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REPORT

WORKSHOP ON DATING
OLD GROUND WATER

March 16-18, 1978

The University of Arizona
Tucson, Arizona 85721

This report was prepared by The University of Arizona under subcontract 19Y-55412V with Union Carbide Corporation, Nuclear Division, under contract number W-7405-eng-26 with the Department of Energy. The subcontract was administered by the Office of Waste Isolation.

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WORKSHOP ON DATING
OLD GROUND WATER

March 16-18, 1978

The University of Arizona
Department of Hydrology and Water Resources
Tucson, Arizona 85721

Conference Chairman:
Stanley N. Davis

Cooperating University Departments:
Geosciences
Hydrology and Water Resources
Physics

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May 20, 1978

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INTRODUCTION

A workshop on methods which might be used to date very old ground water was held on March 16-18, 1978, in Tucson, Arizona. The workshop was sponsored by the Office of Waste Isolation of Union Carbide Corporation as part of studies supported by the United States Department of Energy which are designed to evaluate the safety of proposed subsurface repositories for nuclear waste. The workshop was convened by the College of Earth Sciences of the University of Arizona with the cooperation of other university departments, particularly the Department of Physics.

The dating of ground water in the vicinity of nuclear repositories is a critical aspect of the safety evaluation of these repositories. The age of the water gives an indication of past rates of water movement which in turn will help evaluate the likelihood of future migration of radionuclides from a given repository. Despite this rather obvious practical application, most of the workshop time was devoted to difficult technical questions related to the actual dating of the water.

The present manuscript was written cooperatively by all participants of the workshop, hence no separate authorships are indicated in the body of the report. A list of the participants with their institutional affiliations are given in the Appendix, Part A. In addition, several participants as well as two researchers who could not attend submitted detailed statements on various aspects of the problem. These contributions are photocopied from the original manuscripts and are given without editing as parts C through L of the Appendix. Authorships of these sections are indicated.

A total of 34 researchers from 24 separate organizations in seven countries participated in the workshop. These individuals brought to the workshop an unusually broad background of training and research experience. The enthusiasm and hard work of all participants, we trust, will be reflected in the summary report which follows.

GENERAL PRINCIPLES

The "age" of ground water can be defined as the length of time that the water has been out of contact with the atmosphere. This age can be estimated by at least six different methods. First, if average prehistoric hydraulic gradients, fluid conductivities, and effective porosities along the entire flow path of the ground water can be determined, then Darcy's law and related equations can be used to determine the average velocities along various segments of the flow path. The lengths of these segments can generally be estimated, so the total travel time to any given point along the flow path can be calculated.

A second method is based on a prior knowledge of the late Cenozoic history of a region. For example, shallow ground water high in dissolved solids might be associated with a dated high stand of the ocean, or anomalously high concentrations of argon in ground water might suggest that the water entered the subsurface during a period of extremely cold weather. In a similar but more complicated way, stable isotope ratios such as $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ might be related to past climatic changes in a given region.

A third and widely used method is to measure the age or time of isolation from the atmosphere by measuring the concentrations in the ground water of radionuclides which are assumed to originate only in the atmosphere. To obtain actual ages, the input activities of the radionuclides must be known. Radionuclides of primary interest for dating very old water are ^{14}C , ^{36}Cl , and ^{81}Kr .

A fourth method uses the accumulation of certain products of radioactive decay in the ground water as an index of age. Although other possibilities exist, helium is the only element used thus far in the United States.

A fifth method might use extrapolated rates of structural changes of certain molecules which are assumed to be dissolved by the ground water during or shortly after the water entered the subsurface. Amino acids in solid materials have been used to estimate ages of these materials. The method could, theoretically, be extended to the dissolved amino acids in ground water.

A sixth method utilizes the disequilibrium between parent and daughter radionuclides as an index of water age. This method has been applied to

$^{234}\text{U}/^{238}\text{U}$ disequilibrium but could be extended to other radionuclides produced by uranium and thorium decay.

All methods except the first were discussed by participants of the workshop. The first method was an important part of the discussions of a recent workshop held in Austin, Texas. No attempt was made to duplicate the earlier workshop. Nevertheless, it cannot be emphasized too strongly that hydrodynamics of ground-water flow must be investigated thoroughly along with radiochemical and other methods of dating. An understanding of the well construction details, sampling methods, presence of drilling fluid, hydrodynamic dispersion and mixing, as well as other hydrologic factors such as natural cross flow between aquifers are important in all dating methods. The relation between dating and dispersion is discussed in Part C of the Appendix.

The workshop held in Tucson centered on methods to date water older than 50,000 years. All workshop participants, however, agreed that methods to date younger water are also very important. Calibration of dates of older water from a given aquifer can be assisted by the availability of younger dates hydraulically upgradient in the same aquifer. Also the detection of younger water along with older water would be one measure of past hydrodynamic dispersion. Finally, the presence of a nuclide of short half-life in a water of great age would, of course, suggest contamination of the sample, perhaps by cross flow in a well or seepage of near-surface water into a spring near its orifice.

An important limitation of the workshop was the requirement that the development time for dating methods be limited to three years or less. This limitation was imposed because of the extreme urgency of waste-disposal problems.

CARBON-14

Principles

^{14}C is a radioactive isotope of carbon. It is produced in the atmosphere by a reaction between nitrogen and the natural cosmic ray neutrons. After it is formed, ^{14}C is oxidized to $^{14}\text{CO}_2$ which mixes rapidly with the atmospheric carbon dioxide. The resulting natural ^{14}C concentration in atmospheric CO_2 is about 10^{-12} , which is equivalent to a specific activity of 13.5 disintegrations per minute per gram of carbon.

Through assimilation of CO_2 , all plants contain the same ^{14}C concentration as the atmospheric CO_2 . In the ground, decomposing plant remains generate CO_2 which dissolves in rain water seeping into the soil. This CO_2 -rich water is able to dissolve carbonates present in the soil, which are generally assumed to be very old and, therefore, contain no ^{14}C . The result is that the ground water of recent age contains ^{14}C at a concentration which is somewhat more than half the atmospheric ^{14}C concentration. The resulting specific activity thus is about 10 dpm/gram of carbon. Assuming a dissolved inorganic carbon content of the ground water of two millimoles per liter (equivalent to about 120 mg of bicarbonate), the activity of recent ground-water is about 0.25 dpm/liter of water.

The ^{14}C activity decreases in the course of time and consequently (during the ground-water flow) at a rate which is very well known: 0.12 %/oo per year, which is equivalent to a half-life of 5,730 years.

Assuming the ^{14}C activity in the atmosphere has been constant over the last few hundred thousands of years--and there are good reasons to believe that this has been very nearly true--the known decay rate in principle allows an age determination by measuring the remaining ^{14}C activity of a water sample.

Due to chemical processes underground in which carbon is involved, the situation is somewhat more complicated for most ground water. However, additional chemical and stable carbon isotopic ($^{13}\text{C}/^{12}\text{C}$) analyses allow us to make reasonable estimates of the original amount of ^{14}C in the ground water. During recent years, several more-or-less generally applicable models have been developed to understand ground-water flow directions and rates, in many cases quite well.

Present State-of-the-Art

Two counting techniques are presently available and have been in routine operation for many years. The one uses proportional gas counters where the ^{14}C activity is measured in the form of carbon dioxide, acetylene, or methane. The other uses commercially available liquid scintillation spectrometers in which the ^{14}C is counted as benzene. Both techniques, consequently, need more-or-less extensive sample preparation set-ups in which the original CO_2 extracted from the ground-water sample is converted into the proper chemical compound.

Both counting techniques require certain amounts of carbon in order to have the apparatus operated on a routine basis. Moreover, the necessary precision of analysis requires a certain amount of sample. In general, the "sizes" of the counters are such that, as a minimum, an equivalent of about 1 gram of carbon is needed. This allows a 1% precision and a maximum measurable age of 40,000 years on a one-sample-a-day basis. In general, therefore, a sample of ground water having a volume of 40 to 100 liters is required.

In order to increase the age range beyond 40,000 years, larger quantities of sample are required. At present, counters are in operation which allow ages to be established up to 60,000 years. In this case, however, the estimated amount of sample required is in the order of 1,000 liters.

Using the thermal diffusion isotope enrichment technique prior to the ^{14}C activity measurement, ages of up to 75,000 years can be obtained, provided 5 m^3 of water sample is available. Although this technique is in operation at two places (Seattle, Washington, and Groningen, Netherlands), it has not yet been applied to dating ground water.

Problems with Interpretation

Accurate measurements of ^{14}C in ground water are essential but not sufficient for the determination of accurate ages of ground water. Other factors such as the mixing of waters of different ages or the loss of ^{14}C from ground water during its passage through aquifers must be considered before ages of different water samples can be deduced from measurements of ^{14}C .

The extent of mixing of older water with younger water can be estimated sometimes by measuring two radionuclides with considerably different half-lives. Thus tritium (^3H) measurements can be combined with ^{14}C measurements. Also, ^{39}Ar measurements (if available) might be used for waters up to 1,000 years old which are mixed with still older waters to be dated by ^{14}C .

Additions of stable carbon to the water and the losses of ^{14}C from the waters to rock will arise with carbonate reactions between the rock and the ground water. Geochemical models of the aquifer can be established from measurements of water chemistry and ^{13}C content of the water and the rock. These models are essential to the correct interpretation of ^{14}C analyses, and significant corrections to the apparent age of the water can result.

Problems may arise where the $\delta^{13}\text{C}$ values of the water are near those of the rock. In which case, very large corrections, with equally large uncertainties, may have to be applied. Corrections in some ground-water systems may not even be possible. In these situations, more reliance must be placed on other data for the establishment of the correct geochemical model. The extent and nature of corrections applied may not only affect the reported ages of water but may also affect the uncertainties of those ages because of uncertainties in all basic data including the ^{14}C counting statistics used in the geochemical models. This point is not always appreciated, but it can be an important limitation on the use of ^{14}C for dating ground water.

Research Objectives

^{14}C measurements to 10^{-2} percent of modern concentrations are now made routinely in two laboratories using thermal diffusion enrichment and gas counting. Sample sizes of 100 grams of carbon (5 m^3 of water of 2 millimoles total dissolved carbon per liter) are required. Recently it has been demonstrated that in the near future equivalent detection limits can be achieved with tandem Van de Graaff techniques but with sample sizes of tens of milligrams of carbon or less. Although not demonstrated, it is highly probable that cyclotrons can achieve similar results.

Waters of great age should be most common in deeply buried sedimentary rocks and rocks of limited permeability nearer the land surface. Water samples of more than a few hundred milliliters would be very difficult to obtain from rocks of low permeability. Therefore, sensitive analytical techniques requiring only small samples would be of great value, and their development should be encouraged.

The tandem Van de Graaff machine presently in use by the University of Rochester is presently limited by instrumental noise to about 0.5% of modern ^{14}C (corresponding to the equivalent of 40,000 years before present). To eliminate the instrumental noise, an investment of about \$230,000 would be required. This initial work would take about one year. Following the improvements, about 100 samples per year of 10 mg carbon could be measured to $10^{-2}\%$ of modern (70,000 year equivalent) and could be analyzed at about \$250 per sample. The probability of success is very high. A precision of detection of $10^{-2}\%$ of modern has already been achieved, but not routinely. The investment would be necessary to guarantee regular sensitivity at this level.

Measurements of ^{14}C have also been made by the cyclotron at the University of California at Berkeley. However, because of instrumental contamination, present dating is limited to samples younger than 10,000 years. The difficulties are understood, and with an investment of about \$60,000 during a period of one year the contamination problems can probably be overcome. A gas source, as used for the cyclotron, may have some advantages over the solid source as presently used in the Van de Graaff accelerator. Further descriptions of both cyclotron and Van de Graaff methods will be found in the Appendix to this report.

Thermal diffusion technology is now routinely used to enrich ^{14}C by a power of ten for conventional gas counting. It would be feasible to thermally enrich samples by accelerators and thus increase their detection limits to $10^{-3}\%$ of modern C (equivalent to 90,000 years). A system capable of enriching 10 samples per month in volumes suitable for acceleration counting would cost about \$50,000 and could be built in one year. Samples initially 40 times larger than needed for the ^{14}C measurements would be required.

As measurements of lower ^{14}C activities are made, the chances for the introduction of contaminants are increased. Oceanographic sampling methods might be adapted for borehole sampling. Such adaptation and testing would require less than one year and cost about \$20,000.

Lastly, the matter of in situ production of ^{14}C should be reviewed carefully. As the detection methods improve, small amounts of non-atmospheric ^{14}C which could be generated in the subsurface by certain nuclear reactions may become significant. A few months' time would be needed to complete a brief theoretical study which would recommend field sampling from selected aquifers, provided detectable in situ production is predicted. Sampling and analytical work would take several months to complete. The question of in situ production could possibly be answered within one year for less than \$20,000. Nevertheless, present sample collection methods might possibly need improvement prior to the field and laboratory part of this study.

CHLORINE 36

Introduction

Chloride is a highly mobile anion in the hydrosphere. Owing to the general lack of sorption of chloride ions, they form an effective tracer in ground-water hydrology. Chlorine-36, which has a half-life of 3.08×10^5 years, is produced continually in the atmosphere. Although small amounts of ^{36}Cl may be produced in the subsurface, present indications suggest that it would be a very useful radionuclide for dating ground water.

Principles

Most chloride in shallow ground water (under natural conditions) has been cycled in the atmosphere together with the water which eventually enters the subsurface to become ground water. Some of the chloride originates from dried particles of ocean spray which form nuclei for atmospheric precipitation; some of the chloride settles to the ground as small, dry dust particles to be subsequently dissolved by rainwater; but only a very small part of the chloride originates from normal rock weathering. Once chloride enters the ground-water system, only minor amounts are likely to be removed by ion exchange, to be trapped as fluid inclusions in precipitating minerals, or to become part of the actual structure of new minerals. Hence, for shallow aquifers and for fractured-rock aquifers, the origin of the chloride in the water is probably as well known as any other dissolved constituent in the water. For deep sedimentary aquifers, the geochemical history of the chloride may be more complex. Chloride concentrations may be related more directly to "connate" water migrating slowly out from adjacent compacting fine-grained sediments, may be related to chloride being concentrated by natural ion-filtration processes, or may simply originate by dissolution of evaporite minerals.

Chlorine-36 originates (a) in the atmosphere by either thermonuclear explosions or isotope spallation by cosmic rays, which convert ^{40}Ar to ^{36}Cl , (b) at the soil surface by activation of chloride in the soil by secondary neutrons of cosmic ray genesis, and (c) in the subsurface by

activation of chloride by neutrons related to natural fission of U. Sub-surface production, except within U and Th ore deposits, is only of minor importance. Therefore if the input of ^{36}Cl can be determined for a region and assumed to be relatively constant in the past, ground-water dating with ^{36}Cl will be possible in aquifers not affected significantly by factors outlined in the last paragraph.

Research Needed

Research should progress simultaneously, first, to develop better analytical methods to determine ^{36}Cl , second, to perfect sampling and separation methods, and third, to determine the recent (but pre-1954) ^{36}Cl distribution in shallow aquifers.

Despite the fact that low-level counting can be used to determine ^{36}Cl , the need for smaller samples, more rapid determinations, and greater precision suggests that the development of accelerator-based techniques might be far superior to counting the low-level activity of ^{36}Cl . The cost of this development could vary from \$50,000 to \$200,000 depending on the system used and whether or not the technique is combined with ^{14}C dating (Van de Graaff) or ^{81}Kr and ^{14}C dating (cyclotron). The total time needed would be from 1 to 2 years.

Sampling and separation methods appear relatively simple but not trivial. Relatively large samples will be needed, so initial separation would probably be with anion exchange columns in the field. Concentration of the chlorine in the laboratory would require careful elimination of ^{36}S and ^{36}Ar which potentially interfere with ^{36}Cl analyses. The sampling and concentration problems could probably be solved for less than \$10,000 and might take less than 6 months.

The field sampling program would require considerable travel in order to study aquifers which are moderately well-known. The program would require about one man-year of professional work. Cost is estimated to be about \$50,000 which would be spread over about two years. This work would need to follow the development of analytical procedure.

Further information concerning ^{36}Cl dating can be found in the Appendix, Parts D, H, and M.

KRYPTON-81

Introduction

Of the various cosmogenic nuclides, ^{81}Kr is an excellent candidate for use in dating ground water having ages in the range of 50,000 to 800,000 years. Besides its ideal half life of 210,000 years, it has a number of special characteristics which lead to confidence in its use. (1) Its atmospheric production rate by cosmic rays has already been measured. (2) Complications due to chemical interactions and climatic variations are absent. (3) Spurious underground production, due to neutrons from natural fission or meson interactions, is quite likely to be low because of the very small concentrations of the precursor nuclide, ^{80}Kr . Also, direct production of ^{81}Kr from natural fission is probably negligible because ^{80}Kr is a shielded nuclide. (4) Identification of ^{81}Kr is unique when using low-level counting spectroscopy because of its characteristic 13 keV emission.

We recommend strongly that ^{81}Kr measurements be combined with measurements of ^{36}Cl , in particular, as well as other indicator nuclides and chemical species. Work should be done on the same samples. This is considered important in that it will conserve sampling efforts, allow optimal development of sampling and separation techniques, and provide a direct comparison of independent methods of measuring the age of water. Owing to the very large sample sizes required, routine use of ^{81}Kr dating may not be practical. Nevertheless, ^{81}Kr dating may play a key role in the calibration of water dating by providing benchmark ages of key ground-water samples which are also dated by other methods.

Principles and Objectives

Overview - The general premise underlying ^{81}Kr use includes the measurement of the $^{81}\text{Kr}/^{80}\text{Kr}$ ratio in dissolved krypton and comparison of that ratio with the modern ratio which represents an equilibrium saturation with atmospheric cosmic-ray production. Age of the sample is then derived from the change in the isotope ratio and the physical half-life of 2.1×10^5 years.

Measurement is very difficult because of the low concentration of ^{81}Kr in modern water. This concentration is only about 1000 atoms/liter of water. If sufficiently large amounts of water can be sampled ($\sim 50 \text{ m}^3$ for accelerator isotope ratio measurement, or ten to twenty times this volume for low-level counting) very reliable dates are expected, however. (This is because of the likely absence of spurious underground production, the relative reliability of the geochemical model, and the known modern isotope ratio.) ^{81}Kr dating is especially promising because the chemical-physical separation techniques have been demonstrated and detection of natural concentrations has already been achieved by low-level counting.

Assumptions - Apart from the relatively secure assumptions concerning the geochemical behavior of ^{81}Kr , the most important remaining assumption for the interpretation of ^{81}Kr ages is the effective cosmic ray production rate. That is, unless production of ^{81}Kr has been almost constant over the last few million years, the ^{81}Kr ages may need to be corrected for cosmic ray variations. An assessment of such variations could come from independent studies of magnetic field intensities and the concentrations of other cosmogenic nuclides such as ^{10}Be in cores of marine sediments.

A detailed discussion of some of the assumptions in counting and quantitative interpretation of the nuclear measurements is also given in the Appendix.

Validation with ^{39}Ar - Because of the inherent reliability of noble gas isotopes with respect to geochemical modeling, we recommend that ^{39}Ar - ^{14}C validation procedures be applied in the same manner as the ^{81}Kr - ^{36}Cl model ("age") validation. (Though ^{39}Ar has a relatively short half-life, 270 years, it will automatically be available from the same water sampling, and its measurement will lend credibility to both those of ^{81}Kr [cosmic ray constancy] and ^{14}C [geochemical behavior/contamination].)

Measurement Procedure - Gases from candidate aquifers should be extracted in the field by professionals and the resulting gas sample delivered to a separation facility for noble gases. As the noble gas fraction will be small and the total gas relatively large, the separation would best be performed by special arrangements with commercial air-reduction plants.

Final purification of the noble gas fraction should be performed in a research laboratory using already developed procedures involving fractional distillation and/or active gas removal by chemical reactions such as with hot Ti, followed by gas chromatographic separation of the krypton fraction.

Two measurement techniques must be considered for final quantitation of the recovered ^{81}Kr : (i) atom counting via cyclotron acceleration, and (ii) activity (decay) counting via advanced low-level techniques. The former method has not yet been fully developed for Kr isotopes, but it should be explored for it offers the potential of sample-size reduction by a factor of ten or more; details of this method will be covered elsewhere. The latter method has been proved - it was used to determine the natural production rate of ^{81}Kr - but attention must be paid to sample-size and background questions. Either method (certainly low level counting) will benefit by isotopic enrichment prior to measurement. Plans for enrichment (e.g., via thermal diffusion) should be incorporated, therefore, following the krypton separation step.*

Counting of the radioactivity will best be accomplished through the use of facilities which incorporate massive shielding, anticoincidence meson cancellation, high-purity small gas proportional counters, and one- or two-parameter nuclear spectroscopy. (If desired, the use of existing facilities could be cost-effective both in terms of capital investment and time required for initial results!)

