UNITED STATES ATOMIC ENERGY COMMISSION

NP-1472

**THE MEASUREMENT OF PALEOTEMPERATURES;
SCIENTIFIC REPORT TO THE GEOLOGICAL SOCIETY
OF AMERICA, THE AMERICAN PETROLEUM INSTITUTE
AND THE OFFICE OF NAVAL RESEARCH**

By
Harold C. Urey, Director, et al.

February 27, 1950

University of Chicago

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Angela Kinsler
Authorizing Official
Date: 2-1-2012

Technical Information Division, ORE, Oak Ridge, Tennessee

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	<hr/> 37

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Introduction

Since the summer of 1947 a group of us have been working on an isotopic paleotemperature scale. The problem proved to be a very difficult one and until December of 1949 we did not believe that we could measure the isotopic ratios of present day organically precipitated calcium carbonate precisely, and for this reason offered no papers for publication. During 1949 we succeeded in solving this problem to our satisfaction, and have accordingly prepared certain papers for publication. These include the first three papers following this Introduction. In addition, Dr. Peter Baertschi of the University of Basel, Basel, Switzerland, investigated the isotopic abundance of O^{18} in igneous and sedimentary rocks, and will publish this paper separately. It is not included in this report. Also, Dr. J. M. McCrea wrote a dissertation on inorganically precipitated calcium carbonate and its isotopic composition, and related problems. This paper is included in the papers presented here. Progress reports on work in progress are also included.

The reports are very extensive and difficult to summarize in any brief way. However, we have shown that it is possible to construct a mass spectrometer adequate for our purpose, with a much higher precision for small differences in isotopic composition than has ever been attained before. We have shown that the isotopic composition of certain fossils has been retained over long periods of time at least since the Jurassic. We have been able to establish a temperature scale which so far as measurements are concerned should be accurate to about $1^{\circ}C$. All difficulties in connection

with the use of this thermometer have been overcome with the exception of the variation in isotopic composition of the ocean, which is a serious difficulty. One method of avoiding this difficulty is under investigation. It is thought that it may be possible by using the isotopic composition of phosphates to eliminate the dependence on the isotopic composition of the water. Only further work can decide whether this is possible. We are also beginning work on the distribution of the hydrogen isotopes in nature, with the objective of using the abundance of the hydrogen isotopes to indicate the abundance of the oxygen isotopes because of the similar fractionation processes involved, namely, the evaporation of water. Also, measurements have been made on the temperatures of the Cretaceous of England and the United States, and some interesting preliminary results have been secured.

This work was supported by two yearly grants from the Geological Society of America and the American Petroleum Institute, and nearly all of the orienting work was done with the support received from these organizations. We are indeed very much indebted to them for aiding us in this work. Since the middle of 1949 the work was also supported by a grant under Task Order XXVIII, Contract N6ori-20 of the Office of Naval Research, and the work in progress is being prosecuted mostly under that contract.

This report is presented to the Geological Society of America, the American Petroleum Institute and the Office of Naval Research. It is in fact more a report to the Geological Society and the Petroleum Institute because of their support of this research for a longer period of time, and it is presented to the Office of Naval Research for their information in connection with an application for a renewal of the contract with the University of Chicago.

The Measurement of Paleotemperatures and Temperatures
of the Upper Cretaceous of England, Denmark, and
the Southeastern United States

H. C. Urey, H. A. Lowenstam, S. Epstein, and C. J. McKinney

Geologists have been able to draw a great many conclusions from the purely qualitative evidence of geological studies in regard to the past climatic conditions on the earth. These deductions are based upon a great variety of evidence and the fact that they have been able to deduce as much as they have in regard to these conditions excites the wonder and admiration of all the uninitiated who have the occasion to examine their work even casually. Palm trees do not grow in Spitzbergen, according to all our evidence, unless the weather is mild, about the same as that of Florida. Heavy shells are deposited in warm water and thin shells in cold water. Tree rings are definite evidence of the existence of seasons. There are many other lines of evidence of a similar kind.

