all the way from that sufficient for reading a newspaper to "barely detectable."

All the minerals that displayed natural thermoluminescence could be made much brighter by additional exposure to γ - or x-rays, and many that did not give any detectable thermoluminescence were made thermoluminescent by a brief exposure to these rays. Of the 65 minerals just mentioned, 47 were thermoluminescent following exposure to γ -rays.

FIG. 4. Glow curves for Escabrosa limestone.

The increase in thermoluminescence resulting from a γ -radiation exposure of 140,000 roentgens is shown in the glow curves of Fig. 4 for the Escabrosa limestone. The No. 2 peak coming in at 300°C is about the same, but the No. 1 peak at 215° is seven times as intense. The No. 3 and No. 4 peaks at lower temperatures are fairly intense in irradiated thermoluminescence, but are completely missing in natural thermoluminescence, because the earth temperature has been high enough to drive all the displaced electrons out of their traps. The time elapsing between irradiation in the laboratory and testing is too short to permit any measurable loss. The high-

temperature peak at 300° involves so great a kinetic energy that most of the trapped electrons have remained trapped over the geological ages, and a still longer exposure to natural radioactivity would of course increase the intensity at peak No. 2 still higher—until saturation is reached.

The thermoluminescence of rocks is apt to be quite heterogeneous—some of the mineral constituents give off light when heated, and others do not. Thin specimens of limestones and granites have been polished and placed on a hot plate, with a camera focused on the surface. The light emitted by the heated specimen (below incandescent red heat) is sufficient to produce a photograph. An example is

environment at the time of crystallization and the physical effects of temperature and pressure on the rocks during their geological history have a great deal to do with the nature and intensity of the thermoluminescence.

STRATIGRAPHY

Because the glow curves are so responsive to chemical and physical conditions at the time a rock is formed, they can be used to determine whether two samples of sedimentary rocks were laid down at the same time in the same environment, even if the samples are widely separated geographically. Fossils and other criteria are now used to determine

FIG. 5. Photographs of thermoluminescence of a typical limestone. Floyd's Knob formation. Left: natural; right, γ -activated.

given in Fig. 5, where the calcareous fossils are clearly shown at the left. The light is due to the release of electrons that were originally dislodged by traces of uranium present and trapped in the calcium carbonate lattice of the fossils. The brighter picture at the right was produced by the same sample after an exposure to 140,000 roentgens of γ -rays. The thermoluminescence patterns displayed by granite surfaces commonly reveal spots of brighter light adjacent to inclusions of material of high radioactivity.

Whereas at high altitudes cosmic radiation may be a factor in some of the activation for thermoluminescence, it becomes practically negligible in comparison with the activation caused by radioactivity in rocks below ground level or in rocks that contain one or more parts per million of uranium or thorium.

The thermoluminescence glow curves of rocks vary greatly—i.e., the heights of the peaks of the glow curves and the temperatures of their maxima change from rock to rock. The greater the concentration of uranium or thorium and the older the rock, the greater is the thermoluminescence, because the rock has been subjected to greater effects from radioactivity. The presence or absence of chemical impurities and the physical imperfections are, however, factors that may be just as important. The chemical

whether two rock samples belong to the same stratum, and these tests have practical value in petroleum exploration. If a certain sequence of strata is found as one drills down from the surface and eventually strikes oil, then a repetition of the sequence in another location may indicate that the geological features are the same as found before. Thermoluminescence glow curves add one more test to those already available for correlating sedimentary formations. In some rock types—e.g., volcanic ash and Pre-Cambrian limestones—no fossils are present to aid in the identification of the strata.

One of the first tests of the reliability of the application of thermoluminescence was carried out in a large limestone quarry, where the various strata can be differentiated visually for nearly half a mile. Thermoluminescence curves of ten samples taken from the same stratum across this half-mile face were identical in shape, but samples from other strata a few feet above or below gave entirely different glow curves (29).

Extensive studies have been made of thermoluminescence as a means of correlating limestones. For this purpose the glow curves obtained after excitation with γ -rays are more useful than the natural thermoluminescence curves, because many more peaks are available for identification in the low-temperature region—peaks that have been an-

nealed out of the natural thermoluminescence at earth temperatures. In general, there are four prominent peaks in the glow curves of most limestones. They occur at 120°-140°, 150°-190°, 210°-250°, and 290°-310°C. Saunders (27, 29) and Bergstrom (30) have made a special study of the correlation of limestones as revealed by their thermoluminescence glow curves. Particular attention has been given to the Pennsylvanian limestone outcrops in Iowa. Parks (31) has made a special study of subsurface stratigraphy as revealed by glow curves, using core samples from areas around southern Indiana and southern Illinois.

AGE DETERMINATION

If suitable corrections can be made for chemical impurities and physical imperfections, and for the light absorption in the rock itself, one should be able to estimate the age of the rock from the thermoluminescence intensity and from the uranium or thorium content as determined from the α -ray activity of the sample. Each α -particle produces a given number of trapped electrons that will emit thermoluminescence. The light emitted should be proportional to the number of α -particles per year multiplied by the number of years since the crystal was formed. This method is much less reliable than the method of radioactive carbon for dating material, but the carbon method is satisfactory only for carbonaceous materials less than 25,000 years old. It is still less reliable than the lead-uranium, helium-uranium, potassium-argon ratios, but these radioactive methods also have their limitations. Any new method for dating rocks and minerals is well worth exploring, and progress is being made in the thermoluminescence method, which can give only the time since the mineral was last crystallized. It has been developed for limestones by Zeller (32) and for fluorites by Saunders (33). The α -activities are obtained with a scintillometer, applied by Ockerman (34) to a large area of the powdered rock. If the uranium content is only 1 ppm, the accuracy in determining the α -activities becomes the limiting factor. The area under a selected high-temperature peak in the natural glow curve is used for comparison—or, in another method, the electron traps thought to be produced by α -particles are filled by saturating with γ -rays. The light absorption of each sample is determined experimentally so that corrections can be made for light losses in samples that are not completely transparent. Limestones of known geological ages are used for a calibration scale.

The greatest uncertainties lie in the presence of chemical impurities and imperfections in the crystal lattice, which will increase or decrease the thermoluminescence. It is hoped that better results will be obtained through the use of a 1-curie polonium source, lent by the Atomic Energy Commission, with which an α -ray bombardment can be given to a thin surface layer in a second, which is equivalent to a

million-year bombardment in the limestone with its mere trace of uranium. With this technique it should be possible to cancel out the effects of impurities; and, except for uncertainties in the radiation damage, the time required for the polonium source to match the natural thermoluminescence of the rock would give a direct measure of the α -particles emitted since the rock was formed. Knowing the rate of α -particle emission per hour and per year in the rock, the time required to produce the observed thermoluminescence could be easily calculated.

The possibility of estimating the dates at which limestones and ancient pottery were heated to high temperatures is now being explored. Many other applications of thermoluminescence to various laboratory techniques and applied problems are under investigation.

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[Reprinted from the Journal of Physical Chemistry, 61, 414 (1957).]

Thermoluminescence of Fourteen Alkali Halide Crystals

By Louis F. Heckelsberg and Farrington Daniels

THERMOLUMINESCENCE OF FOURTEEN ALKALI HALIDE CRYSTALS¹

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Received August 30, 1956

In this investigation the thermoluminescence glow curves of fourteen alkali halides from liquid air temperature to red heat were measured after exposure of the crystals to X-ray or γ -radiation. The effects produced by various amounts of radiation were studied using crystals of LiF and NaCl. The thermoluminescence of mixed crystals containing various alkali halides was also studied.

The alkali halides were chosen for study because they all emit light when heated after previous exposure to γ -rays and because they have simple crystalline structures.

Experimental

Materials.—Large fused crystals of LiF, NaCl, KCl and KBr were obtained from the Harshaw Chemical Company. Crystals of LiCl, LiBr, NaF, NaBr, NaI, KF, KI, RbCl, RbBr and RbI were grown by either the Kyropoulos² method or by the slow cooling of liquid salts in platinum crucibles. In several cases, they were further purified by recrystallization.

Eight crystals containing various mole percentages of NaCl and NaBr were grown. These crystals were grown by first mixing the salts at room temperature and then melting them. The melts were held in a liquid state for 24 hours before the crystallization process was started to ensure uniform distribution of the halogen ions. Six NaCl crystals containing one mole per cent. of a foreign alkali or halogen ion were also grown by this method.

Apparatus.—For the determination of the glow curves a modification of the apparatus described by Boyd^{3,4} was used

for the temperature range of 25 to 500°. For the low temperature range of -186 to 50° the apparatus shown in Fig. 1

Fig. 1.—Apparatus for X-ray exposure at low temperatures.

(1) From the Ph.D. thesis of L. F. Heckelsberg, University of Wisconsin, 1951.

(2) S. Kyropoulos, *Anorg. Chem.*, **164**, 308 (1926).

(3) C. A. Boyd, Ph.D. Thesis, University of Wisconsin, 1948.

(4) C. A. Boyd, *J. Chem. Phys.*, **17**, 1221 (1949).

Fig. 2.—Thermoluminescent "glow curves" of the alkali halides (see Table I).

was used. This apparatus consisted essentially of a 1.2 cm. diameter brass bar mounted in a one-inch diameter Pyrex test-tube. Six feet of No. 22 Nichrome wire was wrapped around one end of the bar while cooling fins were machined on the other end. The thin glass window was obtained by blowing a bubble and then passing a long hot flame across the bubble. The tube was evacuated, by means of a side arm, to prevent condensation on the cold metal. The resulting apparatus was insulated with ground asbestos cement. Liquid air was placed around the brass rod in the upper compartment while the apparatus was mounted vertically and the crystal was exposed to an X-ray beam. After exposure the liquid air was poured off, the apparatus was mounted horizontally and the crystal was heated electrically at a rate of approximately 0.8° per second. The heating rate for the furnace used in the high temperature range was about 1° per second. The light evolved was measured with a photomultiplier tube, RCA 1P21 and the electrical current amplified and recorded with a Brown recorder.

Two different sources of radiation were used. For the low temperature range a copper target X-ray tube operating at 37 kv. and 18 ma. was used. The remaining radiation dosages were obtained from a hollow cylindrical Co^{60} source. The radiation intensity inside the source, where the crystals were placed, was found by three different methods to be approximately 6,500 Roentgen units per hour.

Results and Discussions

Glow Curves.—The thermoluminescence glow curves of fourteen alkali halides, all having the simple NaCl type lattice, were obtained during this investigation. The cesium halides and RbF were not studied because they have a different lattice type. RbCl and RbBr have lattice transition points from the CsCl to the NaCl type lattice below 25° . No attempt was made to grow a LiI crystal because of its low melting point and its extremely hygroscopic nature.

The glow curves which cover a temperature range from 100 to 600°K . are combinations of two separate measurements: a low temperature glow

curve from 100°K . to about 325°K ., activated by X-rays, and a high temperature glow curve from about 300 to 600°K ., activated by γ -rays. Experimental difficulties made it impossible to extend a single glow curve from 100 to 600°K . in a single experiment. In several cases, such as with RbBr, the range of the low temperature glow curve was extended in order to obtain a peak occurring around 350°K .

While the temperature corresponding to maximum light emission is always the same, the height of the peak and the area under it depends on the amount of radiation the crystal receives. Some crystals are more sensitive to radiation than others. For example, in the high temperature peaks of LiF and LiCl, LiCl requires about 300 times more radiation than LiF to emit the same amount of light. Whether this difference in sensitivity is an intrinsic property of the crystal or whether it is due to impurities or to some factor in the process of crystallization is not known. It was also found that the glow curves become more complicated with increasing amounts of radiation. Therefore, to obtain a glow curve characteristic of a crystal the least amount of radiation necessary to activate it was used.

Because of these difficulties some method had to be found to present the glow curves in a manner that will allow comparison between them. The method used here presents the data in the form of relative, composite curves with a supplementary table. The shape of the glow curves can be seen in Fig. 2, and the relative peak heights are given in Table I. The relative peak heights given in this table are calculated roughly by dividing the heights of the peaks by the amount of radiation.

The peak heights in Fig. 2 have no absolute significance because the amount of exposure to radiation was different for the different crystals and for the high and low temperatures. The calculations are only approximate but they are based on a considerable amount of data. For the transparent crystals used in this investigation, the amount of light emitted was found to be proportional to the weight of the crystal, at least, for crystals weighing several grams or less. Experiments with long periods of radiation indicate that the height of a peak is roughly proportional to the amount of radiation received, in the initial phase of exposure. It must be kept in mind, however, that peaks slightly above room temperature will be affected by the thermal draining of the traps.

TABLE I
EXPERIMENTAL DATA FOR THERMOLUMINESCENCE GLOW CURVES

Salt	Range above room temp.	Relative height ^a	γ -Radiation, R.	Range below room temp.	Relative height ^b	X-Ray radiation, min.
LiF		712,000	500		1,000	1.5
LiCl		1,800	70,000		91,000	0.08
LiBr		80,000	9,250		3,700	2.5
NaF		5,500	2,000		650	4.0
NaCl		158	5,000		400	2.0
NaBr		1,540	5,000		11,600	2.0
NaI		3	45,000		24,600	1.0
KF		2	96,000		4,800	0.75
KCl		3,700	5,000		550	5.0
KBr		7	17,000		210	10.0
KI					710	5.0
RbCl		2,040	9,000		15	20.0
RbBr		910	13,500		25	20.0
RbI					500	3.0

^a Height of peak divided by gamma radiation dosage in Roentgens. ^b Height of peak divided by X-ray dosage in minutes.

Recently Sharma⁵ published glow curves for LiCl, NaF, NaI, KBr and KI which were irradiated with low energy electrons. Although he used a faster rate of heating his results are in general agreement with the results of this investigation. His conclusions that the thermoluminescence peaks are related to color centers were borne out during this investigation. This relationship has been observed earlier by Pringsheim⁶ and Dutton and Maurer.⁷ It was found during this investigation that the coloration produced by the γ -radiation at room temperature faded out at temperatures corresponding to the major high temperature peaks. KI and RbI have no coloration at room temperature and have no high temperature peaks. Sharma, in an earlier note,⁸ found that KI radiated at -185° has a peak at 235° K. which was not observed during this investigation. He found that the coloration produced by the radiation at low temperatures faded at this peak temperature. γ -Radiation at room temperature will not activate at 235° K. peak because of

thermal deactivation; and the X-ray radiation used at -185° in the present investigation was probably too weak to give this peak.

From results of the present investigation the low temperature peaks appear to be far more sensitive to radiation than the peaks which occur at temperatures above 25° .

In addition to the fading of the F-centers with thermoluminescence a relationship was found between the major high temperature peaks and the absorption spectra of the F-centers. Ivey⁹ has shown that the absorption spectrum shifts to longer wave lengths, or lower energy values, as the size of the ions and lattice constants increase. Results of this investigation show a marked tendency for the major high temperature peaks in the thermoluminescence glow curves to shift to lower temperatures, or smaller trapping energies, with increasing lattice constants. While it is possible to correlate the major high temperature peaks with F-centers, or missing halogen ions, adequate explanations cannot be offered now for the other peaks which come in at the lower temperatures.

The glow curves of RbCl and RbI are of interest because of a phase change below room temperature from a CsCl to a NaCl type lattice. The low temperature peaks of these salts are very broad compared to the usual narrow peaks found in the low temperature region. Also these crystals required larger amounts of radiation than other crystals.

Effects of Extended Radiation.—The heights of the peaks of a glow curve depend upon the amount of radiation that a crystal receives. The high temperature peaks of LiF and NaCl were found to be ideal for studying this relation. These peaks are initially simple, symmetrical peaks and are thermally stable, that is, the temperature at which the maximum emission of light occurs is high enough to prevent thermal draining of the traps at room temperature.

The effects of exposure to X-rays on the low temperature peak of NaCl were also studied. This low temperature peak appears to reach saturation, or its maximum height, with one to 1.5 minute exposure to X-rays (37 kv. and 18 ma.). Peaks which occur close to the irradiation temperatures should become saturated quickly.

High energy radiation not only affects the heights of the peaks but it also causes considerable alteration in the shapes of the glow curves. The changes in the shape of the glow curves caused by increasing amounts of radiation are shown in Fig. 3. These glow curves are composites obtained during the study of the effects of varying amounts of radiation on the thermoluminescence behavior of LiF. Very similar effects were found with NaCl.

The saturation curves were obtained by exposing a large number of crystals to varying amounts of radiation and then obtaining their glow curves. No crystal was used more than once.

The glow curve labeled 1 (Fig. 3) is the initial curve obtained using a freshly prepared crystal and a small amount of radiation. In the case of LiF a beautifully symmetrical peak could be obtained

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(7) D. Dutton and R. Maurer, *ibid.*, **90**, 126 (1953).

(8) J. Sharma, *ibid.*, **85**, 692 (1952).

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Fig. 3.—Typical "glow curves" showing effects of various amounts of radiation on lithium fluoride.

with radiation dosages as small as ten Roentgen units. Experience gained during this study indicates that the smallest possible amount of radiation should be used in order to obtain a glow curve in which the shape is not influenced by continued radiation.

Glow curve 2 shows the shape obtained at the maximum height of the peak labeled "A." For LiF this maximum is reached at values of 10,000 to 20,000 Roentgen units depending on the origin of the crystals used. In the case of NaCl this maximum was reached with dosages of about 15,000 Roentgen units for the one series of crystals studied. Of interest in this glow curve is the formation of a new peak (labeled "B") on the high temperature side of peak "A."

Glow curve 3 shows the formation of a number of small peaks on the low temperature side of peak "A." These peaks are numerous and are irregular in their locations. Glow curve 4 shows the shape obtained in the crystals which received the largest amount of radiation. In the case of LiF this value was about 100,000 Roentgen units while for NaCl it was about 400,000 Roentgen units. Peak "B" is now the predominant peak. In the case of NaCl, peak "A" completely disappeared in crystals receiving 40,000 Roentgen units. In this glow curve over twenty-five small peaks were observed. These results on NaCl have been confirmed and extended by the recent work of Hill and Schwed.¹⁰

Mixed Crystals.—Eight crystals containing different mole fractions of NaCl and NaBr were prepared. The abilities of these crystals to thermoluminesce are shown in Fig. 4. The log of the relative light intensity was used so as to be able to plot all the points on one graph. Each of these crystals received a radiation dosage of 70,000 Roentgen units of Co⁶⁰ radiation. One experimental difficulty encountered in the mixed crystals was the formation of a white opaque coating on exposure of the crystals to the moisture in the air. This coating, which also appears on pure NaBr, was scraped off the crystal before its glow curve was determined.

Boyd,^{3,4} who did some preliminary work on this system, found on X-ray examination a decided variation in the lattice constants at approximately

Fig. 4.—Relative intensity of light emitted by the NaCl-NaBr system.

Fig. 5.—"Glow curves" of NaCl containing 1 mole % of foreign halogen ions.

75 mole % NaCl (63% by weight). The peak in Fig. 4 occurs at approximately the same composition indicating some relation between lattice spacing and thermoluminescence.

Glow curves of NaCl containing one mole % of various halogen ions are shown in Fig. 5. These crystals received a dosage of 10,000 Roentgen units in the Co⁶⁰ source. The degree of coloration caused by γ -radiation (orange) varied from crystal to crystal. The color of light emitted on heating was always blue.

It will be observed that, within experimental error, no variation appears in the temperature

where maximum light emission occurs. Adding a smaller size halogen ion increases the crystal's ability to thermoluminesce while adding a larger halogen ion decreases it. This same behavior of ion size was observed for NaCl containing one mole per cent. of various alkali ions.

Summary

It is well established that F-centers are due to missing halogen ions and since it has been found that the coloration of the crystal disappears when the major high temperature peak disappears, it is felt that this peak in the glow curves is related to missing halogen ions. In support of this relationship, it is known that the absorption spectrum of F-centers shifts to longer wave lengths as the lattice constants increase, in the same manner as the temperature of the major high temperature peak drops to lower temperatures as the lattice constants increase. No adequate explanation can be offered now for the other peaks.

Saturation experiments show that the height and the shape of glow curves depend upon the

amount of radiation which the crystals receive. For a study of the influence of the crystal on the thermoluminescence the minimum amount of radiation should be used in activating the crystal so as to obtain a characteristic glow curve uninfluenced by the radiation itself.

The thermoluminescence of sodium chloride induced by intense X-rays has been studied by Hill and Schwed,¹⁰ and the thermoluminescence of lithium fluoride, potassium chloride and potassium bromide induced by intense γ -radiation has been studied by Ghormley and Levy.¹¹

Mixed crystal experiments showed that adding foreign alkali or halogen ions to NaCl varied its ability to thermoluminesce but did not affect the temperatures of the peaks. Therefore, the minor peaks in the alkali halides, if related to impurities, are due to impurities other than those of the alkali or halogen family.

The authors are glad to acknowledge support of this research by the Atomic Energy Commission.

(11) J. A. Ghormley and H. A. Levy, *THIS JOURNAL*, **56**, 548 (1952)

[Reprinted from the Journal of Physical Chemistry, 61, 633 (1957).]

Thermoluminescence of Some Inorganic Crystals and Glasses

By James K. Rieke

THERMOLUMINESCENCE OF SOME INORGANIC CRYSTALS AND GLASSES

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Received December 3, 1956

Over fifty inorganic compounds and glasses have been examined for γ -ray induced thermoluminescence. Impurities are important and only limited generalizations can be made now.

When some crystals are exposed to ionizing radiation, and then heated in the dark, light is emitted at definite temperatures below red heat. The emission of light is due to the release of electrons trapped in imperfections in the crystal, and released when the kinetic energy becomes equal to the trapping energy. The light intensity is plotted against temperature (or against time when the crystal is heated at a uniform rate) and a "glow curve" showing a series of peaks is obtained which is characteristic of the chemical and physical nature of the crystal, its imperfections and its impurities. These "glow curves" have been studied intensively in this Laboratory, with lithium fluoride,² alkali halides,^{3a} aluminum oxides,^{3b} sulfates, carbonates and oxides,⁴ and many limestones and minerals.

This communication records the results of a survey of the thermoluminescence of over fifty inorganic compounds and glasses in an attempt to find how wide-spread the phenomenon of radiation-induced thermoluminescence is and to try to obtain data from which wider generalizations can be made.

Experimental

The inorganic crystals taken from fresh bottles were mostly of analytical reagent quality. Usually the purity as

given on the bottle was over 99.5% and frequently it was better than 99.9%. Thermoluminescence frequently is affected by traces of impurities less than 0.01%.

All samples except a few which were in the form of powders, were ground in a porcelain mortar to between 100 and 200 mesh, dried at 60° and bottled. They were then exposed to a cobalt-60 γ -source,⁶ giving about 5000 roentgens per hour. Each sample received 5000, 25,000 or 100,000 roentgens at room temperature and was then stored on Dry Ice until used.

The specimens were transferred to small iron dishes 0.75 inch in diameter and 0.15 inch deep and leveled off to give an "infinitely thick" layer. The dish was then placed in the thermoluminescence apparatus⁶ and heated at the rate of 25° per minute, to about 350°.

The apparatus was the result of considerable development of earlier types used in this Laboratory. It consists of a light-tight box divided in the middle by a horizontal shelf with a hole in its center. The furnace in the bottom of the box consists of a pancake arrangement with a coil of No. 20 nichrome wire in spiral grooves of ceramic, covered with a silver block which can be heated up to 1° per second. Holes in the ceramic housing permit air cooling after the completion of an experiment. The temperature of the silver block is recorded with the help of a thermocouple. Vertical internal reflecting rods of clear fused silica 1.1 inch in diameter carry the thermoluminescent light directly from the heated sample to the photomultiplier at the top of the box. This photomultiplier tube (RCA 1P28) is enclosed in a housing through which cooled air can be circulated if necessary to reduce the dark current.

An automatic switch is attached to the door in such a way that the photomultiplier tube is always disconnected when it is exposed to the day-light of the room, thus preserving the high sensitivity of the tube. Corrections are made for

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(2) C. A. Boyd, *J. Chem. Phys.*, **17**, 1221 (1949).

(3) (a) L. F. Heckelsberg and F. Daniels, *THIS JOURNAL*, **61**, 414 (1957); (b) J. K. Rieke and F. Daniels, *ibid.*, **61**, 629 (1957).

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(6) J. K. Rieke, Ph.D. thesis, Chapt. II, University of Wisconsin, 1954.

TABLE I
 THERMOLUMINESCENCE OF γ -IRRADIATED INORGANIC CRYSTALS

Material	5000 roentgens		25,000 roentgens		100,000 roentgens	
	Peak temp., °C.	Area	Peak temp., °C.	Area	Peak temp., °C.	Area
Li ₂ O	111	9	109	8	114	11
	180	49	183	57	183	99
	283	136	296	56	282	23
Li ₂ SO ₄	80	9	93	12	106	29
	134	4	146	14	146	41
	302	56	318	25	320	29
Na ₂ CO ₃	100	3050	100	22,000	91	67,000
	133	1450	137	9,400	126	18,800
					158	20,800
K ₂ Cr ₂ O ₇			100	<1	111	2
			196	<1	212	2
			244	<1		
K ₂ HPO ₄	220	5	219	34	225	90
	305	6	320	29	336	51
{ MgCO ₃ 60% MgO 40%	334	118	350	216	350	424
MgO	115	..	115	..	115	..
	200	..	225	..	215	..
	325	..	335	..		
MgF ₂	91	81	100	200	93	200
	153	200	150	570	144	1820
			268	140	264	620
			338	450	350	1480
Ca ₃ (PO ₄) ₂	108	825	110	4780	114	10,400
BaO	106	1300	105	2440	103	2710
	184	1240	192	1580	196	1790
BaCO ₃	84	29	79	80	95	145
	158	43	112	68	147	445
			153	270	183	165
Ba(NO ₃) ₂					85	1
	192	1	234	1	211	7
BaCl ₂	90	10	89	20	91	
	330	164	345	240	347	524
BaBr ₂	87	168	89	266	86	370
AlPO ₄	265	4	171	2		
	305	<1	250	14		
			325	18		
MnO ₂ ^a	97	1	102	2	159	13
	173	<1	175	4	210	26
MnO ₂ ^a			138	4	135	4
			202	3	192	4
Pb(NO ₃) ₂			114	2	114	4
					194	4
					247	3
PbCl ₂	66	2	60	1	..	..
	102	1	96	2	..	..
			156	4		

^a Chemical, from different sources.

dark current by closing a shutter for brief intervals during the determination of the thermoluminescence glow curve, and for black body radiation by making the same determination in an empty dish.

The current from the photomultiplier tube is amplified by a Leeds and Northrup model 9836-A D-C amplifier with a wide range of sensitivities. The amplification is raised to give maximum deflections without going off the scale and the amplification is checked periodically with a standard tritiated phosphor button imbedded in clear plastic. The intensity of the thermoluminescence light and the temperature of the sample are recorded on a continuous two pen

recorder Model 153, manufactured by the Brown Instrument Co.

The temperature increase is controlled by hand with a Variac or with an automatic device consisting of a Brown Model 152 circular chart proportionating control with an integral mounted Electro-line relay, connected to a slide wire and valve control of a Brown model MS.801 industrial reversing motor geared to a 10 ampere Variac.

The recorder chart was operated at the rate of 1 inch per minute. The temperature of the maximum and the area under each peak was determined. The areas in arbitrary units are proportional to the light emitted within the tem-

perature range and are probably correct to within 20% and the peak temperatures to within 10°.

Results

The results are summarized in Table I.

The following materials exhibited no thermoluminescence detectable with this apparatus even after exposure to 100,000 roentgens: $K_2S_2O_8$, $K_3Fe(CN)_6$, $K_2S_2O_5$, $KHSO_4$, K_2CrO_4 , $KMnO_4$, KNO_3 , NH_4NO_3 , $(NH_4)_2Cr_2O_7$, MnO_2 (electrolytic), $MnCO_3$, $MnCl_2$, $FeCl_2 \cdot 4H_2O$, Fe_2O_3 , NiF_2 , $CuCl_2$, $Cu_3(PO_4)_2 \cdot 3H_2O$, CuI , Ag_2O , Ag_2SO_4 , $HgCl_2$, $HgBr_2$, $PbBr_2$, PbI_2 .

In addition to exploring thermoluminescence of several inorganic salts, a few glasses containing varying amounts of iron were studied. It is known that exposure of some glasses to X-rays or γ -rays gives coloration, which disappears on heating. Such glasses exhibit thermoluminescence and provide information concerning the types of imperfections which can act as electron traps. Six plates of glass were exposed to 240,000 roentgens and run in the thermoluminescence apparatus with a 1P21 photomultiplier tube. The glass plates and the chemical analyses were supplied by Mr. J. V. Fitzgerald of the Pittsburgh Plate Glass Company. All the glasses had the following approximate composition: Na_2O , 20%; CaO , 20%; SiO_2 , 60% with varying traces of iron oxide.

The results are summarized in Table II.

TABLE II
THERMOLUMINESCENCE OF GLASS

% iron oxide	Peak temp., °C.	Peak area, arbitrary units
0.01	170, 210	82
.05	190	45
.10	215	20
.10 ^a	208	43
.10 ^b	185	50
.50	..	3

^a All oxidized. ^b All reduced.