Two-parameter (energy and pulse shape analysis) is especially attractive for ^{81}Kr measurement because of very significant background reduction and positive ^{81}Kr identification. This latter point might be considered crucial with respect to the question of credibility: if the characteristic "signature" of ^{81}Kr is seen in the spectrum, one can be certain of the nuclide giving rise to the signal. To further explain, ^{81}Kr decays by electron capture, and this leads to a short-range pulse

* Cooperative measurements between accelerator and low-level counting laboratories would be especially fruitful at the final measurement stage. Only ~ 10% of the krypton fraction need be taken for accelerator measurement. This would provide independent measurement and/or intercalibration.

in the counter (hence, pulse shape discrimination) having the characteristic K-electron binding energy of ~ 13 keV.

Finally, because of the very low levels of activity and consequent long measurement times, the counting system must be coupled to a data acquisition system capable of storing the two-parameter data and providing positive evidence of long term stability. Also, the computational approaches for extracting the net x-ray peak from the continuous baseline merit careful attention, particularly with respect to possible systematic model error, in the assumed shape of the baseline. Obviously, internal and external quality control are mandatory. These can be by means of replication, standards and laboratory intercomparison.

Costs and Time Needed

The start up costs for new laboratory gas-purification, low-level counting facilities for ^{81}Kr dating would be approximately \$200,000. Total costs including field sampling equipment could be on the order of \$250,000. Cost of dating with a cyclotron was not estimated during the workshop. If the cyclotron is used, cost of development might also be shared with the development of other dating methods such as ^{14}C and ^{36}Cl .

URANIUM ISOTOPIC DISEQUILIBRIUM

Introduction

There are several attractive aspects of the use of U-234/U-238 disequilibrium as a means of dating old water (greater than 50,000 years): . . .existing technology is adequate, a body of data and experience has already been accumulated, and the observed variations of aquifer patterns suggest that this approach may be applicable to several types of ground-water systems. In addition, required sample sizes are small, and the time span afforded by the approach is appropriate. At best a concerted effort might show that not only will $^{234}\text{U}/^{238}\text{U}$ yield reliable ages, but also that related techniques such as Th-234/U-234 may also be useful. In any event, the uranium isotope variations will be applicable as tracers in evaluating water sources, mixing proportions, and water-rock interactions.

Geochemical Principles

A typical aqueous uranium cycle involves moderate uranium concentrations in shallow and surface waters of the order of one part per billion (ppb). Here uranium occurs in the +6 oxidation state as a soluble carbonate complex. At deeper levels the oxidation state is reduced to +4 which is much less soluble, and old ground waters typically have concentration levels of only 0.01 ppb.

The observed wide variation from about 0.5 to 15 in the alpha activity ratio U-234/U-238 of dissolved uranium (A.R.) is at first surprising inasmuch as the equilibrium value is 1.0, and physico-chemical mass fractionation is negligible. Leaching alone is not deemed to be sufficiently selective to yield the higher A.R.'s, even considering the radiogenic origin and consequent lattice displacement of the daughter product, ^{234}U . A number of lines of evidence suggest that alpha recoil, involving daughter nuclide translations of about 2×10^2 angstroms in crystal lattices may cause the transfer of the daughter isotope (Th-234, which quickly decays through Pa-234 to U-234) from the aquifer grains

to the interstitial water. This produces a high A.R. in the water and eventually a low A.R. in grain boundary regions. The relative excess of U-234 in ground water is thus a function of (a) the ratio of uranium in aquifer minerals to that in the aquifer waters, (b) the relative surface area of the solid portion of the aquifer, and (c) most importantly, the time of co-existence of the two phases. The approach to such a "steady state" of disequilibrium follows a curve governed by the half life of U-234 which is 250,000 years. It is this characteristic which, combined with other data, should allow age determination in the range of 50,000 to 1.5 million years.

The movement of water from the ground surface through the oxidized part of the aquifer (Figure 1a) to greater depths results in the asymptotic approach of A.R.'s toward steady state values determined by the parameters described previously (See Figure 1b and Appendix, Part I).

Of particular note are the rising curves in high uranium environments such as volcanic ashes or crystalline rocks and also the sharply rising curve at reducing barriers where uranium accumulates as it drops out of solution, producing simultaneously a relative increase in recoil-generated U-234 (the numerator of the ratio) and a decrease in dissolved U-238 (the denominator).

If the deeper aquifers are less uraniferous than at shallower levels, then a falling curve from earlier high A.R.'s (generated at reducing barriers) will result. Two kinds of uranium isotopic evolutionary patterns are thus expected in static or slow moving ground waters. Those in which the water is oxidizing and the host rock is relatively high in uranium will generally display increasing A.R.'s with age. Those with a reducing barrier and a low uranium host rock will display down gradient a decreasing A.R. with age.

Examples of both kinds of pattern are recognized. A volcanic ash-rich aquifer in Japan and a fractured granite percolation system in Sweden are of the first kind, and at least two sandstone aquifers in Texas and a limestone aquifer in Russia are of the second kind. Other examples based on fewer data points have been postulated.

Figure 1a. Simplified cycle of uranium in ground water from infiltration from the surface to old age. (After J. K. Osmond)

Figure 1b. Possible changes of $^{234}\text{U}/^{238}\text{U}$ in ground water as a function of time and position within an aquifer. The steady-state disequilibrium values, or asymptotes, and the curve slopes are a function of the uranium content of aquifer minerals and water, and the effective surface area of aquifer grains. Scales are arbitrary. (After J. K. Osmond)

Research Objectives

The assignment of more exact ages to these waters awaits a better understanding of the fractionation models and the determination of the necessary aquifer characteristics such as porosity, uranium concentration, distribution of U between rock and solution, etc. These questions should be the objectives of future research aimed at developing tools for dating ground water. It should be noted that even if other geologic data are absent to the extent that absolute ages are not obtainable, relative ages and/or flow velocities may be estimated.

Model testing should be pursued both in the field and in the laboratory. In the latter case, relatively simple tests of the efficacy of recoil in affecting isotopic ratios of dissolved uranium can be conceived, and some have already been attempted.

The field tests should involve the use of standard hydrologic analysis, determination of overall water geochemistry, and recovery and geochemical analysis of rock materials from the aquifer itself. Less systematically collected, old static and connate samples should also be studied, e.g., deep oil field or over-pressured brines.

Although there are reasons to believe that Th-230 with a half life of 75,000 years may prove useful, the problems of detection and measurement may be too severe to expect early results. Nevertheless, Th methodology development may be worthwhile.

Measurement Techniques

With respect to the disequilibrium functions $^{234}\text{U}/^{238}\text{U}$ or $^{230}\text{Th}/^{234}\text{U}$, research for the development of models will be necessary, but measurement techniques are well-established -- at least in the case of uranium.

Alpha spectrometry requires at least ten nanograms of uranium and more is preferred. At a few parts per trillion (ppt), a normal value for reducing waters, several liters of sample and several days counting are required. Fifty-liter samples and a field pre-concentration procedure have been used. Isotope dilution with U-232 permits activity ratios

and concentrations to be determined on a single run.

If Th-230 is deemed of interest, measurement will be more difficult. Thorium has been detected at trace levels (as Th-232) in only a few water samples. One can anticipate that a hundred liters or more of sample might be required for alpha spectrometry. Field concentration methods are simple if water supply is not a problem.

Long counting times are normal using alpha spectrometry. Most labs doing alpha spectrometry have several of the relatively inexpensive counting systems running continuously.

Mass spectrometry requires less sample by perhaps a factor of 100. Part of the sample is used to determine the $^{234}\text{U}/^{235}\text{U}$ ratio ($^{235}\text{U}/^{238}\text{U}$ is constant) and a lesser part of the sample is used to determine the uranium concentration by isotope dilution with U-233. Clearly, if sample size is limited, mass spectrometry will be the preferred method, even though somewhat more costly.

A summary account of requirements of mass spectrometry as an analytical tool for the determination of uranium and thorium appears in the following table.

Information on the Method for Measuring
Nuclides in Water by Mass Spectrometer

<u>Nuclides</u>	<u>Method</u>	<u>Sample Size, cc.</u>	<u>Remarks</u>
$^{234}\text{U}/^{238}\text{U}$	Mass spectrometry with pulse counting detection and high abundance sensitivity of 10^6 .	10	for 10 ppb U
		200	for 0.005 ppb U
Total U	Isotope dilution employing ^{233}U and mass spectrometry.	10	good to 0.005 ppb U, total U
		100	good down to 0.0005 ppb
$^{230}\text{Th}/^{234}\text{U}$	Mass spectrometry as above and alpha-spectrometry	500	

Time and Cost Considerations

The costs of uranium isotopic research are not excessive, particularly if combined with other isotopic and geochemical and hydrologic studies.

We estimate, aside from unusual and often unpredictable collecting expenses, that costs for analyses would be about \$30,000 per 100 samples by alpha spectrometry, and \$50,000 if by mass spectrometry. Existing facilities could handle several hundred samples per year. Laboratory experiments in alpha recoil mechanisms could be performed at a level of about \$10,000 per experiment. Significant results toward establishing a dating technique should be available within 1 or 2 years.

Recommendations

1. Obtain samples and analyses of fluid-bearing rocks as well as waters of interest, for all studies.
2. Test buildup and decay models using aquifer systems which are well characterized hydrologically and geochemically, such as the Carrizo in Texas.
3. Test models of recoil/leaching mechanisms for activity ratio buildups, in laboratory experiments.
4. Extend application of the technique to rock types of a variety of mineralogies.
5. Sample waters (and host rocks) known to be old, stagnant, and/or isolated from other groundwaters.

ACCUMULATION OF RADIOACTIVE DECAY PRODUCTS

Introduction

The use of accumulation products of radioactive decay for dating old ground water has a distinct advantage over several other dating methods in that their abundance becomes greater with age. The noble gases are particularly useful for this purpose in that they are non-reactive with earth materials. A preliminary list of the isotopes that might be useful in order of importance are ^4He , Xe, Kr, $^{21,22}\text{Ne}$, and ^{40}Ar . By far, the element that holds the most promise for dating old ground water is ^4He because of its demonstrated abundance in old ground water. (See Appendix K.)

Another advantage of using the accumulation of radioactive decay products over several other dating techniques is that no knowledge of previous climatic conditions is presupposed inasmuch as the products begin to accumulate in significant quantity only after the water has entered the ground.

The analytical techniques and instrumentation are all well developed and no new effort in this direction is required.

Principles

Water virtually devoid of uranium and thorium decay products will enter the ground from the atmosphere and will flow with the ground water. Because uranium and thorium are nearly ubiquitous in rocks and undergo continual radioactive decay, the decay products are generated continually within the rock. Some of the decay products will be retained by the rock, but some will enter the water. If the generation rate of the decay product is known and the uranium and thorium content of the rock is known, then a minimum residence time of the water in contact with this type of rock can be calculated from the amount present in the water.

The assumption involved in this calculation is that the transfer rate of the decay product into the water from the rock is the same as

the generation rate. For a hydrogeologic system subject to new conditions, such as initial saturation or radical change in salinity, this assumption may be suspect. However, if the hydrogeologic history of the region shows that the ground-water system has not undergone significant change, the release rate of the decay products from the rock to the water may have reached a steady state that is proportional to its generation rate.

To the extent that the decay product continues to accumulate in the rock-forming minerals or diffuses through the rock and is lost to the atmosphere, the water may be older than the age calculated. To the extent that helium migrates into the aquifer of interest from deeper zones in the earth, the calculated age may be too old.

Another assumption required for accumulation dating of water is that the uranium and thorium content of the rock along the entire flow path is known. To the extent that geology is relatively homogeneous over the flow path, this is not a complicating assumption. Even if the geology is unknown, minimum ages can be calculated from assumed uranium and thorium contents obtained from the literature.

Objective

The use of the accumulation of decay products of uranium and thorium to date ground water has not been practiced in very many places. Perhaps the most immediate research need to develop this method into a viable, cogent technique for dating old ground water is to develop more data in different types of rock and in different hydrogeologic settings. A secondary research objective is to develop a better understanding of the transfer mechanism whereby the decay product is released from the rock into the water.

Work to be Completed

(1) Work has been done on helium dating of water in the crystalline rock beneath the Savannah River Plant near Aiken, South Carolina (Appendix K). Five wells that are within $1\frac{1}{2}$ miles of each other were sampled and these samples had different helium contents. It is now known that the

removal of injected drilling water from several of these wells was not complete, and this affected the observed helium content. Although the helium variation is explained, the dating method would gain in credibility if these wells were pumped to remove the drilling water and it were shown that all wells gave consistent results. Several wells that lie at different points along the flow path should be sampled.

At the same time that these wells are being sampled for helium, the samples should also be analyzed for xenon, krypton, neon, and radon to develop correlative information on the usefulness of these elements.

Samples should also be collected for other methods of dating that are being pursued if it is feasible to do so; for example, for amino acid analysis, chlorine-36 analysis, or uranium 234/238 ratio measurements.

(2) To aid in planning for additional work in this field it would be useful to develop a graph showing the buildup of various decay products in representative rock types in a form similar to that shown below.

This graph or table could be developed in a very short period of time from literature values and would indicate the potential usefulness of each element in determining the age of the water. This would determine the effort that should be expended on each.

(3) Data should be developed in selected rock types under a small variety of hydrogeologic conditions. It seems reasonable that areas should be sampled where hydrogeological field work is being conducted and where the water may be of great age. It is highly desirable that the flow system be reasonably well known and that other types of hydrogeologic field work be in progress. For example, samples might be collected as part of ongoing programs from basalt at Hanford, Washington, from granite gneiss at Chalk River, Ontario, from granite at Stripa, Sweden, and Pinawa, Manitoba, and from carbonate rocks, at the Nevada Test Site. Samples could also be obtained from existing holes in Triassic mudstone at the Savannah River Plant.

(4) Research should be done to understand better the transfer mechanism by which the decay product moves from the rock to the water. These would initially be simple laboratory studies, such as placing a rock of known helium content in a water with zero helium content to determine the rate of equilibration, or a laboratory experiment on the diffusion rates of helium through rock under different concentration gradients.

Cost

Because the analytical techniques are well developed using mass spectrometers, no capital or developmental money would be needed for analytical techniques. Existing mass spectrometer services, which are commonly available at large laboratories, would be used. Samples will be collected from existing wells, thus no costs need be designated for well drilling. Money would be needed for well pumping equipment and sampling effort in areas where field investigations are not in progress, such as at Savannah River. In areas where sampling programs are active, such as at Stripa or Hanford, the sampling might be incorporated into ongoing field investigations.

The coordination, sample collection, and analytical service would probably amount to \$80,000 for the first year.

Time to Develop Method

Because no difficult technical problems are expected, probably only a one year program would be needed to determine if this dating method is viable. One year is basically the time required to sample some well studied hydrologic sites and evaluate the data. The principles are simple and can be readily understood by those with little technical expertise.

The principal difficulty that can be envisioned at this time is in the knowledge of the ground-water flow system. However, difficulties arising from this ignorance will be common to any dating technique.

AMINO ACIDS

Introduction

Amino acids in living systems exist predominantly as the L-isomer. After death of the organism, the L-forms reversibly convert to the D-forms, a chemical reaction known as racemization:

This reaction has been the basis for estimating ages of geologic and archeologic specimens such as bones and shells. When the racemization reaction reaches equilibrium, equal amounts of the D and L-isomers are present. As with any chemical reaction, the rate of racemization is a function of temperature. The rate of racemization will approximately double for every 4-5°C increase in temperature. The table below gives estimates of the minimum age of waters, at different temperatures, in which representative free amino acids would be present at equilibrium. These times represent the upper limit of the method at various temperatures. At least another six amino acids could be added to this list.

Estimated Age of Waters in which Equilibrium
Will be Established (years)

<u>Amino Acid</u>	<u>0°C</u>	<u>25°C</u>	<u>40°C</u>
Phenylalanine	1,000,000	10,000	1,000
Aspartic Acid	2,000,000	20,000	2,000
Alanine	5,000,000	50,000	5,000
Isoleucine	20,000,000	200,000	20,000
Valine	30,000,000	300,000	30,000

Based on the results of some recent analyses of spring waters and oil well brines in which concentrations of approximately 100 nanomoles per liter for each amino acid were found, it is likely that many ground waters contain sufficient concentrations of amino acids to be easily measured. Soil organic matter, the likely source of the dissolved amino

acids in ground water from igneous and metamorphic aquifers and many sedimentary aquifers, has very low D/L amino acid ratios with the exception of those amino acids produced by bacteria (e.g., D-glutamic acid, D-alanine, and D-aspartic acid).

Objectives

The objectives of this project will be to determine if amino acid racemization reactions can be used to: (1) estimate a minimum age of old ground water; (2) estimate a relative chronology of various ground waters, possibly related to a known age from independent methods; (3) estimate absolute ages.

Proposed Plan of Research

Water samples for measurement of D/L amino acid ratios would be obtained from aquifers from a variety of rock types including the major sedimentary rocks (limestone, shale, sandstone) and representative igneous and metamorphic rocks. Sedimentary rocks are likely to contain amino acids that could be leached into the ground water thereby making the water appear older than it is. The addition of such rock-derived amino acids could be corrected, or established to be unimportant, by assuming that these amino acids are contributed to the ground water in direct proportion to the inorganic ions also derived from dissolution of rock. Igneous and high grade metamorphic rocks will not contribute amino acids to ground water.

Because of the temperature dependence of the racemization rate, it is desirable to collect waters of known thermal history. These should include both cold and warm waters. Priority should also be given to analyses of any waters whose age is known from independent methods such as C-14 or U and Th decay product accumulation, etc., to establish an absolute value for the rate of racemization and the general reliability of the method.

Previous geochemical racemization studies have been conducted on samples such as bone and shell where the amino acids are protected from bacterial activity by the inorganic matrix in which they are embedded. For this reason, the effect of bacterial activity in "open" systems like

natural waters is not known. It is our opinion that bacterial effects will not be important; however, in view of the uncertain significance of, and even the presence of a variety bacteria in aquifers, we would propose that any study of bacteria in aquifers be carried out as a separate project.

Samples, preferably from existing wells, must be collected with particular care to avoid contamination. For this reason only persons specifically trained to collect samples or knowledgeable of proper collecting procedures by virtue of experience in amino acid analyses should be employed. Samples should be evaporated preferably by freeze-drying. When this cannot be done immediately, samples should be shipped and stored frozen.

Instrumentation for amino acid analyses will be standard ion exchange and/or gas chromatography. No modification to present instrumentation will be necessary, although the addition of a nitrogen detector to gas chromatographs will give increased sensitivity and will be more specific for the nitrogen containing amino acids than the general purpose flame ionization detector.

Duration and Budget

A detailed investigation designed to answer all the objectives of this proposed research would require two to three years if the entire project including sample collection was carried out entirely by one research group. If on or near-site personnel could be utilized for a major portion of the collecting and preliminary processing, the time for completion would be shortened by as much as half. If only the first objective is to be attained, completion could be in less than one year.

A budget for the entire project to be completed by a single research group is estimated at \$200,000 to \$300,000. If cooperating, on-site sample collectors are utilized, the budget could be reduced by about half, and if an answer to only the first objective is to be sought, the cost could be reduced by a factor of ten.

STABLE ISOTOPIC CHRONOLOGIES

Introduction

The use of stable isotopic or geochemical chronologies as dating tools is not a method which may be applied at present on a global scale, but it is extremely specific to the site or continental region being studied. The fundamental principle of such an approach is to identify a major trend or pulse in the composition of the ground water which may be related to an event or process that can be dated by other techniques. The nature of the events controlling the trends may be highly variable such as major changes in drainage patterns, in elevations of mountains, in the position of coastlines, and in the extent of the land surface covered by continental ice. However, detailed understanding of the events is not needed for pragmatic use of the trends as a means of dating old ground waters.

Principles

Cyclic changes in the ^{18}O and ^2H (deuterium) content of ocean water during the Pleistocene and late Pliocene are recorded in the composition of foraminifera tests and amount to 1 to 2 per mil in $^{18}\text{O}/^{16}\text{O}$ ratio (equivalent to 8 to 16 per mil in $^2\text{H}/^1\text{H}$ ratio). These variations reflect principally the tie up of the lighter isotopes in the continental ice caps during world-wide periods of glaciation. Major global cycles lasting roughly 10^5 years are interspersed with shorter fluctuations of roughly 10^4 years and even shorter minor fluctuations of 10^3 years or less.

During the last decade, geochemists have documented variations of ^{18}O and ^2H in ground water samples and speleothems which appear to correlate with world-wide temperature fluctuations. Samples studied extend roughly from 40,000 to 200,000 years before present. However, dated ground waters have not shown the clearly defined isotopic record found in ocean sediments. The apparent absence of significant changes

in the isotopic composition of ground waters as old as 30,000 years is not explained as yet. However, should further work identify, say, the 10^5 year "cycle" in the stable isotopic composition of ground water, a method of dating water as old as 2 million years might be possible.