During the last fifteen years a very considerable amount of study has been placed by a number of people on the different chemical properties of isotopic substances. These include the demonstration of differences in the chemical properties of the hydrogen isotopes, the first calculations in regard to such differences in the case of other of the lighter isotopes, extensive applications of such differences to the separation of isotopes, and considerable evidence in regard to such differences from surveys of the abundances of the lighter isotopes in nature. From the standpoint of the natural abundances the early demonstration that deuterium was not constant over the surface of the earth, and with it the demonstration

by Dole (1935, p. 2731; 1935, p. 268) that oxygen also varies, particularly in the air, and the variation of carbon as between inorganic and organic sources by Nier (1939, p. 697; 1941, p. 771), made early contributions to the science of geology. Recently Thode, MacNamara and Collins (1949, p. 361) have demonstrated substantial variations of the sulfur isotopic abundances, and these authors and Lossing (1948, p. 3008) have demonstrated such variations in the case of boron. It is the purpose of the present paper to present a way in which the natural variations in the abundances of the lighter isotopes makes possible, in principle at least, the measurement of paleotemperatures in a quantitative way and thus another contribution to the science of geology.

Differences in the chemical properties of the elements such as differences in vapor pressures, differences in equilibrium constants of exchange reactions, are at least partially if not wholly responsible for these variations in the lighter isotopes in nature. It is quite certain that the variation of the hydrogen and oxygen isotopes in the fresh waters of the earth as compared with

the sea is due to the difference in vapor pressures of the varieties of water containing hydrogen and deuterium or the three oxygen isotopes, oxygen 16, 17, and 18. The variation in the abundance of the carbon isotopes discovered by Nier cannot certainly be assigned to this cause. He found that carbon 13 exists in organic matter in a decreased abundance as compared with the carbon in carbonates. Whether the photosynthetic process concentrates the carbon isotopes by some equilibrium or near equilibrium process or not is not certain. Since the oxygen isotopes of the air are not in equilibrium with the oxygen isotopes of the sea or fresh water, it seems probable that this effect is also produced by the photosynthetic process or by the oxidation of organic matter by atmospheric oxygen*, and if a vital selection of the isotopes occurs

*However, Dole has recently proposed other explanations for this effect. See Science 109, 77 (1949).

in the case of one of these isotopes it may well do so in the case of others.

Variation in isotopic abundances which are due to differences in thermodynamic properties, i.e., processes which are in equilibrium or very close to equilibrium, are understood completely in principle and in many cases in exact detail. On the one hand, it is necessary to know the quantum states of these molecules, and on the other it is necessary to have the exact theories of statistical mechanics in order to relate these quantum states to the physical chemical properties. For molecules in the neighborhood of ordinary temperatures and above, it is unnecessary to consider the

rotational quantum states, since these are very close to classical at these temperatures in the case of all molecules except those involving the hydrogen isotopes. In this case the entire difference in the chemical properties resides in the differences in the vibrational energy levels. A great many calculations covering exchange reactions of the lighter elements were made by Urey and Greiff and have been recalculated by Urey (1935, p. 321; 1947, p. 562), together with the mathematical formulae and spectroscopic data by which the calculations are made. In general it is found that differences of a few percent in the ratio of isotopes in two chemical compounds which are brought to equilibrium with each other with respect to the exchange of isotopes are possible for elements even as high as chlorine in the periodic system. The heavier elements can be expected to show but very slight effects of this kind. The calculations indicate that there should be differences in the ratio of the oxygen isotopes in water and carbonate ion, water and sulfate ion, and water and phosphate ion, as shown in Table 1 for two temperatures.

Table 1*

Calculated Fractionation Factors for O^{16} and O^{18}

<u>t°C</u>	<u>$CO_3^{=}$ - $H_2O(\psi)$</u>	<u>$SO_4^{=}$ - $H_2O(\psi)$</u>	<u>$PO_4^{=}$ - $H_2O(\psi)$</u>
0	1.0220	1.0204	1.0104
25	1.0176	1.0157	1.0087
Ratio K_O/K_{25}	1.0044	1.0047	1.0017

*McCrea (Doctoral Dissertation, Chicago, 1949) by attempting to include the effects of the potential fields in crystals instead of assuming no such fields as was done by Urey (loc. cit.) secures slightly different values for the $CO_3^{=}$ - H_2O constants.