In general, the thermoluminescence decreases as the iron content increases, at least after a minimum amount is present. The presence of 0.5% iron oxide practically destroys the thermoluminescence. There is little difference in the thermoluminescence whether the iron is in the form of the oxidized ferric or reduced ferrous compound. There is a difference, however, in the absorption color of the glass. After irradiation, the 0.01, 0.05 and 0.10% iron oxide glasses are brown-black, brown and light brown, respectively. All become colorless after heating. The glass with 0.50% iron oxide is very light brown after irradiation, and after heating it retains the same light color. The reduced iron at 0.10% gives a very light brown with no apparent change on heating; whereas the oxidized iron gives a dark brown after irradiation, which disappears completely on heating.

A dozen other glasses of varying compositions

were studied also. With exposures of 5000 roentgens most of them did not exhibit thermoluminescence; but with 300,000 roentgens most of them did.

Discussion

In view of the large number of alkali halides, oxides, carbonates and sulfates, and the thousands of mineral samples that have shown radiation-induced thermoluminescence in this Laboratory, it was somewhat surprising to find so many inorganic compounds which exhibit no thermoluminescence. Probably many of these would show thermoluminescence at temperatures below room temperature if exposed to radiation at still lower temperatures.

The presence of chemical impurities greatly affects thermoluminescence, sometimes increasing it and sometimes decreasing it. The relation between impurity content and thermoluminescence has been studied in calcium carbonate. Impurities so low in concentration as to be undetectable by many standard methods of analysis can still affect thermoluminescence. But impurities are not the only factors. The type of crystal, the physical treatment of the crystal and the extent of the exposure to γ -radiation are variables which affect thermoluminescence.

Only tentative generalizations can be offered now. Radiation-induced thermoluminescence is more apt to occur in hard, colorless crystals with simple lattices and small cations and anions as indicated in Table III.

TABLE III
ROUGH CLASSIFICATION OF THERMOLUMINESCENCE INTENSITIES

Anions	Cations
High intensity	
F^- , Cl^- , CO_3^{2-} , SiO_3^{2-} , O^{2-}	Li^+ , Na^+ , K^+ , Mg^{++} , Ca^{++} , Sr^{++} , Al^{+++}
Intermediate intensity	
HPO_4^{2-} , Br^- , I^- , PO_4^{3-}	Pb^{++} , Cd^{++} , Ba^{++}
Low intensity	
CrO_4^{2-} , $Cr_2O_7^{2-}$, $S_2O_8^{2-}$, $Fe(CN)_6^{4-}$, HSO_4^- , MnO_4^- , NO_3^-	Fe^{+++} , Fe^{++} , Mn^{+++} , Mn^{++} , Co^{++} , Ni^{++} , Cu_2^{++} , Cu^{++} , Ag^+ , Hg^{++} , NH_4^+

These generalizations are only tentative and much more needs to be done, particularly with crystals of extraordinary purity before firm conclusions can be drawn. Although the thermoluminescence glow curves are reproducible for a given sample of material, there may be great differences in the glow curves for a given chemical compound prepared under different conditions and with different impurity contents.

The author is glad to acknowledge the advice of Professor Farrington Daniels and the support of the Atomic Energy Commission, Contract AT-(11-1)-178 in this work.

[Reprinted from the Journal of Physical Chemistry, 61, 636 (1957).]

Thermoluminescence of Sodium Sulfate and Lead Sulfate, and Miscellaneous Sulfates, Carbonates, and Oxides

By Louise E. Moore

THERMOLUMINESCENCE OF SODIUM SULFATE AND LEAD SULFATE, AND MISCELLANEOUS SULFATES, CARBONATES, AND OXIDES¹

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Received December 3, 1956

Radiation-induced thermoluminescence has been studied for several sulfates, carbonates and oxides. The thermoluminescence of sodium sulfate is affected by the method of dehydration and by the impurities taken up on crystallization. Lead sulfate is not thermoluminescent, but is rendered so by the addition of certain impurity ions.

The thermoluminescence of crystals has been studied in this Laboratory,^{3a} particularly the alkali halides^{3b} and calcium carbonate. After exposing the crystals to γ -radiation they are heated in the dark and the temperatures at which light is emitted are recorded, giving a "glow curve."

The glow curve of calcium carbonate is markedly affected by the impurities in the solution from which the material is precipitated. Maxima in the light intensity-temperature curves can be induced, increased or decreased by the addition of various impurities. In some cases, impurity content can be predicted from the glow curve and *vice versa*. This fact suggested that thermoluminescence might be useful as an analytical tool in studies of nearly pure crystalline compounds. It is sensitive to very small quantities of impurities—reagent grade purity is far from thermoluminescence purity.

Thermoluminescence may or may not be an inherent property of the host crystal. The pure crystal may give a basic thermoluminescence pattern which is modified by imperfections, or the thermoluminescence may arise from the presence of impurity ions or from effects of radiation on the crystal.

The purpose of this investigation was to determine the thermoluminescence of the sulfates, and to study particularly sodium sulfate which can be easily purified, and lead sulfate which is free from the complication of hydrate formation. Other salts such as carbonates and oxides were measured also in an exploratory study.

Experimental

Reagent grade sulfates were used with the exception of calcium sulfate and manganese sulfate, both of which were described as "purified." "Specpure" samples obtained from the Jarrell-Ash Company, designated as "spectroscopically pure," were used for the carbonates and oxides.

Any samples which were not powders were ground and sieved to 100 to 200 mesh. The "Specpure" samples were neither dried nor ground.

Sodium sulfate was recrystallized from distilled water and from conductance water. The recrystallizations from conductance water were made in polyethylene containers (except for the filtration steps) by cooling from room temperature to 0°. The lead sulfate precipitations and the preparations of sodium sulfate with added impurities were carried out in Pyrex containers.

Sodium sulfate samples were ground to 100 to 200 mesh. Lead sulfate samples precipitated as powder. All lead sulfate samples and most of the sulfates, except sodium sulfate, were dried at 150°.

Sulfates were tested for thermoluminescence before and

after irradiation in a cobalt-60 source.⁴ The radiation level within this source is approximately 3000 roentgens per hour. Most of the sulfates were irradiated for periods of 24, 48 and 72 hours. The sodium sulfate samples were irradiated for 24 hours and the lead sulfate samples for 72 hours. The samples were irradiated in gelatine capsules and stored on Dry Ice until used.

Samples were then packed in a thin silver dish, 1.2 cm. in diameter and 1 mm. deep, and were heated in a light-tight box from 0 to 400°. A linear temperature rise of about 1° per second was provided by manual operation of a Variac which controlled the furnace current. The furnace consisted of heating coils of Nichrome wire, electrically insulated from the silver plate on which the sample dish was placed.

Light was detected with an RCA 5819 phototube with a maximum response in the blue. The current from the phototube was passed through a Leeds and Northrup amplifier to a Speedomax recorder. This responded alternately to the light impulse and to the output of a copper-constantan thermocouple. The sensitivity to thermoluminescent light could be varied 300-fold.

Results

Sulfates.—The peak temperatures at which maxima occurred in the glow curves of the sulfates are recorded in Table I.

TABLE I

RADIATION-INDUCED THERMOLUMINESCENCE OF SULFATES

Compound	Peak temp., °C.	Compound	Peak temp., °C.
Li ₂ SO ₄ ·H ₂ O	85–120	3CdSO ₄ ·8H ₂ O	110–130
	230–260 ^a	PbSO ₄	110–130
Na ₂ SO ₄ ·10H ₂ O	80–130	Tl ₂ SO ₄	60–80
K ₂ SO ₄	80–100	Ag ₂ SO ₄	None
MgSO ₄ ·7H ₂ O	120–145 ^b	MnSO ₄	80–110
	90–120	NiSO ₄ ·6H ₂ O	None
SrSO ₄	120–135	CuSO ₄ ·5H ₂ O	None
CaSO ₄	120–140	Fe ₂ (SO ₄) ₃ ·6H ₂ O	None
BaSO ₄	100–120		
	180–190		

^a High temperature peak only after grinding. ^b Low temperature peak only after heating to 260°.

Drying sometimes increased and sometimes decreased the area of the thermoluminescence peaks. The peak temperature and the peak area could not be correlated either with the position of the element in the periodic table nor with the impurity content given by the manufacturer.

Dried LiSO₄·H₂O always exhibited a very small peak between 85 and 120°. This was a very low, broad peak; and it was impossible to determine precisely the temperature of the maximum. When the material was ground, either before or after drying, a second, large peak appeared at 230 to 260°. This peak could be found only in samples which

(1) Supported by the U. S. Atomic Energy Commission, Contract AT(11-1)-178.

(2) Armour Research Foundation, Chicago, Illinois.

(3) (a) J. K. Riecke, *THIS JOURNAL*, 61, 633 (1957); (b) L. F. Heckelsberg and F. Daniels, *ibid.*, 61, 414 (1957).

(4) D. F. Saunders, F. F. Morehead and F. Daniels, *J. Am. Chem. Soc.*, 75, 3096 (1953).

were dried and ground. Since 12 hours or more of heating at 150° did not destroy the effects of grinding, a relatively permanent type of trap must have been produced. The production of a new peak in radiation-induced thermoluminescence by grinding has been observed before and will be discussed in another communication.

In the case of calcium and manganese sulfates (which were less pure), thermoluminescence peaks were observed *before* irradiation. This crystallization-induced thermoluminescence has been noted before.⁵ These peaks appeared against a background rising to red heat. The peak for manganese sulfate, previously dried at 260°, came in at 290°. The curve for calcium sulfate had a peak at 310° before drying. After the material was dried at 150°, two peaks appeared at 345 and 355°. These pre-irradiation peaks were usually not observed in the irradiated samples, probably because of a high background from the larger peaks induced by radiation.

Carbonates and Oxides.—Table II shows the effect of different radiation periods on a group of "Specpure" carbonates.

TABLE II
INFLUENCE OF γ -RADIATION EXPOSURE ON
THERMOLUMINESCENCE

Compound	Approx. peak temp., °C.	Peak height after exposure to	
		145,000 r.	215,000 r.
Li ₂ CO ₃	140	0.025	0.103
Na ₂ CO ₃	110	1.3	2.8
	230	4.4	4.6
Tl ₂ CO ₃	100	0.0077	0.0153
CaCO ₃	155	4.8	4.9
	235	1.3	1.3
	340	1.5	1.2
BaCO ₃	125	0.25	0.29
	165	0.14	0.14

For about half of these materials there was little change in peak height produced by additional radiation beyond 145,000 roentgens. The electron-traps were largely filled by this exposure. The greatest increase produced by additional radiation was observed for lithium carbonate which had a very low peak. With sodium carbonate a 50% increase in radiation did not affect a high temperature peak, but it doubled the intensity of light emitted at a low temperature peak.

Figure 1 shows the relative thermoluminescence peaks induced in a number of "Specpure" compounds obtained from the Jarrell-Ash Company by exposure to 145,000 roentgens. Each bar indicates the temperature of the maximum light intensity of a peak, and the length of the bar represents the relative height of the peak. It is to be emphasized that the scales of the ordinates are not the same for the different materials.

The following samples of "Specpure" materials gave no thermoluminescence detectable with the present apparatus after exposure to 145,000 roentgens: BeCO₃, Cs₂CO₃, K₂CO₃, Ag₂O, Bi₂O₃, CdO,

Fig. 1.—Relative thermoluminescence peak heights of thermoluminescent "Specpure" carbonates and oxides.

Cr₂O₃, CuO, Fe₂O₃, Mn₃O₄, MoO₃, Sb₂O₄, SiO₂, SnO₂, Ta₂O₅, TiO₂, Tl₂O₃, U₃O₈, V₂O₅, WO₃ and Si.

Sodium Sulfate.—Sodium sulfate was studied in more detail because it is easy to recrystallize. The study is divided into two parts—drying and recrystallization. Since the material crystallizes as the decahydrate, it is necessary to consider the effect of drying on the thermoluminescence pattern. Removal of the water of crystallization from the solid creates crystal defects which contribute electron traps. This complicates any basic thermoluminescence pattern and its interpretation.

Samples of anhydrous sodium sulfate were used to test reproducibility and to determine the limits of the apparatus and of the method of determining area and peak temperature. Variations of 5 to 20° are possible for the maximum of a peak. The area under the peak, determined by planimetry, varied by about 10%.

Anhydrous sodium sulfate also was used to test the irradiation time necessary for saturation and to show that storage on Dry Ice for periods up to a week does not reduce the thermoluminescence. The peak area after 72, 48 and 24 hours of irradiation was essentially the same. Twenty-four hours, about 70,000 roentgens, was sufficient for saturation.

Samples of the decahydrate from a single bottle were dried at 70, 120, 320°, and at room temperature over concentrated sulfuric acid for periods ranging from one hour to 52 days. Peak temperatures and areas varied with drying time and tem-

(5) E. J. Zeller, J. L. Wray and F. Daniels, *J. Chem. Phys.*, **23**, No. 11, 2187 (1955).

Fig. 2.—Glow curve of sodium sulfate recrystallized three times and glow curves with additions of lead (p.p.m. referred to Na_2SO_4). Intensity is in arbitrary units.

perature, but for any given method the reproducibility was fair. Areas generally increased with heating time. For samples heated first at low temperatures, the area increased with drying at 320° . Usually the area for a sample heated for 24 hours at 320° was approximately twice that of a sample heated for 1 hour at 320° .

Usually drying at temperatures below 320° produced one peak at $110\text{--}140^\circ$. Increasing the time of heating tended to lower the temperature of this peak and to cause a second peak to appear between 150 and 280° . The contribution of such an unresolved peak would raise the apparent maximum of the low temperature peak. In addition a very low temperature peak appeared between 40 and 60° in all samples heated at 320° except those previously dried for 52 days over concentrated sulfuric acid. This room temperature drying was associated with a pink coloration of the sample after irradiation.

Apparently, the defects produced by drying play an important role in the production of thermoluminescence in this hydrate. Two or three types of traps can be produced during drying. When water was removed slowly at room temperature by standing over concentrated sulfuric acid, the decahydrate did not go into solution and recrystallize. After prolonged treatment over sulfuric acid, no high temperature peak developed even after later heating at 320° . Apparently when much of the water was carefully removed at room temperature, fewer defects were produced. It may be that the 110° peak is characteristic of the material and that the peaks at $150\text{--}280^\circ$ and at $40\text{--}60^\circ$ are produced by rapid removal of part of the water.

In general, recrystallization of sodium sulfate from distilled water or conductance water decreased the thermoluminescence, but in each series of recrystallizations the area increased at least once. This occasional increase may have been due to variations in crystallization or drying, or possibly to accidental traces of impurities. The addition of traces of K_2SO_4 , CaSO_4 and PbSO_4 to solutions of the products of several such series gave erratic results although checks on each individual sample agreed well. The difficulty probably was due in part to differences in the amount of impurity taken up in the crystal.

The product of the third recrystallization of a sample of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was used to determine the effect of impurities on the glow curve. All samples were dried at 120° and later at 320° . The samples without added impurities showed a single, sharp peak. All samples have a background of many impurities, as shown by spectrographic analysis.

Addition of lead sulfate in small amounts produced a second peak, the area of which increased roughly with the concentration of the lead sulfate, as shown in the thermoluminescence glow curves given in Fig. 2. Addition of potassium sulfate produced a second peak which was smaller than that produced by lead sulfate. Calcium sulfate apparently did not affect the thermoluminescence pattern.

Lead Sulfate.—Lead sulfate was chosen for further study because it is not complicated by water of crystallization. Reagent grade lead sulfate showed very little thermoluminescence. Precipitation of lead sulfate by mixing $0.1\text{ }M$ $\text{Pb}(\text{NO}_3)_2$ with $0.1\text{ }M$ H_2SO_4 gave a material with no measurable thermoluminescence. A thermoluminescence peak at $110\text{--}140^\circ$ could be induced in this material by deliberate addition of certain impurities. In all experiments the lead sulfate was subjected to γ -radiation of 215,000 roentgens.

A series of lead sulfate precipitates was prepared in which silver nitrate, cupric sulfate pentahydrate, ammonium sulfate, potassium sulfate, lithium sulfate monohydrate, nickel sulfate hexahydrate or hydrated ferric sulfate was added to the solution. Equal volumes of $0.1\text{ }M$ lead nitrate and a solution $0.1\text{ }M$ in sulfuric acid and $0.1\text{ }M$ in the impurity salt were mixed. The precipitates from solutions containing ammonium sulfate, potassium sulfate or lithium sulfate gave a thermoluminescence peak at about 120° .

The thermoluminescence is not due to that of the added impurity alone. Pure lithium sulfate showed less thermoluminescence than lead sulfate precipitated in the presence of lithium sulfate. Silver sulfate, calcium sulfate, strontium sulfate, magnesium sulfate and manganese sulfate were also used as impurities and none of the lead sulfates prepared with these impurities gave thermoluminescence peaks although most of these sulfates alone, as reagent grade chemicals, are thermoluminescent.

Concentration effects were studied with added sodium sulfate. Equal volumes of $0.1\text{ }M$ lead nitrate and $0.1\text{ }M$ sulfuric acid containing various amounts of sodium sulfate were mixed. The precipitated lead sulfate was not thermoluminescent.

if the sodium sulfate concentration in the sulfuric acid was 6×10^{-5} to $3 \times 10^{-2} M$. It was thermoluminescent if the concentration of sodium sulfate in the sulfuric acid was raised to 0.2 to 0.8 M . If the precipitating solution contained only sodium sulfate, a thermoluminescent lead sulfate could be prepared by mixing equal volumes of 0.1 M lead nitrate and 0.1 M sodium sulfate. As the sodium sulfate solution was increased to 0.8 M , the area of the thermoluminescence peak increased. In each case the thermoluminescence of lead sulfate precipitated from a solution containing a given concentration of sodium sulfate was greater if no acid was added.

Two concentration series were run with potassium sulfate. When potassium was the added impurity, an increase in acid concentration increased the area of the thermoluminescence peak. The area also increased with increasing concentration of potassium in the solution. If a small amount of silver sulfate was added to the solution of potassium sulfate, the thermoluminescence area was changed. For high potassium concentrations it usually increased, while for low concentrations it generally decreased. If sulfuric acid was present, the decrease in area seemed to be greatest for high potassium concentrations. Both acid and silver sulfate alone gave lead sulfates with no thermoluminescence.

The results may be due to complex combinations of the effects of several impurities in the lattice or to changes in the amount of impurity taken into the lattice when other impurities are present in the solution.

Lead sulfate was precipitated from solutions containing one of several sodium or potassium salts. The salt was added to the sulfuric acid solution in each case. Lead sulfate precipitated in the presence of chlorides, bromides and acetates was not thermoluminescent, but lead sulfates precipitated in the presence of iodides and hydroxides were thermoluminescent. Potassium carbonate, potassium nitrate and potassium phosphate gave thermoluminescent precipitates while the corresponding sodium salts did not.

These results indicate that anion impurities also affect the thermoluminescence pattern. All samples gave the lead sulfate X-ray pattern with some modifications. Samples from the solutions containing iodides showed the X-ray pattern of lead iodide in addition to that of lead sulfate. There were minor changes in line intensities, perhaps due to the substitution of sodium or potassium for lead.

Conclusions

Radiation-induced thermoluminescence glow curves provide a means for studying factors in crystallization and the purity of the crystals. Many of the sulfates exhibit thermoluminescence even when highly purified. Others definitely require the presence of impurities.

The quantity of impurity which affects the thermoluminescence may be so low as to be difficult to measure by analytical methods.

The effects on thermoluminescence of various impurities at different concentrations are very complicated. In order to affect thermoluminescence, the impurities must be taken up into the crystal structure to give special types of imperfections.

In one reagent bottle of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ of high quality, different crystals in the bottle gave widely varying thermoluminescence glow curves. The variations probably were due to slight differences in impurities taken up by the crystals at different stages in the crystallization process or to differences in the physical conditions of crystallization. Thermoluminescence measurements might be used as a control for uniformity in certain types of crystallization operations.

The thermoluminescence of sodium sulfate is changed by the method of heating the decahydrate. Apparently the rate of heating affects the defects in the crystal and their ability to trap electrons. The nature and concentration of foreign ions taken up into the sodium sulfate crystal also affects the glow curve. Lead and potassium produce an additional high temperature peak.

Pure lead sulfate is uncomplicated by dehydration. It does not exhibit radiation-induced thermoluminescence. Large amounts of impurities of sodium, ammonium, potassium, lithium and iodide and hydroxide added to the solutions from which lead sulfate is precipitated, produce a thermoluminescence peak while many other impurities are without effect. The peak temperature in lead sulfate is always the same with the different impurities, and the area depends on the concentration of sulfuric acid at the time of precipitation and on an interaction of both cation and anion impurities.

It is hoped that studies of thermoluminescence will lead eventually to a better understanding of the up-take of impurities and the nature of imperfections in crystals.

Acknowledgments.—The author wishes to express her gratitude to Dr. Farrington Daniels who directed this work and to the U. S. Atomic Energy Commission which supported it.

[Reprinted from the Journal of Physical Chemistry, 61, 629 (1957).]

Thermoluminescence Studies of Aluminum Oxide

By James K. Rieke and Farrington Daniels

[Reprinted from the Journal of Physical Chemistry, **61**, 629 (1957).]
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THERMOLUMINESCENCE STUDIES OF ALUMINUM OXIDE¹

BY JAMES K. RIEKE AND FARRINGTON DANIELS

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin

Received December 3, 1956

Gamma-ray induced thermoluminescence of aluminum oxides depends on the extent of hydration and the crystal form produced by different calcining treatments. A peak at 236° depends on sodium impurity. Surface thermoluminescence can be induced by visible light in partially hydrated alumina.

The influence of structure and impurities on the thermoluminescence glow curves of aluminum oxides was the object of this investigation. It is part of a broader program in this Laboratory in which an attempt has been made to understand better the factors which determine the thermoluminescence of crystals and to find chemical applications for this phenomenon. These glow curves may have

a bearing on the catalytic behavior of aluminum oxides.

Experimental

Thirty samples of aluminum oxide, representing various crystal phases, degrees of hydration and chemical purity have been studied. They were prepared and characterized by Dr. Allen S. Russell of the Aluminum Company of America and kindly given to us for this investigation. In general, the samples were crystalline powders ranging in size from 5 to 100 mesh. The samples were ground uniformly to pass a 100 mesh screen and be retained on a 200 mesh screen.

(1) Adapted from a portion of a Ph.D. thesis by James K. Rieke, filed in the University of Wisconsin Library, 1954.

TABLE I
 DESCRIPTIONS OF Al_2O_3 SAMPLES

Sample No.	Name ^{1,4}	Description	Purity
1	α -Alumina trihydrate	Monoclinic, from Na_3AlO_3 (Bayer)	0.38% Na_2O
2	β -Alumina trihydrate	Monoclinic, rapid ppt. with CO_2 at 40° from Na_3AlO_3	0.28% Na_2O
3	α -Alumina monohydrate	Digested no. 1 with H_2O at 200°	
5	High purity, α -monohydrate	Orthorhombic, hydrolyzing pure Al isopropoxide	<0.10% impurity
6	Alcoa, Alumina A-1	Calcined no. 1 at 1100°	0.5% Na_2O
7	Alcoa alumina A-14 (porous alpha)	Calcined hydrate	0.04% Na_2O
8	Alcoa alumina F-10	Catalyst support, $120 \text{ m}^2/\text{g}$.	0.1% Na_2O
9	Alcoa alumina T-61	Highly calcined hydrate	0.02% Na_2O
10	χ - Al_2O_3	Cubic (not spinel), calcined 600°	
11	γ - Al_2O_3	No. 1 calcined at 700°	
12	ϵ - Al_2O_3	Cubic (spinel), no. 2 calcined at 800°	
13	δ - Al_2O_3	Orthorhombic, no. 1 calcined at 900° in steam, almost anhydrous	
14	θ - Al_2O_3	Hexagonal, no. 2 calcined at 1000° in steam	
15	κ - Al_2O_3	Orthorhombic, no. 8 calcined at 850° in steam	
16	α - Al_2O_3	Hexagonal, no. 8 calcined at 1000° in steam, anhydrous	
31	Sapphire	Powder fused in electric arc	

γ -Irradiation of about 145,000 roentgens was accomplished by exposure of 1-gram samples in gelatine capsules to a cobalt-60 source.² The samples were placed in glass containers and stored on Dry Ice until their thermoluminescence glow curves were determined. The thermoluminescence apparatus of improved design is described elsewhere.³ The samples were heated at the rate of 25° per minute to 450° and the intensity of emitted light recorded.

Effect of Light.—In this investigation it was first found that thermoluminescence in crystals sometimes occurs without previous exposure to γ -rays or other high energy radiation. For studying this phenomenon samples of aluminum oxide powder were placed in the thermoluminescence apparatus (without previous exposure to γ -radiation) and heated to between 350 and 400° until the emission of light practically ceased. These "drained" samples were then cooled in the dark in a desiccator evacuated to 0.1 mm . of mercury. Repeated heating and cooling failed to activate the aluminum oxide to give thermoluminescence, but exposure to the light of the room or to a AH-4 mercury lamp did activate the samples so that they exhibited glow curves when heated in the thermoluminescence apparatus. A beam of light from the mercury lamp was focussed through the thick Pyrex desiccator and onto the sample. After such an exposure the sample exhibited thermoluminescence glow curves with broad maxima around 350° . Visual observation showed that the thermoluminescence light is pale blue or blue-green. In some cases, the light was emitted for as long as ten minutes when kept at 370° . In other experiments, before exposing to the light, the drained samples were exposed to water vapor in the desiccator at 1 mm . and at 15 mm .

Description of Aluminum Oxides.—The thirty samples are described in Tables I and II.

Samples 17 to 30 were prepared from monoclinic alumina trihydrate, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, by calcining under conditions recorded in the tables which follow.

Results

Typical examples of glow curves are shown in Figs. 1–3 from the thirty curves which are available. These curves have been corrected for dark current with shutters at periodic intervals and for black body radiation using an empty dish. In these figures the light intensity of the actual experiments measured with the photomultiplier cell, has been reduced by a suitable factor so as to get all the curves on a comparable scale. The reduction factor is labeled on each curve. Thus, in sample 22 of

Fig. 3, the relative intensity of the low temperature peak is 4×10 or 40 , whereas the high temperature peak is 31×40 or 1240 . The areas under the various peaks of the original glow curves were measured with a planimeter. Different determinations of area for a given material agreed within about 10%.

γ -Ray Induced Thermoluminescence.—Thermoluminescence glow curves are produced after irradiation with γ -rays for nearly all samples of aluminum oxide, but the intensity of light and the peak temperatures at which maxima occur, vary greatly. The quantity of light emitted generally increases as the degree of calcination increases from the lower hydrates through α -alumina and is greatest for synthetic sapphire, made in an electric arc, which is highly crystalline α -alumina.

All the thermoluminescence peaks are found to lie in one of four temperature ranges; $103 \pm 5^\circ$, $123 \pm 5^\circ$, $164 \pm 5^\circ$ and $236 \pm 5^\circ$. The 103 and 123° peaks do not usually occur together in the same sample. The thermoluminescence behavior is recorded in Table II.

Light-induced Thermoluminescence.—Thermoluminescence sometimes occurred without previous exposure to γ -radiation as already described. This phenomenon was observed in the hydrated or partially hydrated aluminas and did not occur in the highly calcined samples or the sapphire. Several experiments were carried out with sample 22 which had been heated to 220° for two hours and originally consisted of a mixture of α -trihydrate and α -monohydrate. The material was heated to 370° for varying periods of time to convert more of the trihydrate to monohydrate and then exposed to the light for varying periods of time before obtaining the thermoluminescence glow curves. The results are recorded in Table III.

Similar experiments were carried out with sample 20 which also showed light induced thermoluminescence except that after calcining at 370° the aluminum oxide was exposed to water vapor for 160 minutes and then exposed to the light for 130 minutes. The blank run without water vapor gave a light induced thermoluminescence area of 15.0 (square inches on the chart) whereas the one with

(2) D. F. Saunders, F. F. Morehead and F. Daniels, *J. Am. Chem. Soc.*, **75**, 3096 (1953).

(3) J. K. Rieke, *This Journal*, **61**, 633 (1957).

(4) A. C. Stumpf, A. S. Russell, J. W. Newsome and C. M. Tucker, *Ind. Eng. Chem.*, **42**, 1398 (1950).