A stable isotopic chronology, if it can be developed, offers two major advantages over most other chronologies. First, ^2H and ^{18}O behave conservatively in ground water with temperatures below 100°C . Second, ^2H and ^{18}O are major, not trace, constituents. The concentration of ^{18}O in fresh waters is almost 2000 mg/l and that of ^2H is about 140 mg/l. Hence, these constituents will not be as subject to serious natural contamination, say by cross flow between aquifers, as would most other trace constituents of potential use in ground-water dating.

Objectives

Objectives of a program to develop a stable isotopic continental chronology should be to:

1. Develop ^{18}O and ^2H records for North America which will extend backward in time for about 2 million years. This may be done by expanding in the speleothem studies which have been done by researchers at McMaster University and other institutions. Also, calcite veins which were once feeders for former springs are being studied by researchers of the U.S. Geological Survey with the objective of investigating variations of ^{18}O and ^2H during the past few million years. Dating of the speleothems and fossil spring deposits has been done by $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ clocks.
2. Attempt correlation of major stable isotopic cycles (if any) in these deposits with each other and with the oceanographic record.
3. Look for these major cycles in old ground water and date these waters by matching cycles.

4. Attempt to define and date unidirectional trends which can be related to regional events such as mentioned in the introduction to this section.

Possible Costs

Work presently underway by the U.S. Geological Survey in Death Valley will provide a stable isotopic record covering the period 2×10^5 to 3×10^6 years before present. This work should be completed within the next 18 months. It appears at this writing (March, 1978) that this record may not demonstrate the desired fluctuations and further work in this area on ^{18}O and ^2H may not be justified. If major fluctuations are found, spending as much as \$100,000 per year for 4 years might be justified. Much of the work would be related to meticulous field sampling and laboratory determinations. Fundamental instrumental development is not needed.

Addendum

Although the above discussion is centered on the use of ^{18}O and ^2H analyses, concentrations of other constituents found in water may also supply information concerning past surface environmental conditions. For example, the solubility of Ar is very temperature sensitive, so variations of from about 0.5 to 1.0 mg/l might be measured and correlated with past changes of climate provided the water in the aquifer has not undergone severe heating or some other form of degassing since it was recharged.

DISCUSSION AND CONCLUSIONS

The workshop participants considered that the development of a ^{36}Cl method of dating and the continued development of ^{14}C dating presented the most promise for dating very old ground water. Despite the requirement for very large water samples, a ^{81}Kr method was considered desirable for validation of the ^{36}Cl dates because the half-life of ^{81}Kr is ideal and its geochemical history is not complicated. Three additional methods, amino acids, uranium disequilibrium, and helium accumulation, also were considered to have strong possibilities of being useful. The development of a stable isotope chronology was considered very favorably, but the regional nature of the method and the work needed to establish local standard trends suggest that a period of many years may be needed for development. Thus, the development time needed is not within the three-year limitation given in the original goals of the workshop.

All workshop participants agreed that more than one method of dating should be developed and that none of the major dating methods considered should be eliminated from further consideration at this time.

APPENDIX

Notice for Appendix, Parts C through P

The following manuscripts have been submitted as supporting documents for the workshop on dating old ground water. Material contained in the manuscripts is provisional and subject to revision. Contents should not be quoted. Authors of individual parts should be contacted for updated information.

PART A

WORKSHOP ON DATING VERY OLD GROUND WATER

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PART B

WORKSHOP ON DATING OLD GROUND WATER

Second General Description

March 16, 17, and 18, 1978

Tucson, Arizona

Introduction:

The purpose of the workshop will be to recommend research into possible methods of determining the length of time which ground water has been isolated from the earth's surface. Attention will be focused on dating water which is more than 50,000 years old. Although funding for the workshop has been provided by the Office of Waste Isolation, the workshop will not cover methods of hazard evaluation nor general aspects of radioactive waste repositories.

Topics to be Covered:

The age of ground water can be estimated by several methods including:

- (a) Travel time of the ground water calculated from assumed flow paths and hydraulic gradients using Darcy's law or related equations.
- (b) Time of isolation of the ground water calculated from the decay of certain radionuclides which are assumed to originate only in the atmosphere.
- (c) Residence time of the ground water in an aquifer based on the total accumulation of certain products of radioactive disintegration.
- (d) Time of isolation of the ground water based on extrapolated rates of structural changes of certain molecules which are assumed to originate at or near the land surface.
- (e) Residence time of the ground water in an aquifer estimated from the degree of disequilibrium present in the concentrations of one or more of the uranium or thorium daughter products.
- (f) Time of origin of the ground water could be based on its unique hydrochemistry. For example, connate water in the shallow subsurface might be associated with a dated high stand of the ocean, or anomalously high concentrations of argon might be correlated with recharge during a certain late glacial substage.

The workshop will concentrate its interest on items b, c, d, and e. Item a was covered rather thoroughly in a workshop held recently in Austin, Texas. Item f is mostly a problem of late Cenozoic geology and may not be too useful for ages in excess of 50,000 years.

Limitations of Workshop:

Besides human limitations (even 20 to 30 individuals cannot cover all relevant aspects of the topics listed above), participants should be aware of several other limitations of the workshop. The most important is that we will not attempt to complete even a general description of the entire topic of dating ground water. The objective is to prepare recommendations for government-supported research which will have a possibility of producing useful results within a period of two or three years. Although highly speculative discussion will be encouraged and may eventually lead to new and important innovations, the research which will be recommended by the group as a whole must be feasible within a relatively short span of time. Another restriction of the workshop will be a lack of time during the meetings for formal presentations. A maximum amount of time must be reserved for the exchange of ideas and discussions among various experts. Finally, all participants are very busy and will not be able to participate in the writing and editing of a long manuscript. Therefore, the formal report will be as concise as possible. All participants, however, are urged to submit separate statements which can be duplicated and attached as appendices to the general report. Thus, the appendices will give detailed descriptions, diagrams, references, equations, etc., which cannot be placed in the body of the recommendations.

Examples of General Questions for the Workshop:

The following are a few of the questions which will certainly be raised during workshop discussions:

1. Are there radionuclides of possible interest which originate in the atmosphere in addition to ^{14}C , ^{36}Cl , and ^{81}Kr ? Some radionuclides with interesting half-lives and moderate to high mobility in water are ^{41}Ca , ^{60}Fe , ^{79}Se , ^{99}Tc , and ^{135}Cs .
2. Besides ^4He and ^{40}Ar , what other gases could accumulate in ground water as a result of nuclear processes? For example, detectable amounts of Xe in the subsurface have been postulated to come from geologically recent natural fission, and the reaction $^{19}\text{F}(\alpha, p)^{22}\text{Ne}$ has been suggested as a source of anomalous amounts of ^{22}Ne in the subsurface.
3. Could extremely small, but still significant, amounts of ^{14}C , ^{36}Cl , ^{81}Kr , and other radionuclides of interest be produced in the subsurface by the very low natural flux of n or α particles as well as natural fission of uranium?
4. Which analytical procedures might be best to detect very small concentrations of ^{14}C , ^{36}Cl , ^{81}Kr , and other radionuclides and compounds of potential interest? Be prepared to give, if possible, rough estimates of cost, precision, accuracy, speed of analyses, and current state of development.
5. Besides amino acids, are there other natural compounds found in water which undergo predictable, time-dependent changes?

6. What difficulties of field sampling and storage might preclude the use of certain radionuclides and/or chemical compounds for dating ground water?

All participants should formulate their own lists of critical questions for the workshop. Numerous disciplines will be represented including chemistry, physics, geochemistry, civil engineering, nuclear engineering, and hydrogeology. We trust, therefore, that a large number of questions brought by any single individual can be answered by other workshop participants.

Meeting Schedule:

(All meetings including the reception will be at the Arizona Inn.)

Wednesday Evening (early), March 15 -- Reception

Thursday Morning, March 16.

Greetings -- Dr. Kassander, Vice President for Research, University of Arizona

Introduction -- (OWI representative)

General Scope of the Meeting -- S. N. Davis

Organization of Working Groups

General Discussion of Topic of Water Dating

Thursday Afternoon, March 16.

Working groups organized more-or-less according to professional specialization. Exact categories will be established during the morning session. Each working group will appoint a reporter for the closing general session.

Each working group will consider a series of general questions related to its field of specialization.

Thursday Evening, March 16.

Generally free time, but several informal, ad hoc groups will probably meet to discuss specific problems.

A visit to the University of Arizona's Laboratory of Isotope Geochemistry can be arranged for those who may be interested.

Friday Morning, March 17.

Working groups organized according to specific geochemical bases of dating will meet to discuss various questions. Again, a reporter will be appointed for each group. It is premature to designate groups at this point, but, as an example, two possible groups would be those working with ^{14}C and amino acids.

Friday Afternoon, March 17.

Combined session of all groups in which the reporters give summaries of the main conclusions of each working group. Also, time will be reserved for a general discussion from all participants.

Friday Evening, March 17.

Free time for most participants. Selected members will meet with S. N. Davis to work on a general outline of the report.

Saturday Morning, March 18.

Various working groups will meet to write a rough draft of the report. A typist will be present to help with the task.

All participants who have had financial assistance provided for the workshop are requested to work Saturday morning. Others are invited to help also, but will be excused if their schedules are too pressing to stay.

The rough draft completed Saturday morning will be assembled and circulated to all participants for their corrections and additions prior to final typing.

PART C

DISCRETE-STATE COMPARTMENT MODELS: PART I, COMPUTATIONAL PROCEDURES

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Abstract

This is the first of three papers that describe the properties and applications of a quasi-physical discrete-state compartment (DSC) model, consisting of a set of interconnected compartments or cells of any desired size, in any desired configuration, through which the transport of mass is represented by a sequence of discrete states. The transformation from one state to the next is governed by a set of recursive equations. Several idealized examples are given to illustrate model properties. A computer program was written that will accept up to 100 cells in 1-, 2-, or 3-dimensional networks. Computer time required for simulation experiments is small.

Introduction

For more than two decades, hydrologists have been using mixing cells and discrete reservoirs as a basis for modeling hydrologic systems (Craig, H., 1957; Dooge, J.C.I., 1959; Eriksson, E., 1971). For the most part these models are solved analytically which places a constraint on flexibility. That is, in order to achieve solutions of multi-cell models, it is necessary to assume constant cell volumes and simple cell networks. In mass transport studies it is also necessary to assume constant flow (Himmelblau and Bischoff, 1968, Chapt. IV). It is possible to greatly increase the flexibility and usefulness of such models by obtaining solutions by recursive equations. In this way it becomes possible to model systems that, as a function of iteration number, exhibit (a) a steady or non-steady flow, (b) steady or non-steady cell volumes, and (c) steady

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or non-steady concentrations (or mass) of dissolved substances. In addition, a large number of cells can be accommodated, the volumes and interconnections among cells may be as complex as desired, and the cell networks can be arranged in one, two, or three dimensions. Energy and mass transport can be modeled simultaneously.

We call our procedure a "Discrete-State Compartment Model" or DSC model.² It is "discrete-state" in the sense that the computational procedure imposes a finite limit to the "sample space" of changes, depending on the number of significant figures specified in the computer print-out. Each compartment is a "mixing cell" in a sense that no concentration gradient may exist in any cell, even though a DSC model may be designed in whole or in part for pure piston flow of discrete fluid volumes. This paper is Part I of a three-part series. Part II examines the role the DSC model can play within a water resource systems framework, in particular with regard to managerial decision-making under various uncertainties. Part III concerns itself with a "real-world" application to a two-dimensional model of the Edwards Limestone aquifer, Texas, calibrated against the distribution of tritium. This series is a generalization and extension of material presented at a seminar in karst hydrology at Dubrovnik, Yugoslavia (Simpson and Duckstein, 1976; Duckstein and Simpson, 1976) and includes new material developed by Campana (1975).

In the DSC model a hydrologic system is divided into a network of interconnected cells, where each cell represents a specified region of the system. The movement of water and dissolved matter through the cells is described by a finite sequence of states. The transformation from one state to the next is governed by a set of recursive equations based on the equation of continuity. In addition, at each iteration, operations may be performed on any or all cells to account for changes of state governed by radioactive decay and/or chemical reactions. The initial or "first guess" design of a given network of cells is based on

²In the Dubrovnik and earlier papers, the model was called "Finite-State Mixing Cell" or FSM. However, "finite-state" has a different connotation in Systems terminology, and hence our change of name.

a priori knowledge of the flow system. The initial design is then modified as appears necessary and reasonable through trial-and-error calibration procedures. A computer program was written that will accept up to 100 cells (a minor modification of the program will increase the maximum number of cells), in one, two, or three-dimensional arrays; cell volumes may be different from one cell to the next, and/or from one iteration to the next. (The program called FISTMO, is not made part of this report, but listings are available from Dr. M. E. Campana, on request.)

Definitions and Basic Equation

The word tracer will indicate any measurable substance dissolved in water (including water molecules containing deuterium, tritium, or oxygen-18) whose distribution in nature can aid in the calibration of a DSC model. A numerical tracer is a dimensionless number used in DSC model simulation experiments, whose magnitude is related to the amount or concentration of the real-world tracer. Mass, S , is the magnitude of a numerical tracer in a cell, when it is a measure of amount rather than concentration. The particular relationship between a given DSC model and the real-world system it represents will determine the meaning (in grams, curies, counts per minute, etc.) of the numerical tracers. Tracers in the model and in the real world are assumed to occupy zero volume. Cell volume, VOL , is a number, implicitly having the dimension of volume, whose magnitude is expressed as a multiple of an arbitrary unit reference volume, the URV. The size of the URV is chosen to give convenient VOL numbers for calculation. For example, in modeling a large aquifer system, a suitable URV might be 10^9 cubic meters. Cell volume and the volume of water contained therein are identical. If the model is steady mass but non-steady volume, then cell state is defined by VOL . If the model is non-steady mass and non-steady volume, then cell state is defined by the 2-element set (S, VOL) . In the case of a multi-cell model containing m cells, the state at each iteration is defined by a set containing $2m$ elements.

The basic equation for any cell in an array of cells is:

$$S(N+1,X) = S(N,X) + (BRV(N+1,X) * BRC(N+1,X)) - (BDV(N+1,X) * BDC(N+1,X)) + R(N+1,X) \quad [1]$$

where, S = mass or amount of tracer in cell,
 BRV = boundary recharge volume (input volume of water to cell),
 BRC = boundary recharge concentration (input concentration of tracer),
 BDV = boundary discharge volume (output volume of water from cell),
 BDC = boundary discharge concentration (output concentration of tracer),
 R = tracer source or sink within cell,
 X = matrix location or cell number,
 N = iteration number, and
 $*$ = multiplication.

As was the case with cell volume, VOL , the volumes BRV and BDV are expressed as multiples of an arbitrary unit reference volume, the URV . When the input BRV is from the outside environment (system boundary) it is designated $SBRV$, and when the output BDV is to the outside environment it is designated $SBDV$. The same convention holds for boundary BRC s and BDC s.

Equation 1 states that the amount of tracer in cell X at iteration $N+1$ equals the amount of tracer in the cell at iteration N , plus the amount that came in at iteration $N+1$, minus the amount that went out at iteration $N+1$, plus or minus the amount that was "created" or "destroyed" at iteration $N+1$. In other words, equation 1 is a discrete form of the continuity equation.

Steady state is the condition where both the mass, S , and the volume, VOL , of every cell of the DSC remains constant from one iteration to the next. If S or VOL or both in at least one cell changes with iteration number, the regimen is non-steady state. Steady mass, non-steady mass, and steady volume, non-steady volume are as above for S and VOL separately. Steady flow is the condition where the volumetric output from at least one cell changes with iteration number.

Fluid element. In an analysis of this kind it is necessary to assume that the water may be subdivided into a large number of small elements, herein called fluid elements, each of which retains its identity in moving through the array of cells, and to each of which may be assigned a very small, but finite and constant volume. Each fluid element, as it enters the DSC, is associated with a contained amount of tracer. The contained amount of tracer may be any finite amount down to and including zero. "Retains its identity" means that the amount of tracer associated with a fluid element does not change except by chemical reaction with other contained tracers, or by reaction with solids in the flow system, or by radioactive decay. In other words, fluid elements do not intermix with one another.

Change of state or of flow is affected by the number of significant figures specified in the computer print-out. For example, when approaching steady state a system described in three significant figures will reach steady state before an identical system described in five significant figures. A model regimen is defined by a specific combination of the following: steady or non-steady mass, steady or non-steady volume, steady or non-steady flow. Thus eight combinations exist but two are not physically possible (i.e., combinations containing non-steady volume, steady flow). It is possible to pass from one regimen to another as iteration progresses, or to restrict the model to a given regimen.

Real Time. In and of itself, the DSC model bears no relation to real time. A relationship may be established, however, by choosing values for the volumetric system input, SBRV, that corresponds to real system input, $\bar{Q} * \Delta t$, where $\bar{Q}$ is the volumetric rate of input averaged over the real-time interval Δt . The magnitude of Δt will depend on the kind and amount of data available and on the purpose of the model. For most purposes Δt can be taken as a constant, but this is not a necessary constraint. If $\bar{Q}$ is a function of time and varies from one Δt interval to the next, we have

$$\begin{aligned} \text{SBRV}(N) * \text{URV} &= \bar{Q}(t) * \Delta t \\ \text{or} \quad \text{SBRV}(N) &= \frac{\bar{Q}(t) * \Delta t}{\text{URV}} \end{aligned} \quad [2a]$$

if $\bar{Q}$ is constant, then

$$SBRV = \frac{\bar{Q} \cdot \Delta t}{URV} \quad [2b]$$

By equations 2a and 2b, each iteration, N, of the DSC model represents a real-time interval Δt .

First order chemical reactions and radioactive decay. A first order reaction is one in which the rate of the reaction is proportional to the mass of reactant. As of this writing we have not attempted to model a system that includes a chemical reaction but we have done so for radioactive decay. The following equations refer to decay but may be applied to first order chemical reactions if the reaction rate is known. The equation for radioactive decay may be written

$$S(N+1) = S(N) \cdot RD \quad [3a]$$

where, $RD = e^{-\lambda(\Delta t)}$

$$\lambda = \text{decay constant} = \frac{\ln 2}{T_{1/2}}$$

$$T_{1/2} = \text{half-life of isotope}$$

$$\Delta t = \text{real-time interval (constant) represented by each iteration, N, in same units as } T_{1/2}$$

The program is written to first calculate the changes in state that result from flow; then, as an intermediate step each cell is operated on to account for radioactive decay. Therefore, in algorithm form, equation 3a becomes

$$S(N+1) = S(N+1) \cdot RD \quad [3b]$$

If the magnitude of Δt is small compared to $T_{1/2}$ it will not be necessary to adjust the value of RD to account for the difference in decay at the beginning and at the end of the interval Δt . Otherwise, RD should be calculated for a time less than Δt .

Selected Hydrologic Regimens: Examples

In this paper it is not our purpose to attempt an examination of all regimens that can be modeled by DSC models. The following examples will serve to demonstrate the range of possible applications as well as to

further develop the procedures involved.

Steady Volume, Steady Flow, Non-steady Mass Regimen. If the model is restricted to steady volume and steady flow, then at each iteration, by definition, $BDV = BRV = \text{a constant for each cell}$. The mass may be steady or non-steady, depending on the history of tracer input, $SBRC(N)$. The BRV as well as the BRC either are specified inputs to the model from the outside environment, or are the calculated outputs (temporarily stored in computer memory) from one or more upstream connecting cells within the model. If, for the time being, it is assumed that $R = 0$ in equation 1, then the only unknown on the right side of that equation is the value of the BDC . The value of the BDC may be specified by writing an equation describing the manner in which the input mixes with the tracer already in the cell. Two alternative equations are possible. One alternative describes a cell analogous to a mixing cell and herein termed a simple mixing cell or SMC ; the other alternative describes a cell somewhere between the SMC and pure piston flow. This cell is called a modified mixing cell or MMC .

In the first case, that of the SMC , it is assumed that at each iteration the cell walls expand to accommodate the incoming water. The tracer and incoming water mixes completely with the contents of the cell. Following that, the cell walls contract to their original shape and the cell discharges a volume of water equal to the volume that entered (Figure 1a). The BDC will be identical to the concentration of tracer in the cell in its expanded condition. Thus,

$$BDC(N+1) = \frac{S(N) + (BRV(N+1)*BRC(N+1))}{VOL+BRV(N+1)} \quad [4a]$$

In the second case, that of the MMC , it is assumed that the cell walls are rigid, and that at each iteration the incoming water first displaces a volume of cell water equal to the incoming volume, and then the incoming water mixes with the remaining cell content (Figure 1b). The BDC at iteration $N+1$ is, therefore, identical to the concentration of tracer in the cell at iteration N . Thus,

$$BDC(N+1) = \frac{S(N)}{VOL} \quad [4b]$$

It will be noticed that the MMC approaches pure piston flow as BRV approaches VOL, and approaches simple mixing as BRV approaches zero. The BRV may equal VOL but should not exceed it, else negative masses may result. For non-steady volume cases, the VOL term in equations 4a and 4b should be replaced by VOL(N).