TABLE II
CORRELATIONS OF AREA UNDER DIFFERENT PEAKS

Sample no.	Temp. of calcination, °C. ^a	Area under peak	% crystal forms		Surface area m. ² /g.
123° Peak					
1	140	0.4		100 monoclinic	
28	200	1.4	25 orthorhombic	75 monoclinic	
22	220	1.9	35 orthorhombic	65 monoclinic	7
21	230	1.9	40 orthorhombic	60 monoclinic	45
24	245	2.2	50 orthorhombic	50 monoclinic	169
27	250	2.0	50 orthorhombic	50 monoclinic	110
25	400	3.3	50 orthorhombic	50 cubic	400
26	300	3.0	90 orthorhombic	10 cubic	300
23	282	3.7	95 orthorhombic	5 cubic	282
3	200(s)	8.2	100 orthorhombic		
10	600	0.2	99 cubic	1 gamma	
17	500	1.0	95 cubic	5 gamma	310
18	740	...	60 cubic	40 gamma	172
19	830	0.9		100 gamma	134
11	700	3.0	100 cubic		
12	800	5.7		75 gamma	
13	900(s)	8.7	25 orthorhombic		
15	850(s)	13.0	100 orthorhombic		
6	1100	22.5			
14	1000(s)	64.0			
103° peak					
18	740	0.4	60 cubic	40 gamma	
20	1000	3.9	100 gamma		
15	850(s)	11.6	100 orthorhombic		
30	1100	7.2	100 theta		
29	1200	46.0	100 hexagonal		
9	...	25.0	100 hexagonal		
164° peak					
28	200	0.9			
10	600	0.2			
20	1000	3.2			
13	900(s)	7.5			
15	950(s)	13.0			
6	1100	9.0			
30	1000(s)	7.2			
14	1000	82.0			
29	1200	65.6			
16	1000(s)	152			
7	...	200			
9	...	240			
236° peak					
9	...	13.0	100 alpha		% Na ₂ O
7	...	25.0	100 alpha		0.02
16	1000(s)	62.0	100 alpha		.04
29	1200	141.2	100 alpha		.1
					.3

^a (s) indicates that the calcination was carried out in steam.

TABLE III
RELATIVE AREAS UNDER GLOW CURVES OF THERMOLUMINESCENCE INDUCED BY LIGHT FOR SAMPLE 22

Time of heating at 370°, min.	Time of subsequent exposure to light, hr.	Relative thermoluminescence, glow curve area	Time of heating at 370°, min.	Time of subsequent exposure to light, hr.	Relative thermoluminescence, glow curve area
20-30	5	23.6	50-60	2	9.2
20-30	10	19.8	60-70	1	6.5
20-30	1	18.4	90-100	3	9.3
30-40	2	11.7	Over 100	10	7.3
30-40	0.5	5.3	Over 100	10	5.7
40-50	4	9.3	Over 100	1	5.0
50-60	10	11.1			

1 mm. of water vapor gave 1.3 and the one with 15 mm. of water vapor gave 1.2.

Discussion

The glow curves indicate that thermoluminescence is induced by high γ -irradiation, but that the locations of the maxima and the areas under the maxima vary markedly. The quantity of thermoluminescent light increases as the removal of water increases. It is largest with synthetic sapphire which is highly crystalline α -Al₂O₃ without water.

The thermoluminescence glow curves can be re-

Fig. 1.—Thermoluminescence of Al_2O_3 (samples 1,2,3,5-9).

solved into four peaks occurring at approximately 103, 123, 164 and 236°. The 123° peak is the most characteristic peak for aluminum oxide, hydrates and partial hydrates. It is found in almost all samples until a very high degree of calcination has been reached and then with further removal of water it disappears abruptly. To a limited extent, the area under the curve can be correlated with the crystal phases of the material. The area increases as the orthorhombic phase replaces the monoclinic alpha trihydrate and it reaches a maximum for orthorhombic α -monohydrate. As the temperature is increased and the orthorhombic phase disappears, the peak continues, but to a lesser extent than in the case of the α -monohydrate. The peak area again increases as the orthorhombic α -phase forms at still higher temperatures and continues to increase as the theta phase appears. It then disappears rapidly with further calcination.

The 103° peak occurs in most samples which do not show the 123° peak, except in no. 7 and no. 16. Only in no. 15 do both peaks appear. Both the 103° peak and the 164° peak appear at intermediate stages in the calcination which removes water from the crystal.

The 164° peak appears first when the alumina has been calcined to 600° and then increases progressively as the calcination increases. It is greatest for samples 7 and 8 and the synthetic sapphire. No correlation with impurities was found.

Fig. 2.—Thermoluminescence of Al_2O_3 (samples 10-17). Fig. 3.—Thermoluminescence of Al_2O_3 (samples 22,28,30,31).

The 236° peak occurs only in samples which have been calcined above 1000°. The thermoluminescence area increases in an approximately linear manner with concentration of sodium ion present as an impurity. The synthetic sapphire no. 31 shows an additional peak at 300°.

The 103, 123 and 164° peaks appear to be characteristic of lattice imperfections rather than impurity imperfections. The fact that the thermoluminescence shifts to higher temperatures as the degree of calcination increases indicates that the 103 and 123° trapping centers are in regions of partial hydration. The loss of water during calcination would tend to make these regions more posi-

tive and these centers may be of the $\text{Al}(\text{OH})_2^+$ type. The 164° peak may be related to $\text{Al}_2(\text{O})_x^{+(6-2x)}$ where x is between 2 and 3. The 236° peak which occurs only in the presence of sodium and complete dehydration is probably connected with a sodium ion trapping center.

The light-induced thermoluminescence is found in the partially hydrated samples. The fact that it is quickly quenched by adsorbed water suggests that the trapping centers are predominantly surface sites and that H_2O must be chemically bound. Anderson⁵ observed that luminescence occurs at aluminum anodes after an oxide film has been built up. Phosphorescent after-glow decayed rapidly after the current was stopped. Anderson concluded that the oxide layer acts as an excess conductor under these conditions. Work by Charlesby⁶ supports this view and indicates that the traps are at or near the crystal surface. Ewles^{7,8} studied the excitation

and emission spectra of several oxides. He found that the wave length of the exciting light most effective in producing luminescence lies in the spectral region where the hydroxyl ion is absorbing. Ewles found further that by chemical analysis there was marked oxygen deficiency at the surface. The emission maxima observed by Anderson and by Ewles were 4590 and 4500 Å., respectively. The visible light produced by light-induced thermoluminescence also lies in this spectral region. The electron transition which produces light emission appears to be the same in all three cases, and it is likely that the emission centers occur in surface regions where OH radical or ions exist.

The authors are grateful to Dr. Allen Russell of the Aluminum Company of America for furnishing the samples of aluminum oxide and characterizing them. They are also appreciative of the financial support for this research program by the Atomic Energy Commission under Contract AT(11-1)-178.

(5) S. Anderson, *J. Appl. Phys.*, **14**, 611 (1943).

(6) A. Charlesby, *Proc. Phys. Soc. (London)*, **66B**, 317 (1953).

(7) J. Ewles and G. C. Farnell, *ibid.*, **62A**, 216 (1949).

(8) J. Ewles and C. N. Heap, *Trans. Faraday Soc.*, **48**, 331 (1952).

Thermoluminescence Induced by Pressure and by Crystallization

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(Received September 12, 1955)

IN trying to determine the age of coral limestones from the intensity of thermoluminescence and the alpha-ray activity it was found that the younger limestones gave abnormally bright thermoluminescence. This observation led to the unexpected discovery that calcium carbonate, freshly precipitated in the laboratory, is also thermoluminescent, even without exposure to radiation. A variety of related phenomena are under further investigation in this laboratory.

When calcium carbonate is precipitated from calcium nitrate by sodium carbonate and the washed and dried crystals exposed to gamma radiation, prominent peaks are found in the thermoluminescence glow curve which are associated with impurities, such as iron, manganese, strontium, barium, and magnesium. The middle fraction of the precipitated crystals contains the fewest impurities¹ and does not show radiation induced (gamma-ray) thermoluminescence. However, the precipitated CaCO_3 crystals, whether exposed to gamma radiation or not, exhibit some thermoluminescence around 250° shortly before blackbody radiation obscures further detection. A typical glow curve of this type is shown in Curve 1, Fig. 1.

When the crystals are subjected to high pressure (50 tons per square inch) the thermoluminescence observed on heating is much greater as shown in Curve 2, Fig. 1. This pressure-induced thermoluminescence, without previous exposure to radiation, occurs even with the highly purified calcium carbonate which shows no radiation-induced thermoluminescence.

In old limestones (older than 100 million years) the thermoluminescence induced by alpha particles from uranium is always decreased by application of high pressures. This pressure effect is useful because it distinguishes between the radiation-induced thermoluminescence on which the age determination is based and the complicating crystallization- or pressure-induced thermoluminescence. The radiation-induced thermoluminescence is decreased while the crystallization-(nonradiation) induced thermoluminescence is increased.² New possibilities are opened up for determining the age of minerals based on the several different types of thermoluminescence and the influence of pressure.

More experimental facts are being accumulated on which to base a theory of pressure-induced and crystallization-induced thermoluminescence. It is suggested now that high pressures applied to a mass of crystals creates, by friction and point contact effects, high electrostatic voltages in local areas which are greater than the voltage necessary to release electrons in the crystal lattice. Triboluminescence is a well-known phenomenon in which light is emitted in the crushing of certain crystals such as cane sugar. The presence of pressure-induced thermoluminescence sug-

FIG. 1. Curve 1. The natural glow curve of a calcium carbonate precipitate before exposure to radiation or pressure. Curve 2. The glow curve of the same precipitate after pressure of 50 tons/sq in. but without exposure to radiation. Curve 3. Blackbody radiation curve.

gests that triboluminescence was produced initially, and that accumulated thermoluminescence is easier to detect than transient triboluminescence.

The crystallization-induced thermoluminescence merits further study. One theory suggests that strains of crystal growth may be set up which generate local electrostatic charges sufficient to release electrons; and according to another hypothesis a double layer involving ions attached to a growing crystal surface may, under certain conditions, generate a high enough charge to release electrons and give rise to subsequent thermoluminescence. Where crystallization-induced thermoluminescence exists, it is suggested that crystallization luminescence may be detected at the time of crystallization if the detection techniques with photomultiplier tubes are sufficiently improved. The pressure effects, in addition to releasing electrons in the crystal, may also create new holes or imperfections for the trapping of electrons, leading to new peaks in the thermoluminescence glow curves. Moreover, under certain conditions the application of pressure, causing plastic flow, may "heal" some of the imperfections already present and cause a decrease in some types of radioactivity-induced thermoluminescence.

The effects on thermoluminescence of pressure and crystallization described here are very small and could easily escape detection in earlier work with less sensitive equipment. By analogy with γ -induced thermoluminescence, it is estimated³ that of the order of one electron may be released and trapped among 10^9 atoms.

¹ E. J. Zeller and J. L. Wray, Bull. Am. Assoc. Petroleum Geol. (to be published).

² E. J. Zeller, Symposium on Geochemistry, American Chemical Society, Minneapolis, Minnesota (September 12, 1955).

³ Morehead and F. Daniels, J. Phys. Chem. 56, 546 (1952).

Thermoluminescence Dosimetry

By

William P. Riemen and Farrington Daniels

(Forthcoming Publication)

VI. Crystals -- Radiation Damage, Polymorphous Crystals
and Kinetics of Solid Reactions between Crystals

[Reprinted from the Journal of Physical Chemistry, 56, 546 (1952).]

Storage of Radiation Energy in Crystalline Lithium Fluoride and Metamict Minerals

By Frederick F. Morehead, Jr., and Farrington Daniels

STORAGE OF RADIATION ENERGY IN CRYSTALLINE LITHIUM FLUORIDE AND METAMICT MINERALS¹

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Received February 25, 1952

Measurements have been made on the energy of thermoluminescence obtained when lithium fluoride is exposed to 30,000 roentgens of γ -radiation and then heated to 500°. The bluish light emitted is equivalent to 1.5×10^{-6} calorie per gram and amounts to a storage in electron traps of about 0.005% of the γ -radiation. Metamict minerals have their crystal lattices so damaged by alpha rays from radioactive elements for millions of years that they fail to exhibit an X-ray diffraction pattern. When the temperature is raised to 450°, however, the crystal lattice is restored and at the same time, it has been found in this investigation that there is an evolution of about 25 calories of heat per gram, as measured with a thermal analysis apparatus.

The mechanism by which energy from α -, β - and γ -rays is stored in a crystal lattice is a matter of theoretical interest for studying the nature of the solid state, and it is a matter of practical importance for developing materials for nuclear reactors which will withstand the intense radiation.

When a crystal or semi-conductor is subjected to γ -rays or X-rays part of the energy is absorbed in displacing electrons from their atoms. Some electrons return immediately to their normal positions giving off fluorescent light; others become trapped in lattice imperfections or holes. The trapped electrons give rise to the so-called F-centers which absorb definite wave lengths of light. When the crystals are heated, the increased kinetic energy drives the electrons out of their traps from which they fall eventually to positions of lower energy with the emission of light, a phenomenon known as thermoluminescence.

The thermoluminescence of rocks, which contain uranium, and alkali halides which have been exposed to γ -radiation, has been under investigation in this Laboratory in an attempt to understand better the various ways in which the energy of radiation can be stored. Lithium fluoride has been studied thoroughly and the absolute energy of its thermoluminescence is reported here. It is small, 1.5×10^{-6} calorie per gram, amounting to 0.005% of the γ -radiation absorbed. Although the energy stored in trapped electrons is small it seemed likely that the atoms of the lattice might be displaced also and that this displacement would involve much more energy. In general, where there is light there is apt to be more energy present in the form of heat, but the measurement of small amounts of heat is much more difficult than the measurement of an equivalent amount of light energy. In order to study the storage of energy in crystal lattices attention was turned to metamict minerals which have been exposed for millions of years to α -particles from the considerable amounts of uranium and thorium which they contain. The crystal lattice of metamict minerals has been so damaged by radioactivity that the minerals do not show an X-ray diffraction pattern, but the pattern is easily restored by heating to a sufficiently high temperature. The evolution of energy by the restoration of atoms to their normal positions in the crystal lattice should evolve more heat than is evolved by

the release of trapped electrons. Energy storage as large as 25 calories per gram was found, and other minerals will be examined in the hope of finding still larger amounts of stored energy.

Measurements of Thermoluminescence.—The apparatus for measuring thermoluminescence^{2,3} consists of a light-tight box containing an electrical plate heated at the rate of 1° per second, a photomultiplier tube (RCA 1 P21) and a suitable optical system. The current through the photomultiplier tube is amplified and recorded with a potentiometer in which the intensity of the light is plotted automatically as a function of the time. The temperature of the hot-plate as recorded by a thermocouple is automatically plotted on the same graph, and the heating current is controlled so as to give a linear rise in temperature.

The light intensity as recorded by the photomultiplier tube was calibrated with monochromatic light from an AH-4 mercury lamp at a distance of 25 meters. The energy of this light in turn was calibrated at a distance of one meter with a thermopile which in turn was calibrated with a standard carbon filament lamp provided by the Bureau of Standards. Application of the inverse square law showed that for blue light at 4300 Å. the highest sensitivity for one recorder gave a deflection amounting to 4.1×10^8 divisions per erg per second, and for a second recorder 1.1×10^6 divisions. Farrand interference filters were used with the mercury lamp for 4300 and 5500 Å. and the ratio of the calibrations at these two wave lengths (2.36) agreed within 4% with the ratio of relative values given by the manufacturers.

The crystals of lithium fluoride, 1 cm. square and 1 mm. thick, were obtained from large, clear crystals grown from the molten material by the Harshaw Chemical Company. They were irradiated in a hollow aluminum cylinder surrounded by cobalt powder which had been exposed in the pile of the Oak Ridge National Laboratory and calibrated directly with ionization meters as will be described in a later communication. The density of γ -radiation within the cylinder was 6000 roentgens per hour as determined by three different methods which gave an average deviation of less than 10%.

A spectrogram of the weak thermoluminescent light extends from about 4005 to 4823 Å. It shows regions of varying intensity but no structure can be detected with the instruments used. The midpoint of the emission is taken as 4400 Å.

The sensitivity of the recorder is such as to give a deflection of 1.1×10^6 divisions for one erg per second. The graph paper travels at the rate of 1 inch in 40 seconds. Since there are nine divisions per inch on the recording graph paper, one square inch under the thermoluminescent curve corresponds to $9 \times 40 / 1.1 \times 10^6$ or 3.3×10^{-4} erg. The lens which focuses the light from the crystal onto the photomultiplier tube is 4.5 cm. in diameter and 10.5 cm. from the crystal. Assuming that there is no reflection from the perfect crystal, the total light in all directions for each square inch under the curve of thermoluminescent light intensity, as recorded on the graph paper, is

$$\frac{4\pi(10.5)^2}{\pi(4.5)^2/4} \times 3.3 \times 10^{-4} = 2.9 \times 10^{-2} \text{ erg}$$

(1) Further details of this research may be obtained from the Master's thesis of Frederick F. Morehead filed in the Library of the University of Wisconsin, June, 1951.

(2) F. Urbach, *Weiner Ber.*, **139**, 353 (1930).

(3) C. A. Boyd, *J. Chem. Phys.*, **17**, 1221 (1949).

For crystals which had a γ -ray exposure of exactly 5 hours, amounting to 30,000 roentgens, the area under the thermoluminescent curve was 2000 square inches per gram when converted to the highest sensitivity. The total light energy emitted is then $2000 \times 2.9 \times 10^{-2}$ erg or 58 ergs or 1.4×10^{-6} calorie. Assuming that the energy of the trapping level is about 10 electron volts above the highest ground level in lithium fluoride, as it is in sodium chloride, the energy of one 4400 Å. photon is 4.5×10^{-12} erg, the number of photons emitted per gram is 1.3×10^{13} , we find that the energy stored by the trapped electrons is 5×10^{-6} cal./g.

Lattice Displacements in Metamict Minerals.—Differential thermal analysis, long used for studying cooling and heating curves in metallurgy, has found extensive use recently in the analysis of clays. The ceramic material can be identified by means of heat effects at definite temperatures due to the melting or oxidation of some of the ingredients. An instrument manufactured by the Eberbach Company was modified for the present investigation. It consists of a metallic block 3 cm. in diameter which contains two cylindrical holes, one for the inert or deactivated (heated) material and the other for the material under investigation. A chromel-“P”-alumel thermocouple measures the difference in temperature between the two, and a second thermocouple measures the temperature of the metal block. A furnace with nichrome coils fits over the metal block and heats it by radiation while the energy input is kept constant by a voltage regulator. A sensitive galvanometer was substituted for the millivoltmeter, and the whole furnace and block was mounted in a gas-tight box so that oxygen could be removed by evacuation or by displacement with nitrogen. The return of the displaced atoms to their normal positions in the lattice at a definite temperature evolves heat, and the object of the experiment is to measure this heat. It is necessary then to eliminate all other sources of exothermic heat such as the oxidation of sulfides.

When there is no evolution or absorption of heat the differential thermocouple reads zero, but if there is a lattice transition, a fusion, or a chemical reaction in one of the two samples of material there will be a galvanometer deflection indicating the absorption of heat or evolution. If one plots this temperature difference against the temperature for a given rate of heating, a minimum in the curve indicates the temperature of heat absorption such as fusion, and a maximum indicates the evolution of heat.

A simple mathematical analysis¹ shows that the area under the curve in which temperature differences are plotted against temperature, is nearly proportional to the heat evolved by the active material. The area under such a curve within a definite temperature range is calibrated in terms of calories with materials of known heats of fusion as follows: tin at 232°, bismuth at 268°, lead at 327°, zinc at 419° and lead chloride at 485°.

A given weight of one of these powdered metals or salts was mixed with inert lithium fluoride powder in one of the holes in the heated block. The calibrations ranged from 2.19×10^{-3} calorie per cm. deflection (scale division) $\times$ degrees at 232° to 3.49×10^{-3} at 485°.

Two radioactive minerals were studied exhaustively by this method. One a polycrase mineral (a titanoniobate) designated as D-100 was a metamict mineral supplied by Dr. J. C. Rabbitt of the U. S. Geological Survey. The thermal analysis curve for this mineral is shown in the upper half of Fig. 1. The other mineral, shown in the lower half of Fig. 1, came from a radioactive inclusion in a quartz core of pegmatite collected in Ontario by Dr. Donald F. Saunders. It exhibited radial cracks with decreasingly intense smoky color with increasing distance from the radioactive inclusion. The metamict minerals have complex lattice structures containing rare-earth elements.

The metamict mineral shows an exothermic peak at 460° which was the same in air, in nitrogen and in a vacuum of 4 mm., thus showing that it does not involve air-oxidation. The fact that it involves a true change in the crystal lattice is proved by the fact that X-ray diffraction measurements of the mineral showed no patterns with the original mineral, but did show patterns corresponding to a definite crystal lattice after heating above 460°. This peak has an area equivalent to 2700 cm. degrees for a sample weighing 0.5 g. and the energy evolved is $2700 \times 3.5 \times 10^{-3}/0.5$ or 21 calories per gram.

Holland and Kulp⁴ have reported the evolution of heat on heating a metamict crystal.

Fig. 1.—Thermal analysis curves.

In the sample of radiation-damaged quartz there are two endothermic transitions or fusions clearly evident but the exothermic peak at about 440° in air disappears when the heating is carried out in nitrogen or in a vacuum. It is probably due to the oxidation of iron or sulfur, and is similar to the peak found by Rowland and Lewis⁵ in the thermal analysis of certain pyritic clays. There is no evidence for exothermic changes in the crystal lattice. It is highly important to exclude the possibility of chemical reactions, particularly air-oxidations, when looking for heat effects which are due to radioactive damage of the crystal lattice.

The present equipment is not sensitive to less than about 1 calorie per gram and all attempts failed to measure the heat evolved when an irradiated crystal of lithium fluoride was heated. One crystal was irradiated with the high voltage electron accelerator at Brookhaven National Laboratory through the courtesy of Dr. A. O. Allen. Although this crystal was nearly black in color it failed to give a measurable quantity of heat when tested in a manner similar to that used for the metamict mineral.

Two additional metamict minerals supplied by Dr. J. C. Rabbitt were run by Mr. Warren E. Thompson in this Laboratory. One (samaraskite) gave no evolution of heat; the other (eschybite-prionite) gave about 20 calories per gram.

Conclusions

The amount of energy stored as trapped electrons in lithium fluoride is very small— 5×10^{-6} calorie or 0.005% of the 30,000 roentgen exposure. This corresponds to 1.3×10^{13} photons of blue light per gram or 4×10^{14} photons per mole. Optical and density measurements of crystals exposed to γ -radiation for long periods of time lead to esti-

(4) H. D. Holland and J. L. Kulp, *Science*, **111**, 132 (1950)

(5) R. A. Rowland and D. R. Lewis, *American Mineralogist*, **36**, 80 (1951).

mates of a saturated value of about 10^{18} trapped electrons per mole. It is not clear why the stored energy capable of producing thermoluminescence is only about one ten-thousandth of the amount expected on the basis of F-center studies. It will be shown in a later communication that thermoluminescence in lithium fluoride does not reach saturation until about 100,000 roentgens and an exposure to γ -radiation much in excess of 32,500 roentgens would have given somewhat greater thermoluminescence, but not more than three times as much. The extremely low efficiency is comparable in magnitude to the efficiency of the production of X-rays by means of electron bombardment of a metal target.

It has been calculated¹ from the geometry of the cobalt source with 6000 roentgens per hour that 4.8×10^7 photons of γ -rays were absorbed per second by the lithium fluoride crystal 1 cm. square and 1 mm. thick. This is equivalent to 0.33×10^{13} photons absorbed per gram during the 5.00 hour exposure of 30,000 roentgens. Since 1.3×10^3 photons of blue thermoluminescent light were emitted, it is seen that 5 photons of thermoluminescent light are emitted for every photon of γ -radiation absorbed.

The experiments with metamict minerals show that the storage of energy from radioactivity, mostly from α -particles, can be very much greater. The mechanism of energy storage is quite different. Although the samples studied thus far give a maximum of 25 calories per gram, other samples of old minerals rich in uranium or thorium will be

studied to ascertain if still greater amounts of energy can be stored under certain conditions. The possible storage of radioactive energy in rocks is a matter of interest in geology.

This investigation was carried out as a cooperative research with the U. S. Atomic Energy Commission under contract number AT(11-1)-27.

REMARKS

Professor Daniels, in reply to a question by Professor Burton concerning the thickness of the lithium fluoride crystals which were used for the dosimeter tests, said: The crystals were 1 cm. square and 3 mm. thick. It is true that in very thin crystals a considerable amount of energy may be lost by the escape of electrons released by γ -rays. In these experiments, however, crystals three mm. in thickness were stacked up in a pile inside the cobalt γ -irradiator, and so the thin crystals were behaving essentially as thick crystals and any loss of electron energy from one crystal was offset by a similar addition of energy from the adjoining crystal.

Professor Daniels, in reply to a question concerning the effect of impurities, said: The presence of impurities in the crystal lattice is certainly a factor in the thermoluminescence glow curves. Sometimes, however, impure crystals give nearly the same glow curves as purer crystals. Unfortunately the thermoluminescence can be so much more sensitive than other physical or chemical tests that it is difficult to connect the thermoluminescent glow curve peaks with traces of specific impurities. Sometimes samples from the same crystal 2 cm. apart will vary by 50% in their thermoluminescent intensity, presumably due to different amounts of trace impurities.

The areas under the peaks are proportional to the number of electrons released from traps. If the peaks are narrow, the peak heights are nearly proportional to the areas. A rapid rate of heating produces sharp narrow peaks, a slow rate gives broad flat peaks but the areas are practically the same.

STORAGE OF ENERGY IN METAMICT
MINERALS

BY
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Reprinted from *American Mineralogist* 42:91-99 (1957)

STORAGE OF ENERGY IN METAMICT MINERALS*

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ABSTRACT

A number of radioactive minerals have been studied by means of differential thermal analysis. The amount of heat evolved in heating under nitrogen and the radioactivity of these minerals have been quantitatively determined.

Metamict minerals are capable of storing appreciable quantities of energy from radioactivity in the form of atomic displacements within the crystal. These minerals which were originally crystalline, have had their crystal structures partially destroyed by the radioactive disintegration of uranium, thorium and their radioactive decay products which are present in the mineral. The fast moving alpha particles and recoiling parent nuclei interact with the atoms present at the lattice sites, displacing them and causing the partial disordering of the crystal structure. Accompanying this rearrangement of the crystal lattice is the storage of energy together with marked changes in the physical and optical properties of the minerals.

If the disordered crystal is annealed by raising the temperature, the original crystal structure is reconstituted with the evolution of heat. Faessler, in making a calorimetric study of the mineral gadolinite, observed the evolution of heat amounting to 89.1 cal./gm. (2). Kerr and Holland (4) also noted the evolution of heat in performing thermal analysis experiments on davidite, fergusonite, priorite and other metamict minerals.

Morehead and Daniels (5), using differential thermal analysis, reported the evolution of heat amounting to 25 cal./gm. for one polycrase mineral. The experimental work described herein is an extension of this work, carried out with improved apparatus, in an attempt to find still larger quantities of stored energy.

DIFFERENTIAL THERMAL ANALYSIS

The theory underlying the use of thermal analysis to determine heats of reaction is discussed by many investigators (5, 9, 10, 13). Two samples are placed in adjacent holes within a metal sample block. One sample is thermally active, (i.e. exhibits an absorption or evolution of heat) the other is thermally inert. Both samples are then heated at a uniform rate. If heat is absorbed by the active sample, by fusion or a polymorphic transition, the temperature will fall below that of the inert material.

* More complete details of this investigation may be obtained from the Ph.D. thesis of Sheldon F. Kurath filed in the library of the University of Wisconsin, 1953.

Such temperature differences, measured with a differential thermocouple, appear as minima in the curve when plotted against the temperature. Similarly the evolution of heat from a chemical reaction or the release of energy stored in the displacement of crystal units will place the active sample at a temperature higher than the inert sample and give a maximum in the curve. Such maxima and minima are shown in the differential thermal analysis (DTA) curves of Fig. 1. The areas under the peaks are proportional to the heat evolved (10).

FIG. 1

EXPERIMENTAL

The apparatus used in this investigation is similar to an improved differential thermal analysis apparatus developed by Whitehead and Breger (11). A small stainless steel cylinder 1" by $\frac{7}{8}$ " in diameter contained two holes $\frac{1}{4}$ " in diameter which served as sample holders. One hole is the holder for the thermally active material and the other contains thermally inactive alumina. A thermocouple, placed in a small hole between the two sample holes, serves to measure the mean temperature of the sample holder. The temperature difference between the inert and active samples is measured by means of a chromel—"P"—alumel differential thermocouple. The out put potential from the differential thermocouple is fed in to a Liston Becker Model 14 D.C. amplifier. After amplification,

the potential is recorded on a Brown Model 142 two-pen continuous potentiometric recorder. The differential temperature and the temperature of the sample holder are recorded simultaneously. The sample holder is heated by means of a nichrome wound alundum tube furnace. Both sample holder and furnace were constructed to fit inside of a heavy steel cylinder. The cylinder was made so that it could be evacuated, purged with nitrogen and then operated under nitrogen at reduced pressures.

The most convenient manner in which to evaluate the area under the thermal analysis peaks, is to run heating curves on substances having known melting and inversion points. If the weight of the sample and the heat of fusion are known, the area under the curve can be evaluated in terms of cal./cm.² /gm. as described by other authors (1, 5, 12). The sample weights ranged from 0.1 to 0.01 g. The following materials whose heats of fusion are well known were used for calibration in the present work; Bi, Pb, anhydrous CdCl₂, PbI₂, Zn and Al.

All samples were heated from room temperature up to 700° C. under nitrogen at reduced pressure, (10 mm). Mineral samples which had been annealed for reference material under nitrogen at 700° C. to remove exothermic maxima or peaks in the *DTA* curves were also analyzed thermally. The differential thermal analysis curves of both active and annealed samples were then compared before determining the area under the peaks of the active samples.

Measurements of the radioactivity exhibited by the minerals were also carried out. The apparatus used in radioactivity measurement included a scaling unit model No. 162 made by Nuclear Instruments and Chemical Corporation, and was equipped with a radiation counter type D-33 operated at 1200 volts D. C. and having a mica window with a stopping power of 3.5 mg./cm.². Samples were placed 0.2 mm. from the mica window of the geiger tube. Checks were made with scintillation counters, sensitive only to alpha particles, to convert the readings into alpha ray activity. The alpha activity of these minerals, which are in radioactive equilibrium, was from $\frac{1}{4}$ to $\frac{1}{6}$ of the total activity determined by geiger counting. The alpha activity was estimated by multiplying the geiger count values by the appropriate factor.

RESULTS

The results of thermal analysis experiments and radioactivity measurements are presented in Table 1. The temperatures at which *DTA* peaks were observed are reported along with the heat evolved or absorbed. The radioactivity is reported in terms of alpha counts/min./cm.² emitted from the surface of the sample. Typical differential thermal analysis curves are shown in Fig. 1 for several samples of ellsworthite.

TABLE 1. RADIOACTIVITY AND STORED ENERGY IN METAMICT MINERALS

Sample	Peak temperature °C.	Heat evolved cal./gm.	Radioactivity α counts/min./cm ²
<i>Ellsworthite</i>			
A ^a	none	none	2,170
B ^b	flat	18.6	2,220
	112-517° C.		
C	197	1.8	2,200
	302	5.5	
	405	13.9	
	608	43.1	
		Total	64.3
D ^b	215	5.4	2,280
	395	4.0	
	615	28.3	
		Total	37.7
<i>Fergusonite</i>			
A ^c	680	49.4	1,080
	543	7.8	
		Total	57.2
B ^{d,e}	210-417°	7.2	900
	440	15.2	
		Total	22.4
C ^e	440	4.6	770
D ^{d,e}	none	none	700
E ^f	633	64.9	800
	360	2.2 ^g	
	183	1.9 ^g	
		Total	64.9
F ^g	680	36.6	150
	619	27.3	
	347	1.0 ^f	
	176	1.8 ^f	
		Total	63.9

^a Samples from MacDonald Mine, Bancroft, Ontario, collected by Dr. D. F. Saunders.

^b Examined by x-ray and found to yield no x-ray diffraction pattern.

^c Sample from Dr. J. C. Rabbitt of the U. S. Geological Survey.

^d Examined by x-ray and found to yield no x-ray diffraction pattern.

^e From J. J. Goll Mine, Madawaska, Ontario.

^f Heat was absorbed instead of evolved.

^g From Baringer Hill, Texas, collected in 1902 by Marshall Hanks.

TABLE 1—(continued)

Sample	Peak temperature °C.	Heat evolved cal./gm.	Radioactivity α counts/min./cm. ²
<i>Sammarskite</i>			
A ^c	640	3.2 ^t	1,000
	510	5.2	
	200	9.4	
		—	
B ^c	650	Total 14.6	1,450
		44.2	
<i>Euxenite</i> ^a			
	610	32.8	1,900
	395	15.4	
	305	0.9 ^t	
	135	6.0 ^t	
		—	
		Total 48.2	
<i>Exchynite-priorite</i> ^c	515	46.3	870

Ellsworthite: Experimental data on four samples of ellsworthite ($\text{CaO} \cdot \text{Nb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$) are given in Table 1. Typical *DTA* curves for samples *B* and *D* are shown in Fig. 1. They indicate evolution of heat at several different temperatures. Although the samples were obtained from the same locality and had similar amounts of radioactivity, they failed to yield the same peak structure in the heating curve. Surprisingly, sample *A* yielded no peak structure even though highly radioactive. The failure of this sample to evolve heat is probably due to the fact that the sample was not heated to a high enough temperature. Other investigators have noted exothermic peaks as high as 980° C. (4), but it was not possible with the present equipment to go above 700° C. In the case of sample *C* the differential thermal analysis yielded four distinct peaks.

All of these samples were imbedded in salmon colored calcite which was found to exhibit a high degree of thermoluminescence. Thermoluminescence glow curves labelled *TL* are presented in Fig. 1 for the calcite adjacent to the ellsworthite for samples *B* and *D* as obtained with a photomultiplier tube.

Fergusonite: Sample *A* was kindly given to us by Dr. J. C. Rabbitt of the U. S. Geological Survey. Three samples, *B*, *C* and *D*, were obtained from the J. J. Goll Mine at Madawaska, Ontario. Samples *E* and *F* were given to us by Mr. Marshall Hanks from a collection which he had made in a pegmatite cerium mine in 1902 at the Baringer Hill of Texas.

The results are given in Table 1. As in the case of ellsworthite, samples *B*, *C* and *D* from the same location yielded different thermal analysis peaks although they all had about the same radioactivity. Sample *D* showed no evolution of heat even though it was highly radioactive and metamict in character as shown by the absence of x -ray diffraction patterns. Presumably this sample would have yielded an exothermic heat of reaction at temperatures above 700° C. (2). Samples *E* and *F* gave small endothermic peaks which may be due to dehydration.

Samaraskite, Euxenite-Polycrase, Eschynite-Priorite: A limited number of samples of other minerals were also found to evolve heat when their temperatures were raised. Two samples *A* and *B* of samarskite were kindly given to us by Dr. J. C. Rabbitt of the U. S. Geological Survey. The euxenite sample came from the MacDonald Mine at Bancroft, Ontario. The eschynite-priorite sample was given by Dr. J. C. Rabbitt. The results are presented in Table 1. All of these minerals were highly radioactive and evolved large amounts of heat during differential thermal analysis. As in the case of fergusonite, endothermic peaks may be traced to the evolution of water of hydration.

Minerals Indicating No Energy Storage

Two samples of allanite were found to have no stored heat releasable below 700° , even though they had radioactivity counts of 103 and 81 counts/min./cm.² respectively. Two samples of cyrtolite yielded radioactive counts of 525 counts/min./cm.² and gadolinite and zircon had counts of approximately 50 counts/min./cm.². These minerals are found in the metamict state and probably have energy peaks well above 700° C. (4, 6).

Several samples of purple fluorite showed no stored energy although nearly black in color. Uraninite (UO_2) and xenotime similarly exhibited no stored energy. All these minerals had high alpha ray activity. These results support the generalization that highly ionic materials are not found in the metamict state.

DISCUSSION

The majority of the minerals exhibiting energy storage showed complex peak structures in the differential thermal analysis curves. The fact that all of these experiments were carried out in nitrogen, after previous evacuation, precludes air oxidation as a factor in these exothermic peaks. The appearance of a multiple peak structure can be compared with the mineral thorium silicate in which the appearance of several phases was noted (6).

The low-temperature peaks are probably associated with the produc-

tion of crystalline components of the metamict mineral while the other components remain in their amorphous state. Similarly, the peaks which appear at the higher temperature correspond to the conversion of the other materials to their crystalline form or to the reaction of crystalline components with the surrounding isotropic medium to form an entirely crystalline medium.

In some instances, no energy evolution was observed even though the mineral was highly radioactive. There are a number of explanations for this lack of heat evolution. In the case of zircon, gadolinite, and cyrtolite the energy evolution, in all probability, does not take place in the temperature range from room temperature to 700° C. It is known, for example, that gadolinite evolves energy in the neighborhood of 800° C. (4). This limitation to low temperatures probably accounts for the fact that one fergusonite sample which was known to be metamict, failed to evolve heat in these experiments. Other minerals may have been geologically too young to have sufficient radiation damage to detect and in other cases in which heat was not evolved the radioactivity may have been too low to cause appreciable structural damage (e.g. gadolinite, 50 α counts/min./cm²).

The data presented in previous sections may be used to estimate the time necessary for a mineral to become metamict. Making the qualified assumption that all the energy from radioactive decay is spent in disrupting the crystal structure, Pabst (6) estimated that it would take a sample of gadolinite (Ytterby), at least 110,000 years to become metamict.

An alternate approach to estimating the time of metamictization is given in the following paragraph. A sample of powdered fergusonite in a deep layer in a 5.3 cm.² dish gave 3,580 alpha counts per minute. Assuming that the alpha particles have an energy of 5.0 mev with a range of 3.5 cm. in air, that the "atomic number" of fergusonite is 70, that the density is 5.7 g. per cc. and that the "atomic number" and density of air are 7.2 and 1.23×10^{-3} respectively, the range of the alpha particles in fergusonite is given by the relation

$$\text{range} = \frac{3.5 \times 1.23 \times 10^{-3}}{7.2} \left(\frac{70}{7.2} \right)^{1/2} = 22.6 \times 10^{-3} \text{ cm.}$$

It can be shown that 25 per cent of the alpha particles within 2.26×10^{-3} cm. of the sample surface may escape to be counted (3). If all the alpha particles that escape the surface of the sample are counted, the alpha particles that are emitted per year per gram of sample may be estimated at

$$\text{alphas/year/gm.} = \frac{3.580 \times 60 \times 24 \times 365}{0.25 \times 2.26 \times 10^{-3} \times 5.3 \times 5.32} = 1.10 \times 10^{11}.$$

A 5 mev alpha particle will give about 10,000 electron-volts of energy in collisions and the recoil atom will transfer about 60,000 electron volts as collision energy making a total of 70,000 ev. (8). If all of the collision energy of the alpha particle and the recoil atom are stored, then every alpha count should represent an energy storage of about 70,000 ev. The rate of energy storage in the fergusonite sample is, therefore,

$$1.10 \times 10^{11} \times 7 \times 10^4 \times \frac{(1.6 \times 10^{-12})}{(4.18 \times 10^7)} = 2.95 \times 10^{-4} \text{ cal./gm./year}$$

where $1.6 \times 10^{-12} / 4.18 \times 10^7$ is a factor to change electron volts per alpha particle into calories. Since the heat evolved upon thermal analysis was 57.2 cal./gram, a minimum time for this highly radioactive mineral to become metamict may be estimated at

$$\frac{57.2}{2.95 \times 10^{-4}} = 198,000 \text{ years.}$$

This estimate is to be regarded as a minimum value because only part of the collision energy from the disintegration process will appear as stored energy, much of it being dissipated immediately as heat. Many metamict minerals have a considerably lower content of radioactive elements and would require a much longer time than this to become metamict. Moreover, the efficiency of energy storage decreases as the mineral becomes more metamict and the crystal structure becomes more disordered.

According to other views (7, 8), a 5 mev alpha particle and its recoil atom might produce less than 890 interstitial atoms and if each interstitial atom involves the storage of approximately 10 ev, there would be an energy storage of 8,900 ev per alpha particle. This value is considerably less than the 70,000 ev used in the preceding calculation and would lead to a much longer time requirement for metamictization.

The fact that many of the highly radioactive minerals, which have reasonably simple crystal structures, do not store any energy in the crystal structures suggests that there is something about the complicated crystal lattices of the metamict minerals which holds a dislocated ion or atom of the lattice in its abnormal position so that the disorder will not be annealed out at earth temperature.

ACKNOWLEDGMENT

The author is glad to acknowledge the help of Professor Farrington Daniels under whose direction this research was carried out. He is indebted to the Atomic Energy Commission for financial support of the project which provided him with a research assistantship. He wishes to

also thank Dr. Donald F. Saunders, and Dr. John C. Rabbitt who provided some of the metamict minerals.

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Manuscript received June 2, 1956.

[Reprinted from the Journal of Physical Chemistry, 61, 917 (1957).]

Differential Thermal Analysis of Inorganic Hydrates

By Hans J. Borchardt and Farrington Daniels

DIFFERENTIAL THERMAL ANALYSIS OF INORGANIC HYDRATES¹

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin

Received January 8, 1957

Differential thermographs are presented for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$. Two kinds of anomalous peaks were observed. One originates from the formation and subsequent vaporization of liquid water when a hydrate decomposes. This situation has sometimes led to the erroneous interpretation of data in the literature. The other type of anomalous peak is due to the sudden change in the thermal conductivity of a sample when liquid forms. X-Ray measurements were used to determine the origin of the peaks in the differential thermographs. The X-ray data are given for the compound $\text{CuSO}_4 \cdot \text{CuO}$ and new lines are given for $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$.

Introduction

Differential thermal analysis (DTA) is a useful tool for studying the processes which occur in a material on heating. The difference between the temperature of a sample of powder and that of a standard powder is recorded as the two are heated simultaneously. Endothermic processes such as melting or dehydration are shown by minima or "peaks" in the curve in which temperature differences are plotted against the temperature. Certain conditions, however, may influence the differential thermograph and lead to misinterpretations. Inorganic hydrates, for example, where non-equilibrium conditions exist, may give rise to extra peaks as will be described.

The copper sulfate-hydrate system was studied with DTA by Taylor and Klug.² These authors obtained a differential thermograph of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, for the temperature range 40 to 160°, essentially the same as that shown by the solid line in Fig. 1. The product formed at 120° after the double peak was identified as $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$. Since the transition from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ occurred in two stages, as evidenced by the appearance of a double peak, these authors concluded that an intermediate phase existed. Chemical analysis of the product after the first peak of the doublet gave a Cu to H_2O ratio of 1:4. Thus Taylor and Klug reported the existence of $\text{CuSO}_4 \cdot 4\text{H}_2\text{O}$. More recently, Ghosh³ reported evidence for this compound as a result of thermogravimetric studies. Its existence is mentioned in several authoritative texts.⁴⁻⁶

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as well as $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ were studied in this Laboratory with DTA. The differential thermograph of each of these com-

pounds, with the exception of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, showed one more peak than would be expected on the basis of their commonly known hydrates. An intensive effort to find corroboration for new phases using X-ray techniques led, without exception, to negative results. Further observation made it apparent that when these unexpected peaks occur the hydrate does not go directly to water vapor and the next lower hydrate, but that liquid water is formed. The subsequent vaporization of this water gives rise to the extra peak. The occurrence of this phenomenon is determined by the phase relationships of the hydrate and the procedure followed in differential thermal analysis.

Experimental

DTA Apparatus.—The DTA apparatus was a modification of that reported by Whitehead and Breger⁷ which makes use of radiation shields in place of conventional insulation so that a vacuum can be attained readily. Pt-Pt 10% Rh thermocouples are used in a ceramic sample holder. The sample well was 5/32 inch in diameter and 5/8 inch deep, having a capacity of 0.1 to 0.2 g. With such small samples, the heat effect is very small and hence considerable amplification is necessary. An amplification factor of the order of 2000 was used most frequently. The high amplification in turn required special techniques to assure exact centering of the differential thermocouple in the furnace. To achieve this, a device was incorporated which allowed the position of the furnace to be varied continuously by small increments. Details are given elsewhere.¹

The furnace is wound with nichrome wire. Different gases may be introduced by evacuating the furnace and bleeding in the desired gas.

The output from the differential thermocouple is amplified by a Liston-Becker model 14 d.c. breaker amplifier and is then recorded on a Brown recording potentiometer having a scale 0 to 20 millivolts. The rate of temperature rise was programmed on a Brown Potentiometer Pyrometer which also gave a record of the sample temperature. For most work a rate of temperature rise of 10° per minute was used. Commercial C.P. material was used without further purification. The samples for DTA were ground to 100-200 mesh and diluted with an equal weight of calcined alumina. Alumina also served as reference material. Some aspects of the procedure are discussed in greater detail in another paper.⁸

X-Ray Analysis.—All X-ray work was performed on a North American Philips Type 12045 diffraction instrument using a copper target and nickel filter. For identification purposes a Philips 52057A, 57.3 mm. diameter camera was used. For the patterns reported herein a Philips 52056, 114.59 mm. camera was employed. The patterns were checked on a Norelco diffractometer. For work at ele-

(1) Presented in part at the 129th meeting of the American Chemical Society, Dallas, Texas, April, 1956. Further details may be found in a Ph.D. thesis by Hans J. Borchardt, filed in the Library of the University of Wisconsin, June, 1956.

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(5) S. Bowden, "The Phase Rule and Phase Reactions," The Macmillan Co., New York, N. Y., 1938, p. 71.

(6) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford Press, 1950, p. 155. (Sidgwick erroneously cites Taylor and Klug² as a reference for $\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$. These authors make no mention of a dihydrate.)

(7) W. L. Whitehead and I. A. Breger, *Science*, **111**, 279 (1950).

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Fig. 1.—Differential thermograph of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

vated temperatures, two devices were used. One was a Norelco high-temperature camera. Samples for this camera were sealed in quartz capillaries, 0.3 mm. in diameter. The other device was a brass sample holder, 0.5 inch long, 1 inch wide and 1.5 inches deep, open at the top and wound around with nichrome wire so that it could be heated directly. It contained a thermocouple in its interior. This sample holder is mounted on the Norelco diffractometer, the diffractometer shield being removed to accommodate the sample holder. In this manner, diffraction lines of the sample were scanned while the sample was being heated.

Results and Discussion

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.—The differential thermograph of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is shown in Fig. 1. No peaks appeared between 275 and 725°. Above 750° the two-stage decomposition of CuSO_4 to CuO with $\text{CuSO}_4 \cdot \text{CuO}$ as an intermediate is observed. The identity of CuSO_4 and CuO was established by X-ray analysis and reference to standard patterns. A weight-time plot of CuSO_4 heated at 720° showed a sharp break at the composition $\text{CuSO}_4 \cdot \text{CuO}$. The X-ray data for the $\text{CuSO}_4 \cdot \text{CuO}$ compound are given in Table I.

TABLE I

X-RAY DATA FOR THE COMPOUND $\text{CuSO}_4 \cdot \text{CuO}$

Line no.	1	2	3	4	5 ^b	6	7	8
<i>d</i>	6.46	4.91	4.75	4.63	4.02	3.63	3.41	3.29
<i>I/I</i> ₀ ^a	78	6	25	14	4	100	15	8
—band—								
Line no.	9	10	11	12	13	14	15 ^b	16 ^b
<i>d</i>	3.15	2.83	2.78	2.67	2.62	2.54	2.47	2.38
<i>I/I</i> ₀ ^a	16	21	47	8	94	34	10	8
Line no.	17 ^b	18	19	20	21	22	23	24
<i>d</i>	2.32	2.25	2.14	2.02	1.97	1.86	1.82	1.76
<i>I/I</i> ₀ ^a	6	52	5	26	10	4	7	23
Line no.	25	26	27	28	29	30	31	32
<i>d</i>	1.70	1.67	1.64	1.62	1.61	1.60	1.58	1.55
<i>I/I</i> ₀ ^a	5	15	4	7	11	14	16	5
—band—								
Line no.	33	34	35	36	37	38	39	
<i>d</i>	1.53	1.51	1.48	1.47	1.45	1.41	1.39	
<i>I/I</i> ₀ ^a	5	4	9	15	7	8	17	
—band—								

^a The relative intensities (*I/I*₀) are the ratios of peak heights on the diffractometer trace. The designated bands appeared as a broad line in the X-ray photograph but were resolved in the diffractometer trace. ^b These lines correspond to intense lines in the CuSO_4 or CuO X-ray pattern. They may be due to the presence of these materials as impurities.

The low temperature portion of the pattern lacked reproducibility in early experiments. The first two large peaks (solid line, Fig. 1) appeared on some days as a single peak as shown by the dotted line. The small initial peak, coming before the two solid-line peaks, appeared only when the doublet (solid line) was observed and then only at high heating rates ($> 15^\circ/\text{minute}$). This difference in behavior was traced to the variation in atmospheric humidity, the doublet occurring

only in periods of high relative humidity. The observation was verified by controlling the atmosphere in the furnace. With an initially dry atmosphere, a single peak always occurred. With a furnace atmosphere initially saturated with water vapor, the doublet always appeared.

In order to determine the origin of the extra peak, samples of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were partially dehydrated and X-ray diffraction photographs taken. All lines could be assigned to the lines reported in the literature for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$. Since the extra peak occurred only at higher vapor pressures, a procedure was followed to give high pressures of water vapor. An intimate mixture containing approximately 55 mole % $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 45 mole % $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ was sealed in a quartz capillary. On the basis of the size of the capillary and the amount of sample taken, no significant quantity of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dissociated, when the partial pressure of water vapor in the capillary reached 1 atmosphere. This capillary was maintained at 90° for several hours in a high temperature X-ray camera. No new lines appeared. It was further heated to approximately 95° where a blank photograph resulted. Examination of the capillary showed that liquid was present and only a little salt remained. By shifting the position of the capillary a feeble X-ray pattern of the remaining salt was obtained. The pattern corresponded to $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$.

In order to observe portions of the X-ray pattern continually while $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was heated, the previously described sample arrangement on the diffractometer was used. The sample temperature was followed as a function of time at a constant heating rate. Breaks in the time-temperature curve occurred at 92.5° , 102° and 115° . The line of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ having a Bragg *d* value of 3.70 was scanned during heating. No significant changes were observed until the sample had been heated at 92.5° for approximately one minute. At this point the sample shrank and was not available to the X-ray beam. The shrinking and visible wetting of the sample showed clearly that liquid water was forming. Even more convincing was the observation of water vapor steaming from the sample holder for the duration of the 102° break in the heating curve. Since the breaks in the heating curve correspond to the peaks in the differential thermograph, the doublet observed by Taylor and Klug³ and in this investigation is not due to a tetrahydrate, but simply to the processes

These findings are consistent with the classical vapor pressure-temperature diagram of the CuSO_4 -hydrate system (Fig. 2). On heating $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ above its dissociation temperature, trihydrate and water vapor form. This water vapor does not diffuse away from the sample at an appreciable rate. The resulting increase in the local partial pressure of water as the temperature is raised would be given by the dotted line if the system were in equilibrium. In DTA the temperature is probably somewhat higher than indicated since relatively large rates of temperature rise are

employed. When the partial pressure of water vapor becomes somewhat greater than 568 mm., the vapor pressure at the quadruple point (A),⁹ the remaining $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ becomes unstable with respect to the trihydrate and saturated solution. This transition gives rise to the first large peak in the differential thermograph (Fig. 1) and the first break in the heating curve. On further heating, the vapor pressure of the saturated solution increases until it reaches atmospheric pressure, at which point (B) water boils off and the second peak appears, these two peaks comprising the doublet. The next two peaks in Fig. 1 result from the transition of trihydrate to mono (130°), and monohydrate to anhydrous salt (250°), respectively, at a vapor pressure equal to atmospheric pressure.

The failure of a double peak (occasioned by the production of liquid water) to appear when the initial gas is dry, is attributed to the fact that the partial pressure of water vapor in the tube never gets as high as the vapor pressure of the saturated solution and all of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is dissociated before a pressure of 568 mm. is reached.

The other evidence for $\text{CuSO}_4 \cdot 4\text{H}_2\text{O}$ is Taylor and Klug's³ chemical analysis and Ghosh's⁴ thermogravimetric work. With regard to the former, one can only conclude that their sample may have consisted of a fortuitous mixture of $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ and adhering solution.

Ghosh relied quite heavily on sudden deflections of a simplified thermobalance. His method indicated the presence of $\text{CuSO}_4 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 4\frac{1}{3}\text{H}_2\text{O}$ as well as $\text{CuSO}_4 \cdot 4\text{H}_2\text{O}$, neither of which have been observed in any other studies.

Other Hydrates.—The occurrence of extra peaks in the differential thermal analysis of hydrates due to formation of saturated solution is not uncommon. Figure 3 shows the differential thermographs of five other hydrates. The processes giving rise to the peaks are summarized in Table II. Confirmatory X-ray analyses were performed to show when new phases were present and when they were not.

In the course of this work two distinct new lines were found in partially dehydrated $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$. These were traced to $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$, being the first two lines exhibited by this compound and occurring at Bragg d values of 5.64 and 4.55. They are the second and third most intense lines, having relative intensities of 79 and 90, respectively. The X-ray data are given in Table III. The lines are consistent with the structure of $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ reported by Jensen,¹⁰ corresponding to reflections from the 200 and 011 planes, respectively.

The necessary requirements for the appearance of a liquid phase in the differential thermal analysis of a hydrate are (1) that the hydrate system contains a quadruple point where hydrate, next lower hydrate, saturated solution and water vapor are in equilibrium; (2) that this quadruple point occurs at a water vapor pressure which is less than atmospheric pressure; (3) that the rate of dissociation of the hydrate be rapid (if the sample tem-

Fig. 2.—Vapor pressure-temperature diagram of the CuSO_4 -hydrate system. The areas 5, 3 and 1 represent the stable regions of the penta-, the tri- and the monohydrate.

Fig. 3.—Differential thermographs of several hydrated salts. The second peak in each of the top four thermographs is a "false" peak due to vaporization of water.

perature has attained a value greater than the boiling point of saturated solution before appreciable local vapor pressures are established, no liquid can form); and (4) the water vapor which is evolved must be confined to the immediate vicinity of the sample.

Conditions (3) and (4) require that an intermediate rate of temperature rise be employed if a liquid phase is to be observed. With very rapid heating rates the system is too far from equilibrium and condition (3) will not be met. Very low rates of temperature rise will allow time for the water vapor to diffuse away from the sample.

The temperatures and pressures at the quadruple point for the hydrates are summarized in Table IV. All samples comply with the requirement that the pressure at the quadruple point must be below atmospheric. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ is the only material studied where condensation failed to take place, as indicated by the absence of an extra peak in the DTA curve. The relatively small difference between the vapor pressure of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ at the quadruple point and atmospheric pressure requires close adherence to equilibrium conditions if the formation of liquid is to be observed. This condition, obviously, was not met.

(9) E. M. Collins and A. W. C. Menzies, *THIS JOURNAL*, **40**, 379 (1936).

(10) K. Jensen, *Danske Vidensk. Selsk. Mat. Fys. Medd.*, **20** (No. 5), 22 (1942).

TABLE II
PROCESSES WHICH GIVE RISE TO THE PEAKS IN FIG. 3

Hydrate	Peak No. and temp. ^a	Process
CoCl ₂ ·6H ₂ O	1 (49°)	CoCl ₂ ·6H ₂ O(s) → CoCl ₂ ·2H ₂ O(s) + 4H ₂ O(l)
	2 (99°) ^b	4H ₂ O(l) → 4H ₂ O(g)
	3 (137°)	CoCl ₂ ·2H ₂ O(s) → CoCl ₂ ·H ₂ O(s) + H ₂ O(g)
	4 (175°)	CoCl ₂ ·H ₂ O(s) → CoCl ₂ (s) + H ₂ O(g)
MnCl ₂ ·4H ₂ O	1 (55°)	MnCl ₂ ·4H ₂ O(s) → MnCl ₂ ·2H ₂ O(s) + 2H ₂ O(l)
	2 (102°) ^b	2H ₂ O(l) → 2H ₂ O(g)
	3 (135°)	MnCl ₂ ·2H ₂ O(s) → MnCl ₂ ·H ₂ O(s) + H ₂ O(g)
	4 (210°)	MnCl ₂ ·H ₂ O(s) → MnCl ₂ (s) + H ₂ O(g)
SrCl ₂ ·6H ₂ O	1 (66°)	SrCl ₂ ·6H ₂ O(s) → SrCl ₂ ·2H ₂ O(s) + 4H ₂ O(l)
	2 (122°) ^b	4H ₂ O(l) → 4H ₂ O(g)
	3 (132°)	SrCl ₂ ·2H ₂ O(s) → SrCl ₂ ·H ₂ O(s) + H ₂ O(g)
	4 (183°)	SrCl ₂ ·H ₂ O(s) → SrCl ₂ (s) + H ₂ O(g)
BaBr ₂ ·2H ₂ O	1 (110°)	BaBr ₂ ·2H ₂ O(s) → BaBr ₂ ·H ₂ O(s) + H ₂ O(l)
	2 (118°) ^b	H ₂ O(l) → H ₂ O(g)
	3 (209°)	BaBr ₂ ·H ₂ O(s) → BaBr ₂ (s) + H ₂ O(g)
BaCl ₂ ·2H ₂ O	1 (125°)	BaCl ₂ ·2H ₂ O(s) → BaCl ₂ ·H ₂ O(s) + H ₂ O(g)
	2 (200°)	BaCl ₂ ·H ₂ O(s) → BaCl ₂ (s) + H ₂ O(g)

^a These temperatures bear an uncertainty of about $\pm 5^\circ$. ^b Water boiling from saturated solution.

TABLE III
X-RAY DATA FOR SrCl₂·2H₂O

Line no.	1 ^a	2 ^a	3	4 ^b	5	6	7	8	9
<i>d</i>	5.64	4.55	3.98	3.28	3.20	2.88	2.80	2.71	2.66
<i>I/I</i> ₀	79	90	47		100	24	45	27	71
Line no.	10	11	12	13	14	15	16	17	18
<i>d</i>	2.65	2.61	2.54	2.48	2.44	2.27	2.26	2.19	2.14
<i>I/I</i> ₀	34	24	32	34	15	24	32	11	3
Line no.	19	20	21	22	23	24	25	26	
<i>d</i>	2.115	2.103	2.025	1.985	1.973	1.927	1.886	1.857	
<i>I/I</i> ₀	27	40	29	8	31	5	19	15	

^a These lines are not reported in the A.S.T.M. index. ^b Line 4 appears as a separate line in the photograph but did not resolve completely from line 5 in the Geiger counter diffractometer trace at a chart speed of 1/4°/minute using 1° slits. Hence, its relative intensity is not reported. It is a very weak line.