Thus, given a rule for cell mixing (either equation 4a or 4b), the state of a cell at any iteration $N+1$ may be computed by knowing the state at iteration N and the inputs to the cell at iteration $N+1$. In multi-cell models, interior cells receive their inputs from upstream cells until, eventually, the upstream cell (or cells) is a boundary cell and receives its input from the outside environment. Therefore, to operate a model in a steady volume, steady flow regimen one must know (or assume) the initial mass, S , for all cells, and know (or assume) the value of the SBRV (independent of N) and the inputs SRBC (tracer concentrations) which are functions of iteration number. The model output is the succession of states of the cells that constitute the model and of the concentration of tracer in the water discharged to the outside environment (the SBDC). The mass of any cell may be converted to tracer concentration simply by dividing by cell volume. Hence, the model output can be given as the changes in concentration of tracer both within the model and in the water discharged by the model.

Based on the concept of fluid elements two distribution functions may be defined: (1) a normalized transit-number distribution $T(N)$ and, (2) a normalized age-number distribution $A(N)$. To clarify the meanings of these two distributions, assume that each fluid element as it enters the DSC automatically displays a positive integer, starting with integer one. Subsequently, the integer automatically increases by one unit at each iteration, and continues to increase so long as the fluid element remains within the model. This integer is the "age-number" of the fluid element. The maximum age-number a given fluid element exhibits is that which it has at the iteration of its discharge from the DSC model (or, if so desired, from some sub-region of the model). This maximum age-number is the "transit-number" of the element. That is, each fluid element receives a number, called its age-number, that increases by one unit for each iteration of the model, to a maximum value called the

transit-number, which is the number that coincides with the discharge of that element from the model (or, if so desired, from some sub-region thereof).

For any model in a steady flow, steady volume regimen, both the age-number and the transit-number distributions will reach constant values after a sufficient number of iterations have occurred following the start of the steady flow, steady volume regimen. The size of a "sufficient number" of iterations will depend on the degree of precision desired (i.e., on the number of significant figures specified). Conceptually, the transit-number distribution may be determined by collecting the water discharged from the system at any iteration (after the "sufficient number"), grouping the fluid elements contained therein according to the transit-number they display, and then dividing the number of fluid elements in each group by the total number of elements collected. One would then have, for each transit-number group, the fraction of elements within that group, and

$$\begin{aligned} N_m \\ \sum_{i=1}^{N_m} T(N)_i &= 1 \end{aligned} \quad [5a]$$

where, $T(N)_i$ = fraction of elements in transit-number group i , and
 N_m = maximum transit-number in population.

Similarly, at any given iteration (after the "sufficient number"), if all the fluid elements within the DSC were collected, the normalized age-number distribution could be determined, and

$$\begin{aligned} N_m \\ \sum_{i=1}^{N_m} A(N)_i &= 1 \end{aligned} \quad [5b]$$

where, $A(N)_i$ = fraction of elements in age-number group i .

The average transit-number and the average age-number may be obtained directly from the first moments of the distributions:

$$\bar{T} = \sum_{i=1}^{N_m} i T(N)_i \quad [6a]$$

$$\bar{A} = \sum_{i=1}^{N_m} i A(N)_i \quad [6b]$$

where, $\bar{T}$ = average transit-number, and

$\bar{A}$ = average age-number.

In equations 5a through 6b, and throughout the rest of this paper, the group number i is identical to the iteration number N .

For any FSM in steady flow, steady volume regimen, with no "dead space" (see illustrative example II for definition of dead space) and with a single SBRV and single SBDV, the following is valid:

$$\frac{SBRV + \Sigma VOL}{SBRV} = \bar{T} \quad [7a]$$

where, ΣVOL = sum of all cell volumes.

In the special case of an FSM consisting of a single simple cell (equation 4a) the following is valid:

$$\frac{SBRV + VOL}{SBRV} = \bar{T} = \bar{A} \quad [7b]$$

Illustrative example I. Assume a steady volume, steady flow model consisting of three simple mixing cells in series, with $VOL = 2$ for each cell (Figure 2). Let the $SBRC = 10,000$ at $N=1$ and zero for all $N>1$. Let the $SBRV = 0.01$ (constant). At iteration $N=1$, 100 tracer units ($SBRC \cdot SBRV = 10,000 \cdot 0.01 = 100$) will enter the DSC model. Nominal concentration is defined as the number of tracer units in a cell divided by the nominal (or unexpanded) volume of that cell. In this example the nominal concentration of tracer units entering cell 1 is 50. However, after inflow, mixing, and discharge from the cell, the nominal concentration (to 4

significant figures) is 49.75, the difference having gone out with the discharged fluid. It is evident that 0.005 part of the nominal volume ($SBRV/VOL = 0.01/2 = 0.005$) of cell 1 is "tagged" by the entering numerical tracer. At the end of iteration 1, 49.75/50.00 fractional part of the entering age-number 1 is $49.75 \times 10^{-4} ((49.75/50.00) * 0.0005)$. At all subsequent iterations $SBRC = 0$; that is, no more "tagged" fluid elements enter the model. At any subsequent iteration, N , the concentration of numerical tracer remaining in any cell is a measure of the fractional amount of fluid elements of age-number N in that cell. That is for any cell,

$$A(N)_i = \frac{C(N)_i}{C'} * \frac{BRV}{VOL'} \quad [8]$$

where, $C(N)_i$ = concentration of numerical tracer in a cell at iteration $i(=N)$.

C' = "instantaneous" nominal tracer concentration at iteration $i = 1$, entering boundary cell.

VOL' = volume of boundary cell receiving tracer.

By iterating the model until $C(N)_i$ is zero (to the number of significant figures desired), the distribution $A(N)$ may be determined. The same is true for the distribution $T(N)$, except that it is computed with relation to the concentration of tracer in the discharged fluid. For the SMC rule, the concentration in the discharged fluid and the concentration in the effluent boundary cell (or cells) is identical. The computations of $C(N)$ for the model of Figure 2 is given in Table 1. The distributions of $A(N)$, computed by equation 8, are shown in Figure 2. These distributions depend on the magnitude of flow and the design of the model and are independent of the particular value chosen for the BRC pulse in the simulation experiment.

As a check on the computer program, the concentration in cell 3 may also be calculated by the analytical solution given by Himmelblau and Bischoff (1968, Chapt. IV). It is only necessary to note that $t/\bar{t}$ in the analytical solution is equivalent to $N/\bar{N}$ in the model. The results are given in the last column of Table 1.

TABLE 1. Concentration C(N) of numerical tracer in cells of DSC shown in Figure 2.

N	Cell 1	Cell 2	Cell 3	Cell 3, H.&B.
1	49.75	0.25	0.00	-----
100	30.36	15.11	3.80	3.79
200	18.44	18.35	9.17	9.20
400	6.80	13.63	13.50	13.53
600	2.51	7.49	11.19	11.20
800	.93	3.68	7.34	7.33
1,000	.34	1.70	4.23	4.21
2,000	.00	.02	.12	.11
5,000	.00	.00	.00	.00
$\bar{A}$	201.00	401.00	601.00	-----

Note: By equation 9, $A(N)_i = \frac{C(N)_i}{50} * \frac{0.01}{2} = C(N)_i * 10^{-4}$

The computer program calculates the mean age-number of any cell, the mean age-number of the entire model, and the mean transit-number of the model. The calculated results are shown on the bottom row of Table 1. The mean age-number for the entire model is the mean of the individual cells, in this case 401. The mean transit-number, in this case, is the same as the mean age-number for cell 3, or 601. The program also computes the variance (not shown) for each distribution.

Illustrative example II. Assume a model of identical total volume as in the previous case, but divided between a volume of active flow and a volume of "dead space." Each of the 3 cells in the active flow region is interconnected with the dead space (Figure 3). At each iteration a fraction of volume from each active cell flows to the dead space, mixes with the water in the dead space, and then returns to the active cell. The volume fraction that exchanges in this way is called XVOL. In this example XVOL = 0.10 for each cell. As in the previous case the age-number distributions are obtained by pulsing the DSC model. The results are given in Table 2.

Since cell 3 (the only discharge boundary cell) is a simple mixing cell its average age-number, $\bar{A}$, (in this case 573.76) is also the average transit-number, $\bar{T}$, of the DSC. Here, however, the average transit-number,

as calculated by the program (FISTMO), is not given by equation 7a. Perhaps five significant figures is not enough, in this case, to define a "sufficient number" of iterations.

TABLE 2. Concentration C(N) of numerical tracer in cells of DSC shown on Figure 3.

N	Cell 1	Cell 2	Cell 3	Cell 4
1	89.43	1.12	0.34	3.04
10	38.83	10.46	7.87	14.15
50	14.62	16.07	16.57	15.46
200	11.02	12.31	12.81	11.84
400	7.71	8.61	8.96	8.28
600	5.40	6.03	6.27	5.80
1,000	2.64	2.95	3.07	2.84
2,000	.44	.50	.52	.48
3,000	.07	.08	.09	.08
5,000	.00	.00	.00	.00
$\bar{A}$	524.02	569.82	573.76	565.24

Note: By equation 9, $A(N)_i = \frac{C(N)_i}{100} * \frac{0.01}{1} = C(N)_i * 10^{-4}$

Illustrative example III. In many field investigations the decay age of carbon-14 in groundwater is obtained in order to estimate age of the groundwater in the aquifer. However, decay age and groundwater age are not identical except in the special case of zero mixing (i.e., "piston" flow). Decay age may be related to groundwater age only within the framework of a specific population balance model. The DSC model offers this possibility in a simple manner. Suppose a spatial distribution of adjusted C-14 ages has been obtained from the groundwater in an aquifer. The distribution of ages, together with other information, may be used to formulate and calibrate a DSC model. To illustrate the method, assume an alluvial aquifer in a semi-arid region receiving recharge both along its periphery (mountain-front recharge) and through the channel bottoms of streams (Figure 4). Information on flow distribution is available, and it is desired to obtain an estimate of long-term average annual

recharge. As a first guess the aquifer is divided into a series of cells (based on hydrogeological data) and values of SBRV, representing average annual recharge, are chosen. The system boundary recharge concentration, SBRC, of C-14 at each of the two recharge locations is made equal to 100 (constant). The model is iterated until steady state is reached. At each iteration the state of each cell is changed in accord with equation 3b to account for radioactive decay. The results are shown in the table of Figure 4. These ages may be compared with the field data, and the modeler makes changes, as may be necessary, to obtain a better fit between model and data. In making these changes, he will use all sources of information at his disposal -- quantitative, qualitative, and intuitive. After a satisfactory model is achieved, it may be pulsed as in examples I and II to obtain the average age, $\bar{A}$, of the water. As is expected, in all cases where mixing occurs, C-14 ages are lower than average age of the water. In this example the differences between the two ages are small, because mixing is relatively small, but in cases where young water mixes with old water the differences are significant.

Non-steady Volume, Non-steady Flow, Non-steady Mass. The volume of any or all cells of the model may be changed from one iteration to the next by applying a rule other than $BDV = BRV$. As mentioned previously, cell volume is always identical to volumetric liquid content; that is, there is no empty space in any cell. The particular rule chosen will depend mainly on the kind of system being modeled. For example, excess rainfall-runoff relationships on a watershed may be modeled by a network of linear reservoirs (Dooge, 1973) where the discharge from a reservoir at any instant is directly proportional to the storage in the reservoir.

In DSC notation, we have,

$$VOL(N+1) = FAC * BDV(N+1) \quad [9a]$$

or,

$$BDV(N+1) = \frac{VOL(N+1)}{FAC} \quad [9b]$$

The storage equation may be written

$$VOL(N+1) = VOL(N) + BRV(N+1) - BDV(N+1) \quad [9c]$$

FAC is a constant of proportionality whose magnitude will be determined by trial-and-error calibration. In a multi-cell network, where each cell represents a portion of the watershed, FAC may be different for different cells. In this case,

$$BDV(N+1, X) = \frac{1}{FAC(X)} * VOL(N+1, X) \quad [9d]$$

Equations 9a through 9d can be easily modified to include threshold effects in which a cell will begin to discharge only after a minimum volume is exceeded (Campana, 1975, p. 211).

Illustrative example IV. Assume a watershed of, say, 60 km^2 area, divided into six equal parts, each represented by a cell (Figure 5). A storm produces a uniform rainfall excess of 3 cm in a 50-minute interval. Let each N represent one minute. The total input to each cell is $3 \text{ cm} \times 10 \text{ km}^2 = 30 \text{ cm-km}^2$. If the unit reference volume is taken as 60 cm-km^2 , then the SBRV at each iteration from $N = 1$ to $N = 50$ will be 0.01, and zero thereafter. In addition, the model was pulsed with a numerical tracer at $N = 1$. Figure 5 shows the resulting stream hydrograph for $FAC = 10.0$, and also the tracer concentration, both at the output of cell 6. (The computer printout provides data for all 6 cells.)

Example IV is the simplest possible, with only one parameter, FAC, to be evaluated, for any given cell network. It is possible to make the model increasingly complex, by having cells represent unequal areas, by having FAC change in magnitude from cell to cell, etc., and the input to the system can be made variable both in time and in space. A physical meaning can be attached to the tracer distribution of example IV only if the dispersive properties of the real watershed correspond to model assumptions. As of this writing we have made no attempt to simultaneously model dispersion of tracers and volumetric discharge of surface waters of a real-world system. If instead of being a constant, FAC varies with iteration number according to some rule (for example, as some function of VOL) then a non-linear system will result. Some of these possibilities are outlined by Campana (1975) including the possibilities for modeling

energy transport and flow in ground-water reservoirs, but we have not yet applied them to real-world systems. The program written by Campana is flexible and can accommodate a wide range of different assumptions.

Discussion and Conclusion

The DSC model represents a compromise between a wholly operational and a wholly physical model. To the extent that it provides a basis for prediction in spite of ignorance of the physical system, it is operational. Equally, to the extent that it accounts for the distribution of mass and energy within the system in a manner that is in harmony with chemical and physical laws, it is physically based.

The model is, in general, non-linear, since separate impulses are not necessarily additive. In spite of this characteristic, it is simple, flexible and inexpensive to operate. Models of up to about 12 cells can be programmed for desk calculators, such as the Wang 700. Beyond that number a digital computer is required. About 10 seconds on a CDC 6400 is needed for a typical run. The model's flexibility may be a source of uneasiness because much depends on the skill and intuition of the modeler in devising a model based on incomplete and scattered data. The DSC model is not capable of manufacturing observations, but it appears to have a potential for helping with the interpretation of available scant data. At the very least, it provides a quick and easy method for testing the consequences of alternative hypotheses in a wide range of hydrologic and hydro-geologic settings. In addition, we make the following comments:

(1) The DSC model is particularly useful wherever the real system cannot be described by a manageable set of partial differential equations (such as flow through karstic aquifers),

(2) The model can deal with two different kinds of data: mass transport (many different "tracers") and energy transport (hydrographs and change in storage),

(3) The model is a vehicle for interpreting data and reproducing experiments. Because of its recursive structure the stage is set for Markov chain models in which all of its elements would be redefined in probabilistic terms, and

(4) The model possesses features that may lead to useful managerial applications -- for example, estimates of the probability distribution

function of pollutant concentration in a watershed or of storage volume in a karst aquifer.

The second paper in this series discusses applications to water resources management and the third paper describes an application to modeling groundwater flow.

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(a) SIMPLE MIXING CELL, SMC.

(b) MODIFIED MIXING CELL, MMC.

Figure 1. Alternative unit cells in discrete-state compartment models.

Figure 2. Illustrative example of steady volume DSC model consisting of 3 cells in series.

Figure 3. Illustrative example of steady volume DSC model consisting of 3 cells in series interconnected with a dead space.

CELL NO.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
PERCENT C-14	99.01	95.70	93.07	90.16	87.01	80.02	87.69	85.21	82.62	79.91	77.11	74.24	71.30	66.33	65.33	62.31
C-14 AGE	167	353	591	852	1151	870	1084	1324	1580	1854	2149	2456	2796	3151	3523	3911
A, WATER	168	368	601	868	1162	901	1121	1361	1621	1901	2201	2521	2861	3221	3601	4001

Figure 4. Illustrative example of relation between decay age of C-14 and average age of water.

Figure 5. Illustrative example of DSC model applied to rainfall-runoff relationship.

PART D

ON THE USE OF NEGATIVE IONS AND ELECTROSTATIC ACCELERATORS
FOR THE STUDY OF LOW CONCENTRATIONS OF LONG LIVED RADIONUCLIDES*

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Abstract

Ultrasensitive mass spectrometry can benefit from the strongly specific properties of negative ions and the exploitation of the tandem accelerator principle to increase the energy of the ions so that individual particle identification becomes possible. The complete disintegration of molecular ions during the process of charge exchange at high energies also simplifies the particle identification.

The study of the radioactive isotopes ^{10}Be , ^{14}C , ^{26}Al and ^{36}Cl is discussed in particular although the general ideas are more widely applicable.

*Report prepared for the "Workshop on Dating of Old Ground Water" to be held at the University of Arizona, March 16th to 19th, 1978.

INTRODUCTION

The recent successes in directly detecting^{1,2} and measuring^{1,3} ^{14}C atoms at near natural abundances, using nuclear physics derived techniques, has stimulated the discussion and the planning for the detection of other long lived radio-active nuclei. The direct detection of ^{10}Be atoms has been reported quite recently^{4,5}. It is quite likely that the detection and accurate measurement of other long lived radio-active nuclei will be possible and this report summarizes the state of our thinking on the detection and measurement of the radio-active nuclei ^{10}Be , ^{26}Al and ^{36}Cl together with a summary of the situation for ^{14}C . The detection and measurement of ^3H and ^{32}Si is discussed in an appendix.

DETECTION of ^{14}C

The negative ion of carbon is stable and exists in two forms whereas the negative ion of nitrogen is unstable¹. This is shown in Table 1. Table 2 lists the negative ion fluxes expected for the long-lived radioactive nuclei. Complete separation between ^{14}C and ^{14}N is therefore possible at the negative ion source of a tandem accelerator. The mass-14 molecular ions $^7\text{Li}_2^-$, $^{13}\text{CH}^-$ and $^{13}\text{CH}_2^-$ also emitted by the ion source are broken up, during the charge exchange process, in the terminal of a tandem accelerator. It has been shown recently that the molecule $^{12}\text{CH}_2^{+2}$ is metastable⁶ and so could interfere with $^{14}\text{C}^{+2}$ determination. However as long as charge state +3 or greater is used there appears to be no interference of molecular fragments with the detection of ^{14}C ions^{6,7}.

There are, of course, numerous developmental problems such as ^{14}C background from contamination, both natural and artificial^{1,3} and with instabilities in the ion sources¹ but these problems are not surprising because the devices used were not designed solely for the detection and measurement of ^{14}C concentrations in natural carbon. Figure 1 shows the separation achieved between ^{14}C , ^{14}N , ^{13}C and ^{12}C ions in a recent experiment at Rochester¹. This figure illustrates two important problems that will be encountered in the future with other long lived radioisotopes.

First of all there are the other carbon isotopes which interfere with the detection of ^{14}C . These are generated mainly from the $^{13}\text{CH}^-$ and $^{12}\text{CH}_2^-$ molecules which strip twice, once in the terminal and once in the residual gas of the high energy acceleration tube. Though this process is improbable, less than 1 in 10^{+6} , there are enough molecules injected into the accelerator to generate ^{13}C and ^{12}C ions of the same magnetic rigidity as the ^{14}C ions. These ions can be eliminated by electrostatic analysis and so are not a fundamental limitation. Such ^{13}C and ^{12}C ions can also be generated if the resolution, $\frac{M}{\Delta M}$, of the accelerator inflection magnet is not high enough.

Secondly there are interfering ^{14}N ions. These are generated either during machine instabilities following the injection of some $^{14}\text{NH}^-$ into the accelerator or else by a second charge exchange in the acceleration tube. Adequate stabilization of the accelerator voltage and higher ion source magnet resolution would eliminate this source of background although the Rochester Heavy Ion detector⁸ can readily discriminate between ^{14}N and

^{14}C of the same energy and the ^{14}N yield is observed to be very low.

Detailed work on the design of a dedicated ^{14}C measuring tandem system is in progress⁹.