Fig. 4.—Differential thermograph of NaNO₃ showing a small peak at about 275° due to a second-order transition, and a large peak at 310° due to fusion. The solid line is obtained with a temperature rise of 15° per minute. The dotted exothermic peak appears when the temperature is raised at the rate of 30° per minute. It is due to increased thermal conductivity caused by fusion.

Small Initial Peaks.—A small initial endothermic peak is observed with CuSO₄·5H₂O as well as with

TABLE IV
TEMPERATURE AND PRESSURE AT QUADRUPLE POINT FOR HYDRATES

Hydrate	T° C.	P, mm.	Ref.
CoCl ₂ ·6H ₂ O	52.4	48.5	11
MnCl ₂ ·4H ₂ O	58.1	63.2	12
SrCl ₂ ·6H ₂ O	61.6	89.7	9
BaBr ₂ ·2H ₂ O	107.9	664	9
BaCl ₂ ·2H ₂ O	101.9	684	9

the other hydrates when high heating rates ($> 15^\circ/\text{min.}$) are used. A similar phenomenon is observed when fusion occurs except that the peak is in the exothermic direction as shown schematically by the dotted line in Fig. 4. These peaks are explained as follows: The formation of liquid in the sample holder is accompanied by a sudden change in the thermal conductivity of the material, inasmuch as it becomes a continuous medium, hence a much better heat transfer agent. This increased heat conductance causes a small surge of heat to the thermocouple junction as the thermal gradient in the sample diminishes. This gives rise to an exothermic peak. In the case of the hydrates, the occurrence of this exothermic peak, while an over-all endothermic reaction is taking place, makes it ap-

(11) "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, p. 361.

(12) A. von Benrath, *Z. anorg. allgem. Chem.*, **247**, 147 (1941).

pear as if two endothermic peaks are occurring.

This explanation is consistent with the observation that the small peak occurred in the pattern of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in Fig. 1 only when the doublet appeared, that is, only when liquid formed in the sample and only at high rates of temperature rise.¹³ Since the sample wells in this work are very small, thermal gradients are reduced to a minimum. In order to establish an appreciable gradient high heat-

(13) Taylor and Klug² observed several small peaks prior to dehydration which they attributed to second-order transitions in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. These were observed at sensitivities much higher than those used in the present work and are apparently not the same as the anomalous peak described above.

ing rates are necessary.

The results of this investigation emphasize precautions which are necessary in the interpretations of some differential thermal analysis measurements.

Acknowledgments.—The X-ray work was conducted with the helpful advice of Professor Sturges Bailey of the Department of Geology, University of Wisconsin.

The authors are grateful for the support of this research by the Atomic Energy Commission Contract AT(11-1)-178 and by a grant for fundamental research by the E. I. du Pont de Nemours Company, Inc.

Thermoluminescence and Coloration of Lithium Fluoride
Produced by Alpha Particles, Electrons, Gamma Rays and
Neutrons

By

Frederick F. Morehead and Farrington Daniels

Journal of Chemical Physics 25, December (1957)

FACTORS INFLUENCING PRECIPITATION OF CALCIUM CARBONATE

BY

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Reprinted for private circulation from
THE BULLETIN OF THE AMERICAN ASSOCIATION OF PETROLEUM GEOLOGISTS
Vol. 40, No. 1, January, 1956

FACTORS INFLUENCING PRECIPITATION OF CALCIUM CARBONATE¹

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ABSTRACT

Aragonite, calcite, and vaterite have been precipitated under conditions of controlled temperature, pH, and impurity ion concentration. Results from X-ray diffraction studies, spectrographic analyses, microscopic examination, and thermoluminescence studies have provided information regarding the factors affecting the formation of the various crystalline forms. The immediate factor influencing the form of calcium carbonate precipitates is the impurity content of the crystals. The impurity content has been found to be greatly affected by the pH, temperature, impurity ion concentration in the original solution, the solubility of the polymorphs, crystal size, and the time the precipitate remains in contact with the solution. All of these factors are closely interrelated. The factors influencing the artificial precipitation of calcium carbonate are believed to be applicable to studies concerning the origin of carbonate sediments.

INTRODUCTION

Although calcium carbonate is one of the most commonly occurring geologic materials, its chemistry and mineralogy are so complex that many of their details are still not clearly understood. A series of X-ray diffraction studies, spectrographic analyses, microscopic examinations, and thermoluminescence studies has provided information regarding the extent to which conditions of controlled temperature, pH, and impurity ion concentration affect the artificial precipitation of aragonite, calcite, and vaterite. This direct approach through the chemistry of formation of the polymorphs of calcium carbonate has seemed more appropriate to the problem than some of the early attempts to study the mineralogical and chemical composition of samples in an effort to infer their mode of origin. The findings reported here are not in conflict with most of the results of previous studies by other workers; however, serious question is raised as to the interpretation of some of the earlier work. Techniques employed in this study have differed somewhat from those of other workers, and although they have been essentially of a laboratory nature, their prime concern has been with the interpretation of geologic phenomena.

The writers recognize that the factors involved in the precipitation of calcium carbonate, both in nature and artificially, are not direct and simple but, rather, indirect and extremely complex. Many workers have attempted to determine the factors controlling the formation of the various crystalline forms of calcium

¹ Manuscript received, May 31, 1955.

² Department of Chemistry, University of Wisconsin. The writers thank Professor Farrington Daniels, Department of Chemistry, University of Wisconsin, whose advice and insight have prevented them from becoming lost in the complex chemical aspects of this problem. Their appreciation is also extended to Sturges W. Bailey, Department of Geology, University of Wisconsin, who provided the many X-ray diffraction determinations, and to Oiva Joensuu, Department of Geology, University of Chicago, who performed the spectrographic analyses. The writers are indebted to the Atomic Energy Commission, Research Division, for its support of a research program of which this work is a part.

carbonate. Notable is the early work of Credner (1870). Johnson, Merwin, and Williamson (1916) made a rather complete investigation of the chemistry of formation of calcium carbonate. A comprehensive summary of much of the early work was compiled by Mellor (1923). More recently, studies of artificial calcium carbonate have been made by deKeyser and Dugeldre (1950).

Studies of factors relative to naturally occurring calcium carbonate have been numerous in recent years. Among these, the occurrence of strontium in sediments and fossils has been considered by Odum (1950), Kulp, Turekian, and Boyd (1952), Turekian (1955), and Imbrie (1955). Chave (1954) has reported on the biogeochemistry of magnesium. The influence of temperature on the formation of calcium carbonate has been noted by Lowenstam (1954). Conditions controlling the deposition of calcite and aragonite in caves have been studied by Murray (1954).

In addition, it is particularly noteworthy that much information concerning the chemistry of formation of carbonates can be obtained in many recent textbooks on inorganic chemistry.

EXPERIMENTAL PROCEDURES

The laboratory experiments were carried out with the use of ordinary chemical apparatus. Basically, it consists (Fig. 1) of a 2,000-milliliter separatory funnel equipped with a stirring device. This vessel was enclosed in a thermostatically controlled water bath in order that its temperature might be regulated. Solutions inside the separatory funnel were kept under a nitrogen atmosphere, at ordinary pressure, to exclude carbon dioxide present in the air of the laboratory from the vessel. The calcium carbonate precipitates were produced either through the controlled addition of dilute sodium carbonate from a burette to a dilute solution of calcium nitrate in the vessel or through the simultaneous addition of sodium carbonate and calcium nitrate to water in the vessel. In each case the solution in the precipitating vessel was being rapidly stirred.

In the common procedure for forming the precipitates, 1,000 ml. of approximately 0.1 molar calcium nitrate solution, containing either its inherent impurities or specific amounts of added impurities, were placed in the separatory funnel. The temperature of this solution was held constant and the contents of the vessel agitated. In addition, the solution was kept under a nitrogen atmosphere. The pH of the solution was measured, then 20 ml. of 1 molar sodium carbonate were slowly added from a burette to the stirred solution at a rate of about 2 ml. per minute. Agitation of the solution and the resulting precipitate was continued for 24 hours, at the end of which time a pH measurement was made. The solution and the precipitate were then removed from the separatory funnel and filtered in order to recover the precipitate. The precipitate was washed and allowed to dry in air. The filtrate was returned to the precipitating vessel and 20 ml. of sodium carbonate were added. The precipitating procedure, as outlined, was repeated. The addition of sodium carbonate in 20 ml. increments was carried out

until all of the calcium carbonate had been precipitated. The concentration and quantity of the reagents being used in each case resulted in the formation of about 6 precipitates.

Variations of the procedure consisted primarily in changes of temperature, and changes in the impurity content of the calcium nitrate. Other modifications of this experimental technique consisted in the slow simultaneous addition of

FIG. 1.—Apparatus for precipitating calcium carbonate.

both sodium carbonate and calcium nitrate solutions to either sea water or distilled water that was being agitated in the separatory funnel.

The solutions of calcium nitrate used in all of these experiments were made either from analytical reagents, or from limestone or crystals of calcium carbonate dissolved in nitric acid. The precipitating agent, sodium carbonate, was made from analytical reagent material. All of these solutions contained their inherent impurities (Tables I and II).

The crystalline nature of the precipitates obtained from these experiments was identified by the use of X-ray diffraction studies and through petrographic microscope examination. The impurity content of the calcium carbonate precipi-

TABLE I. IMPURITY CONTENT OF Na_2CO_3 AND $\text{Ca}(\text{NO}_3)_2$ ANALYTICAL REAGENTS

	<i>Spectrographic Analysis (ppm)</i>				
	Fe_2O_3	MnO	SrO	BaO	MgO
Na_2CO_3	20	3	X	X	100
$\text{Ca}(\text{NO}_3)_2$	20	5	(20)	(4)	100

tates was determined by spectrographic analysis. In addition, thermoluminescence studies were conducted on many of the precipitates.

RESULTS AND INTERPRETATIONS

Impurity effect.—If carbonate ions are continuously added to a solution containing several metallic ions, the pH of the solution will rise and the metallic ions will precipitate in the order in which the solubility products of their carbonates are exceeded. Hydroxyl ions resulting from hydrolysis will tend to complicate the picture if the hydroxides of any of the metallic ions are less soluble than their carbonates. In the system studied the writers were able to determine the sequence of precipitation for each of the geologically common impurity ions. Iron is the first to begin to precipitate, followed by manganese, strontium, barium, and finally magnesium. In an environment in which calcium ions predominate to a very high degree over other metallic ions, those present in low concentration may be considered impurities. If enough carbonate ions are added to such a solution, the calcium ions together with the impurities will be precipitated as insoluble carbonates or hydroxides. The impurities will be taken out of solution either through

TABLE II. SPECTROGRAPHIC ANALYSES OF SAMPLES OF NATURALLY OCCURRING CALCIUM CARBONATE

<i>Sample</i>	<i>Location</i>	<i>Spectrographic Analysis (ppm)</i>				
		Fe_2O_3	MnO	SrO	BaO	MgO
SCB-1 Aragonite	Pseudo-oölites from Bahama Banks	90	2	12,500 (1.25%)	7	1,300
AR-S Aragonite	Cianciana, Sicily	20	60	1,400	4	100
AR-U Aragonite	Tooele County, Utah	20	6	600	8	15,000 (1.5%)
ST-A Aragonite	Stalactite from cave near Cuba, Missouri	30	3	250	105	300
ST-C Calcite	Stalactite from cave near Cuba, Missouri	30	3	100	100	100,000 (10.0%)
SL-1 Aragonite	Oölites from Great Salt Lake, Utah	1,100	25	5,000	140	12,000 (1.2%)

their direct precipitation in the form of crystals of their own carbonates or hydroxides, or through their inclusion as impurity ions in the crystal structure of calcium carbonate.

About 80 precipitates of calcium carbonate were prepared by the techniques outlined in the foregoing section using solutions of calcium nitrate that contained only their inherent impurities. The results of some of these experiments are summarized in Table III. In addition, a solution of calcium nitrate was spiked with ferric iron, manganese, strontium, barium, and magnesium nitrates such that it was approximately 0.001 molar with respect to each of these ions. Precipi-

TABLE III. SELECTED SAMPLES OF ARTIFICIALLY PRECIPITATED CALCIUM CARBONATE

Sample	Crystalline Structure (Per Cent)	pH	Temperature °C.	Spectrographic Analysis (ppm)				
				Fe ₂ O ₃	MnO	SrO	BaO	MgO
2B	Calcite 100	6.7		20	450	300	5	4,200
10B	Calcite 100	7.1	25	20	9	220	9	7,000
15B	Calcite 20 aragonite 80	8.1		20	3	800	60	43,000
B1	Calcite 90 vaterite 10	7.7	10	35	25	7	4	80
B6	Calcite 10 vaterite 90	10.1		25	3	160	40	700
C1	Calcite 100	7.5		20	34	5	4	50
C6	Calcite 90 aragonite 10	8.3	72	25	3	65	15	160
D1	Calcite 95 aragonite 5	7.5		25	22	5	4	50
D3	Calcite 75 aragonite 25	7.6		30	3	8	4	50
D5	Calcite 50 aragonite 50	8.0	52	45	3	60	30	90
D6	Calcite 5 aragonite 95	10.3		30	25	600	420	200
AR-15	Calcite 100	7.5	15	35	170	5	5	100
ARS-25-1	Calcite 80 vaterite 20	6.5		30	3	700	60	50
ARS-25-2	Calcite 90 aragonite 10	8.7	25	30	3	17,000	30	50
ARS-13-A	Calcite 10 vaterite 90	8.4	13	40	4	600	12	90
ARS-44-C	Calcite 40 aragonite 60	8.7	44	30	3	6,500	12	90
ARU-44-F	Calcite 10 vaterite 10 aragonite 80	9.7	44	30	12	1,100	12	2,500

Selected samples of artificially precipitated calcium carbonate, indicating the crystalline structure, spectrographic analyses, pH, and temperature at time of formation. Varying concentrations of impurities were present in the solution from which each group of precipitates was precipitated.

tation was carried out at a temperature of 44°C . in six stages by the methods already described. X-ray investigation and spectrographic analysis of each precipitate were made and the results are listed in Table IV.

This experiment clearly indicated the sequence in which the impurities were precipitated as the pH rose. Almost all of the iron was removed in the first precipitate formed at pH 6.9. Only about half of the manganese was brought down with the first precipitate. Barium and strontium were present in quantities less than 0.5 per cent and only a trace of magnesium appeared in the first precipitate. The second precipitate, formed at pH 7.1, contained only a trace of iron. The

TABLE IV. ARTIFICIALLY PREPARED CALCIUM CARBONATE

Sample	Spectrographic Analysis (Per Cent)					
	pH	Fe_2O_3	MnO	SrO	BaO	MgO
E-1	6.9	4.60	3.60	0.25	0.35	0.01
E-2	7.1	0.02	1.45	0.30	0.50	0.015
E-3	7.4	0.008	0.47	0.35	0.50	0.022
E-4	8.1	0.006	0.08	0.42	0.60	0.06
E-5	8.6	0.005	0.004	0.55	0.50	0.12
E-6	10.9	0.005	0.0003	2.50	2.00	1.15

X-ray Investigation

Results indicate that all samples are calcite. In addition, E-6 has a small amount of vaterite. There is a slight shift of d-spacings in some of the samples.

E-1	decreased $d = 3.029 \text{ \AA}$	(could be due to substitution of smaller cation for calcium)
E-2	normal $d = 3.04 \text{ \AA}$	
E-3		
E-4	increased $d = 3.054 \text{ \AA}$	(could be due to substitution of larger cation for calcium)
E-5		
E-6		

Samples E-1 and E-6 had a higher background than the other samples. This may be due to amorphous material or a distortion of the lattice due to substitution. In the case of E-1, fluorescence from iron may also contribute.

manganese content was less than half of that in the first precipitate. Barium and strontium remained about the same. The third precipitate, formed at pH 7.4, contained no significant iron and approximately 0.5 per cent of manganese, barium, and strontium. By the time pH 8.1 had been attained in the formation of the fourth precipitate only 0.08 per cent of manganese was present in the sample. Barium and strontium had increased slightly, but in general the fourth precipitate was the purest of the series.

In the fifth precipitate, formed at pH 8.6, strontium showed a slight increase, but barium continued to precipitate at nearly the same rate as before. Magnesium was just beginning to appear in quantities large enough to suggest that it was actually coming out of solution. The sixth and final precipitate, formed at pH 10.9, contained 2.5 per cent strontium and 2 per cent barium. The magnesium content had risen to 1.2 per cent.

The sequence of precipitation for the five impurity ions studied was exactly that which would be expected from the relationships of the solubility products of the compounds under investigation. Nevertheless, the experimental results

deviate considerably from the theoretical results computed from solubility product data as outlined in Table V.

Solubility product computations indicate that under the conditions of this experiment the iron could be expected to have been precipitated by the time pH 4 had been attained. Furthermore, the iron would have been precipitated as the hydroxide and not as the carbonate. The iron would not have been effective in influencing the crystal form of the calcium carbonate since it would have been almost wholly removed from solution before the calcium carbonate began to

TABLE V. THEORETICAL SOLUBILITY VARIATIONS

<i>Compound</i>	<i>Moles Per Liter pH 6</i>	<i>Moles Per Liter pH 8</i>
Fe(OH) ₃ Fe ₂ (CO ₃) ₃	4×10^{-14} *	4×10^{-20} *
Mn(OH) ₂ MnCO ₃	* 1.9×10^{-4}	7.1×10^{-3} 1.9×10^{-6}
Sr(OH) ₂ SrCO ₃	* 2×10^{-3}	* 2×10^{-6}
Ba(OH) ₂ BaCO ₃	* 1.1×10^{-2}	* 1.1×10^{-4}
Mg(OH) ₂ MgCO ₃	* *	* (**) .2

Theoretical solubility variations in hydroxides and carbonates for Fe⁺⁺⁺, Mn⁺⁺, Sr⁺⁺, Ba⁺⁺, and Mg⁺⁺. Calculated from solubility product data and expressed in moles per liter.

* Indicates that calculated value is in excess of one mole per liter.

(**) At pH 10 the calculated solubilities indicate that Mg(OH)₂ is soluble to 5.5×10^{-4} M/l while MgCO₃ is soluble to 3×10^{-8} M/l.

precipitate. Some colloidal particles of iron hydroxide were probably in suspension at the time of formation of the calcium carbonate precipitates, but it is difficult to evaluate their influence on the type of structure which would form.

It is apparent from the theoretical calculations that the manganese did precipitate as the carbonate and could have influenced the crystal form of the calcium carbonate through direct coprecipitation. Under these conditions the manganese acted either as an impurity incorporated directly into the calcium carbonate crystal structure or as a seed crystal of manganese carbonate around which the calcium carbonate lattice was built. In either case, precipitation of calcite rather than aragonite was favored. The ionic radius of manganese is smaller than that of calcium and tends to favor the more compact ionic arrangement of the calcite unit cell. Manganese carbonate (rhodochrosite) has a hexagonal crystal form, and if small crystals of this compound serve as the nuclei of the calcium carbonate being precipitated, the hexagonal calcite lattice will be favored over the orthorhombic aragonite lattice.

Strontium and barium undoubtedly act together and their effects are clearly

similar. Both tend to come out of solution at a pH higher than that at which the main body of the calcium carbonate is precipitated. Examination of the experimental results indicates that their actual concentration in the precipitate was almost 0.5 per cent and does not vary greatly from pH 6.9 to pH 8.6. Not until the final precipitate, formed at pH 10.9, was there a significant increase. The fact that both barium and strontium carbonates are fairly soluble at pH 6.9 suggests that a mechanism other than the solubility of their individual carbonates is affecting their removal from solution. The consistently high content of these impurities in the precipitates formed at relatively low pH strongly suggests coprecipitation by direct lattice inclusion. Both barium and strontium have ionic radii which are larger than that of calcium and thus they tend to favor the more open ionic arrangement of the unit cell of aragonite. Also, both of their carbonates, witherite and strontianite, have the orthorhombic crystal form of aragonite.

Magnesium precipitates only in the higher pH ranges and in this particular set of experiments the pH was not raised to a level which would be necessary to force most of it out of solution. Solubility product data make it clear that under the conditions of this experiment, magnesium hydroxide and not the carbonate would be obtained. The effect of the presence of small particles of magnesium hydroxide upon the formation of the calcium carbonate lattice can not be readily evaluated.

Temperature effect.—Temperature has long been considered to be one of the prime factors affecting the calcite-aragonite ratio in recent sediments and in the shells of calcium carbonate secreting organisms. In order to test its effects upon artificial precipitates, four sequence precipitations were run at varying temperatures. Each of these precipitations was carried out with the same reagents in the same concentrations. These reagents contained only their inherent impurities (Table I). Every effort was made to maintain identical conditions except for the temperature variation.

The first group consisted of six precipitates formed at 10°C. All of the precipitates were mixtures of calcite and vaterite. No aragonite was present in any of them. The vaterite showed a general tendency to increase with rising pH. The second group of precipitates was formed at 23°C. All were calcite. No trace of aragonite or vaterite was found in any of the precipitates either by X-ray diffraction or microscopic examination.

The third group of six precipitates was formed at 52°C., and all of the precipitates were found to be mixtures of aragonite and calcite. The percentage of aragonite in each precipitate is indicated in Figure 2. The fourth group, formed at 72°C., showed only calcite present in all but the final precipitate, which contained a trace of aragonite. As in all of the experiments, the precipitates were allowed to remain in the precipitation-vessel for 24 hours, and each was held at a constant temperature during this time.

Viewed entirely by themselves, the results of these experiments provide a

falsely simple picture of the effects of temperature upon the crystal form of the precipitates. In subsequent experiments, changes in concentration and purity content of the reactants permitted large quantities of aragonite to be precipitated under conditions of high pH at a temperature of 20°C. In several experiments involving precipitation in the presence of sea water, it was possible to obtain aragonite in the first precipitate formed at pH 7.2 at 20°C.

FIG. 2.—Percentage of aragonite in precipitates formed at 52°C.

Rate processes.—In view of these conflicting data it seems that the influence of temperature upon the crystal phase of the precipitate operates primarily through its effects upon the impurities which can enter and remain in the crystal structure of the precipitates. The entry into and retention in the structure by the critical impurities are governed by three physical rate processes. These are termed the aggregation velocity, the orientation velocity, and the rate of recrystallization (Kolthoff and Sandell, 1952).

The aggregation velocity is the rate at which the precipitate aggregates from the initial colloid formed at the instant of reaction. In solutions of the concentrations and temperatures of those with which the writers worked the aggregation velocity appeared to be very rapid.

In the process of making experimental precipitations it was observed that the pH of the solution tended to fall sharply during the first hour after precipitation at room temperature. This observation called the writers' attention to the fact that the first formed precipitates were amorphous aggregates. It was later possible to verify this conclusion by X-ray diffraction studies. The fall in pH is coincident with the crystallization of the precipitate and results from the decreased solubility and resultant decreased hydrolysis of the crystalline phase as compared with the amorphous phase. The process described has been termed the orientation velocity and may be defined as the rate at which the ions of an amorphous precipitate tend to orient themselves in definite crystal forms. Orientation velocity is clearly temperature dependent. Analytical chemists frequently make use of this phenomenon when they boil solutions containing colloidal aggregates in an effort to render them crystalline and hence more readily filterable.

1/10 M

16. g per liter

16 cc per liter formulated ppt.

$$\begin{array}{r} \text{Sr } \frac{87}{103} \times 20 = .000017 \\ \underline{\quad \quad \quad 16} \\ \quad \quad \quad \underline{102} \\ \quad \quad \quad \underline{17} \\ .000272 \end{array}$$

~~0.27~~

0.00027 g Sr per liter

$$.0001 \text{ Sr(NO}_3)_2 = \frac{87}{103} \times .0001 \frac{\quad}{1000} = .0000087 \text{ g Sr per cc}$$

5 and 6

Pat — Please leave two pages for
Introduction

Introduction

$$\frac{1}{6} \times 10 = 1.6 \text{ g ppt last ppt } \text{CaCO}_3$$

$$1.6 \times .025 = .04$$

$$\begin{array}{r} 16 \\ 150 \\ \hline 28 \end{array}$$

Probably the most important of the three rate processes is the rate of recrystallization. It is the recrystallization process which produces the most marked effect upon the impurity content, crystal form, and crystal size of the precipitate. In a solution containing crystals of the same compound but of different sizes, the large crystals tend to grow at the expense of the smaller ones because the finer crystals are more soluble. After 24 hours the results of this process were clearly evident in the particle sizes of the four sets of precipitates previously described. The average particle size in the first group precipitated at 10°C. was much smaller than the crystal size of the group precipitated at 72°C.

Of primary concern is the tendency of the precipitates to lose their impurities in the recrystallization process. Under conditions of high aggregation and orientation velocity, precipitates were generally very finely divided and highly impure. Any ions which are roughly the same size as the lattice ions can be trapped in the rapidly growing crystals and will influence their crystal form. Upon recrystallization, however, only those ions which are very closely similar in size are able to enter the structure of the slowly growing larger crystals. As the precipitates recrystallize and become more coarsely crystalline, most of the impurities are rejected to the solution. Only the nuclei of the large crystals contain all of the impurities which were included in the first-formed crystals. Nevertheless, if the critical impurities are present in the initial nuclei they will dictate the ultimate form of the large crystals which result from recrystallization. In this way it may be possible for very small quantities of impurity ions to determine the crystal form of the precipitate without necessarily appearing in significant quantities in spectrographic analyses.

It has been stated (Noll, 1934), and many times repeated, that the impurity uptake of calcium carbonate is determined by the crystalline form. In light of our results this statement would appear to be a confusion of cause and effect. The pH and impurity effects are closely related and appear to be significant factors influencing the crystalline form of the precipitate.

Solubility effect.—Of the factors governing the crystal form of the calcium carbonate precipitates, one of the most important is the differing solubility of the three polymorphs. There seems to be general agreement that aragonite and vaterite are more soluble than calcite. The exact solubility of vaterite is not known, but it is thought to be slightly more soluble than aragonite. In view of the differing solubilities of the three polymorphs, it seems that the least soluble form could be expected to grow at the expense of either of the two more soluble forms. Experimental results confirm this conclusion, and it was found that a mixture of approximately 90 per cent vaterite and 10 per cent calcite could be converted entirely to calcite by boiling for 3 hours. Microscopic examination made at intervals during this time showed a gradual reduction in size of the vaterite rosettes with an attendant increase in size of the calcite rhombs. Mixtures of aragonite and calcite can also be converted entirely to calcite by boiling, but the conversion is not as rapid as in the case of vaterite.

The fact that all of the precipitates were held in the precipitating vessel at constant temperature for 24 hours undoubtedly accounts for the relatively high proportion of calcite which was present in most of the samples. Vaterite was favored by low temperatures, probably because at high temperatures in the 24-hour period after precipitation was complete, any vaterite present would have been converted to calcite or aragonite.

Thermoluminescence.—Thermoluminescence studies indicate that there appear to be marked differences between the glow-curves of calcite and aragonite. The impurity content strongly influences the thermoluminescence characteristics of both calcite and aragonite, but they are thought to be affected only by those impurities which are directly included in the crystal structure. Research is in progress to determine the nature and extent of these impurity effects.

GEOLOGIC IMPLICATIONS

In recent years numerous workers have attempted to determine the factors influencing the origin of carbonate sediments and shells, particularly with respect to paleoecological studies. In general, it appears that the interpretations of many of these studies have been over-simplified, and in some cases the basic principles concerning the chemistry of formation of the material have been given little or no attention. The writers have emphasized that many factors—temperature, pH, impurity ion concentration, solubility, crystal size, the time element—can directly or indirectly affect the formation of the polymorphs of calcium carbonate and the concentration of certain related elements. To consider only one of these factors in a genetic analysis to the exclusion of the others seems grossly in error.

Although the scope of this study has not included a systematic application of the laboratory findings to natural conditions of limestone development, certain suggestions can be made. In light of the results it appears that certain physical conditions of sedimentation can be inferred by a study of the impurity elements present in carbonate rocks. Though the study of trace elements is certainly not new, an evaluation of their presence and abundance in terms of principles relative to their chemistry seems appropriate.

Even though this work has not been directly concerned with strontium-calcium ratios in carbonate materials, certain interpretations are evident. The results of spectrographic analyses for strontium, in more than 50 calcium carbonate precipitates formed under controlled conditions, indicate that several variables can affect the Sr/Ca ratio, although pH, temperature, and the amount of strontium in the initial solution seem to be the most important. Odum (1950) suggests that there is a direct relationship between the Sr/Ca ratio in carbonate sediments and shells and the Sr/Ca ratio in the solution from which they were derived.

Turekian (1955) states that the salinity of the water could be a significant independent factor in determining the Sr/Ca ratio in shells and sediments. Imbrie

(1955), following this hypothesis, has attempted to relate the Sr/Ca ratio to the abundance of certain fossil groups and indicates that these reflect the salinity of the sea. Since neither author defines the meaning of salinity, it is assumed that they accept the usual broad definition of the term (Sverdrup *et al.*, 1942, p. 50), which may be simply stated as the weight per unit volume of *all* of the dissolved metallic salts. No one could reasonably disagree with their hypothesis in view of the all inclusive nature of the term. On the other hand, they have not indicated just *how* this factor affects the Sr/Ca ratio. The chemical effects of variations in salinity are so complex that they could not possibly be reduced to a single influence.

Lowenstam (1954) has suggested that the aragonite-calcite ratio in the shells of marine organisms is controlled by temperature. Evidence seems to indicate clearly that colder waters favor the precipitation of calcite, whereas warmer waters tend to favor the precipitation of aragonite. The temperature of natural waters, which are exposed to the atmosphere, is the principal factor controlling the amount of carbon dioxide which can be held in solution. Increased temperature results in a loss of carbon dioxide with an attendant rise in pH through the reduction in the bicarbonate ion in solution, as well as carbonic acid and the carbonate ion. The pH of sea water is known to vary between approximately 7.5 and 8.4, warm waters nearest the surface usually having the highest pH (Sverdrup *et al.*, 1942, p. 194). The writers have found that temperature has an important influence upon their artificial precipitates, but not to the exclusion of the other factors involved.

It is apparent from these laboratory experiments that a sedimentary environment that would provide conditions of high pH could produce carbonate rocks that would be expected to contain appreciable trace amounts of strontium, barium, and magnesium. Conditions of high pH might be expected in shallow marine waters and basins with restricted circulations.

Solubility product data indicate that the quantity of strontium, barium, iron, and manganese present in a carbonate rock at the time of deposition would remain essentially unchanged after lithification because the preferential leaching of these elements on a large scale is impossible without the complete solution and removal of calcium carbonate. Magnesium, on the other hand, is soluble at a pH which would permit it to go into solution under certain conditions allowing it to be selectively removed from the calcium carbonate.

CONCLUSIONS

These studies indicate that the immediate factor influencing the form of calcium carbonate precipitates is the impurity content of the crystals. The impurity content has been found to be greatly affected by the pH, temperature, impurity ion concentration in the original solution, the solubility of the polymorphs, crystal size, and the time the precipitate remains in contact with the solution. All of these factors are closely interrelated and even under the most favorable labora-

tory conditions it is often impossible to isolate the effects of one from the effects of the others. The writers consider the factors controlling the precipitation of calcium carbonate, as observed in the laboratory, to be applicable to studies concerning the origin of carbonate sediments.

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[Reprinted from the Journal of the American Chemical Society, 79, 2031 (1957).]

Precipitation of Calcite and Aragonite

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Precipitation of Calcite and Aragonite

By JOHN L. WRAY AND FARRINGTON DANIELS

RECEIVED OCTOBER 22, 1956

The two common polymorphs of calcium carbonate, calcite and aragonite, have been precipitated by mixing soluble carbonate solutions with solutions of calcium ions under conditions of controlled temperature, concentration and aging. Results from these experiments have provided new information regarding the factors affecting the formation of these two crystalline varieties.

Introduction

Although the preparation of calcium carbonate has been described many times in the chemical and geological literature, the products usually have not been well defined and they have varied considerably with the experimental conditions. Among the important early workers who have attempted to determine the factors controlling the formation of the various crystalline varieties of calcium carbonate are Credner,¹ and Johnson, Merwin and Williamson.² A comprehensive summary of much of the early work was compiled by Mellor.³ More recently, studies of artificial calcium carbonate have been made by deKeyser and Dugueudre.⁴ Calcium carbonate can be precipitated in the laboratory in different crystalline forms as calcite, aragonite or vaterite, although calcite is the only thermodynamically stable form of pure CaCO_3 at room temperature and atmospheric pressure. The factors which are involved in the formation of the polymorphs of CaCO_3 apply then to the kinetics of metastable forms, rather than to equilibrium conditions.

The purpose of this investigation was to determine the conditions necessary to precipitate pure calcite, pure aragonite, or specific mixtures of the two. There is practical significance also for such a study. Calcium carbonate is finding extensive

use in chromatography and the efficiency in such work depends not only on the size of the particles, but also on the calcite-aragonite ratio. Again, calcite and aragonite are found in nature and their origin is important in the interpretation of geologic phenomena.

Experimental

Calcium carbonate was precipitated in 500-ml. round-bottom flasks by mixing soluble carbonate solutions with solutions of calcium ions with rapid mixing by a motor-driven stirrer. Reagent grade calcium nitrate manufactured by Merck and Co. was used. Spectrographic analysis of selected impurities in this material given in parts per million are as follows: MgO , 80; Fe_2O_3 , 20; MnO , 3; SrO , 30; Pb <3; and BaO <3. Sodium carbonate manufactured by the Baker Chemical Co. gave MgO <10, Fe_2O_3 <10, MnO <3, SrO <3, Pb <5, and BaO <3. The experiments were carried out at temperatures from 30 to $70 \pm 1^\circ$ and the precipitates were aged for periods from 6 minutes to 18 hours. The solutions were mixed to give precipitates of calcium carbonate as shown in Table I.

TABLE I
CONCENTRATIONS OF SOLUTIONS USED IN PRECIPITATING CaCO_3

Expt. series	Soln. added	Addn. rate, ml./min.	Soln. in flask
1	20 ml. 1.0 M $\text{Ca}(\text{NO}_3)_2$	5	200 ml. 0.1 M Na_2CO_3
2	20 ml. 1.0 M Na_2CO_3	5	200 ml. 0.1 M $\text{Ca}(\text{NO}_3)_2$

Additional experiments were performed in which 1.0 M $\text{Ca}(\text{NO}_3)_2$ and 1.0 M Na_2CO_3 were mixed. At selected temperatures and aging periods, calcium chloride was substituted for calcium nitrate in experiment series 1 and 2.

The pH of each solution was determined with a glass electrode. At the end of each aging period the precipitate was filtered immediately through a Büchner filter, thoroughly washed with distilled water, and dried at room temperature.

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The per cent. of calcite, aragonite and vaterite in the precipitates was determined by X-ray diffraction measurements and by examination with a petrographic microscope, in which the relative areas of rhombs of calcite, needles of aragonite, and spherulitic growths of vaterite were estimated with the aid of a linear scale. The limits of error in these determinations, both by X-ray diffractometer and petrographic microscope, may be as great as $\pm 15\%$.

Results

Table II gives the results of experiment series 1.

TABLE II
CRYSTAL PHASES PRODUCED BY ADDING 1 *M* $\text{Ca}(\text{NO}_3)_2$ TO 0.1 *M* Na_2CO_3

Temp., °C.	Digestion time, hr.	Crystal phase (%)		Vaterite
		Aragonite	Calcite	
30	0.1	..	5	95
	0.5	..	10	90
	3.0	..	20	80
	10.0	..	20	80
	18.0	..	100	..
40	0.1	5	95	..
	0.5	..	100	..
	3.0	..	100	..
	10.0	..	100	..
	18.0	..	100	..
45	0.1	70	30	..
	0.5	30	70	..
	3.0	2	98	..
	10.0	..	100	..
	18.0	..	100	..
50	0.1	100	..	..
	0.5	100	..	..
	3.0	95	5	..
	10.0	85	15	..
	18.0	70	30	..
70	0.1	100	..	..
	0.5	100	..	..
	3.0	100	..	..
	10.0	100	..	..
	18.0	100	..	..

The pH of the initial sodium carbonate solution was 10.9 at 30° and after complete precipitation with calcium nitrate it was 9.1. The sizes of the CaCO_3 particles ranged from about 10 to 15 μ .

The aragonite-calcite components of this series after various periods of aging, which are given in Table II between 40 and 50°, are shown graphically in Fig. 1.

Table III gives the results of experiment series 2.

The pH of the 0.1 *M* $\text{Ca}(\text{NO}_3)_2$ was 6.3 at 30° and increased to 9.1 with the addition of the 1 *M* Na_2CO_3 . The grain size varied from about 10 to 20 μ .

The effect of increasing the concentrations of the reagents, using 1 *M* solutions of both $\text{Ca}(\text{NO}_3)_2$ and Na_2CO_3 , was to give a finer grained precipitate (5–10 μ) and products that contain a much greater proportion of calcite and vaterite than aragonite when precipitated at high temperatures and allowed to age only for brief periods. For example, a precipitate containing 70% calcite, 20% vaterite and 10% aragonite was obtained at 70° after 6 minutes aging when 100 ml. of 1 *M* Na_2CO_3 was added to 100 ml. of 1 *M* $\text{Ca}(\text{NO}_3)_2$.

TABLE III
CRYSTAL PHASES PRODUCED BY ADDING 1 *M* Na_2CO_3 TO 0.1 *M* $\text{Ca}(\text{NO}_3)_2$

Temp., °C.	Digestion time, hr.	Crystal phase (%)		Vaterite
		Aragonite	Calcite	
30	0.1	..	5	95
	0.5	..	5	95
	3.0	..	5	95
	18.0	..	25	75
40	0.1	..	15	85
	0.5	5	45	50
	3.0	5	95	..
	18.0	..	100	..
50	0.1	30	70	..
	0.5	25	75	..
	3.0	20	80	..
	10.0	10	90	..
	18.0	..	100	..
60	0.1	95	5	..
	0.5	95	5	..
	3.0	90	10	..
	10.0	50	50	..
	18.0	..	100	..
70	0.1	100	..	..
	0.5	100	..	..
	3.0	100	..	..
	10.0	..	100	..
	18.0	..	100	..

Essentially the same results, as shown in Tables II and III, were obtained when calcium chloride was substituted for calcium nitrate. This reagent grade material was manufactured by Mallinckrodt Chemical Works and analyzed (in p.p.m.): MgO , 25; Fe_2O_3 , 25; MnO < 3; SrO , 60; Pb < 3; BaO < 3.

Many of the precipitations in experiment series 1 and 2 were repeated with reagent grade calcium nitrate manufactured by the General Chemical Company. This material analyzed (in p.p.m.): MgO , 25; Fe_2O_3 , 35; MnO , 3; SrO , 40; Pb < 3; BaO < 3. These results were within $\pm 15\%$ of the products obtained with the Merck calcium nitrate shown in Tables II and III.

Discussion

It is evident from the results of this investigation that it is easy to control temperature, pH and time so as to get either calcite or aragonite. It is surprising to find, as shown in Fig. 1, that the temperature range is so small and so critical. At 40° the precipitate is nearly pure calcite. At 45° it is 30% calcite and 70% aragonite, but changes during two hours digestion to more than 90% calcite. At 50° the precipitate is mostly aragonite. At temperatures between 45 and 50°, with suitable periods of digestion, one can obtain practically any ratio of calcite to aragonite. Although the precipitate suspended in solution may go rather rapidly to the more stable calcite, this change is stopped by filtering and drying the material. The rate of change in the dry state is indefinitely slow in the laboratory.

The temperature at which dry aragonite changes spontaneously into calcite at atmospheric pressure is quite high (usually above 400°). At very high pressures, aragonite is thermodynamically stable

at lower temperatures, even at room temperature. The phase equilibrium diagram for the different crystalline varieties of calcium carbonate has been fully worked out.⁵

There is much geological and laboratory evidence to show that the aragonite crystal structure is favored by the inclusion in its lattice of cations as impurities which are larger than the calcium ion, such as strontium, barium, and lead.^{6,7}

The ionic radii of the cations of the calcite and aragonite groups are given in Table IV.

TABLE IV

IONIC RADII OF CATIONS, ÅNGSTRÖM UNITS ⁸									
	Mg	Fe	Zn	Mn	Cd	Ca	Sr	Pb	Ba
Calcite type	0.78	0.83	0.83	0.91	1.03	1.06	..	..	..
Aragonite type	..	..	..	..	..	1.06	1.27	1.32	1.43

In this Laboratory, it was found⁹ that aragonite generally has a higher content of strontium than calcite, and that the formation of aragonite is induced by adding strontium, barium or lead under conditions, namely, high pH, such that they will be co-precipitated with the calcium carbonate. Only in case these ions are incorporated into the lattice would they be expected to produce the aragonite. It was pointed out that the presence of these larger ions under the proper conditions tends to produce the aragonite, rather than that the aragonite is produced from other causes and takes up the strontium, barium, or lead which happen to be in solution.

In studying the aging process, it is important to distinguish three different stages¹⁰ in the mechanics of crystallization: (a) an aggregation velocity in which the ions are brought together and precipitated; (b) an orientation velocity in which the ions in colloidal or amorphous material of the precipitated particles form crystals; and (c) a rate of recrystallization.

In the present work the aggregation velocity is considered to be infinitely rapid, the orientation is probably complete in a few seconds or minutes, and the recrystallization takes place in minutes, hours or days, and longer depending on conditions.

With the facts and generalizations discussed here, it is possible to explain the experimental results and to point out the factors which affect the production of calcite or aragonite.

The formation of the unstable aragonite having a larger crystal structure than calcite is favored by the incorporation of larger-sized cations, Sr⁺⁺, Ba⁺⁺ or Pb⁺⁺, into the CaCO₃ lattice. The concentration of these ions may be very low, because once a seed crystal of aragonite or calcite is formed, the rest of the crystal growth tends to follow the same crystal pattern.

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(9) E. J. Zeller and J. L. Wray, *Bull. Amer. Assoc. Petrol. Geol.*, **40**, 140 (1956).

(10) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., The Macmillan Co., New York, N. Y., 1952, p. 113.

Fig. 1.—Influence of temperature and aging on the crystal form of precipitated calcium carbonate.

At low pH values, strontium, barium and lead carbonates do not precipitate, and the first colloidal particles of calcium carbonate to form do not contain these larger ions. Calcite is precipitated under these conditions. At higher pH values, however, these larger ions are co-precipitated with the calcium carbonate and there is a tendency to form aragonite.

At the instant of precipitation, the strontium ions as well as the calcium ions are brought from a large volume of solution into the small volume of the first colloid particles to form, thus giving in these aggregates a high concentration. In a matter of seconds or minutes, the colloid aggregate undergoes orientation leading to crystal formation. If there is sufficient time between precipitation and crystallization, the strontium (and barium and lead) ions can diffuse out of the colloidal particles into the strontium-depleted solution which surrounds them. Factors which tend to shorten this time for escape of strontium ions tend to produce aragonite, and those which lengthen the time before crystallization give more opportunity for the escape of strontium ions and thus tend to produce calcite.

At the higher temperatures, the rate of crystallization is accelerated rapidly and the strontium ions do not have time to escape and thus they are incorporated into the CaCO₃ lattice giving the larger structure—aragonite. In series 1, calcite is formed at temperatures below 40° and aragonite is formed at temperatures above 50°. At temperatures between these limits, the incorporation of strontium in the lattice is intermediate and a mixture of aragonite and calcite is formed.

The greater the concentration of precipitating

ions the greater the tendency to form colloidal precipitates and the longer the time available for expulsion of strontium ions before crystallization. Accordingly, when all other conditions are the same, an increase in concentration tends to favor calcite formation rather than aragonite, as was found when 1 molar solutions were mixed.

Thus far only the first two stages have been discussed—the formation of aggregates and the orientation or first crystallization. The work of de Keyser and Dugueudre⁴ was concerned only with these first two steps, but extensive changes from aragonite to calcite can take place by further contact with the solution from which the precipitates were formed. The transformation of the solid aragonite to solid calcite all in the same crystal is an exceedingly slow process at room temperature, but if these crystals are in contact with water, the more soluble aragonite goes into solution and recrystallizes as the less soluble calcite. Moreover, the redissolved calcium carbonate produced by the solution of the aragonite brings its strontium into solution where it is diluted so that it is less likely to produce aragonite.

Spectrographic analyses showed a higher per cent. of strontium (80 p.p.m.) in the 70% aragonite precipitated at 45° (Fig. 1) than in the recrystallized calcite (25 p.p.m. strontium) after 10 hours of standing in the solution.

The removal of strontium ions from aragonite which is undergoing recrystallization is believed responsible for the formation of calcite. This hypothesis was confirmed with additional experiments. Pure aragonite precipitated at 50° and its surrounding solution was divided equally and placed in two separate flasks and maintained at 50°. To one of these was added 100 ml. of 0.1

M Sr(NO₃)₂. In this flask there was no trace of calcite formation after 20 hours, whereas in the flask to which strontium nitrate had not been added, about 50% of the aragonite had changed to calcite in the same period of time.

The fact that similar results were obtained with calcium nitrate of two different manufacturers probably indicates that after a certain minimum concentration of strontium and other critical impurities are reached, higher concentrations have but little further effect.

At first sight, it would be expected that the recrystallization from aragonite to calcite would go faster at high temperatures, but an examination of Fig. 1 shows that at 40° the 95% calcite changes to 100% calcite in half an hour, at 45° it changes from 30 to 100% in about 10 hours, and at 50° it changes only from zero to about 35% in 18 hours. The number of calcite crystals to act as nuclei for further growth is much less in the precipitates formed at the higher temperatures. The slowness to go from aragonite to calcite at the higher temperatures is thus explained as due to the relative absence of calcite seed crystals. This hypothesis was checked by taking out a precipitate of 50% aragonite and 50% calcite slowly changing at 45°. When this precipitate in its solution was heated to 70° the change to calcite was complete in two hours, whereas at 45° it required ten hours. If sufficient seed crystals are present, the higher temperature does give a faster rate of transformation to the stable calcite, as would be expected.

Acknowledgment.—The authors are indebted to the Atomic Energy Commission, Contract AT-(11-1)-178, and to a grant for fundamental research by the E. I. du Pont de Nemours Company.
MADISON, WISCONSIN

[Reprinted from the Journal of Physical Chemistry, 61, 802 (1957).]

Kinetics of Solid State Reactions of Silver Sulfate with Calcium and Strontium Oxides

By William P. Riemen and Farrington Daniels

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KINETICS OF SOLID STATE REACTIONS OF SILVER SULFATE WITH CALCIUM AND STRONTIUM OXIDES¹

BY WILLIAM P. RIEMEN AND FARRINGTON DANIELS

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin

Received February 11, 1957

The rate of the reaction $\text{Ag}_2\text{SO}_4 + \text{CaO} \rightarrow \text{Ag}_2\text{O} + \text{CaSO}_4 \rightarrow 2\text{Ag} + \frac{1}{2}\text{O}_2 + \text{CaSO}_4$ has been studied in solid powders between 500 and 600°. A similar reaction with SrO has been studied between 400 and 450°. The fraction reacted is measured by loss in weight of oxygen and by amount of soluble silver remaining. The data and rate constants are in agreement with a kinetic formula. The reactions are abnormally fast at first probably due to a rapid surface reaction.

Most researches in chemical kinetics have been concerned with reactions in solution or in the gas phase. Progress in solid state physics suggests interesting studies in solid state chemistry, and several researches in this field have been carried

(1) Further details of this research may be obtained from part of a Ph.D. thesis by William P. Riemen, filed in the Library of the University of Wisconsin, Madison, Wisconsin, in 1955.

out in this Laboratory. Reactions of solids to give solids would be exceedingly slow except for imperfections in the crystals which act as centers for the diffusion of materials through the crystal structure. Reactions between solids are significant in geological phenomena where long periods of time have been available, and in the preparation of crystals of high purity. They are important also in catalysts

parently quite general for the reactions between silver sulfate and calcium oxide or strontium oxide. The fact that the curve can be divided into two straight lines with different slopes suggests that the reaction proceeds in two stages. The later stage, after the initial stage of the reaction is complete, is controlled by diffusion into the interior of the solids. The other mechanism may be surface diffusion.⁹ Presumably, the surface reaction occurs first and is a fast reaction which is completed in a short time. After the surface is covered and the surface reaction is completed, the dominant mechanism is volume diffusion. This phase of the reaction is adequately described by the spherically symmetrical diffusion rate equation given earlier. This equation does not take surface diffusion into account.

Another explanation for the deviations from the rate law for spherical diffusion which occur in the initial phase of the reaction is based on the fact that the solid state reactions are exothermic. Since the heat capacities and conductivities of solids are usually low, the powder mixture becomes heated during the reaction. The initial heat liberated will raise the reaction mixture almost immediately to a temperature higher than the furnace temperature. From this maximum temperature, the mixture gradually cools down to the furnace temperature. On this basis, the initial part of the reaction would be expected to go at a faster rate than after the mixture had cooled down. This idea was first formulated by Jander.¹⁰ Calculations indicate that if the reaction were adiabatic there would be a sufficient rise in temperature to account for the increased rate at the beginning. However, on this hypothesis, a more gradual change to the slower rate would be expected.

Experiments indicated that surface reactions do occur rapidly in the reaction between silver sulfate and calcium oxide. Large particles of silver sulfate were placed in crucibles and completely surrounded by very small particles of calcium oxide. The large particles were about 0.5 cm. in diameter and the small particles were about $50\ \mu$ in diameter. These mixtures were heated to 625° for periods of time which varied between one and three days. A similar experiment was performed in which the large particles were calcium oxide and the small particles were silver sulfate. After each of these

(9) S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(10) W. Jander, *Z. anorg. Chem.*, **166**, 33 (1927).

Fig. 4.—Fraction of reaction completed *versus* time for reaction $\text{SrO} + \text{Ag}_2\text{SO}_4$ at temperatures 400 and 450° .

Fig. 5.—Rate constant k multiplied by time *versus* time, for reaction $\text{SrO} + \text{Ag}_2\text{SO}_4$ at temperatures 400 and 450° .

mixtures was heated for one day, it was removed from the furnace and a few of the large particles were taken from each crucible for visual examination. All the particles were completely covered with a grayish-black surface. The particles were then placed on a microscope slide and secured in place with Canada Balsam. They were subsequently thin-sectioned and observed under a microscope. No evidence was observed for diffusion into the interior of either calcium oxide or silver sulfate. This procedure was repeated after two days of heating and the results were the same. After three days of heating a small ring of gray silver was observed in the interior of the calcium oxide particles.

The evidence indicates that a rapid surface reaction does occur at first. However, the possibility of the heat build-up hypothesis as a partial explanation for the rate curves is not excluded.

Acknowledgment.—The authors are pleased to acknowledge support of this research by the U. S. Atomic Energy Commission through Contract AT(11-1)-178.

and other materials having particular impurities.

Pioneer work has been summarized by Hedvall,² Cohn,³ and Rees.⁴ The kinetics of the reactions between some of the alkali halide crystals around 450° has been studied in this Laboratory by Mason⁵ in which the rate of the reaction was measured by the changing X-ray patterns.

The purpose of this investigation was to study a solid-solid reaction which can be followed by simple chemical means. It is not easy to find suitable reactions because further chemical changes are apt to take place during the chemical analysis which destroy the kinetic significance of the analysis. Reactions involving a loss of a product as a gas or the change in concentration of a chemical element are suitable for direct analysis. The reactions between a powder of silver sulfate and a powder of calcium oxide and strontium oxide, giving a product gas and metallic silver, were chosen for this investigation.

Theoretical.—Exchange reactions of this type proceed by diffusion through two different product layers. Several factors may be involved in the kinetic behavior, including phase boundary processes and the rates of diffusion of the reactants through each other and through the products. Jander⁶ gave a mathematical treatment of diffusion assuming diffusion through a concentric shell of product on the outside of a sphere. Serrin and Ellickson⁷ published a more rigorous diffusion-controlled rate equation. Mason⁵ has derived this equation, and subjected it to experimental test with very good results.

The equation is

$$1 - x = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 kt}$$

where $k = \pi^2 D/a^2$, x is the fraction of the reaction completed at time t , D is the diffusivity based on Fick's law, a is the radius of the particles, and k is the rate constant for the solid state reaction based on diffusion into a sphere. This equation has been solved by Mason⁵ for numerical values of kt from 0.01 to 1.20 and the corresponding values of $1-x$ from 0.8727 to 0.1844 with the help of an I.B.M. calculator.

In using this equation, x is determined by chemical analysis and the corresponding value of kt is obtained from the tables. Then kt is plotted against time. The resulting line should be straight if the process is diffusion controlled and the assumptions of the derivation are valid. The slope of the line gives the value of k . Straight lines have been obtained frequently in this Laboratory, even though the particles are not spherical and the diffusion law is not entirely applicable. Thus, the equation may be used as an empirical equation for powders.

(2) J. A. Hedvall, "Einführung in die Festkörperchemie," F. Vieweg and Sons, Braunschweig, 1952.

(3) G. Cohn, *Chem. Revs.*, **42**, 527 (1948).

(4) A. L. G. Rees, "Chemistry of the Defect Solid State," John Wiley and Sons, New York, N. Y., 1954.

(5) H. F. Mason, Ph.D. Thesis, University of Wisconsin, 1954; *This Journal*, **61**, 796 (1957).

(6) W. Jander, *Z. anorg. Chem.*, **166**, 33 (1927).

(7) B. Serrin and R. T. Ellickson, *J. Chem. Phys.*, **9**, 742 (1941).

Experimental

The reaction between silver sulfate and calcium oxide in the solid state was first studied by Hedvall⁸ who applied the method of thermal analysis rather than the more convenient chemical method of gas evolution. Moreover, he gave no kinetic data which could be used to calculate a rate constant.

Solid silver sulfate reacts with solid calcium oxide in the temperature interval from 500 to 600°. Below 500° it is too slow to follow. Consequently, this research was restricted to the temperature interval of 500 to 600°. The reaction can be considered as a double decomposition reaction, as

At temperatures above 300°, silver oxide is completely dissociated into elemental silver and gaseous oxygen. In these studies carried out at temperatures above 500°, the above reaction should then be written

Two means are available for following the course of this reaction. The first measures the loss in weight of the reaction mixture which occurs when oxygen is evolved. The second determines the remaining, unreacted silver sulfate.

Analytical grade materials were used throughout the research. The calcium oxide was prepared by heating calcium hydroxide at 1000° for 24 hours. This ensured that all the hydroxide was converted to the oxide. Both chemicals were heated independently at 500° for two hours to ensure complete drying. They were then ground in a millite mortar and sieved. The fraction of the powder which passed through a 200-mesh screen and lay on a 320-mesh screen was collected and stored in a desiccator. The sieve screens were heated on a hot plate before use to remove the possibility of moisture being picked up by the powders.

At room temperature this reaction is very slow if the reactants are kept in a dry condition. Consequently a large amount of an equimolar mixture of the powdered calcium oxide and silver sulfate was prepared by weighing out the appropriate amounts of each and mixing thoroughly by passing three or four times through a sieve whose openings were several times larger than the size of the particles. These mixtures were stored in desiccators until used.

The kinetic data were obtained by the following procedure: 3.6790 g. of the reaction mixture was weighed into crucibles which had been previously dried and weighed. These crucibles were placed in a Lindberg muffle furnace controlled to $\pm 4^\circ$ for times which varied from 5 to 1000 minutes. After the reaction time had elapsed, the crucible was removed, cooled in Dry Ice to stop the reaction quickly, and reweighed. The loss of weight which represented oxygen evolution was taken as a measure of the extent of the reaction.

The procedure was repeated with another set of crucibles at the same temperature and the soluble silver sulfate which remained unreacted, was determined. The reaction mixture was treated with a dilute solution of ammonium hydroxide and filtered. Using litmus as an indicator the dissolved silver was precipitated from this filtrate with dilute hydrochloric acid, care being observed not to add too great an excess of the acid. This precipitate was allowed to digest at 80° for 1 hour. It was then filtered off into Gooch crucibles, washed and dried at 110° for 1 hour. The weight of the silver chloride was converted into silver sulfate. This value was used to obtain another measure of the extent of the reaction.

The silver analysis was not used as much as the oxygen evolution method. However, checks were made at each temperature to ascertain whether there was agreement. The comparison between the results of the two methods gave good agreement and the average difference amounted to about 5%. This difference showed no trend indicating that one method was always lower or higher than that of the other. Hence, it was concluded that the oxygen method was quite acceptable. The results of the two methods appear in Table I.

The data are summarized in Table II and presented in graphical form in Figs. 1 and 2. The rate constants for the reaction are calculated from the slopes of the curves which represent kt versus time. In Fig. 3, $\log k$ is plotted against

(8) J. A. Hedvall, *Z. angew. Chem.*, **39**, 781 (1931).

Fig. 1.—Fraction of reaction completed *versus* time for reaction $\text{CaO} + \text{Ag}_2\text{SO}_4$ at temperatures 500–600°.

Fig. 2.—Rate constant k multiplied by time *versus* time for reaction $\text{CaO} + \text{Ag}_2\text{SO}_4$ at temperatures 500–600°.

Fig. 3.—Log rate constant *versus* reciprocal of absolute temperature for reaction $\text{CaO} + \text{Ag}_2\text{SO}_4$.

the reciprocal of the absolute temperature, giving an activation energy of 41,000 cal. per mole.

The reaction between silver sulfate and strontium oxide in the solid state is similar to the reaction between silver sulfate and calcium oxide. The details of the experimental procedure were the same as those which were used in the calcium oxide and silver sulfate reaction with the exception that 4.2545 g. of a 50:50 molar mixture of the reactants was used as the reaction mixture.