DETECTION OF ^{26}Al

The successful detection of ^{26}Al should closely parallel the detection of ^{14}C because there is a strong indication¹⁰, although at present no proof, that the $^{26}\text{Mg}^-$ ion is unstable. The properties of Mg^- and Al^- are shown in Table 1. Undoubtedly the $^{25}\text{MgH}^-$ and $^{24}\text{MgH}_2^-$ molecular ions will form part of the injected molecular ion current as will $^{13}\text{C}_2^-$ and possibly others¹¹. However these molecular ions will be destroyed during the charge exchange process to form positive ions and although a second charge exchange process will undoubtedly generate ^{24}Mg , ^{25}Mg and ^{13}C ions of the same magnetic rigidity as the ^{26}Al ions they can be eliminated by an electrostatic analyser. However in this case it is necessary to improve the resolution of the ion source inflection magnet over the usual value of $\frac{M}{\Delta M} \sim 25$ for an MP Tandem ion source because $^{26}\text{MgH}^-$ ions will undoubtedly be injected in small but significant numbers and a second charge exchange after molecular disintegration will yield ^{26}Mg ions of the same magnetic rigidity as the ^{26}Al . Also the tail of the intense $^{27}\text{Al}^-$ beam will undoubtedly contribute, making the discrimination of ^{26}Mg and ^{26}Al by dE/dx measurements very difficult. The proposed¹²

$\frac{M}{\Delta M} \sim 100$ injection system for the Rochester Tandem will undoubtedly solve this problem as well as making possible rapidly sequential measurements of both ^{27}Al and ^{26}Al ion intensities.

It has been observed recently¹⁰ that Al^- ions are generated most readily by charge exchange in sodium vapour. The equilibrium fractions of Al^- and Mg^- at 20 keV energy are 0.12 and $< 10^{-6}$ respectively. Ion currents of Al^- generated by this method are likely to be much higher than from the solid aluminum of the sputter source¹¹. The reason for this is not known at present.

Using the microampere beams from charge exchange in sodium, the detection of ^{26}Al at the level of 1 part of ^{26}Al in 10^{14} parts of ^{27}Al should present no problems provided a higher resolution inflection magnet is used. Expected $^{26}\text{Al}^-$ fluxes from some samples are given in Table 2. The presence of Mg^- ions would, of course, modify this assertion and clearly, as in the case of the detection of ^{14}C in the presence of ^{14}N using negative ions, an experiment will give the final answer to this problem.

The Rochester Heavy Ion detector⁸ will discriminate between ^{26}Mg and ^{26}Al ions of the same energy but it is worth noting that in this case the range separation method used at Berkeley³ to discriminate between ^{14}C and ^{14}N ions will not work because the ^{26}Al ions have a shorter range than the ^{26}Mg ions.

DETECTION OF ^{10}Be

The negative ions of ^{10}Be and ^{10}B have both been observed¹⁰ and microampere beams of Be and B have been accelerated by a tandem accelerator¹³. Some of the properties of these negative ions are shown in Table 1. ^{10}Be has been detected using a cyclotron^{4,5} and the range separation technique³ is useful here for separating the ^{10}Be and ^{10}B ions. However the tandem accelerator is quite competitive with the cyclotron and in fact it has the great advantage of being able to cycle rapidly between ^9Be and ^{10}Be to measure the isotopic ratio accurately.

If $^{10}\text{Be}^{+4}$ and $^{10}\text{B}^{+4}$ ions are accelerated in an MP tandem accelerator then energies of 50 MeV are easily obtained. There could be as many as 10^7 $^{10}\text{B}^{+4}$ ions per second if the B contamination is 1 part in 10^6 parts of beryllium. This high counting rate cannot be handled by the Rochester Heavy Ion detector. However at 50 MeV the ions can be passed through a thin carbon foil and this reduces the $^{10}\text{B}^{+4}$ flux by a factor of 30 but has little effect on the $^{10}\text{Be}^{+4}$ flux because all the electrons have already been removed¹⁴. Three such charge exchanges each followed by a magnet to remove the $^{10}\text{B}^{+5}$ ions would reduce the $^{10}\text{B}^{+4}$ flux by a factor of 2.7×10^4 . The remaining flux of 3.2×10^2 $^{10}\text{B}^{+4}$ ions per second can easily be handled by the Rochester Heavy Ion detector. As it happens three magnets are already available at Rochester before the final detector so that the procedure could be implemented as soon as a sodium charge exchange ion source becomes available. Range separation³ is also possible in this case. $^{10}\text{Be}^-$ fluxes expected from samples are given in Table 2.

DETECTION OF ^{36}Cl

The negative ions $^{36}\text{Cl}^-$ and $^{36}\text{S}^-$ both exist as shown in Table 1 and although ^{36}S is a rare (0.014%) isotope nevertheless it will represent an obstacle to the detection of ^{36}Cl at the level of 1 part in 10^{14} of chlorine.

Tens of microamperes of Cl can be generated quite readily by a sputter ion source¹¹ and a resolution of $\frac{M}{\Delta M} \sim 100$ is necessary to avoid the injection of $^{35}\text{Cl}^-$ and $^{37}\text{Cl}^-$ ions. Even with the higher resolution $^{35}\text{ClH}^-$ ions¹⁵ and $^{18}\text{O}_2^-$ ions will be injected. It is expected that $^{36}\text{Ar}^-$ ions will be unstable but this can only be decided by experiment. The molecular ions will, of course, be destroyed and present no problem. However, the fluxes of ^{36}S ions could be as large as 10^3 to 10^4 second and this combined with the smaller difference in dE/dx between S and Cl than for Al and Mg will make the problem difficult but not impossible to solve. Improvements to the Rochester Heavy Ion detector are possible and care with the purity of the chlorine from sulphur could make the detection of ^{36}Cl in the presence of ^{36}S possible as well as the measurement of the ratios $^{35}\text{Cl} : ^{36}\text{Cl} : ^{37}\text{Cl}$ in 10^{14} parts of ^{35}Cl . Typical $^{36}\text{Cl}^-$ fluxes are given in Table 2. However much more research into the detection of ^{36}Cl in the presence of ^{36}S is necessary. Unfortunately the range of ^{36}S is greater than the range of ^{36}Cl so the range separation technique³ cannot be used in this case. A speculative solution to the ^{36}S problem is given in Appendix 1.

CONCLUSIONS

It appears that the recently developed atom counting method for the detection of ^{14}C atoms can be extended quite readily to the measurement of ^{10}Be and ^{26}Al with tandem accelerators and possibly to ^{36}Cl . For ^{26}Al and ^{36}Cl the use of a higher resolution, $\frac{M}{\Delta M} \sim 100$, inflection magnet will be necessary and in the case of ^{36}Cl it will be necessary to solve the problem of ^{36}S contamination. Some speculations on more advanced methods for decreasing the background ions for all three cases are given in the Appendix 1. A brief discussion of the detection of the radioactive nuclei ^3H and ^{32}Si by atom counting is given in Appendix 2.

ACKNOWLEDGEMENTS

We are indebted to Dr. K.H. Purser, Professor H.E. Gove and several of our colleagues for many stimulating discussions. This work was partly supported by the National Research Council of Canada.

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APPENDIX 1

There are a number of techniques and ideas being developed at present which may have important applications to the detection of radio active nuclei at very low levels of abundance (less than one part in 10^{14}) in the presence of the isobar.

The time of flight of heavy ions has been measured¹⁶ with time resolutions of about 100 picoseconds by using the pulses of electrons emitted when a heavy ion passes through a thin foil. This is a potentially powerful technique and may be especially useful in the early stages of studying the problems of detecting an unfamiliar isotope. The time of flight technique generates a complete velocity spectrum of the heavy ions and after a magnetic deflection makes the identification of charge to mass ratios possible over a wide range. As a result the setting up of the beam transport system could be simplified. Unfortunately combining dE/dx measurements with time of flight measurements, although theoretically possible, has not yet been studied thoroughly.

Some time ago an interesting idea was proposed by Cramer¹⁷. This was dubbed the charge enforcer and is a type of storage ring which allows the maximum charge state to build up as a result of successive traversals of the same foil by a heavy ion beam. The idea was proposed for high beam currents but variations on the idea are possible as part of a detector for ultra-sensitive mass spectrometry.

A simplified version is shown in Figure 2, for a device which would separate ^{36}Cl from ^{36}S . The mode of operation of the device is obvious from the figure. The chlorine atom can reach charge state +17 whereas the sulphur atom can only reach charge state +16 so that after many passes through the stripping foil, limited only by multiple scattering and energy spread increase, a large fraction of the ^{36}Cl atoms could be detected.

It is worth noting that with a total flux of 10^3 $^{36}\text{S}^{+9}$ and 1 $^{36}\text{Cl}^{+9}$ injected per second there will still be only one ion circulating at any time most of the time. One circuit could take approximately $1\ \mu\text{s}$ so that hundreds of circuits for each ion are possible before the next ion arrives¹⁸. In this case the electron pulse from each passage of the stripping foil is recorded so that the detailed history of each ion for many circuits is possible. This would make the ejection of an ion after a given number of circuits feasible. The criterion for ejection might be that the multiple scattering or energy spread is becoming too large.

Many variations on this type of device are possible and much ion optical work would have to be carried out before it could be realized. However it does, we think, illustrate the point that if it is necessary to detect ^{36}Cl in the presence of ^{36}S that there are probably solutions to the problem.

APPENDIX 2

DETECTION OF TRITIUM*

Negative ion sources that produce at least 178 μA of H^- exist. At this current there are 4 tritons per hour per Tritium Unit (TU). This is to be compared with 4 beta rays per hour per TU from 1 gram of hydrogen. Negative ion sources capable of generating at least 1.78 mA of H^- exist¹⁹ and enrichment of tritium to 100 TU is routine consequently 4×10^3 tritons per hour could be counted if it wasn't for the existence of $^3\text{He}^-$.

After acceleration to 4 MeV nearly 99% of $^3\text{He}^+$ can be converted to $^3\text{He}^{++}$ on passing through a thin foil²⁰ so that 99% of the ^3He beam could be eliminated with the help of a simple magnetic analyser. N foils plus magnetic analysers would reduce the ^3He flux by a factor of 100^N . After an appropriate number of attenuations range separation should be possible.

*Prepared with help from H.W. Lee.

DETECTION OF ^{32}Si

Negative silicon beams of several micro amperes are readily available from a sputter ion source¹¹. Unfortunately sulphur also readily makes negative ions so that $^{32}\text{S}^-$ ions could seriously interfere with the detection of ^{32}Si . Although it may be possible to reduce the sulphur contamination it will always limit the ability to detect ^{32}Si at very low levels.

The ^{32}S contamination can be reduced by possibly a factor of 10^6 by noting that there are isomeric states of the $^{32}\text{Si}^-$ ion, Table 1. Also one of these isomeric states can be dissociated readily by an electric field because of the low binding energy²¹. Consequently if we start out with $^{32}\text{Si}^-$ ions and neutralize them in an electric field only neutral ^{32}Si atoms will be formed because of the high binding energy of $^{32}\text{S}^-$ and the absence of isomeric states of $^{32}\text{S}^-$. The $^{32}\text{S}^-$ can be eliminated by a magnetic field and the neutral ^{32}Si reconverted to $^{32}\text{Si}^-$ in sodium vapour. They can then be accelerated and detected in the normal manner using for example the Rochester Heavy Ion detector which would have no difficulty separating ^{32}Si and ^{32}S because they differ by two charges.

TABLE 1

RADIOISOTOPE	HALF LIFE YEARS	POSSIBLE DATING RANGE YEARS	NEGATIVE IONS OF ISOBARS [†]
^{14}C	5730	$0 - 10^5$	$^{14}\text{C}^- [^4\text{S}(1.27), ^2\text{D}(0.035)]$ $^{14}\text{N}^- [^3\text{P}(-0.05)^* ?]$
$^3\text{H}^\#$	12	$0 - 120$	$^3\text{H}^- [^1\text{S}(0.74)]$ $^3\text{He}^- [^4\text{P}(0.07)^*]$
^{10}Be	2.5×10^6	$0 - 2.5 \times 10^7$	$^{10}\text{Be}^- [(0.24)^*]$ $^{10}\text{B}^- [^3\text{P}(0.28)]$
^{26}Al	7.4×10^5	$0 - 7.4 \times 10^6$	$^{26}\text{Al} [(0.46)]$ $^{26}\text{Mg} [(0.32)^*]$
$^{32}\text{Si}^\#$	~ 650	$0 - 6500$	$^{32}\text{Si}^- [^4\text{S}(1.39), ^{32}\text{S}^- [^2\text{S}(2.097)]]$ $^2\text{D}(0.51)? ^3\text{P}$ or $^2\text{S}(0.035)$
^{36}Cl	3.1×10^5	$0 - 3 \times 10^6$	$^{36}\text{Cl}^- [^1\text{S}(3.615)]$ $^{36}\text{S}^- [^2\text{S}(2.077)]$

[†] Configuration of state given together with binding energy in eV

* Metastable with lifetime long for $^3\text{He}^-$ and $^{10}\text{Be}^-$ and very short for $^{14}\text{N}^-$ and $^{26}\text{Mg}^-$.

[#] Discussed in Appendix 2.

TABLE 2

ISOTOPE	ACTIVITY	CONCENTRATION	NEGATIVE IONS PER MICROAMP
^{10}Be	3.8 to 7.6 $\frac{\text{dpm}}{\text{cm}^3}$ ⁽¹⁾	$(7.2 \text{ to } 14.4) \times 10^{-10}$	$10^3 \text{ sec}^{-1}\dagger$
^{26}Al	0.65 $\frac{\text{dpm}}{\text{g}}$ ⁽²⁾	1.7×10^{-12}	$2 \text{ sec}^{-1}\dagger$
^{36}Cl	2.1 $\frac{\text{dpm}}{\text{g}(\text{Cl})}$	2.2×10^{-11}	10^2 sec^{-1}
^{14}C	15 $\frac{\text{dpm}}{\text{g}}$ ⁽⁴⁾	1.2×10^{-12}	7.5 sec^{-1}

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†Assumes no enrichment of beryllium or aluminum. Estimates only.

Figure Captions

Figure 1. The number of ions is shown as a function of the total ion energy and the ion energy in the final section of the Rochester Heavy Ion Detector.

Figure 2. A schematic diagram of an atom identifier for ^{36}S , ^{36}Cl is shown.

W-3703 MT. SHASTA

4590 ± 250 yrs. (USGS)

ATOM IDENTIFIER

(SCHEMATIC)

Fig. 2

THE IONEX CARBON-14 DATING SYSTEM
by K. H. Purser and P. R. Hanley

INTRODUCTION

Recent experimental results on the application of tandem accelerators to carbon-14 dating⁽¹⁻³⁾ have motivated the design of a compact, automated carbon-14 dating system intended for routine laboratory use. This paper describes the IONEX Carbon-14 Dating System which is designed to employ either solid carbonaceous or gaseous CO₂ samples. These samples are ionized and mass selected to produce $^{14}\text{C}^-$ ions which are then accelerated to high energy and counted individually. This technique, which has been discussed by several previous authors (1-3), can provide the ultimate sensitivity for ^{14}C measurements. In order to make useful dating measurements, it is necessary to arrange that it be possible to compare the ratios of the ^{14}C nuclei present in the sample with the quantities of the other two stable isotopes ^{12}C and ^{13}C . This ratio decreases by a factor of two for every 5730 years. The $^{13}\text{C}/^{12}\text{C}$ ratios are only essential for very precise measurements as they make possible corrections for changes in the isotope uptake of the sample material at the time of its formation. The problem of time variations in ion source output and variations in the transmission efficiency of the complete apparatus from ion source to detector is obviated by arranging that individual bursts

of ^{12}C , ^{13}C , and ^{14}C ions can be injected, with no changes in the source parameters, in a rapid, controlled time sequence. Because ratio information is all that is needed for dating, slow variations in either source or transmission efficiency have no effect on the result.

The system has a good transmission efficiency for the ^{14}C atoms that are present; for a sample of recent origin it will be possible to measure between 15 and 30 ^{14}C events per second with less than 1 mg/hour consumption of material. 1% statistics should be available within 15 minutes; 0.1% statistics should be available from a measurement taking between 10 and 24 hours. Because of the rapid production possible with this system, automation and computer control is essential from the insertion of a suitable sample to the final determination of an age.

APPARATUS DESCRIPTION

The system which is shown in Figure 1 divides itself naturally into four sections:

1. An ion preparation section where bursts of ^{12}C , ^{13}C , ^{14}C ions free of unwanted mass contaminants are prepared in the form of negative ion beams of equal emittance selected in a computer controlled time sequence.
2. A region where the particles are accelerated in two stages to an energy of 8 MeV with an intermediate stripping of the negative ions to multiply charged positive ions. During charge changing molecular components are dissociated.

3. An analysis stage where a combination of electric and magnetic constraints are used to eliminate almost all unwanted particles.
4. A gas counter which makes an independent check of detected particle parameters from which values for the mass, atomic number and charge state can be derived.

Solid Ion Source

The ion source is a critical element in any direct measuring ^{14}C detection system. Two separate types will be available with the present instrument. The first of these is an improved version of the sputter ion source that has been used for the ^{14}C measurements to date that have been made using tandem accelerators⁽⁴⁾.

The principles of this device are shown in Figure 2. An incident beam of cesium positive ions having an energy of ~ 20 keV is focused through a small aperture and reflected in the negative ion extraction electrostatic field to a small spot where the cesium is deposited and carbon is sputtered from the surface. C^- ions are produced at this location and are accelerated by the extraction field. Sputter sources have the following advantages:

1. High efficiency ($\sim 1\%$ conversion of the carbon material into useful C^- ions).
2. Solid materials are used so that comparatively little preparation is needed between sample collection and its introduction to the ion source.

3. Rapid change from sample to sample is possible. Forty samples can be loaded at any one time for sequential processing by the dating machine.

A serious disadvantage of the solid sputter source is that it appears that the samples are very susceptible to surface contamination and this must be removed by sputtering before the data stabilizes and a reliable date can be obtained.

CO₂ Source

The second source that will be available is a Penning discharge system⁽⁵⁾ designed to run on CO₂ gas incorporated as a tracer into pure argon (Figure 3). The use of CO₂ as the source gas has several advantages:

1. The ¹⁴C atoms in the CO₂ gas is representative of the volume composition of the original sample rather than the surface composition.
2. CO₂ can be prepared in clean laboratory conditions using well-established techniques and maintained in sealed enclosures until dating. Thus, it can be completely free of recent contaminations such as ash and cigarette tars.
3. Using careful designs and replaceable anodes, Penning discharge sources can be designed to have a short memory so that previous measurements have little influence on current measurements.

The Penning Source produces positive ions and these must be made negative before injection into the acceleration section. This negative

stage is essential to eliminate the ubiquitous ^{14}N contamination. Without ^{14}N elimination the measurement would be virtually impossible. The production of C^- ions from C^+ ion beams from the gas source can best be achieved without degrading the beam emittance by charge exchange in an alkali vapor cell. Measurements from Aarhus⁽⁶⁾ indicate that sodium is the best material. A sodium cell is provided near the exit from the first electrostatic analyzer (see Figure 1). The efficiency of conversion of negative ions to positive at this point can be as high as 20% and we estimate that from the Penning Source with 30 uA of mixed C^+ ions, using CO_2 as the feed gas, ~ 6 uA of C^- will be available for injection into the dating machine. For carbon samples of recent origin this will produce a counting rate of ~ 10 /second for the final ^{14}C events. The charge exchange cell that is used is shown in Figure 4. This device is an extension of an Oxford design⁽⁷⁾ recently adapted for use with the IONEX Helium Backscattering System. The canal provides a sodium target having an integrated thickness of $\sim 6 \times 10^{14}$ atoms/cm². This is done by heating sodium metal in the central boiler from which the vapor passes through the exit tubes and condenses back to liquid on the wicking surfaces for return to the boiler. Such a device has a measured lifetime of approximately 1000 hours.

Inflection Optics

The double element inflection system used on the ^{14}C analysis machine serves the following purposes:

1. An electrostatic deflector insures that only atoms of the expected energy are introduced into the analysis system and completely eliminates high and low energy tails.
2. A high resolution magnetic element ensures that there is virtually complete rejection of the adjacent masses 13 and 15 when ^{14}C ions are being injected.
3. The mass selection system allows any one of the masses 12, 13, and 14 to be rapidly introduced to the system with similar emittances by changing the mass selection voltage. This feature permits rapid cycling and ratio measurements of high accuracy.

The first electrostatic deflector serves to provide an energy resolution of better than 1 part in 50 for the extracted ions. In this way high and low energy tails, which originate from charge exchange transitions within the electrostatic fields or from close encounters between C atoms and the incident Cs ions, can be completely eliminated. The effect of such tails is to cause mass 12, 13, and 15 particles to have similar magnetic rigidity ME/q^2 as ^{14}C . The electrostatic deflector eliminates this effect by insuring that only a single energy is accepted.

The major analysis component in the injection system is a high transmission 90° magnet for momentum dispersion which has a mass resolution, $M/\Delta M$, greater than 150. The contamination from adjacent isotopes such as $^{13}\text{C}^-$ and $^{14}\text{NH}^-$ is virtually zero and can be easily handled by the later post acceleration optics and the gas counter.