TABLE I
COMPARISON OF ANALYTICAL METHODS

Time, min.	Temp., °C.	Fraction of reaction completed	
		By silver anal.	By oxygen anal.
105	500	0.32	0.37
900	500	.48	.47
285	570	.58	.61
45	600	.55	.58
225	600	.76	.73

TABLE II
KINETIC DATA FOR REACTION $\text{Ag}_2\text{SO}_4 + \text{CaO}$

Time, min.	Fraction reaction completed	kt	Time, min.	Fraction reaction completed	
Temp., 500°			Temp., 530°		
5	0.19	0.03	5	0.23	0.05
15	.25	.06	15	.30	.09
45	.27	.07	45	.37	.15
105	.35	.13	225	.45	.23
220	.38	.17	500	.49	.28
500	.42	.20	825	.52	.34
900	.48	.27			
$k = 1.6 \times 10^{-4} \text{ min.}^{-1}$			$k = 2.2 \times 10^{-4} \text{ min.}^{-1}$		
Temp., 570°			Temp., 600°		
5	0.26	0.06	5	0.29	0.09
15	.33	.12	15	.43	.22
45	.41	.18	45	.56	.42
105	.48	.28	105	.64	.56
285	.59	.49	225	.74	.89
600	.67	.62	425	.86	1.47
885	.72	.77			
$k = 7.9 \times 10^{-4} \text{ min.}^{-1}$			$k = 27 \times 10^{-4} \text{ min.}^{-1}$		

The reaction between silver sulfate and strontium oxide occurs at a measurable rate in the temperature interval of 400 to 450°. The reaction may be represented as

The data are summarized in Table III and presented in graphical form in Fig. 4 and 5. The rate constants k are calculated from the slopes of the lines of Fig. 5. A plot of $\log k$ against the reciprocal of the absolute temperature gives an activation energy of 14,000 cal. per mole.

TABLE III
KINETIC DATA FOR REACTION $\text{Ag}_2\text{SO}_4 + \text{SrO}$

Temp., 400°			Temp., 425°			Temp., 450°		
Time, min.	Fraction reaction completed	kt	Time, min.	Fraction reaction completed	kt	Time, min.	Fraction reaction completed	kt
5	0.22	0.04	5	0.23	0.05	5	0.27	0.07
15	.28	.07	15	.29	.09	15	.33	.12
45	.34	.12	45	.36	.13	45	.35	.13
100	.42	.18	100	.40	.18	75	.41	.18
230	.48	.27	250	.45	.23	195	.45	.22
500	.52	.34	500	.57	.41	350	.57	.41
690	.58	.45	650	.60	.48	500	.68	.67
$k = 4.9 \times 10^{-4} \text{ min.}^{-1}$			$k = 5.6 \times 10^{-4} \text{ min.}^{-1}$			$k = 10 \times 10^{-4} \text{ min.}^{-1}$		

Discussion

It is observed that all the curves representing kt *versus* time give straight lines after the initial part of the reaction. The initial part of the reaction is also very nearly a straight line which passes through the origin. The slope of this line is greater than the slope of the straight line representing the major portion of the reaction. This behavior is ap-

[Reprinted from the Journal of Physical Chemistry, 61, 813 (1957).]

Kinetics of the Reaction Between Silver and Sulfur in the Solid State

By William P. Riemen

KINETICS OF THE REACTION BETWEEN SILVER AND SULFUR IN THE SOLID STATE¹

By WILLIAM P. RIEMEN²

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin

Received February 11, 1957

Reactions in the solid state have been reported from this Laboratory.^{3,4} The reaction between

Fig. 1.—Fraction of reaction completed versus time, for reaction $2\text{Ag} + \text{S} \rightarrow \text{Ag}_2\text{S}$ at 25° .

Fig. 2.—Rate constant k multiplied by time versus time, for reaction $2\text{Ag} + \text{S} \rightarrow \text{Ag}_2\text{S}$ at 25° .

silver and sulfur is an excellent solid reaction to study because it proceeds with measurable velocity at room temperature and it can be followed readily by dissolving out the unreacted sulfur with carbon disulfide. It has been studied before.⁵⁻⁸ Further research is reported here because the measurements fit a kinetic formula^{1,3,4} and they bring out quantitatively the influence of particle size on reaction velocity.

(1) More details are available in a portion of a Ph.D. thesis by W. P. Riemen filed in the Library of the University of Wisconsin, 1955.

(2) U. S. Rubber Company, Passaic, New Jersey.

(3) H. F. Mason, Ph.D. Thesis, University of Wisconsin, 1954, THIS JOURNAL, 61, 796 (1957).

(4) W. P. Riemen and F. Daniels, *ibid.*, 61, 802 (1957).

(5) K. Fischbeck, *Z. anorg. Chem.*, 165, 55 (1927).

(6) F. Hohn, *ibid.*, 99, 118 (1917).

(7) J. Smith, *Bull. soc. chim.*, 7, 706 (1940).

(8) F. Taradoire, *Bull. soc. chim. France*, 147, 623 (1932).

Fig. 3.—Rate constant k versus reciprocal of square of particle radius for reaction $2\text{Ag} + \text{S} \rightarrow \text{Ag}_2\text{S}$.

The silver was precipitated from silver nitrate with copper, washed thoroughly, and dried at 200° for an hour. The sulfur was prepared by melting flowers of sulfur, cooling and grinding the crystals in a mullite mortar. Both sulfur and silver were sieved to give uniform sizes.

2.1576 grams of silver powder was thoroughly mixed with 0.3206 g. of sulfur powder of the same size placed in weighed sintered glass-bottom crucibles at 25° for periods of time ranging from 1 to 50 days. At suitable time intervals a crucible was extracted five times with about 10 ml. of fresh carbon disulfide and the loss in weight gave the amount of sulfur still unreacted.

Experiments were also carried out in which the powders were pressed into pellets under pressure of 3 tons per sq. inch, as in the experiments of Fischbeck.⁶ There was no significant difference in reaction rate between the pressed and unpressed powders and the act of compression gave no appreciable reaction. This lack of action on compression was unexpected because preliminary work on KBr and AgNO_3 indicated that compression under high pressures does bring about some reaction.

The data on the reaction between silver and sulfur at 25° are given in Fig. 1.

These data fit well the rate equation for solids, based on diffusion, as derived by Mason³ and checked by him on $\text{NaBr} + \text{KCl}$ and $\text{CsCl} + \text{KBr}$, and checked by Riemen and Daniels⁴ on $\text{Ag}_2\text{SO}_4 + \text{CaO}$ and SrO . The formula is

$$1 - x = 6/\pi^2 \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 kt)$$

x is the fraction of the reaction at time t , D is the diffusivity, a is the radius of particles, and k is the rate constant $= \pi^2 D/a^2$; kt is evaluated from $1 - x$ by I.B.M. calculations.³

Figure 2 shows the kt plot against time which permits a calculation of k . For 55μ particles, k is 0.039 day^{-1} , for 85μ , k is 0.019 day^{-1} and for 285μ , k is 0.002 day^{-1} .

Figure 3 shows that the rate constant k is inversely proportional to $1/a^2$ in agreement with the formula.

The author is glad to acknowledge the help of Professor Farrington Daniels with whom this research was carried out and to acknowledge the support of the U. S. Atomic Energy Commission through Contract AT(11-1)-178.

VII. Experimental Techniques

[Reprinted from the Journal of the American Chemical Society, **75**, 3096 (1953).]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

A Convenient Source of Gamma Radiation

BY DONALD F. SAUNDERS, FREDERICK F. MOREHEAD, JR., AND FARRINGTON DANIELS

RECEIVED OCTOBER 15, 1952

A simple irradiator is described which gives intense and uniform gamma radiation from Co^{60} for laboratory experiments involving objects of relatively small size.

An intense and uniform source of γ -rays capable of irradiating large numbers of small specimens was needed in a research program on the thermoluminescence of crystals. A hollow Co^{60} cylinder has solved the problem so successfully that a description of it may be of help to others. Thousands of irradiations have been carried out with this simple and inexpensive source since its development in 1949.^{1,2} The γ -ray flux is uniform because of the geometrical characteristics, and it is intense because the samples to be irradiated are placed inside the source and receive radiation from all sides. The γ -radiation extending outward from the source is of sufficiently low enough intensity that safe handling and shipping may be carried out easily. An unshielded 3-curie source giving a radiation intensity of approximately 4 roentgens per hour at a distance of 1.0 meter will provide an intensity of about 6,000 roentgens per hour inside the source.

Similar cylindrical Co^{60} γ -ray sources have been prepared in other laboratories for studies in radiation chemistry³ and to develop new applications for fission products.⁴ The high activity of these other sources (300 to 1,000 curies) requires that special apparatus and techniques be used for safe preparation and handling. The smaller size of the sources described below produces a high radiation intensity per unit of radioactivity, making high γ -ray fluxes available to laboratories not possessing specialized facilities.

A hollow cylinder of cobalt metal powder was prepared by filling the space between two concentric aluminum cans. The aluminum container must be absolutely tight to pre-

vent the escape of any trace of radioactive cobalt powder. The powder was used because it is easily available whereas the machining of cobalt metal is very difficult.⁵

A plan of the apparatus is shown in Fig. 1. The cylindrical aluminum cans were welded from standard aluminum containers used for neutron irradiations in the nuclear reactor at the Argonne National Laboratory. The outer aluminum cylinder has an outer diameter of 3.1 cm. and the inner cylinder has an inner diameter of 2.2 cm. The height is 13.5 cm. The top and bottom of the concentric cylinders are closed with a thick aluminum ring to which the two cylinders are welded after filling up the space between them with pure chemical-grade cobalt powder.

The first model of this apparatus was placed in the nuclear reactor at the Argonne National Laboratory and exposed to a neutron flux for a sufficient time to produce 0.7 curie of radioactive cobalt. Radioactive cobalt (Co^{60}) has a half-life of 5.3 years and decays with the emission of weak β -rays and 1.17 and 1.33 mev. γ -rays.

A second gamma source of the same type was irradiated at the Oak Ridge National Laboratory to produce 3 curies of radioactive cobalt.

Specimens are placed in an aluminum rack which fits in the source. This rack holds several solid pieces, 1 cm. square and a few millimeters thick, sawed from a rock or cleaved from a crystal, or it can hold 40–50 gelatine capsules containing powdered specimens. It has been used for irradiating biological material including live bumble bees and fruit flies. The 0.7-curie and 3-curie irradiators are kept in separate compartments of a lead container with walls seven inches thick. This is set in the floor of an isolated basement room. A mirror is placed at an angle of 45 degrees about 1.0 meter above the irradiators. The specimens are lowered into the irradiator and removed with a "fish pole."

The relative and absolute radiation intensities in the irradiators were determined by using the thermoluminescence of lithium fluoride crystals as dosimeters as will be described in detail in a forthcoming communication. Lithium fluoride, as well as other alkali halides, emits light on heating after an exposure to high energy radiation such as X-rays, γ -rays and α - or β -particles. This thermoluminescence is measured by recording the changes in light intensity as measured by a multiplier phototube while the temperature of the specimen is increased at a rate of about 1° per second. The resulting light intensity-time curve or the

(1) Farrington Daniels and D. F. Saunders, *Science*, **111**, 462 (1950).

(2) D. F. Saunders, Ph.D. Thesis, University of Wisconsin (1950).

(3) J. A. Ghormley and C. J. Hochanadel, *Rev. Sci. Instruments*, **22**, 473 (1951).

(4) B. Manowitz, *Nucleonics*, **9**, No. 2, 10 (1951).

(5) It has been learned that cylinders of cobalt metal can be made by Technical Fabrications Co., Cambridge, Massachusetts, and by Eldorado Mining and Refining (1944) Ltd. Ottawa, Canada.

Fig. 1.—Gamma source.

replotted light intensity-temperature curve (glow curve) passes through a series of maxima.

The height of the lithium fluoride glow curve maximum at 220° was used as a measure of the amount of light emitted by any particular specimen. This value was corrected to a standard weight of lithium fluoride. All the specimens used for calibration were obtained by cleaving plates 1 cm. square by 1–2 mm. thick from a large single crystal of lithium fluoride obtained from the Harshaw Chemical Co. By measuring the thermoluminescence of specimens placed in the same position within one of the irradiators as a function of time of exposure to gamma radiation, an equation was found which related the amount of thermoluminescence to the amount of γ -radiation. For very short exposures the thermoluminescence was nearly proportional to the square of the time of exposure, but became directly proportional for slightly longer exposures.

The relative radiation intensities along the length of each irradiator were determined by measuring the thermoluminescence of lithium fluoride specimens which were distributed along the axis of the source and given equal exposure times. By comparing these measurements with the curve of thermoluminescence as a function of exposure time, it was possible to construct radiation intensity distribution curves as shown in Fig. 2 for the 3-curie source. The γ -intensities are given in arbitrary units. This curve agrees quite well with relative values as calculated from geometrical considerations of the distribution of activity in the source. The differences between the curves are attributed to compaction of the cobalt powder at the bottom of the source.

In order that absolute γ -intensities in roentgens per hour might be calculated other specimens of lithium fluoride were exposed to γ -radiation outside the 0.7-curie source at a distance of 1.0 meter. The radiation intensity at this point was determined by a standardized ionization-type survey meter. The thermoluminescence produced was compared with that obtained from the specimens exposed inside the irradiators. By combining these data with the known equation for the increase of thermoluminescence with the amount of γ -radiation and the ratio of the times of irradiation in the two instances, it was possible to calculate the intensity of radiation inside the source. The values obtained were about 1,400 roentgens per hour at the center of the 0.7-curie source and about 6,000 roentgens per hour at the center of the 3-curie source.

Calculation of Radiation Intensity.—As a check on the measured radiation intensity in the 3-curie source, we have calculated the radiation intensity

Fig. 2.—Intensity distribution along axis of source.

distribution along the axis of the source and in a plane perpendicular to the axis at the center.

In these calculations, one assumes that the annulus containing the Co^{60} is sufficiently thin so that one may use an "area" rather than a "volume" distribution of the Co^{60} . That is, the Co^{60} is assumed to be uniformly distributed over the surface of a cylinder of radius R , where R is the mean radius of the two aluminum cans, 1.35 cm. in this instance. The height, h , is approximately 12 cm., which includes only the portion containing Co^{60} .

The radiation intensity, I , in roentgens per hour produced by a point source of 1 curie of Co^{60} at a distance D cm. in dry air at 0° and 760 mm. is given by

$$I = \frac{(3.7 \times 10^{10})(3600)(1.17 \times 3.53 \times 10^{-6} + 1.33 \times 3.41 \times 10^{-6})}{4\pi D^2(6.77 \times 10^4)} \\ = \frac{1.356 \times 10^4}{D^2} \text{ roentgens per hour}$$

Here $1/4\pi D^2$ is the fraction of energy emitted by the Co^{60} passing through a 1-cm.² area at D cm. The absorption of 6.77×10^4 mev. is the equivalent of 1 roentgen. The absorption coefficients of 1.17 and 1.33 mev. gammas are $3.53 \times 10^{-5} \text{ cm.}^{-1}$ and $3.41 \times 10^{-5} \text{ cm.}^{-1}$, respectively,⁶ neglecting photoelectric and pair production absorption.

If Z is the position on the cylinder axis and r the radial distance from the axis to the point at which it is desired to know the radiation intensity, then the intensity, I_s , due to surface element $R d\theta dZ^1$ located at Z^1 , R and θ is

$$I_s = \frac{(N R d\theta dZ^1)(1.356 \times 10^4)}{D^2}$$

where

$$D^2 = (Z - Z^1)^2 + R^2 + r^2 - 2Rr \cos \theta$$

and N is the surface concentration of the source in curies per square centimeter. If we set $r = 0$ we get the radiation intensity along the axis, I_a , by integrating over θ and Z^1 .

(6) R. E. Evans, *Nucleonics*, 1, No. 4, 32 (1947).

$$I_a = H \int_{h/2}^{h/2} \int_0^{2\pi} \frac{d\theta dZ^1}{D^2}$$

$$= 2\pi H \int_{-h/2}^{h/2+Z} \frac{d(Z-Z^1)}{(Z-Z^1)^2 + R^2} =$$

$$\frac{2\pi H}{R} \left[\tan^{-1} \frac{h/2 - Z +}{R} \tan^{-1} \frac{h/2 + Z}{R} \right]$$

where $H = NR (1.356 \times 10^4)$.

Fig. 3.—Radial intensity distribution at center of source ($Z = 0$).

For the 3-curie source, the radiation intensity at the center ($Z = 0$) is calculated to be 6750 roentgens per hour which agrees reasonably well with the value of 6,000 roentgens per hour as measured by the thermoluminescence method. The relative intensity distribution along the axis of the source is shown in Fig. 2.

The radial intensity distribution at any point is found by first integrating over θ .

$$I_r = 2NR(1.356 \times 10^4) \int_{-h/2}^{h/2} \int_0^\pi \frac{d\theta dZ^1}{a + b \cos \theta}$$

$$= 4\pi NR(1.35 \times 10^4) \int_{-h/2}^{h/2} \frac{dZ^1}{\sqrt{a^2 - b^2}}$$

$$\text{where } a = (Z - Z^1)^2 + R^2 + r^2$$

$$b = -2Rr$$

The integration over Z^1 is most easily done graphically, and the result for $Z = 0$ is shown in Fig. 3. The relative uniformity of the intensity when r is less than 0.7 roentgen has been shown experimentally. A photograph of the thermoluminescence emitted by a large crystal of lithium fluoride irradiated in the source showed almost completely uniform blackening except for an increase at the edges, which was shown to be due to internal reflection. The same blackening increase at the edge was present for a crystal whose edges were cleaved off after irradiation and before photographing.

One may check the figure thus obtained for the intensity at the center by comparing the intensity measured with a survey meter at a point directly above the source with a value calculated from the formula for the intensity along the axis, corrected for the self-absorption of the Co^{60} . The measured value was 0.80 roentgen per hour while the calculated was 0.805 roentgen per hour.

Secondary electrons produced by the gammas in the cobalt and aluminum have been neglected in the above calculations. The thermoluminescence of lithium fluoride crystals wrapped tightly in heavy foil metal (cadmium) did not differ from that of unwrapped crystals given an equal exposure. It has been found that the thermoluminescence of lithium fluoride is extremely sensitive to exposure to low energy electron beams (~ 6 kev.). Hence, neglect of the secondary effects would seem to have some empirical justification.

During the past three years of research on the thermoluminescence of crystals these γ -irradiators have been in constant use and have given very satisfactory service.

We are particularly indebted to Dr. E. W. Rylander and to the Argonne National Laboratory for their cooperation in preparing this γ -ray source and irradiating the first source. We are indebted also to the Oak Ridge National Laboratory for irradiating the second source. This investigation was carried out with the help of a grant from the Atomic Energy Commission.

MADISON, WISCONSIN

Fluorometric and Colorimetric Microdetermination of Uranium in Rocks and Minerals

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Reprinted from

ANALYTICAL CHEMISTRY

Vol. 26, Page 1635, October 1954

Fluorometric and Colorimetric Microdetermination of Uranium in Rocks and Minerals

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A system of operations and manipulations has been developed for analyzing geologic specimens containing less than 10 p.p.m. of uranium. Means of opening the sample, as well as cellulose chromatographic and ethyl acetate extraction procedures for the separation of uranium from interfering elements, have been investigated and compared. The fluorometric procedure has been critically studied and compared with Yoe's colorimetric procedure. In general, samples containing less than 10 p.p.m. of uranium are best analyzed fluorometrically; more than 10 p.p.m. colorimetrically.

IN THE past few years many articles have appeared on the determination of uranium. Most of these articles have dealt with the determination of macro or semimicro amounts of uranium. For microdeterminations of uranium, the fluorometric method was intensively investigated and developed. The Trace Elements Laboratory of the U. S. Geological Survey has published a number of investigations (5) in this field of fluorometry, as has the New Brunswick, N. J., laboratory of the Atomic Energy Commission (8-10).

For the past 3 years this laboratory has been engaged in studies of the geochemistry of uranium. These studies necessitated the determination of uranium in a large variety and

number of rocks and minerals, most of which contained only 0.1 to 10 p.p.m. While making several thousand such determinations, various methods and procedures were investigated. The optimum conditions for several important steps were quantitatively determined. A system of procedures has been developed which permits the routine analysis of many different types of geologic specimens. The presentation of these procedures and their comparison are the purpose of this paper.

OPENING OF SAMPLE

The specimens dealt with in this work were mostly natural silicates and the opening of the sample played an important part in determining the uranium content. Radioautographic techniques (2) show that generally uranium may occur in rocks either as a "paint" around the individual crystalline grains of a rock or it may be bound within the crystalline lattices. Usually, the paint is easily taken into solution with dilute acid, while crystalline silicates—e.g., zircons—are difficult to bring into solution.

HYDROFLUORIC-NITRIC ACID TREATMENT

The conventional procedure of hydrofluoric-nitric acid treatment was used for the opening of siliceous materials such as granites and obsidians because it leaves much less salt than does an alkali fusion. For a 1-gram sample, three hydrofluoric-nitric acid treatments followed by three nitric acid treatments were sufficient to open most specimens, excluding zircons.

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Table I. Effectiveness of Nitric Acid Reflux Action and Comparison of Separation and Determination Techniques

Sample	Uranium Analysis, P.P.M. from Other Laboratories	Uranium Found, P.P.M. (Fluorometric Method)	
		Cellulose column separation	Ethyl acetate separation
P-108 W (granite)	50 ^a	54.7 ± 1.8 ^b	54.0 ^b
P-118 W (granite)	30-40 ^a	23.2 ± 3.6 ^b	21.5 ^b
Rubideaux granite	2.3-3.2 ^a	2.6 ± 0.3 ^b	2.2 ^b
New Brunswick std. car- notite No. 5	930 ^c	910 ^d	955 ^b
New Brunswick std. phosphate No. 1	247 ^c	227 ± 4.3 ^d	288 ^b
Phosphate rock U.S.G.S. No. 47595	100 ^a	96.2 ± 4.2 ^d	
Uncompahgre granite	3.4 ± 0.1 ^c		3.1 ± 0.3 ^b

^a Trace Elements Laboratory, U. S. Geological Survey.^b Opened using HF-HNO₃ treatment.^c New Brunswick, N. J., Atomic Energy Commission.^d Opened using HNO₃ reflux treatment.^e Isotope dilution method, G. R. Tilton, analyst (11).

NITRIC ACID REFLUX ACTION

Samples in which uranium occurs as a paint around the crystal, or in materials low in silica and soluble in nitric acid, such as fluorites and phosphate rocks, may be opened by refluxing the solid sample in concentrated nitric acid (1 to 1). A 125-ml. round-bottomed borosilicate glass flask and reflux condenser were used. Two hours of refluxing with 50 ml. of nitric acid solution completely dissolved several grams of fluorite with some attack on the glassware by the hydrofluoric acid evolved. The very small residue from the fluorite refluxings was examined under the petrographic microscope to confirm the complete solution of the fluorite. The fluorite was easily identified by its isotropic characteristics and low index of refraction. The insolubles, which were found to contain an insignificant amount of uranium in most specimens of this type, were removed by filtration through Whatman No. 40 filter paper. The filtrate was diluted to the desired volume (usually 100 ml.) with water. Aliquots were then removed in preparation for the separation of uranium from elements that interfere with the methods of determination.

Approximately 100 fluorites, numerous phosphate rocks, and carnotites were opened effectively using this procedure. Results obtained on standard samples may be found in Table I.

An attempt was also made to open the P-108 W granite using the nitric acid reflux action; however, the results were over 50% low, after 4 hours of refluxing.

SEPARATIONS

The success of both the colorimetric and fluorimetric procedures for the analysis of uranium in the range of 0.1 to 10 p.p.m. is very dependent upon the effectiveness of the separation of uranium from interfering ions. Since interference ions, such as iron, are present in much larger quantities than is uranium, the selectivity of the separation must be exceptionally high. Three means of reducing the ratio of interference ions to uranium were used successfully.

Ethyl Acetate Extraction. This procedure depends upon the selectivity of the ethyl acetate in extracting uranium quantitatively from a solution of high nitrate salt concentration. The procedure below is essentially that of Grimaldi *et al.* (5), except that less free nitric acid is present in the aluminate nitrate phase.

REAGENTS. Ethyl Acetate, A. R. grade.

Preparation of aluminum nitrate stock solution. Four hundred fifty-three grams of reagent grade aluminum nitrate enneahydrate were dissolved in distilled water and the solution was diluted to a volume of 520 ml. The solution was extracted once in a separatory funnel with 150 ml. of reagent grade diethyl ether to remove any uranium; 453 grams of aluminum nitrate enneahydrate have been found to contain from 2 to 14% of uranium. After separation of the two phases, the aluminum nitrate solution was recrystallized to increase the purity and to reduce the nitric acid content of the salt. A saturated solution of the purified

aluminum nitrate was prepared and an aliquot was analyzed gravimetrically by slow evaporation to dryness and ignition to alumina. The analyzed solution was then diluted to a concentration of 10.0 ± 0.5 gram of aluminum nitrate enneahydrate per 10 ml. of solution. Aluminum nitrate enneahydrate especially purified for this uranium extraction procedure is now commercially available (4).

Uranium stock solution. Prepared in a concentration of 1 mg. of uranium per ml. from uranyl nitrate hexahydrate and an aliquot was analyzed gravimetrically by evaporation and ignition to urania. Another aliquot was analyzed by redox titration with ceric solution after having been converted to the sulfate and passed through a Jones reductor. Solutions of greater dilution were prepared from the stock solution.

Extraction efficiency. As shown by Figure 1, the efficiency of the extraction is dependent upon the aluminum nitrate concentration; 9.5 grams per 10 ml. of solution was found to be the lower effective limit for the aluminum nitrate enneahydrate concentration. Optimum conditions were determined to be 10.0 grams of aluminum nitrate enneahydrate per 10 ml. of solution with less than 3% nitric acid (70% volume per volume) present. The efficiency and precision of the extraction at these concentrations were found to be good and 0.4 % of uranium could be extracted from 10 ml. of aluminum nitrate enneahydrate solution with greater than 90% efficiency.

Figure 1. Ethyl Acetate Extraction of 1, 10, 50, and 100 P.P.M. of Uranium as a Function of Aluminum Nitrate Enneahydrate Concentration

The efficiency of the extraction of uranium was determined by evaporating a solution of known uranium nitrate content to near dryness in a 25-ml. flask. Ten milliliters of aluminum nitrate solution were added, followed by 10.0 ml. of ethyl acetate; the mixture was shaken for 2 minutes, allowed to stand for 5 minutes, and the ethyl acetate phase was then decanted through a double-fold filter paper into a 20-ml. vial. The filter paper served to absorb any water droplets that may have been suspended in the ethyl acetate. An aliquot of the ethyl acetate solution was then analyzed fluorimetrically.

The analytical procedure was as follows. The residue resulting from either the hydrofluoric-nitric acid treatment or the evaporation of an aliquot from the nitric acid reflux action, was taken up in 10.0 ml. of aluminum nitrate solution and transferred to a 25-ml. glass-stoppered flask. Heat was applied to aid in dissolving the residue. Ten milliliters of ethyl acetate were added from an automatic pipet and the solution was extracted immediately by shaking vigorously for 2 minutes. The flask was allowed to stand for 5 minutes to permit the phases to separate. After filtering as described above, an aliquot of the ethyl acetate phase was used for either the fluorometric or colorimetric procedure. The glassware, especially the pipets, must be dry to prevent the stripping (reversed extraction) of uranium from the ethyl acetate into an unsalted aqueous phase. Ethyl acetate is slowly hydro-

lyzed by acid solutions and the contact time with the aluminum nitrate solution should be minimized.

Nitrated Cellulose Chromatographic Separation. An alternative procedure for the separation of the uranium from interfering ions makes use of an activated cellulose column. This separation is effected by the selective elution of uranyl nitrate from activated cellulose with diethyl ether containing 5% by volume of concentrated nitric acid (70%).

Arden *et al.* (1) found in early work that uranium could be separated from foreign ions by using paper strips and organic solvents containing nitric acid. Recent work by Burstall and Wells (3) indicates that uranium may be separated from nearly all of the other metal ions by the use of a cellulose column using diethyl ether and nitric acid as the eluent. The procedure used in this laboratory was similar to that proposed by Kennedy (6).

REAGENTS AND EQUIPMENT. Diethyl ether, A. R. grade.

Nitric acid, A. R. grade (70%).

Preparation of cellulose pulp. Fifty grams of Whatman No. 1 or S. and S. No. 598 filter paper were cut into small strips, placed in a 3-liter bottle nearly full of distilled water, and shaken in a mechanical shaker to disintegrate the paper. The pulpy mass was transferred to a Büchner funnel and sucked dry. The semi-dry mat was broken up and placed in a liter of boiling 5% nitric acid (70%, volume per volume) and boiled for 10 minutes, stirring constantly. The pulpy mass was transferred again to a Büchner funnel, sucked dry, and washed with a liter of absolute alcohol, followed by 1500 ml. of diethyl ether. The pulp was then sucked dry, broken up and stored in a tightly stoppered container.

Preparation of extraction tube. The column used was 20 cm. high and 2 cm. in diameter. A stopcock at the bottom regulated the flow, and a separatory funnel at the top served as a reservoir. To prevent channeling of eluent down the inside of the tube, it was coated with silicone grease dissolved in carbon tetrachloride. A mat of glass wool was placed at the bottom of the tube and enough eluent (ether containing 5% nitric acid, 70%, volume per volume) added to half fill the tube. Nitrated cellulose was added in half-gram portions and packed with the aid of a glass plunger, using a vertical motion. Two and a half grams of nitrated pulp were then added and packed to a height of 8 cm. The use of the glass plunger facilitates even packing which is essential for a smooth rapid flow of eluent. One hundred milliliters of eluent were passed through the column before using.

PROCEDURE. With a sample opened by hydrofluoric-nitric acid treatment, the residue was taken up in 5 to 10 ml. of 25% nitric acid (70%, volume per volume) and transferred directly to the top of the column; or, if the sample was opened by nitric acid reflux, an aliquot of this solution was placed on the column. In the first instance, the crucible was rinsed with the eluent and the solution transferred to the column. Enough ether-nitric acid solution was added to the reservoir at the top of the column so that the total volume passing through the column was 100 ml. This quantity of eluent was passed through the column in 20 minutes. A stream of air passing over a 100-ml. beaker containing 25 ml. of water at the bottom of the column served to remove the ether, and concentrated the uranium in the aqueous phase. The solution was then diluted to a desired volume and an aliquot was removed for either fluorometric or colorimetric analysis.

Table II lists data obtained from pure solutions and shows that repeated use of the column is possible for small samples and that the precision of the method is good. The uranium was analyzed fluorometrically. Although repeated use is possible, for accurate work on large samples with little uranium, a new column should be prepared for every run. Table I shows a comparison of results obtained with the ethyl acetate and cellulose column separations.

Dilution Method. Price (7) has described the dilution method whereby large dilution factors reduce the concentration of interference ions and still permit the fluorometric analysis of uranium. This procedure is applicable if the uranium-quencher ion ratio is above a certain level. With the instrumentation described below, the dilution method required a uranium-iron ratio greater than $1/100$ to give a reading six times above blank (10.0 γ of iron could be tolerated in the dish and 0.1 γ of uranium gave a reading of six times blank). Quenching of the fluorescence is dependent solely on the absolute amount of quencher present, not the uranium-quencher ratio (7).

Table II. Extraction of Standard Uranium Solutions Using an Activated Cellulose Column

(Analyses done fluorometrically)

Sample	Column	Uranium Added, γ	Uranium Found, γ	Recovery, %
1	A	1.0	0.99	99
2	A	2.0	1.86	93
3	A	3.0	3.10	100
4	A	3.0	2.81	94
5	B	5.0	4.75	95
6	C	10.0	9.6	96
7	C	20.0	20.5	100
8	D	30.0	29.8	99
9	D	30.0	30.7	100
10	E	50.0	50.0	100
11	E	50.0	50.0	100

DETERMINATION

Fluorometric. Many procedures (5, 10, 13, and others) have been described in the literature for the fluorometric method of determining uranium. However, all differ in some respects as to instrument design, methods of separation, effect of gold versus platinum or silver fusion dishes, and other details. The procedure outlined below also differs from published procedures in some important details and is especially adapted to natural silicates containing 0.1 to 10 parts per million of uranium.

Figure 2. Vertical Cross Section of Circular Chromium-Vanadium Steel Die for Forming Gold Dishes

REAGENTS AND EQUIPMENT. **Instrument.** The fluorometer used is the same in principle as the transmission type described by Grimaldi *et al.* (5) except for some details of construction. It was not found necessary to adjust the height of the ultraviolet source more than once every few months and fine adjustments of response were readily made electronically. By keeping the ultraviolet source and the photomultiplier tube 60 to 80 cm. apart, it was not found necessary to use a fan for cooling. The response of the photomultiplier tube was measured with a Photovolt Model 520M line operated instrument. In nearly 2 years of service, this instrument required only occasional adjustments. This particular model has over a hundredfold reserve sensitivity for this application with a Hanovia ultraviolet source (Type SH). A neutral gray filter was placed in front of the photomultiplier tube so that all four scale multiplier ranges could be used.

Fusion dishes. Fine gold disks 0.016 inch thick and 2 inches in diameter were pressed in a steel die (see Figure 2) to form a depression about $1\frac{3}{4}$ inches in diameter and $\frac{5}{16}$ inch deep with a $\frac{3}{16}$ inch rim. The dishes were reformed in the die after each fusion; boiling for a few minutes in 1 to 1 nitric acid cleaned the dishes very effectively.

Dish holder. A holder for the gold dishes was made by wiring silica rods on stainless steel blocks to a plate of stainless steel $4 \times 10 \times \frac{1}{4}$ inches. The tray was supported on three stainless

steel legs $\frac{1}{2}$ inch in diameter and 1 inch high. The V blocks and silica rods were arranged in squares so that the gold dishes were supported by their rims and did not touch any stainless steel. The tray held 10 gold dishes and was manipulated in the furnace by a 2.5-foot detachable handle that just fitted between the legs of the tray.

Furnace. Lindberg Model B-2 with 291 indicating pyrometer and automatic controller, Lindberg Engineering Co., Chicago, Ill.

Flux. As described by Grimaldi *et al.* (5), 9.0 grams of reagent grade sodium fluoride were mixed with 45.5 grams each of reagent grade sodium carbonate and potassium carbonate. This mixture was fused at 660°C . in a platinum dish and the cake was broken up, ground, and sieved through an 80-mesh sieve. Flux with a uniform blank was also made by thoroughly mixing 453 grams of sodium carbonate with 453 grams of potassium carbonate and 89.7 grams of sodium fluoride. This mixture was then fused in batches. The ground flux was stored in a well-stoppered container and placed in a warm place to reduce adsorption of moisture.

Standard uranium solutions. Same solutions as those described above in connection with the ethyl acetate extraction.

Permanent fluorescent standard. A permanent fluorescent standard was made by mounting a 1×1 cm. piece of a Corning No. 3750 filter in a piece of brass that could replace a sodium fluoride-sodium potassium carbonate disk in the fluorometer. By exposing the fluorescent glass through a $\frac{1}{16}$ -inch diameter hole, in the brass, a reading equivalent to 0.60γ of uranium was obtained. This reading varied by $\pm 4\%$ over a period of 18 months, if the glass were kept clean.

PROCEDURE. A 1- or 2-ml. aliquot from the ethyl acetate extraction was placed in a gold dish and flamed off by igniting with a gently burning match. Dishes were placed on an aluminum plate $1\frac{1}{4}$ inches in thickness, to conduct heat away, thus preventing splattering and permitting even burning. Usually six to eight samples were run in one tray with one or two standards, a flux, and a procedure blank. The standards were prepared by placing 1 ml. of a solution containing 1.00 or 10.0 γ of uranium in a gold dish and evaporating under an infrared heat lamp. The aqueous solutions of samples from the chromatographic or dilution procedures were treated the same way as the standard uranium solutions. Flux blanks were made by adding the flux to clean gold dishes. Two and a half grams of flux were added to each gold dish and the set of 10 dishes was placed in the preheated tray. One standard was usually in the front of the furnace and one in the back, to detect any effect caused by temperature gradients in the furnace. An automatic pyrometer in the furnace was set at 660°C . After 3 minutes in the closed furnace, the whole tray was shaken in the furnace by means of the 2.5-foot detachable handle, using asbestos gloves. Shaking was continued with a vigorous swirling motion until the flux in the front dishes became solid. The furnace was then closed and fusion was continued for 27 minutes, the tray was removed, and the flux was allowed to solidify. The solid flux disks were removed from the dishes after the latter had cooled on an aluminum plate. The disks can be conveniently marked with an ordinary pencil. The disks were placed under infrared heat lamps for 10 minutes to stabilize the fluorescence (13), and allowed to cool; their fluorescence was measured in the fluorometer.

The fluorometer was adjusted to read zero when no light was striking the photomultiplier tube. The ultraviolet source was adjusted so that 1 γ of uranium gave a reading of 100 on the $\times 10$ scale. One microgram of uranium standard therefore read 1000 units and the permanent glass standard read about 600 units. The disk containing 1 γ of uranium was arbitrarily set to read 1000 and all the other disks were read, checking the arbitrary and permanent standards again at the end. The uranium content of the samples was calculated as follows:

$$\frac{\text{Sample reading} - \text{procedure blank}}{1000 - \text{flux blank}} = \gamma \text{ of uranium in flux disk}$$

Aliquot factors were then applied. Usually, flux blank = procedure blank = 15 ± 2 units (1 γ of uranium = 1000 units).

Calibration curve. Under the conditions described above, the fluorescence was directly proportional to uranium content from 0.010 to 50.0 γ of uranium in the flux disk. Above 50.0 γ of uranium, linear response failed. This failure is probably due to self-reversal effects and incomplete irradiation of the disk. It is very important that the uranium be uniformly distributed throughout the flux disk; otherwise the linear response will fail at concentrations far below 50.0 γ . Uneven distribution of the uranium in the flux disk can be observed visually. A portable

Mineralight, Model M12, is convenient for visual observation of the fluorescence and 5.0 γ of uranium in the flux disk gives an easily visible fluorescence. Flux disks containing more than 20.0 γ of uranium were regularly checked visually for uniform fluorescence. Uneven distribution of fluorescence in standard disks always correlated with lower than expected fluorescence. It was observed that uniform fluorescence was easier to obtain with ethyl acetate than with aqueous solutions, but vigorous swirling after 3 minutes of fusion (see procedure above) gave uniform disks with very few exceptions.

Effect of Time and Temperature of Fusion. Experiments indicated that the higher the temperature, the shorter the time necessary to reach maximum fluorescence. However, the reproducibility was less satisfactory at higher temperatures. Also there was some quenching or lowering of the fluorescence at higher temperatures, probably because more gold was being dissolved from the dish. Gold is known to be a quencher as well as platinum (5). At 650°C . maximum fluorescence was reached in about 15 minutes as compared with 5 minutes at 900°C . However, the best reproducibility at about 650°C . was obtained with a 30-minute fusion with vigorous swirling after 3 minutes in the furnace. A pyrometer setting of 660°C . was adopted for the fusion temperature because: (1) there was no evidence of enough gold being dissolved to quench the fluorescence; (2) this temperature is easily checked as it is the melting point of aluminum; (3) the time of 30 minutes is not inconvenient for the fusion of ten disks; and (4) this temperature minimized as far as possible the oxidation of the dish tray and heating elements, which have withstood hundreds of fusions without deterioration.

Interfering Elements. Interfering elements have been discussed elsewhere (5, 13). The most common interfering element encountered was iron, which quenches the fluorescence. Experiments showed that under the conditions described about 10.0 γ of iron could be present in the gold dish without causing detectable quenching. Concentrations of 10.0 γ of iron per ml. in the aqueous or ethyl acetate solution could readily be detected by adding a drop of 1% potassium thiocyanate solution to separate portions. The potassium thiocyanate solution also develops a color with many of the other quenching elements. A general quench test was run on about 1 out of 10 samples by a "spiking" technique. A spike, usually 1 γ of uranium, is added to a dish containing a separate aliquot. If there is no quenching, the spiked aliquot will give a reading 1000 arbitrary units minus the procedure blank higher than the unspiked aliquot. Spikes were also added to the aluminum nitrate solution to test both extraction efficiency and quenching.

Precision and Accuracy. Using pure uranium solutions, over 500 determinations by 8 different operators of points on the calibration curve gave an average deviation of $\pm 2.8\%$. With 1.0 γ of uranium in the disk, the lowest and highest value differed by 10% or 0.1 γ of uranium. The average precision of replicate determinations was $\pm 7\%$ of the amount present down to concentrations of about 0.08 γ of uranium in the disk. This is comparable to precision reported elsewhere (5). The use of quenching and extraction plus quenching spikes as described in the previous paragraph indicated that errors do not show a random distribution, but tend to be systematically on the low side. Imperfect extraction and undetected quenching probably offset positive errors caused by evaporation of ethyl acetate or contamination. Contamination was rarely observed in flux or procedure blanks, though it was necessary to work in a room with filtered air and to maintain careful technique. Tables I and III give a comparison of analytical results obtained on the same sample in several laboratories and using various techniques of separation and determination, including isotope dilution. Some of the differences in values shown may well be due to the difficulty of thoroughly homogenizing the samples, rather than to the analytical procedures. The higher than average specific gravity of uranium minerals increases the difficulty of thorough mixing.

Table III. Replicate Analyses on Carnotite Ore

Sample Number		Uranium in Carnotite Ore, %	
		Fluorometric	Colorimetric
07456	A-1	0.21	0.22
	A-2	0.30	0.30
17457	B-1	0.26	0.26
	B-2	0.25	0.25
07458	C-1	0.26	0.27

Figure 3. Relationship of Color Intensity with pH after Reagent Addition and after Final pH Adjustment to 7.0

A. Color intensity of uranium dibenzoylmethane complex vs. pH after reagent addition
 B. Color intensity of same solutions after adjusting to pH 7

The data in Table III illustrate the importance of thorough mixing; A, B, and C in Table III are three different samples taken from an ore stockpile, using a Jones sample splitter. The duplicate analyses on A illustrate the danger of taking small sample weights for analysis. The same ethyl acetate solution was used for the fluorometric and colorimetric determinations.

COLORIMETRIC

Many reagents have been proposed for the colorimetric determination of uranium. Rodden (10) has tabulated a number of such reagents, however the majority of them are neither sensitive nor specific enough for solutions containing less than 5 p.p.m.

Yoe, Will, and Black (12) have recently examined a large group of organic compounds to determine their suitability as colorimetric reagents for uranium. Upon completion of their investigation they proposed using dibenzoylmethane (1,3-diphenyl-1,3-propanedione) as a colorimetric reagent for uranium. This reagent proved satisfactory for solutions having a concentration of from 0.2 to 10 p.p.m. with a reported sensitivity of 0.05 p.p.m. As with other colorimetric methods for uranium, the fact that many other metallic ions develop similar colors with the reagent is a difficulty. Here again the success of the method depends upon the effectiveness of the separation.

Yoe's procedure was investigated and, with certain adaptations, found to be very suitable for some of the work carried on in this laboratory. Yoe suggested using multiple ether extractions; however, this is time consuming and involves certain hazards. Experimentation has shown the ethyl acetate extraction to be efficient, selective, and much faster than the multiple ether extraction.

Procedure. The procedure followed was essentially that as outlined by Yoe with the following alterations. A wave length of 400 m μ was used rather than 395 m μ , as less interference from the light absorbed by the reagent was encountered. The slope of the absorption curve permits this change. Ten-centimeter absorption cells were used when the solutions contained less than 1.0 p.p.m. of uranium, thereby lowering the limits of the method

without resort to evaporations. A solution of 0.25 p.p.m. gave an absorbance of 0.190 using 10.0-cm. cells, while a solution containing 0.04 p.p.m. had an absorbance of 0.028. An aliquot of 5 ml. of ethyl acetate from the extraction procedure outlined above was placed in the alcoholic medium in which the color was to be developed. The addition of ethyl acetate had no effect upon the intensity and stability of the color developed, nor did the quantity of the ethyl acetate added affect the color in any manner.

Yoe also stated that the solution in which the color is to be developed should be adjusted to an "apparent pH" (as measured with a glass electrode) of from 5.0 to 5.5 so as to facilitate maximum color intensity upon the addition of the reagent. It is true that maximum color develops at this apparent pH; however it should be pointed out that hydrolysis of uranium begins to occur slightly beyond this point (pH 6) and that the adjustment of an unbuffered solution to this pH is difficult. As shown by Figure 3, it has been found that although maximum color is not developed at lower apparent pH (2 to 4), it does develop as soon as the final adjustment to apparent pH 7 is made, and that regardless of the pH at the time of the reagent addition the final intensity will be the same.

Under the conditions described, the alcoholic solution after addition of the ethyl acetate from the extraction had an apparent pH of from 3.0 to 3.5 at which point the reagent addition can be made safely, minimizing the possibility of hydrolysis, and omitting the inconvenient procedure of adjusting an unbuffered solution to an apparent pH of 5.5.

Precision and Accuracy. The reagent blank, when compared against a blank composed of ethyl alcohol, ethyl acetate, and water in 10.0-cm. tubes, had an absorbance of 0.130 ± 0.006 . Since the lower limit of the determination has been established at 0.20 p.p.m. this necessitates that 10.0 γ of uranium be present in the 50 ml. of solution in which the color is developed. The absorbance of solutions containing 0.4 p.p.m. of uranium could be read reproducibly with an accuracy of better than $\pm 5\%$.

These additions and adaptations to the method advanced by Yoe greatly reduced the time required for the analysis without impairing its accuracy and yielded a procedure which was faster than the fluorometric. Table III shows the comparative results obtained by using both the fluorometric and colorimetric procedures.

ACKNOWLEDGMENT

The authors wish to acknowledge their indebtedness to Farrington Daniels, the director of this contract, and to the other project personnel who collaborated at one time or another on this work. Thanks go particularly to Charles A. Berridge, James M. Fraser, Thomas J. Katz, and Marjory A. Miller for their experimental work. The assistance and many courtesies of F. S. Grimaldi and his associates at the Trace Elements Laboratory of the U. S. Geological Survey greatly expedited this work.

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RECEIVED for review March 13, 1954. Accepted June 21, 1954. The work described was done under Contract No. AT (11-1)-178, Research Division, U. S. Atomic Energy Commission.

A SPECTROGRAPHIC METHOD FOR THORIUM

Final Report

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United States Atomic Energy Commission Contract

AT (11-1) -178

August

1953

ACKNOWLEDGEMENTS

The author wishes to thank Professors Norris F. Hall and Farrington Daniels for their academic assistance and also Mr. Rubin Shapiro for instruction in the operation of the spectrograph and especially for the information concerning the rotating silver electrode system which he is developing for general use.

A Spectrographic Method for Thorium *

When the problem of analysing for small amounts of thorium was considered, it was noted that the success of the few methods available for the determination of thorium depend on the complete elimination of interfering elements many of which are much like thorium and usually predominate in the minerals and rocks in which thorium is found. The problem of removing these elements would be very difficult and tedious in a case where the thorium was present only to the extent of 50 ppm in a sample which might contain 1-10% zirconia or ceria. For these reasons it was hoped that it would be possible to develop a method of determination which would not be dependent on the complete removal of interferences.

Spectrographic methods are unusually free of interferences and so can be applied in some cases without preliminary separations of any kind. The dispersion of the spectrograph does a very good job of separation.

Spectrographic methods for thorium have not been extensively studied, but it is known that due to the large number of lines in its emission spectra that very few of its lines are sensitive in the usual spectrographic sense. Therefore a certain degree of concentration would be necessary to analyze in even the semi-micro range. Any type of concentration procedure naturally involves some separations but the element sought can be carried on any other convenient element through the separations. Also in the case of a concentration procedure the separations need be made only from the main body of the rock or mineral which may be composed of elements vastly different from the thorium and correspondingly easy to remove. A concentration of this sort needs to be quantitative only in that none of the thorium is lost.

* Thesis submitted for the Master of Science degree, University of Wisconsin, January, 1953.

Because of this necessary concentration the thorium can be most conveniently excited as a solution. There are a number of different methods of spectrographic solution excitation but the so called rotating disk method was used in this series of experiments because of its simplicity and availability.

In this method a rotating graphite disk is used as the lower electrode. The lower edge of the disk is in contact with the solution contained in a porcelain combustion boat; and the discharge is between the top edge of the disk and a 120° pointed 1/4" graphite rod as the counter electrode. The solution is carried into the discharge by the rotation of the disk. The disk itself is 1/2" in diameter, 1/8" thick and has a 1/8" hole for mounting on a steel arbor. The axis of rotation is horizontal and perpendicular to the optic axis of the spectrograph.

In the choice of internal standards the criteria were; the standard must be excited in a manner similar enough to thorium to produce satisfactory working curves and the standard must be dissimilar enough from thorium that there would be little likelihood of it following thorium in any chemical separation procedure or occurring in minerals in which thorium is found, it must also have lines near the thorium analysis line.

The first results in preparing a spectrographic working curve for thorium that were successful to any degree were obtained by using molybdenum as the internal standard. The thorium line used was Th 4019.137A, the most "persistent" line of thorium. The molybdenum line used was Mo 4021.015A. A high inductance spark of about 4.5 amps was used. It was possible to obtain straight-line working curves but it was first necessary to subtract the intensity of a line of the cyanogen band spectrum which coincided with Th 4019.137A. The intensity of CN 4019.1

was calculated from the intensity of CN 4050.7 which was measured at the same time as were Th and CN 4019.1 and Mo 4021.0. However, the presence of this cyanogen interference placed a serious limitation on the sensitivity of the method; and corrections of this type are to be avoided because of the additional errors introduced.

For these reasons a change was made to silver electrodes in order to eliminate the cyanogen band spectra. This had its problems too, for it was difficult to remove the molybdenum from the electrodes between exposures and the results in general were poor. It should be noted that ordinarily silver electrodes can be cleaned simply by treatment with concentrated hydrochloric acid and distilled water; they can be reused indefinitely.

Then manganese was tried as internal standard and good results were obtained using Mn 4018.102. No corrections for background were needed and the curves obtained were good. However, results were not sufficiently reproducible from film to film. This was thought to be due to errors in photographic processing. Errors in the processing are serious at 4000A with the film used, Spectrum analysis no. 1, due to its very high contrast at this wavelength. Using Spectrum analysis no. 2, which does not have this property was not possible since it is not suitable for general work and changing the film was not a simple matter. No problem would be involved on a plate spectrograph. Excitation conditions were similar to those for the method described below. An attempt to decrease the contrast of the film by using soft working developers had little effect.

Another "persistent" line of thorium, Th 2837.299A, was in a more convenient part of the spectrum for photographic processing and could be used with silver electrodes although the use of graphite was almost impossible due to the spark lines C 2836.71 and C 2837.60 which cause interference because of the wide

slit widths needed for quantitative spectra. The use of manganese for the internal standard was no longer feasible since there are no suitable manganese lines near the analysis line.

Chromium was next tried as the internal standard and seemed to show some promise; Cr 2835.633A was the line used. However, it was found that the chromium intensity was varying with the thorium intensity. This was countered by adding excess acid to the solutions so that the pH was near 1.0. This system worked well and it was possible to measure thorium down to a concentration of four micrograms per ml. but corrections were needed for background. This compares with the five micrograms per ml. detection limit obtained by Nachtrieb with similar optical equipment and a copper spark technique. This might well be the lower limit of the sensitivity of thorium analysis unless one used a spectrograph of higher dispersion or one that had much better limitations on stray light in the optical system. The detection limit in most cases is determined by the line to background ratio and the background must be limited in some way if the sensitivity is to be increased. In the final working curve preparations the aperture of the spectrograph was reduced so background corrections would not be necessary. This reduced the sensitivity to about ten micrograms per ml.

The working curve resulting from three separate runs on similar solutions is shown in Figure I and the conditions necessary for its preparation are given as follows:

Spectrographic equipment:

1.5 meter original grating spectrograph
projector -- comparator -- densitometer

arc spark source unit

solution excitation attachment

film developing machine

film drying machine

all of the above are products of Applied Research Laboratories.

Preparation of solutions:

5 ml. of chromium chloride solution - 0.1 mg per ml

0.4, 0.6, 1, 2, 4, 6, and 10 ml. of thorium chloride solution

25 ml. hydrochloric acid diluted 1 to 10 (1 mg per ml)

The above was diluted to the mark in 100 ml volumetric flasks.

It should be noted that all experiments were conducted with chloride as the only anion present; early experiments indicated that nitrate in solution decreases the sensitivity of the thorium.

Excitation conditions:

The silver disk was rotated at seven revolutions per minute. The electrode separation was three millimeters. The slit was set at 60 microns. The input voltage to the source unit was controlled to 240.0 volts. The spark inductance was 1440 microhenries and the capacitance was 0.014 microfarads. The spark transformer was rated at 25,000 volts. The electrodes were presparked for 10 seconds prior to an exposure of 50 seconds. The grating aperture doors were set at 6 and 6.

Photographic processing:

Spectrum analysis no. 1 film was used for all work. After exposure the film was immersed for 10 seconds in water, developed for 3 minutes in D-19, stopped for 10 seconds in 5% acetic acid, and fixed for 1 and 1/2 minutes in F-5.

All of these solutions were thermostated at 20.0°C. and the trays were rocked during processing. The film was washed for two minutes in tap water, rinsed in distilled water, drawn through two damp viscose sponges and dried for two minutes on the drying machine.

The emulsion was calibrated by the two step filter method as described by Churchill. The comparison spectra of iron was run through the step filter on every film processed in order to have a check on the photographic processing.

Calculations:

The calculations were done in the usual manner; the percent transmission of the lines was read on the densitometer and these values were referred to the emulsion calibration curve to obtain relative intensity values. When background corrections were made they were done by subtracting background intensities from the line intensities. The ratios of the intensities of the analysis line and the internal standard line were plotted against concentration on log-log paper.

Conclusions:

The results that were obtained were not completely satisfactory and they probably could be improved by using a higher concentration of chromium in the solutions and a more rigid control of the developing. However, if one were permitted to sacrifice sensitivity better working curves could be obtained by stopping down the aperture of the spectrograph until no background was noticeable. This is the policy in cases where the element to be analyzed has lines of more generous intensity.

In the M. I. T. Wavelength Tables an inferring line would be noted as SC 2837.293A; it is believed that this is not a scandium line but in all probability the thorium line. It is very hard to separate thorium and scandium and 0.006A. Further study of interferences was not possible because of limited time.

Figure I

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Alpha-Particle Autoradiography with Liquid Emulsion

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The problem of track and particle registration, encountered with nuclear emulsion plates, is avoided by liquid emulsions (1, 2) that are not removed from the radioactive specimen throughout the autoradiographic process. Although thin sections of rock were the subject of the present study, the method should be applicable in alpha-particle autoradiography of many different types, e.g., histology and botany.

Procedure

The following procedure was developed during a study of Wisconsin granites and related rocks (3).

1. Thin sections are made of the rock specimen by the standard method, except that the cover glass and its cement are omitted. The excess cement holding the thin section to the microscope slide is scraped off, and debris from grinding is removed by washing with ethanol.

2. After attaining radioactive equilibrium with respect to radon (approximately one month), the thin section is dipped in the emulsion binder solution and dried in a horizontal position.

3. When the emulsion binder is firm, Kodak NTA bulk emulsion, heated to fluidity in a 45° C water bath, is applied as uniformly as possible to the binder-coated top of the thin section. Darkroom conditions must be maintained, as Kodak NTA emulsion is light-sensitive. A medicine dropper is used to apply the emulsion, thickness (50-75 microns) being readily controlled with a little practice.

4. The emulsion layer is dried in an air stream. The loaded specimen is then stored at 5° C in a light-tight box. Exposure time depends upon the alpha-particle flux and the particular problem. With Wisconsin granites, 20 days gave an adequate density of alpha-particle tracks.

5. At the end of the exposure period, the emulsion is developed. The devel-

opment process is: (a) 15 min presoak in 3% chrome-alum hardening solution at room temperature; (b) rinse in distilled water; (c) develop 2 min in Kodak D-8 at 18° C; (d) stop bath—1 min in distilled-water wash at 0° C or 1 min

PHOTOMICROGRAPH-AUTORADIOGRAPH showing alpha-active allanite as core material to pleochroic halo in biotite (magnification: 250×; plane-polarized light); three dark portions of biotite surrounding alpha-emissive allanite are optically continuous

Autoradiographic Materials

Experimental liquid Kodak NTA
Emulsion stored at 5° C

Emulsion binder: dissolve 25 gm of soft gelatin in 250 ml of distilled water at about 60° C; allow it to stand for ½ hr; filter off the unhydrated gelatin; add 2.5 ml of 5% chrome alum and 10 ml of 0.2% wetting agent (Aerosol)

Hardening solution: 3.0% chrome alum in distilled water

Kodak D-8 developer

Prefixer hardening solution: 15 gm chrome alum and 30 gm anhydrous sodium sulfate in 1,000 ml of distilled water

Kodak Rapid Fixer with hardener or Kodak F-5 Fixer

Darkroom conditions: Wratten Series OA filter over 7½-wall safelight

in 3% acetic acid solution at room temperature; (e) 5 min in prefixer hardener at room temperature; (f) fix—twice time to clear in Kodak Rapid Fixer plus Hardener (F-5 is satisfactory, but slower); (g) wash—60 min in running tapwater; (h) dry developed emulsions in a horizontal position to prevent slumping of the softened emulsion and consequent rupture of alpha tracks.

6. When the emulsion is completely dried, the specimen is examined with a petrographic microscope. By focusing on the thin section, the mineral grains can be identified by conventional methods. By focusing on the emulsion above the thin section, alpha-particle tracks can be studied at 210 or 450 magnifications with regard to density and mineral of origin.

Discussion

This procedure produced highly satisfactory autoradiographs (see illustration).

At 450 magnifications it is impossible to detect the emulsion-binder thickness. Curling and peeling of emulsion from the thin section were noted when emulsion binder was not used. Peeling of the emulsion and thin section from the microscope slide occurred when the thin section was not firmly cemented to the microscope slide. After one year, emulsions showed no sign of deterioration.

Background was determined by carrying blank microscope slides through the autoradiographic procedure. Background was about 5 alpha-particle tracks per square centimeter of developed emulsion. The background tracks were produced predominantly from alpha-emitting nuclides in the emulsion itself.

Even when stored at 5° C, the bulk emulsion, air-expressed from Eastman Kodak Company immediately after preparation, did not remain in useable condition indefinitely. After a month or so, it separated.

* * *

The authors would like to thank the Eastman Kodak Company, especially W. F. Swann, for supplying the experimental Kodak NTA bulk emulsion gratis and arranging for its quick delivery. This research was supported by AEC research contract AT(11-1)-178.

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