An important feature of the inflection magnet is that the magnet vacuum chamber is insulated from ground to permit the energy of the beam within the magnetic field region to be varied as a function of time. Because the mass energy product for the system remains constant, increases in energy permit lower masses to be dispersed in proportion to their momentum and selected by the magnetic inflector. For the present analyzer:

$$ME = 280 \text{ AMU.keV}$$

so that for	$E = 20 \text{ keV}$	$M = 14 \text{ AMU}$
	$E = 21.54$	$M = 13$
	$E = 23.33$	$M = 12$

The use of this switching technique makes possible precise measurements of the ratio $^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$ without the need for corrections for long term transmission changes or for ion source efficiency variations.

The energy variations needed for mass switching are made at gap lenses located at the stigmatic entry and exit image positions. The optics of the system are arranged so that the emittance of the selected particles leaving the magnet system is identical from mass to mass so that the transmission through the remainder of the components of the dating system is identical from mass to mass.

Acceleration and Dissociation

The mass selected particles are accelerated through a stable dc potential of 2 megavolts. At the high voltage terminal the negative ions

have an energy of 2 MeV and are stripped of outer electrons to the most probably charge state 3+. This process also dissociates molecular components, such as $^{12}\text{CH}_2^-$, $^{13}\text{CH}^-$ and $^{14}\text{NH}^-$, which may have been injected together with the wanted $^{14}\text{C}^-$ ions. Measurements ⁽⁸⁾ indicate that by using charge state 3+, which is the state for which the dating system has been designed, no molecular contaminants such as $^{12}\text{CH}_2^-$ can make a transition to the 3+ state but are all dissociated. It should be noted that some molecules do make transitions to the CH_2^{++} state, so that the 2+ charge state may not be useful in a ^{14}C analyzer based on the tandem principle.

After charge exchange to 3+ and the elimination of molecules of the same mass by dissociation the particles are further accelerated through a potential of 2 MV to arrive at ground with a final kinetic energy of 8 MeV. It should be noted that molecular contaminants even of the same charge will have lower energy.

SECOND ANALYSIS SYSTEM

After acceleration the particles enter the second identification system which consists of three major components:

1. An electrostatic lens and deflection system whose deflection properties are independent of mass.
2. A high resolution magnetic deflector.
3. An energy and specific ionization sensitive detector which provides atomic number (Z) identification for the particles to eliminate any vestige of nitrogen contamination that may be present.

The operation of the beam transport system excluding the final detector can best be understood by reference to Figure 5. In this plot the quantity $\frac{M}{q}$ ($\frac{\text{mass}}{\text{charge}}$) is plotted as a function of $\frac{E}{q}$ ($\frac{\text{energy}}{\text{charge}}$). The reason that such a plot is useful is that electrostatic devices produce identical trajectories for particles with the same $\frac{E}{q}$ ratio. In contrast, magnetic fields deflect particles identically with the same ($\frac{\text{momentum}}{\text{charge}}$) which can be reduced to $\frac{ME}{q^2}$ ($\frac{\text{mass} \times \text{energy}}{\text{charge}^2}$). Thus, if two such systems operate sequentially on a particle, the constraints of each are superimposed upon the particle's behavior. Even when high-transmission low-resolution geometries are used the rejection of unwanted particles can be virtually complete. Referring to Figure 5, it can be seen that for an electrostatic deflection all particles must lie on the family of vertical lines labeled 1+ to 5+ because of the electrostatic constraints. When the deflector is set to pass only the 3+ charge state, all particles of other charge states coming from the ion source together with any background particles that are produced from within the accelerator will be eliminated. The energy resolution of the system ($E/\Delta E = 300$) is sufficiently high that $^{14}\text{N}^{3+}$ from dissociation of NH^- at the high voltage terminal is eliminated. An $E/\Delta E$ dispersion of 300 corresponds to a selection band with a full width of 27 keV. This 27 keV should be compared to the difference in energy of 114 keV between the energy of ^{14}C from the ion source and the N^{+++} from the dissociation of NH^- .

An important feature of the geometry is that during those periods when other isotopes than ^{14}C are being accelerated, the particles

with the same charge state will be transmitted through the electrostatic deflector section with the same efficiency as the ^{14}C are transmitted. Thus, it is possible to rapidly shift from one isotope to another at the injector without affecting the transmission of the machine so that ratio measurements are possible.

The final magnet separates the three particle groups coming from ^{12}C , ^{13}C , ^{14}C into separate channels. ^{14}C enters the gas detector that will be described in the next section. The other channels collect the current in precision Faraday cups and convert these currents into a high frequency signal proportional to the current. The output from the current to frequency converters is counted to produce an accurate instantaneous current measurement of the ^{12}C and ^{13}C content of the sample. Figure 6 shows the gating sequences to be employed in conjunction with the first analysis system. The background in the ^{14}C channel may increase substantially during the time that the ^{12}C and ^{13}C beams are being injected so that counting of ^{14}C will not be carried out during this period.

The Gas Counter

The final detector carries out the ultimate final series of identification checks on each of the arriving particles. Thus it is not only necessary for the particle to have the correct $\frac{E}{q}$ and $\frac{ME}{q^2}$ ratios defined by the beam analysis systems but it also must satisfy the final detector criteria.

1. That the energy, E , be correct.

2. That the $\frac{dE}{dx}$ (rate of loss of energy) is appropriate to a particle having an atomic number of 6, a mass of 14, and an energy of 8 MeV.

3. That the range is also appropriate.

The final detector counter is derived from counting systems that have been used in nuclear physics for heavy ion detection in the focal planes of magnetic spectrographs.

Basically, the present counter has an ultra-thin window through which the particles enter a region filled with forming gas at a pressure of about 10 Torr where the particles stop. A particle entering the active volume produces ion pairs due to the interaction of the ion with the gas. An electric field across the width of the counter produced by a Frisch grid rapidly moves the electrons from their formation location in times that are of the order of a few microseconds. The transfer of the electrons away leaves a net positive charge which induces a signal on the collector proportional to the total energy of the ion. The electrons which pass through the Frisch grid are also used. In this case, the signals from various sections of the track are collected separately to provide three independent ΔE signals. One of these is from the initial section of the track, the second from the middle, and the third from the termination region. With this technique it is possible to identify uniquely 8 MeV ^{14}C from any residual ^{14}N which may be present in this system due to residual metastables from the ion source or from unexpected charge exchange sequences. Such background events are extremely rare due to the voltages and goo

vacuum that is used. Typically, they can come from the small NH^- tail which has been injected from the ion source, accelerated to 2 MeV, dissociated to $^{14}\text{N}^{4+}$ and H, and then reverted back to $3+$ a short distance down the tube. The final feature of the counter is that a veto signal is provided by the rear wire. Events are vetoed if the particle has a range greater than that of the active volume.

SUMMARY

A system has been described that is now available commercially for the sensitive detection of ^{14}C atoms in materials. For recent samples, the system will have a precision that is expected to be close to 0.1%. The problems of the acceleration of ^{14}N are completely eliminated by the use of negative ions and a final counter that is atomic number sensitive. The problems of molecular contaminants such as $^{12}\text{CH}_2^-$ are eliminated by dissociating the molecules at an energy high enough that the most abundant charge state of the ^{14}C positive ions produced is $3+$. These 8 MeV particles are sufficiently well collimated so that it is possible to use precise electric and magnetic deflection to impose trajectory filtering in the dimensions $\frac{ME}{q^2}$ and $\frac{E}{q}$. Virtually all unwanted particles can be removed at this stage. A final gas counter is used to make elaborate redundancy checks on the particle's identification. This counter permits the energy, $\frac{dE}{dx}$, and the range of the particle to be estimated allowing a unique identification in terms of mass, charge state, atomic number and energy. If these do not all match up with the required parameters the event is rejected.

Simulation measurements indicate that for either the gas or the sputter ion sources the ^{14}C collection rate will be in excess of 10/second.

1% statistics should be available from a recent sample in approximately 15 minutes and 0.1% statistics in a period ranging from 10 hours to 1 day. It is expected that dating to 100,000 years will be possible.

The system can easily be automated so that many samples can be loaded and measurements made automatically. The amount of material that is consumed from each sample will be small. Measurements have already been made with samples of 1 milligram or less in the solid source. It is estimated that the gaseous source proposed will consume CO_2 at the rate of about 1 atm.cc/hr.

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IONEX ¹⁴C DATING SYSTEM

FIGURE 1

SPUTTER NEGATIVE ION SOURCE FOR SOLID SAMPLES

FIGURE 2

PENNING POSITIVE ION SOURCE FOR GASEOUS SAMPLES

FIGURE 3

RECIRCULATING ALKALI METAL CHARGE EXCHANGE CELL

FIGURE 4

ELECTROSTATIC DEFLECTION

$$\frac{E_f}{q} \equiv \text{CONSTANT}$$

$$\frac{E_f}{q} = \frac{eV_i (1+q)}{q}$$

① FOR IONS FROM ION SOURCE

$$\frac{E_f}{q} \text{ ALWAYS } > V_i$$

② FOR IONS ORIGINATING WITHIN INSTRUMENT, WITHOUT CHARGE EXCHANGE DOWN.

$$\frac{E_f}{q} \text{ ALWAYS } \leq V_i$$

MAGNET DEFLECTION

$$B_0 = \frac{\sqrt{2ME_f}}{q}$$

OR FOR ALL TRANSMITTED PARTICLES

$$\frac{ME_f}{q^2} \equiv \text{CONSTANT}$$

ANALYSIS SYSTEM PROPERTIES

FIGURE 5

ANALYSIS SYSTEM GATING SEQUENCES

FIGURE 6

PART F
SUGGESTED INSTRUMENTAL IMPROVEMENTS AT THE UNIVERSITY OF ROCHESTER

K. H. Purser

The recent success in dating carbon samples by directly measuring ^{14}C atoms at levels of one part in 10^{16} has stimulated discussion for the detection of other long lived radioactive nuclei such as ^{36}Cl . Basically, the accelerator technique extends the usefulness of conventional mass spectrometry for the measurement of individual atoms in the following ways:

(1) Molecular interferences, arising from molecules of the same mass as the desired atoms, are completely eliminated by the complete disintegration of molecular ions during the process of charge exchange.

(2) Makes possible the measurement of the atomic number (Z) of an atom by E. dE/dx techniques to separate completely events that would be indistinguishable in a mass spectrometer, i.e., ^{36}S - ^{36}Cl .

(3) At high energies the kinetic energy of the particle can be measured directly to provide substantially more information about the characteristics of individual events.

(4) When a tandem is used, the very specific property of negative ions make possible a number of ways of enhancing the wanted specie and eliminate the unwanted particles (see Part D of this Appendix).

Improvements necessary at Rochester to permit reliable dating using ^{14}C and ^{36}Cl decays:

(1) A new injection system with the following features:

(a) Use of gaseous (CO_2) and solid sources

(b) $E/\Delta E$ selection > 50

(c) Magnetic selection to provide $M/\Delta M$ 7, 150

(d) Rapid mass switching between ^{12}C , ^{13}C , ^{14}C and ^{35}Cl , ^{36}Cl , ^{37}Cl - (\$150,000)

(2) Post Acceleration Components:

(a) Electromatic deflector and lens with $E/\Delta E \gtrsim 300$

(b) Magnetic momentum Selector to give $P/\Delta P \gtrsim 1000$ (\$60,000)

(3) Modified Gas Counter - (\$20,000)

PART G

Proc. Ninth International Conf. on Radiocarbon Dating, R. Berger
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MEASUREMENT OF SMALL RADIOCARBON SAMPLES: POWER OF ALTERNATIVE METHODS FOR TRACING ATMOSPHERIC HYDROCARBONS

L.A. Currie,* J.E. Noakes,** and D.N. Breiter

ABSTRACT

The special problem of measuring very small radiocarbon samples arises whenever samples have a high specific "cost" -- i.e., very limited in supply, or very difficult to collect. One such problem, where collection difficulties are limiting, is the measurement of carbonaceous species in the atmosphere in order to resolve the relative contributions of man and nature. The characteristics of miniature gas proportional and liquid scintillation counters, specially developed for this work, have been evaluated and shown adequate for the measurement of 10 mg of contemporary carbon. A graphical means for assessing the relative performance of an entire set of small counters has been introduced, and used to deduce the equimerit curve for the best gas and liquid scintillation counters. Preliminary results on the carbonaceous fraction of an urban dust sample have been compared with those of earlier workers.

Key Words: Atmospheric pollutants, natural radiocarbon, low-level counting, small gas proportional and liquid scintillation counters, figure of merit.

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SOME COMMENTS ON THE USE OF CHLORINE-36
FOR DATING VERY OLD GROUND WATER

Harold W. Bentley

Introduction

Chloride is a highly mobile anion and has been found to be an effective tracer in ground-water hydrology. Chlorine-36, which has a long half-life of 3.08×10^5 years, is postulated to be produced in the atmosphere at an average rate of 2.8×10^4 atoms per cm^2 column per year (Oeschger et al, 1969, and Schaeffer et al, 1960). Therefore, chlorine-36 is postulated to be a potentially important radionuclide with which to date groundwater (Davis and Dewiest, 1966, and Tamers and Ronzani, 1969).

This paper assesses the relative contributions of the possible sources of chlorine-36 in groundwater, and discusses the possible utilization of chlorine-36 to date very old ground water.

Origin of Chlorine-36

Groundwater chlorine-36 originates 1) in the atmosphere: either by post-1954 thermonuclear explosions or by isotope spallation by cosmic rays, which convert argon-40 to chlorine-36. 2) at the soil surface: neutron activation of chloride in the first meter of the earth surface by secondary neutrons produced by the interaction of cosmic rays with the earth's surface. Feige et al, (1968) suggest an average flux of 8×10^5 neutrons per kilogram year. 3) in the subsurface: neutrons due to natural radioactivity activate chloride in ground water. Although ϕ , the neutron flux, varies with uranium and thorium content and with the aquifer material, a reasonable value for ϕ is 10^4 neutrons per year per kg (Feige et al, 1968).

Meteoric Chlorine - 36

Chloride in ground water is primarily of meteoric origin; the chloride contributed by rock dissolution, except for some special rock types, is generally taken to be zero. The concentration of ground-water chloride depends on the average precipitation chloride concentration, typically tenths of ppm, on the evaporation history of the water prior to reaching the water table; and, in fine grained sediments such as clays and shale, concentration by ion filtration.

where ϕ is the average thermal neutron flux, $\sigma_{th}(i)$ is the thermal neutron cross section of atomic species (i), and $mM(i)/kg$ is the millimoles of element i per kg soil.

Table I gives elemental composition (Horn and Adams, 1966), neutron cross sections, and $\sum \sigma_{th}(i) \frac{mM(i)}{kg}$ for various rock types.

In the general case, taking a ϕ value of 8×10^5 neutrons per yr·kg (Feige et al, 1968) and the data in Table I, the minimum time necessary to attain $N_{36Cl} = 10^8$ is 750 years which, except under unusual geologic and climatic conditions, is an impossibly long period.

The soil surface component of chlorine-36 in a particular area would be assigned on the basis of geologic and paleoclimatologic considerations, but in general can be taken as negligible.

Subsurface Origin Chlorine-36

While ground-water chlorine-36 originating in the atmosphere and soil can be regarded as initial chlorine-36, the decay measurement of which would date the ground water, buildup of chlorine-36 in the subsurface due to neutrons produced by natural subsurface radioactivity will contribute to the error of chloride-36 age determinations.

In the subsurface,

$$N_{36Cl} = N_{36Cl}^{sat} (1 - \exp \Delta t) \quad (4)$$

$$N_{36Cl}^{sat} = \frac{903\phi}{\lambda \left[\sum_i \sigma_{th}(i) mM(i) / kg + \frac{\phi}{\rho} (3300 + 0.9C) \right]}$$

where ϕ equals porosity and ρ equals rock density. In most situations $\frac{\phi}{\rho} (330 + 0.9C)$ is negligible, and

$$N_{36Cl} \approx \frac{903 (1 - \exp \Delta t)}{\lambda \left(\sum_i \sigma_{th}(i) mM(i) / kg \right)}$$

and N_{36Cl} is essentially independent of porosity, chloride concentration, and rock density.

TABLE 1

Igneous rock its elemental composition and neutron cross-sections

Element	Igneous rock mg/kg	Igneous rock mM/kg	σ_{th} $10^{-24} \text{ cm}^2/\text{atom}$	$\sigma_{th} \text{ mM/kg}$
Silicon	285,000	10,146	0.1	1,015
Aluminum	79,500	2,946	0.2	589
Iron	42,200	755	2.4	1,813
Calcium	36,200	903	0.4	361
Sodium	28,100	1,222	0.5	611
Potassium	25,700	657	4	2,629
Magnesium	17,600	724	.054	39
Titanium	4,830	100	5.6	564
Phosphorus	1,100	35.5	.19	7
Manganese	937	17	13.3	226
Chlorine	305	8.6	32	275
Lithium	32	4.6	67	309
Samarium	16	.1	6,500	693
Gadolinium	9.9	.062	45,000	2,833
Boron	7.5	.69	750	520
Hydrogen	variable	variable	0.3	variable
Carbon	320	29.6	.0034	--
$\Sigma \sigma_{th}(i) \frac{\text{mM}(i)}{\text{kg}}$				= 12,474

Sandstone its elemental composition and neutron cross-sections

Element	Sandstone mg/kg	Sandstone mM/kg	σ_{th} $10^{-24} \text{ cm}^2/\text{atom}$	$\sigma_{th} \text{ mM/kg}$
Silicon	359,000	12,780	0.1	3,590
Aluminum	32,100	1,190	0.2	238
Iron	10,600	333	2.4	799
Calcium	22,400	559	0.4	224
Sodium	3,870	168	0.5	84
Potassium	13,200	338	4	1,350
Magnesium	8,100	333	.054	18
Titanium	1,950	40	5.6	227
Phosphorus	539	17	.19	3
Manganese	392	7	13.3	95
Chlorine	15	.4	32	13
Lithium	15	2.2	67	145
Samarium	6.6	.04	6,500	286
Gadolinium	4.4	.027	45,000	1,259
Boron	90	8.33	750	6,250
Hydrogen	variable	variable	0.3	variable
Carbon	13,800	1.277	.0034	4.3
$\Sigma \sigma_{th}(i) \frac{\text{mM}(i)}{\text{kg}}$				= 4,581

Table 1 continued

Shale, its elemental composition and neutron cross-sections

Element	Shale mg/kg	Shale mM/kg	$\sigma_{th}^{10^{-24} \text{ cm}^2/\text{atom}}$	$\sigma_{th}^{mM/\text{kg}}$
Silicon	260,000	9,256	0.1	926
Aluminum	80,100	2,969	.2	593
Iron	38,800	694	2.4	1,667
Calcium	22,500	561	0.4	224
Sodium	4,850	211	0.5	105
Potassium	24,900	637	4	2,547
Magnesium	16,400	674	.054	36
Titanium	4,440	93	5.6	519
Phosphorus	733	23.6	.19	4
Manganese	575	10	13.3	139
Chlorine	170	5	32	153
Lithium	46	6.7	67	444
Samarium	5	.03	6,500	217
Gadolinium	4.1	.026	45,000	1,173
Boron	194	17.96	750	13,472
Hydrogen	variable	variable	0.3	variable
Carbon	15,300	1,416	.0034	4.8
$\Sigma \sigma_{th}(i) \frac{mM(i)}{\text{kg}}$				= 22,223

Carbonate, its elemental composition and neutron cross-sections

Element	Carbonate mg/kg	Carbonate mM/kg	$\sigma_{th}^{10^{-24} \text{ cm}^2/\text{atom}}$	$\sigma_{th}^{mM/\text{kg}}$
Silicon	34	1.2	0.1	
Aluminum	8,970	332	0.2	67
Iron	8,190	146	2.4	351
Calcium	272,000	6,798	0.4	2,719
Sodium	393	17	0.5	9
Potassium	2,390	61	4	245
Magnesium	45,300	1,863	.054	101
Titanium	377	7.9	5.6	44
Phosphorus	281	9	.19	2
Manganese	842	15	13.3	204
Chlorine	305	8.6	32	275
Lithium	5.2	.1	67	50
Samarium	1.1	.007	6,500	48
Gadolinium	.77	.005	45,000	220
Boron	16	1.48	750	1,111
Hydrogen	variable	variable	0.3	variable
Carbon	113,500	10,500	.0034	35
$\Sigma \sigma_{th}(i) \frac{mM(i)}{\text{kg}}$				= 5,481

Table II gives ϕ calculated for the rock types in Table I by the methods of Feige et al (1968).

Table III compares calculated $^{36}_{\text{Cl}}$ with time as a function of rock type. Anomalously high amounts of uranium and thorium would of course lead to much higher ϕ 's and to much larger contributions of subsurface origin chlorine-36. The underground uranium and thorium would have to be determined when a chlorine-36 dating of ground water is attempted.

Figure 1 depicts decay curves of a representative ground-water chloride sample using typical concentration values for the various sources of chlorine-36.

Experimental Approach to Chlorine-36 Dating of Old Ground Water

The advantages to ground-water dating by the chlorine-36 method are that chlorine-36 is meteoric in origin; that the measurement of a decay process is involved; that, unless anomalous thorium and/or uranium are present, interference due to subsurface-origin chlorine-36 are not significant until approximately 10^6 years (see Fig. 1); and that water samples are small - five hundred liters or less by conventional counting, one liter or less by accelerator techniques. Small samples are important in low permeability formations where one liter per hour or less might be all a sampling well could produce.

The disadvantage to the method is that initial concentrations of chlorine-36 must be determined to get accurate dates. Experimental approaches should be designed to determine these initial concentrations.

First, an analysis should be made of present day concentrations of chlorine-36 in a number of aquifers. The procedure would entail the obtaining of tritium free samples (indicating no thermonuclear $^{36}_{\text{Cl}}$ component). Sampling and analytical techniques would be simultaneously perfected. (Development of the accelerator counting techniques should parallel these studies.) An assessment would be made of chlorine-36 concentrations and their variation with climate, latitude, and distance from the ocean. A correlation of chlorine-36 variations with environmental isotopic data should be made.

Table II ϕ calculated for typical granite, sandstone, limestone, and shale by the methods of Feige, Oltman and Kastner.

Table II Neutron Production of Various Rock Types

Rock Type	U (ppm)	Th (ppm)	Natural fission neutron/kg-yr	U-neutrons/kg-yr	Th-neutrons/kg-yr	Total neutrons/kg-yr
Granite	218	11	1,306	6,776	7,755	15,837
Sandstone	1.0	3.9	467	935	1,482	2,884
Shale	4.5	13	2,100	4,110	5,579	11,789
Limestone	2.2	0.2	1,027	1,408	57	2,492

Table III Number of ^{36}Cl atoms/gram Cl (after contact with several rock types for varying times)

Rock type	$\Sigma(\sigma_{th(i)} \frac{MM(i)}{kg})$	$N_{^{36}\text{Cl}} \text{ at } \Delta t$						
		$5 \times 10^4 \text{ yrs}$	10^5 yrs	$2.5 \times 10^5 \text{ yrs}$	$5 \times 10^5 \text{ yrs}$	$7.5 \times 10^5 \text{ yrs}$	10^6 yrs	∞
Granite	12,435	5.44×10^7	1.03×10^8	2.20×10^8	3.45×10^8	4.17×10^8	4.57×10^8	5.11×10^8
Sandstone	14,563	8.46×10^6	1.60×10^7	3.42×10^7	5.36×10^7	6.48×10^7	7.11×10^7	7.95×10^7
Shale	22,187	2.26×10^7	4.30×10^7	9.17×10^7	1.44×10^8	1.74×10^8	1.91×10^8	2.13×10^8
Limestone	5,380	1.98×10^7	3.75×10^7	8.00×10^7	1.26×10^8	1.52×10^8	1.66×10^8	1.85×10^8

Figure 1 Decay curve of representative ^{36}Cl groundwater samples from different aquifers.

The curves rising with time represent the subsurface contribution to ^{36}Cl as a function of aquifer type; the decay curves assume an initial concentration of 2.8×10^9 atoms $^{36}\text{Cl/gmCl}$ (atmospheric component) and 1×10^8 atoms $^{36}\text{Cl/gmCl}$ (soil surface component).

Second, studies should be performed which indicate chlorine-36 variation with time. Experimental work should include comparison of carbon-14 data, environmental isotope data, and other dating techniques with that of chlorine-36. Experiments determining chlorine-36 in Greenland ice (Finkle and Oeschger, 1978) should be continued. Theoretical and experimental studies of past cosmic ray activity should be supported; ^{10}Be variation in sediments would provide such information.

Third, in aquifers of interest, a profile of chlorine-36 concentration should be obtained. These concentrations should be coupled with hydrogeologic data (gradients, conductivities, lithology, uranium-thorium data); environmental isotope studies (to indicate paleoclimatology); and, if sampling problems can be overcome, verification of dates by krypton-81 determinations.

If these procedures were followed, dating of ground-water samples by the chlorine-36 method should be accurate and defensible. Chlorine-36 results from several aquifers would provide further dates to support age determination.

Some preliminary experiments have recently been performed: two chloride samples from tritium-free groundwater from the Tucson basin (provided by the author) were counted by tandem Van de Graaf accelerator at Rochester, N.Y. Naylor et al (1978) describe the counting procedure. The chemical separation involved an AgCl precipitation, the washed precipitate was converted to Ag_2O by boiling NaOH and filtered. The filtrate was taken to near dryness, acidified with concentrated H_3PO_4 , and HCl was distilled into NaOH solution. The sodium chloride obtained by evaporation provided the sample for the sputter source. At a sensitivity of five ^{36}Cl atom in 10^{14} chloride atoms, no counts were observed. Conclusions are premature. Further, verifying experiments are necessary as the low activity is fifty times less than expected from theoretical predictions (Oeschger et al 1969; Schaeffer et al 1960) and other experimental measurements (Tamers et al, 1969; Finkle and Oeschger, 1978).

Development Time and Equipment Cost

Suitable counting facilities are being developed. A dedicated instrument would require one year's development time. Such an instrument could cost as little as \$50,000 if the cyclotron approach were successful to as much as \$600,000 if a tandem Van de Graaf were developed solely for ^{36}Cl detection. An attractive compromise would be the upgrading of a carbon-14 tandem machine at a cost of approximately \$100,000.

Sampling and chemical technology would be developed concurrently. An investigation of sites of interest would take another year, for a total time of two years. One man year of professional work would be required for field sampling; the counting instrumentation would require a full time technician.

Conclusions:

If modern groundwater contains sufficient chlorine-36, and if variations in chlorine-36 with time can be accounted for, then radio-chlorine dating of old ground water is a very attractive possibility. Chlorine-36 dates an interesting time range, and the new particle accelerator counting techniques allow for small samples and short counting times. Although initial chlorine-36 concentrations will be difficult to determine careful supportive experiments should establish them.

Because of recent progress in acceleration counting techniques, the development time of a radiochlorine dating method for old ground water should be relatively short.

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PART I
URANIUM AND THORIUM ACTIVITY RATIOS

Time Dependent Change in U-234/U-238 Alpha
Activity Ratio (A.R.) Due to Recoil

J. K. Osmond

The process of leaching can be expected to produce only moderate deviations from equilibrium; i.e., both isotopes are leached, though not necessarily at the equilibrium ratio. However, the recoil process, which causes the introduction of the daughter isotope only, can have extreme effects, if the amount of original and leached uranium present is very small. This explains some of the scattering of most of the published data. We observe that for the most part, the higher concentration waters have moderate to near equilibrium A.R.'s while the very high A.R.'s are associated primarily with very low concentration waters.

The incremental change of A.R. of dissolved uranium (or other parent-daughter pair) due to the recoil process is semi-quantitatively expressed by

$$\Delta A.R. = \left(\frac{C_S}{C_L} \right) \left(\frac{V_S r_S}{V_L r_L} \right) \left(\frac{L}{4R} \right) \left(1 - e^{-\lambda_{234} t} \right)$$

The first term in parentheses is the ratio of concentration of uranium in the rock (S) to the corresponding concentration in the water (L).

The second term is the ratio of the amounts of solid (rock) and liquid (water) phases in the system. This is primarily a function of aquifer porosity.

The third term describes the proportion of decay events resulting in recoil of the daughter nuclide across the grain/water interface. L is the recoil distance, R the average grain radius, and 1/4 is the average probability of escape of a decaying nucleus located within L distance of the surface of the grain.

The final term is the growth function of a radioactive daughter relative to a steady state of equilibrium, in this case between the daughter

in the liquid and the parent in the solid. Because of the over-riding effect of the first term (solid/liquid concentration ratio) significant changes in A.R. may occur in a time frame much less than, but still proportional to, the half-life ($0.693/\lambda$) of the isotope being monitored (250,000 years in the case of U-234).

From this equation, we can see that, with respect to uranium, moderately high A.R.'s can be expected where low Eh and low $p\text{CO}_2$ conditions keep the amount of dissolved uranium low, and also where aquifer grains are high in uranium and small in size, the over-all porosity is low, and the residence time of water in the system is long. As a result of these factors, many deep aquifer waters, even where the uranium content of the country rock is low, have A.R.'s in the range 2-5.

A possible Th-230 equation:

$$\Delta \text{A.R.} \left(\frac{\text{Th-230}}{\text{Th-232}} \right) = \left(\frac{C_S^{234}}{C_L^{232}} \right) \left(\frac{V_S r_S}{V_L r_L} \right) \left(\frac{L}{4R} \right) \left(1 - e^{-\lambda_{230} t} \right)$$

Pluses: Low C_L^{232} and shorter half life (75,000 years for Th-230) should produce higher A.R.'s. The ratio of Th-230/Th-232 is easier to determine than concentrations.

Minuses: Effective porosity and grain size may be hard to determine (as with the uranium isotope function). Concentration of Th-232 in liquid will be hard to determine.

A possible equation involving ratios of ratios:

$$\frac{\Delta \text{A.R.} \left(\frac{\text{Th-230}}{\text{Th-232}} \right)}{\Delta \text{A.R.} \left(\frac{\text{U-234}}{\text{U-238}} \right)} = \frac{\left(\text{A.R.} \left(\frac{234}{238} \right) S \right)}{\left(\text{Th-232}_{L/\text{U-238}_L} \right)} \frac{\left(1 - e^{-\lambda_{230} t} \right)}{\left(1 - e^{-\lambda_{234} t} \right)}$$

Pluses: Independent of porosity and grain size. A.R.'s are relatively easy to determine.

Minuses: Th-232 in liquid may be hard to measure. Th/U ratio is not as stable as A.R.'s.

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PART J

ISOTOPE DETECTION USING ACCELERATORS

H.E. Gove

As discussed in parts D, E, 3 and M, cyclotrons and electrostatic accelerators can readily be operated in a mode in which they constitute ultra-sensitive mass spectrometers capable in some cases of detecting rare isotopes at a level of one part in 10^{16} or better. The particular isotope being measured need not be radioactive--the systems operate equally well with both stable and unstable species. At one of the working sessions the implications of these new detection techniques were considered.

The panel concerned with the use of accelerators as ultra-sensitive mass spectrometers comprised:

Ken Purser, Chairman	General Ionex Corporation
Harry Gove, Reporter	University of Rochester
Terry Mast	Lawrence Berkeley Laboratory
Dennis Bottomley	Inland Waters Directorate, Ottawa
Bob Laughon	Office of Waste Isolation
Gene Bernstein	Western Michigan University
Stanley Davis	University of Arizona
Douglas Donahue	University of Arizona

Principal discussion concerned the ability of cyclotron and tandem electrostatic accelerator systems to detect a variety of radionuclides and, in particular, those of special significance for dating ground water. These are listed in the order they were introduced, and some brief comments are given on each.

^3He - ^4He (stable)

^3He is assumed to be partly of primordial origin and to be slowly diffusing up through the earth's mantle, becoming dissolved in ground water. Some ^3He originates from the decay of atmospheric ^3H . A measurement of the $^3\text{He}/^4\text{He}$ ratio is of interest and possibly accelerator techniques could play a role, but this is not obvious. It is of interest to note that L.W. Alvarez first detected ^3He using a cyclotron about 40 years ago.

^3H Tritium (12.3 y)

The Lawrence Berkeley Laboratory (LBL) group has already dated water by measuring the tritium content. It is a relatively straightforward thing to do with tandems and cyclotrons. A question we do not have the answer to is at which level of sensitivity are such measurements required and does one really need to use accelerators. Many laboratories, including a group at the University of Witwatersrand in Johannesburg, South Africa, have been measuring ^3H in ground water for the past 20 years or so using conventional counting techniques.

^{10}Be (1.6×10^6 y)

Groups at Orsay and LBL have recently used cyclotrons to detect ^{10}Be . This radioisotope is very important in sedimentation dating but irrelevant for dating ground water since it is essentially insoluble as an element or as a chemical compound.

^{14}C (5736 y)

Accelerators have clearly demonstrated their ability to detect ^{14}C at very low levels (10^{-16}) with very small samples using both Penning sources (CO_2) in a cyclotron and sputter sources (carbon) in a tandem. In the case of a sputter source, a consumption rate of well under 1 mg/hour is required. For a penning source, experience at Berkeley shows that about 1 cc of CO_2 per minute produces over 200 μa of ^{12}C in the +3 state. Both systems produce dates in about 1-hour runs. The efficiency is better with tandems and the background presently lower (thus permitting more ancient dates), but this latter advantage is probably temporary.* The Rochester tandem could be used to date carbon samples from ground water back to 40,000 years or more as the system stands at present. Improvements in the system would extend this to at least 70,000 years or more. The accelerator technique could be combined with isotope enrichment of samples to do an even better job of dating samples at the 100,000-year age, but contamination problems will not be trivial.

* Experimental measurements at Berkeley indicate overall efficiencies of about 10^{-5} . Measurements at Rochester indicate that the comparable number for a tandem is about 10^{-3} .

^{26}Al (7.2×10^3 y)

Probably both types of accelerators could be used to tackle this isotope, but it has little direct significance for ground-water dating. It has, of course, substantial significance for sedimentation dating.

^{36}Cl (3×10^5 y)

This is an excellent candidate for ground-water dating, and both accelerator systems could be employed. Probably one needs sensitivity at the level of one part in 10^{13} or better. Samples could be in the form of chlorine gas or metal chlorides. One problem is distinguishing ^{36}Cl from ^{36}S , ^{36}Ar and from tails of ^{35}Cl and ^{37}Cl . An attempt will be made at Rochester soon to detect this isotope, but ultimately one will need to modify that system to do the job properly. Assuming 10^{-13} ^{36}Cl to Cl and with $30 \mu\text{a}$ of Cl^- (which is no problem) the tandem could achieve about 2 cps of ^{36}Cl . One would thus need 0.5 to 1.0 cc/hr of Cl gas to get 10% statistics in about two hours. The cyclotron system has similar capabilities although it may not be quite as efficient.

^{60}Fe (10^5 yrs), ^{79}Se (6.5×10^4 y), $^{97,98,99}\text{Tc}$ (2.6×10^6 , 4.2×10^6 , 2.1×10^5 y)

All have some possible value for ground-water dating but may have problems as far as accelerator detection is concerned. Accelerator people would need fairly strongly expressed interest by ground-water dating people to develop techniques for these radionuclides.

^{81}Kr (2.1×10^5 y)

Again, this isotope is of interest for ground-water dating. Since Kr does not form a stable (or even meta-stable) negative ion, detection by accelerators is confined to the use of cyclotrons. A problem will be ^{81}Br , but it has a 6% difference in dE/dx . Oeschger says that total Kr in H_2O is 40 atmospheric cc/1000 m^3 of water. Mast estimated 1 cc/min of

Kr $\rightarrow$ 1 cpm of ^{81}Kr in the LBL 88" cyclotron. This would require about 2000 m³ of water for 10% statistics (it could be a factor of 10 smaller), so the problem appears non-trivial. Somewhat later in the meeting, a more accurate lower limit estimate of the amount of water required was 50 m³.

^{129}I (1.57×10^7 y)

This is another interesting possibility for ground water. Accelerator technology would require fairly expensive modifications, however.

^{135}Cs (2×10^6 y)

No discussion was devoted to this.

^{39}Ar (270 y)

This might be good for young ground water--a good cyclotron candidate, probably better than ^{32}Si from a geological point of view.

^{32}Si (280 y)

Again, this radionuclide could be a significant indicator of new water. It is a good accelerator candidate.

^{41}Ca (7.7×10^4 y)

^{41}K will interfere. ^{41}Ca has apparently never been detected in nature.

With respect to ^{14}C and ^{36}Cl , there are questions concerning production in the earth's crust from neutrons and alpha particles from U and Th. In principle, these can be calculated, however.

PART K

THE USE OF HELIUM TO ESTIMATE GROUND-WATER VELOCITIES FOR STUDIES OF GEOLOGIC STORAGE OF RADIOACTIVE WASTE

I. Wendell Marine

Most hydrogeologic tests to determine suitable geologic sites for disposal of radioactive waste are of short duration when compared to the time span required to assess the safety of the facility. Geochemical studies of fluid and rock offer an opportunity to examine natural processes that have been going on for a period of time comparable to that required for safe retention of radioactive waste. In a study of the potential for storing radioactive waste in metamorphic rock at the Savannah River Plant near Aiken, South Carolina, the rate of water movement was determined to be about 0.06 m/yr by analyzing gas dissolved in the water. The gas contained up to 6 percent helium, which originated from the radioactive decay of natural uranium and thorium in the crystalline rock. The residence time of the water in the rock was calculated to be 840,000 years from the quantity of uranium and thorium in the rock, its rate of radioactive decay, and the quantity of helium dissolved in the water. From this residence time and a flow path of 51 km, the average velocity of water through the rock was estimated. This water velocity, which is an average over a broad region (51 km) and a long time period (840,000 years), is more applicable to the assessment of a geologic site for storage of radioactive waste than are velocities estimated from packer tests, pumping tests, or artificial tracer tests, all of which require extensive time and space extrapolations.

(from Geological Society of America Annual Meetings, November, 1977, Seattle, Washington)

PART L

Groundwater Dating at Harwell

G.V. Evans

1. Introduction

The development of groundwater dating is a rapidly moving field in which considerable attention is being placed on measurement methods based on analyses of groundwaters for rock originated or atmospheric originated radioactive nuclides. The interpretation of these measurements has been assisted by increased knowledge of geochemical effects on the concentrations of these nuclides. However, it is important that the limitations of the measurements are recognised and borne in mind in any hydrogeological interpretation of results.

The interest in groundwater dating has been spurred by proposals for disposal of radioactive waste in geological strata, where evidence of the remoteness of a proposed site to man is essential for acceptability. A service for the dating of groundwaters and archaeological samples has been in operation at Harwell for some years based on measurement of the radioactive decay of ^{14}C and a collaborative programme of investigation of major UK aquifers has been undertaken with the Central Water Planning Unit, Reading⁽¹⁻³⁾. Corrections for the fractionation of carbon isotopes are obtained from mass spectrometer measurements of $\delta^{13}\text{C}$ of the water sample and rocks. Because of the age limit of about 30 K-40 K years for this method of measurement (even less with geochemical corrections), attention is being given to the development of longer term dating methods for the application to waste disposal. These methods are based on the use of the Tandem Van de Graaff for more sensitive measurements of ^{14}C and on the measurement of uranium series isotopes. Both of these studies are in their early stages and have yet to be developed to reliable methods of groundwater dating.

2. Uranium/Thorium disequilibrium measurement

Uranium isotope disequilibrium as a hydrogeological tracer and as a method of dating groundwaters has been reviewed extensively^(4,5). Three measurement methods based on measuring the ratios of $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ are under study. These methods depend on the preferential dissolution rates

of the uranium isotopes into groundwaters and measurement of subsequent disequilibria or daughter products following radioactive decay. The relationships used for dating are

$$\left[\frac{^{234}\text{U}}{^{238}\text{U}} - 1 \right]_t = \left[\frac{^{234}\text{U}}{^{238}\text{U}} - 1 \right]_0 e^{-\lambda_{234}t}$$

$$\left(\frac{^{230}\text{Th}}{^{234}\text{U}} \right)_t = \frac{1 - e^{-\lambda_{230}t}}{\frac{^{234}\text{U}}{^{238}\text{U}}} + \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \left(1 - \frac{^{238}\text{U}}{^{234}\text{U}} \right) (1 - e^{-\lambda_{230} - \lambda_{234}t})$$

and $\frac{^{231}\text{Pa}}{^{235}\text{U}} = 1 - e^{-\lambda_{231}t}$

where λ_n is the decay constant for isotope of mass number n
t is the age

and 0 refers to initial conditions.

Sampling and analytical procedures have been identified and measurement equipment utilising an ionisation chamber and alpha spectrometry system has been commissioned. The ionisation chamber and spectrometer calibration are shown in Figs. 1 and 2. An interlaboratory comparison of sample measurements with the University of Bath has verified the equipment and a similar international comparison exercise organised by the University of Southern California, Los Angeles is in progress.

An examination of the use of these isotopes as general hydrogeological tracers is being undertaken in collaboration with Dr. J.W. Lloyd of the University of Birmingham and samples from twelve different sites representing several hydrogeological areas are awaiting analysis.

3. ^{14}C measurement

The established method of ^{14}C dating has been the measurement of the specific activity of samples in which the carbon has been converted into a gas used in a proportional counter or into a liquid used in a liquid scintillation counter. The limit on this method of ^{14}C measurement, without reconcentration, is approximately 30K years which makes it unsuitable for the longer term dating of groundwaters. The Tandem Van de Graaff, when used as a multistage mass spectrometer to measure ^{14}C would provide several orders

of magnitude increase in sensitivity allowing an extension of ^{14}C dating to 100 K years.

Work has consisted of the development of suitable detection and machine stabilisation systems and gaseous ion sources are in the course of preparation.

4. Age corrections

Corrections to the measured ages must be made to allow for geochemical effects on the concentrations of the pertinent nuclides in solution. A clearer understanding is being obtained of the dilution and fractionation of carbon isotopes during the stage of dissolution of carbonates as the water passes through an aquifer. Significant corrections to measured ages can result from these considerations.

Corrections for isotopic effects on ^{14}C are derived from measurements of $\delta^{13}\text{C}$ and the relationship currently used for age determination of groundwaters which have undergone both the congruent and incongruent stages of dissolution is

$$t = 8267 \ln \frac{50}{^{14}\text{C}} \left[\frac{K - \delta^{13}\text{C}_s}{K - \delta^{13}\text{C}_i} \right]^{1 + \frac{\epsilon_{13}}{1000}}$$

where the subscripts s and i refer to the sample solution and input to the incongruent stage respectively, ϵ^{13} is the fractionation factor for ^{13}C and K is $\delta^{13}\text{C}_{\text{rock}} - \epsilon_{13}$.

This correction is not possible when the $\delta^{13}\text{C}$ value of the water is in equilibrium with that of the rock. Then significant losses of ^{14}C to the rock may have occurred resulting in considerable overestimates in groundwater age.

5. Further developments

With the current enthusiasm for new measurement techniques for extending the range of dating methods, it is easy to be led into thinking that we are on the verge of solving our dating problems. However, whilst the sensitivity of these new methods is a great improvement in providing tools for measuring dates between those within the ranges of conventional

^{14}C and $^{40}\text{K}/^{40}\text{Ar}$, their reliability has yet to be proven. For example, the accuracy of ^{14}C measurements will depend on the constancy of ^{14}C production over the last 100 K years. Paleo-magnetic considerations may help to quantify any errors from this source.

Data relating to changes in the geochemistry of water in an aquifer together with a knowledge of the aquifers' properties should assist in providing more reliable estimates of groundwater ages. Use of the uranium series and stable isotopes ($^{18}\text{O}/^{16}\text{O}$, D/H) as hydrogeological tracers may provide useful corroborative data in dating exercises. For example, use may be made of the established relationships between ^{18}O and precipitation temperature combined with knowledge of the history of climatic change of the area.

Apart from obvious developments in measurement and sampling techniques to allow more accurate analyses from conveniently sized samples, developments are necessary in understanding the effect of extraneous factors on interpretations of the measurements.

PART M

Measuring Low Level Concentrations of ^{14}C , ^{36}Cl , and ^{81}Kr With the Berkeley 88-inch Cyclotron

Terry S. Mast
Lawrence Berkeley Laboratory

An enormous increase in the sensitivity of radioisotope dating can be achieved by counting the radioactive atoms directly instead of waiting for them to decay. The table below shows the large numbers of atoms present in a sample with a decay rate of one decay per minute. The isotopes listed are those of interest in dating old ground water at subsurface repositories for radioactive waste.

	<u>Half-life (Years)</u>	<u>Atoms</u>
^{14}C	5730	3×10^9
^{36}Cl	3.1×10^5	1.6×10^{11}
^{81}Kr	2.1×10^5	1.1×10^{11}

Counting these atoms directly (even with low efficiency) can yield many orders of magnitude increase in sensitivity. The two potential benefits of this improved sensitivity are 1) the ability to date older samples and 2) the ability to obtain a date with a greatly reduced sample size.¹

Previous attempts to use mass spectrometers to do this direct counting have been unsuccessful because of the presence of large amounts of contaminating stable isotopes with masses very close to those of the radioisotopes.

	<u>$\Delta m/m$</u>
$^{14}\text{C} - ^{14}\text{N}$	1.2×10^{-5}
$^{36}\text{Cl} - ^{36}\text{S}, ^{36}\text{Ar}$	3.4×10^{-5}
$^{81}\text{Kr} - ^{81}\text{Br}$	3.6×10^{-6}

In the past two years a number of groups have begun to use accelerators

as ultrasensitive mass spectrometers and have applied them to radioisotope dating.^{2,3,4,5} The higher energies of the accelerators allow the separation of the contaminating isotopes with the standard techniques of nuclear physics. Success has been achieved with both electrostatic accelerators^{2,3} and cyclotrons.^{4,5} The potential capabilities and the problems remaining to be solved to achieve them are different for the two types of machines. The capabilities of the electrostatic accelerators are discussed in other papers in this report (see Litherland and Kilius, Purser, and Gove). We describe here the status and future of using the Berkeley - 88 inch cyclotron to measure concentration of the above isotopes.

The capabilities of the Berkeley 88-inch cyclotron as a very sensitive mass spectrometer were demonstrated in a search for quarks where for low masses an abundance sensitivity of 10^{-18} was achieved⁶. Its capabilities for masses over the full range of the periodic table have been studied.⁷ The mass acceptance is comparable to that of a good mass spectrometer ($\Delta m/m \sim 1/3000$). The "abundance sensitivity" (the ability to see small concentrations at masses close to those of abundant isotopes) is extremely good due to the requirement of isochronicity in each of the 100 cycles of acceleration. It is, in effect, like 100 mass spectrometers in series.

Our initial work on radioisotope dating has focused on ^{14}C and is described below. In the past few weeks we have made some successful initial measurements of ^{10}Be . With a half-life of 1.5×10^6 years ^{10}Be will be useful for dating sedimentary rocks. In these initial tests we have measured ^{10}Be at natural levels (in a meteorite) with complete rejection of ^{10}B and no machine sources of background ^{10}Be .

In the sections below we describe for each isotope the status of the running experience, some estimates of the expected count rates and sample sizes, and the time and cost required to fully develop the capability of measuring a large number of samples.

¹⁴C The complete elimination of the abundant ¹⁴N contamination has been achieved by ranging out the ¹⁴N in a cell of xenon gas. The ¹⁴C with a range 30% longer passes through the cell into an isotope identifying detector telescope. The technique and the measurement of a sample of known age are described in Reference 4. Based on the currents and counting rates already achieved a sensitivity is expected which will yield dates of $50,000 \pm 5000$ years with samples of 10 mg. However, at present this sensitivity cannot be achieved due to the presence of a large machine generated ¹⁴C background. The size and variations in this background prevent the use of any subtraction technique. The background comes from the sputtering of graphite blocks (used to protect metal surfaces) which have been in the cyclotron many years and are enriched in ¹⁴C. The construction of an external ion source (presently funded and being designed) will prevent the ionization and acceleration of ¹⁴C generated in the tank. As presently scheduled the external ion source will take 1 to $1\frac{1}{2}$ years to complete. Additional funds for technical support could shorten the completion time to 6 to 9 months.

³⁶Cl The cyclotron has considerable experience accelerating chlorine beams and thus the currents and efficiencies are known. Typically chlorine is introduced in a gas phase as Cl₂ or BCl₃. Sputtering chlorine salts would probably also be successful however sample handling in a gas phase is

easier and less susceptible to contamination. Based on the already achieved currents and efficiencies we estimate 3 mg of Cl would be required to measure a concentration of $^{36}\text{Cl}/\text{Cl}=10^{-11}$ to $\pm 10\%$. (For a fixed precision the required sample size is inversely proportional to the assumed concentration).

The major development work needed to realize this goal is to establish procedures to eliminate contamination from the stable isotopes ^{36}S and ^{36}Ar . The high energy of 5 MeV/nucleon makes this separation feasible. A combination of techniques will be used. Chemical purification will greatly reduce the contamination of ^{36}S (aided by the initial low level of $^{36}\text{S}/\text{S}$). As with ^{14}C an absorber gas cell will be used to separate in energy the ^{36}Ar and ^{36}S allowing the detection of ^{36}Cl in the detector telescope.

The development work required to perfect these separation techniques and to construct a sample handling system capable of measuring about 1000 samples is estimated to take one year and cost \$175,000. The measurement of an individual sample would require 1 hour and cost about \$250.

^{81}Kr Again krypton has been accelerated in the cyclotron and the current available and transmission efficiencies are known. In addition we have measured the stable isotope abundances of Kr as part of our study of the cyclotron as a mass spectrometer.⁷ Based on this experience we estimate that it would require 20 cm^3 of Kr to make a 10% measurement of the concentration for an assumed concentration for $^{81}\text{Kr}/\text{Kr}$ of 6×10^{-13} . No efforts of course have yet been made to improve the ionization, acceleration, and beam optic efficiencies so perhaps as much as an order to magnitude improvement could be made. However, without such improvements the 20 cm^3 is estimated to require 5×10^5 liters of water which may not be feasible for the types of aquifers being considered.

The separation of the contaminating ^{81}Br would be made with the techniques described above for ^{36}Cl although the higher mass here makes the separation more difficult. We feel it would be well worth some exploratory work to assess the separation problems and to estimate the potential improvements in sensitivity. Such an exploratory program would cost about \$50,000 and require about 6 months to complete.

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PART N

SOME COSMIC RAY PRODUCED RADIONUCLIDES OF INTEREST IN DATING OLD GROUND WATER

Hans Oeschger

Radio-nuclides	Half-life years	Initial dpm/liter H ₂ O	Initial concentration atoms/liter H ₂ O	Isotopic ratios	Volume of water sample needed liters	State of method	Hydro-chemical properties	Information to be derived
³⁹ Ar	270	4×10^{-5}	3×10^3	³⁹ Ar/Stable Ar = 8×10^{-16}	1×10^4 to 2×10^4	Has been used for ground-water studies	Good tracer, subject to molecular diffusion	Dating range 50 to 1000 years
³² Si	300	1×10^{-3}	2.3×10^5	?	10^3	Has been used	Probable sorption and/or precipitation in aquifer	Dating range 50 to 1500 years
¹⁴ C	5,730	2×10^{-1}	10^9	¹⁴ C/Stable C = 1.2×10^{-12}	1×10^2 for 5×10^4 years 1×10^3 for 6×10^4 years 5.0×10^3 for 7.5×10^4 years	Available, abundant experience	Problems of dissolution and precipitation. Geochemical models are available to help interpretation	Dating range 10^3 to 7.5×10^4 years
⁸¹ Kr	210,000	0.7×10^{-8}	10^3	⁸¹ Kr/Stable Kr = 5.9×10^{-13} ⁸¹ Kr/ ⁸² Kr = 5.1×10^{-12} ⁸¹ Kr/ ⁸⁰ Kr = 2.6×10^{-11}	0.5×10^6 to 1.0×10^6 (accelerator needs 5×10^4)	Measured in atmospheric samples only	Potentially an excellent tracer. Subject to molecular diffusion	Dating range 5×10^4 to 8×10^5 years
³⁶ Cl	308,000	1×10^{-5} to 2×10^{-4}	2×10^6 to 4×10^7	³⁶ Cl/Stable Cl = 10^{-14} to 10^{-11}	500 (accelerator may need as little as 10)	Has been counted but systematic ground-water studies lacking	Good tracer. Some questions of Cl from connate water and sub-surface production	Dating range 8×10^4 to 1.5×10^6 years

PART 0

PROPOSED COOPERATIVE FIELD PROGRAM

K. O. Münnich

A number of field studies will most likely be undertaken to develop methods to date ground water. In order to compare field and laboratory methods and resulting data, many of these studies should utilize duplicate water samples from the same well taken at the same time. In a previous study, F. J. Pearson, Jr., was able to show a systematic increase of C-14 ground-water ages in a downdip direction in the Carrizo aquifer in Texas. Samples most distant from the outcrop exceeded the dating range of C-14 which existed at the time of his study. The same area as studied by Pearson is suggested as a field area to study not only the possibilities of extended dating capabilities of C-14 but also other methods discussed in the workshop. It is probable that water ages continue to increase rapidly in the downdip direction and that ages in excess of several hundred thousand years can be found in waters from existing wells.

It is proposed that a number of different groups start field work in the Carrizo aquifer as soon as possible. For C-14 techniques, improved field processing equipment for CO₂ extraction from ground water should be tested. A full vacuum extraction system with a continuous flow is under development in Germany at the present time for oceanographic studies. This system could also be tested for ground-water work. The system will be used on the October-December, 1978, cruise of the Meteor and might be shipped to the United States after the cruise.

It should be stressed that the very positive experience from recent cooperative test studies in isotope oceanography (in connection with the U.S. GEOSECS program) suggests a study such as proposed will be a very useful way to increase performance by stimulating competition among different techniques as well as different research groups using similar techniques.

SILICON-32

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Introduction

Like tritium and carbon-14, silicon-32 is another cosmogenic radioisotope. Because of its convenient half life, 300-500 yrs (cf. Lal et al, 1976), this nuclide is extremely useful in dating groundwaters of a thousand years nominal age. This conference is concerned with old groundwaters as deposits for waste disposal. The question immediately arises is what is the relevance of silicon-32, a short half-life isotope, to this problem. We believe that this is an important nuclide which must be studied for delineating "old" groundwaters, as explained in this paper.

During the last few years more than fifty ground-water samples from several sedimentary basins in India have been dated by both the carbon-14 and silicon-32 methods (Lal et al, 1970; Nijampurkar, 1974; and Gupta et al, 1978). In spite of uncertainties concerning the half-life and geochemical behavior of silicon-32 in natural waters, apparent silicon-32 ages of the investigated groundwaters have proved vital. They are generally found to be an order of magnitude lower than the corresponding apparent radiocarbon ages; some of which are as old as 20,000 yrs. Detailed analyses of these results have led us to believe that the C^{14} and Si^{32} data do not fit either (i) the piston flow model or (ii) the completely well mixed reservoir model. Generally, the data can best be understood by a model in which "old" groundwaters receive a component of relatively young groundwater by leakage through semi-confining layers (Gupta et al, 1978).

For earlier discussions of apparent ages of the groundwater for different mixing models, reference is made to Lal et al (1970), Craig (1963) and Oeschger (1972).

Relationship of "Apparent" Ages to "Real" Ages

It is obvious that the interpretation of the radioactive data must be based on an assumed model of transport and mixing for the groundwater.

In one extreme case, the apparent age can be related to the traversal time, i.e. when the groundwater travels without mixing with other ground-water masses; this model is nicknamed as the pipe-line flow for obvious reasons. The age, T_a is given by:

$$A = A_0 e^{-\lambda T_a} \quad \dots(1)$$

where A is the measured concentration of a radionuclide in the ground-water at the point of sampling, A_0 the initial value in the groundwater at "recharge" and λ is the disintegration constant of the nuclide. If, however, the water sampled constitutes a part of a well-mixed larger reservoir with a mean flushing time, τ , for water molecules, the steady state equation for a system as in figure 1 will be:

$$RA_r + qRA_0 = VA\lambda + (1+q)RA \quad \dots(2)$$

or
$$\frac{A}{A_0} = \frac{q + A_r/A_0}{(1+q)(1+\lambda\tau)} \quad \dots(3)$$

FIGURE 1

The effective flushing time of the system is given by:

$$\tau = \frac{V}{(1+q)R} \quad \dots(4)$$

In the above equations, we have assumed for the principal recharge via the underground flow a value for the recharge activity, A_r , different from A_0 ($< A_0$), since away from the recharge area, the waters get progressively "old". A small but finite direct recharge is assumed to occur in the water body, although the activity of this water would be somewhat less than A_0 ; for convenience we have assumed it to be A_0 . This assumption for the " qR " recharge does not lead to any loss of generality since $q < 1$. We examine below the steady state activity for two extreme Cases:

Case I. $A_r \approx A_0$

$$\frac{A}{A_0} = \frac{1}{1+\lambda\tau} \quad \dots(5)$$

Case II. $A_r \ll A_0$

$$\begin{aligned} \frac{A}{A_0} &\approx \frac{q}{(1+q)(1+\lambda\tau)} \\ &\approx \frac{q}{1+\lambda\tau} \quad \dots(6) \end{aligned}$$

Equation (6) differs from (5) by a factor " q " in the numerator. Since q is a small quantity, < 1 , the two expressions are quite different and the physical significance for this major difference should be considered.

In Case I, the simplest of "box" model type water body, the "apparent" age, defined as is normally done using relation (1), gives the true flushing time correctly only for the case:

$$\lambda\tau < 1 \quad \dots(7)$$

in which case equations (1) and (5) are approximately the same:

$$\frac{A}{A_0} = \frac{1}{1+\lambda\tau} \approx e^{-\lambda\tau} \quad \dots (8)$$

However if $\lambda\tau > 1$, the "apparent" age departs from the flushing time, τ ; the departure increases with the value of $\lambda\tau$, as can be seen from fig. 2. It is interesting to note that real old groundwaters, say of 10^6 yrs age, would appear as having $\sim 10^4$ yrs apparent age with the C^{14} and $\sim 10^3$ yrs apparent age using the Si^{32} nuclides as tracers. Such large departures, in fact, can be treated as evidence for the validity of Case I.

FIGURE 2

In groundwaters where $A_r \ll A_0$ and a small but finite leak of relatively young (near zero age) water exists, the system attains a steady-state value of the tracer concentration which is lower than for Case I by a factor q . Consequently, now the apparent ages would be larger than those for Case I (see fig. 3) and in some cases close to the true flushing time. The uncertain parameter here is " q " which can, however, be determined if two suitable nuclides are used. Then the steady state ratio of the concentrations of these nuclides, for example in the case of C^{14} and Si^{32} , relative to zero-age waters would be given by

$$\frac{A(C^{14})/A_0(C^{14})}{A(Si^{32})/A_0(Si^{32})} = \frac{1+\lambda(Si^{32})_\tau}{1+\lambda(C^{14})_\tau} \quad \dots (9)$$

which is independent of q .

FIGURE 3

In either Case (I or II), equation (9) is valid, however the absolute activities for either of the nuclides in Case I would be larger than those in Case II; by a factor of $(\frac{1}{q})$, as discussed before.

Thus it is clear that from simultaneous study of two favourable half-life radionuclides, a groundwater system can be approximated as belonging to either extremes (Cases I and II) or to an intermediate situation. From figs. 2 and 3, we conclude that waters of, $\tau = 10^4 - 10^6$ yrs, as are of interest to this subject, can indeed be suitably studied with C^{14} and Si^{32} .

If the pipeline model is valid, no silicon-32 activity will be found and very little of carbon-14. Absence of silicon-32 in this case would be extremely reassuring, indicating that unless the rock geochemistry was very unfavourable whereby Si^{32} activity was removed by exchange or precipitation in the aquifer material, one could safely use these aquifers for waste disposal. We must mention that our knowledge on the behavior of Si^{32} in different types of aquifer systems is very limited. However, we know, on the basis of analyses of about 50 groundwater samples in granitic, alluvium and basaltic rocks; that the apparent carbon-14 ages of these waters are $(2-20) \times 10^3$ yrs, and apparent silicon-32 ages are $(0.2 - 2) \times 10^3$ yrs. At present we do not have any experience of silicon-32 activity in limestone aquifers. It would therefore be necessary to establish the geochemical behaviour of Si^{32} in limestone and other types of aquifers before assuming its general validity as a useful tracer for characterising old groundwaters.

Conclusion

We have shown that in the absence of knowledge of mixing characteristics of a groundwater body, measurement of just one radionuclide can lead to very erroneous conclusions. In 'old' water the apparent ages can be grossly underestimated as exemplified in this paper. Thus one may discard potentially useful aquifers. It is shown that simultaneous use of another nuclide can shed light on the antiquity of the waters. We have demonstrated this by including the relatively short-lived radionuclide

silicon-32 (half-life $\approx$ 500 yrs). We have chosen this as an example because of our experience and familiarity with its distribution in groundwaters (of India). However, it is quite clear that some radionuclides like Cl^{36} and those belonging to U/Th series will likewise be vitally important considering the importance of simultaneously studying the concentrations of radionuclides of different half-lives in an aquifer. We would like to stress on the necessity of worldwide awareness and the urgency to undertake such studies. We would also like to stress here that Ar^{39} (Loosli and Oeschger, 1968), another cosmic ray produced isotope of half life similar to Si^{32} is ideally suited for delineating antiquity of groundwater, because in this case the question of its fractionation in the ground does not arise. However compared to Si^{32} the task of its measurement is a very difficult one (Oeschger et al, 1974). We therefore recommend a practical solution to the problem, viz., extensive measurements be first carried out of both Si^{32} and C^{14} and the final confirmation be obtained on the basis of Ar^{39} measurements.

FIGURE CAPTIONS

- Fig. 1 Diagram showing the inputs and outputs for a hypothetical mixing cell of a groundwater system.
- Fig. 2 (a) Relationship between the true flushing time and the apparent radiometric age of a mixing cell (Case I: $A_r \approx A_0$).
- (b) Relationship between the apparent silicon-32 and carbon-14 ages for various values of true flushing time of a mixing cell (Case I: $A_r \approx A_0$).
- Fig. 3 (a) Relationship between the true flushing time and apparent radiometric age of a mixing cell (Case II: $A_r \ll A_0$). Different curves for various values of q , the "relative quantity" of direct recharge, with activity A_0 .
- (b) Relationship between the apparent silicon-32 and carbon-14 ages for various values of q , the ratio of direct fresh recharge to old recharge via underground flow (Case II: $A_r \ll A_0$). Points marked A, B and C correspond to the flushing times of 10^3 , 10^4 and 10^5 yrs respectively.

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