In these calculations the results are reported for equilibrium between liquid water and the carbonate ion rather than between the gaseous water and the carbonate ion. It will be noticed that there is a slight difference to be expected in the isotopic composition amounting to a few per cent, and that there are slight temperature coefficients predicted. The calculations show that this difference for the carbonate-water equilibrium should amount to about 0.44% in 25°C, or 0.176‰ per degree C. The calculations are not exact for the reason that experimental data do not supply us with the vibrational energy levels for those molecules containing oxygen 13, and hence the vibrational frequencies of these molecules must be calculated from the known vibrational frequencies of the more abundant oxygen 16 varieties. The calculation depends upon a choice of constants. In fact, in the case of the carbonate ion it is necessary to have five constants in order to describe the potential energy function to the precision of quadratic terms in the coordinates, whereas only four independent frequencies are available for the calculation of these constants from the observed vibrational frequencies of the $\text{CO}_3^{=16}$ ion. A similar situation exists in the case of the phosphate and sulfate ions.

It is immediately obvious that if a relation exists between the oxygen abundances in these compounds, and temperature, and the water in which the compounds were deposited, it should be possible to set up a thermometer for present day organisms living in the sea, if the isotopic composition of the water is known not to differ from the mean of the present seas, or, in case it does, if both the isotopic composition of the carbonate and water are determined.

Thus it would only be necessary after having established an empirical temperature scale to measure the isotopic abundances of oxygen in a shell deposited by an animal in the sea in order to determine the temperature at which the deposition had taken place. This application may be of interest in some cases, as for example in determining the temperature history of an animal, but the process which we shall describe is difficult, and wherever possible ordinary thermometers are likely to be considerably more convenient. On the other hand, it appears possible that these effects may be preserved during geological time, and hence this method affords a possible method for measuring paleotemperatures.

Application to Paleotemperatures

Since the predicted temperature coefficient for the ratio of oxygen isotopes in calcium carbonate relative to water is small, it is necessary to secure mass spectrometers of very great precision and sensitivity for this problem. It would be desirable to measure paleotemperatures within less than a degree Centigrade, which corresponds to a change in the atomic weight of oxygen in the calcium carbonate of 7×10^{-7} atomic weight units, or a change in the abundance of oxygen 18 by 1 part in 2.5 million of oxygen. We have set .01% or better corresponding to about .5°C, or 1°F, as our objective in these experiments. As measurements of the ratio of isotopes have been conducted in the past reports in the literature of 0.1 per cent or 1 γ are about as high a precision as has been attempted. Hence the first problem in the application of this method to paleotemperatures is the construction and operation of very sensitive mass spectrometers.

Since we have examples of animals and plants laying down isotopes out of equilibrium with their surroundings, as for example the carbon of organic material, we may well ask whether the deposition of calcium carbonate by an animal or a plant occurs in such a way as to leave the oxygen isotopes in equilibrium with the water from which the deposition takes place; that is, we may ask whether there is a vital effect. It would seem probable that the equilibrium deposition should be closely approximated in many cases, for the calcium carbonate deposited is constantly bathed with water from the surroundings and hence has every opportunity to exchange its oxygen with the surrounding water during the deposition process. However, one could quite readily imagine mechanisms which would involve the deposition of organic oxygen and thus invalidate these assumptions. The whole question could only be answered by experiment, so far as we can judge from the present state of our knowledge of the physiology of deposition of such substances. The question of deposition of phosphate on the other hand would appear to be even more doubtful than the deposition of carbonate, since phosphate ion does not exchange its oxygen with water in which it is dissolved, and hence it may be that the phosphate deposited by animals generally does not have its oxygen in equilibrium with its surroundings. Since phosphate is so intimately involved in biochemical reactions, its oxygen may be brought to equilibrium with water by them. Only careful experimentation can determine the feasibility of the phosphate thermometer*.

*Dr. Mildred Cohen in a private communication informs us that she has found that some enzymatic hydrolyses of phosphoric esters split the oxygen phosphorus bond though others do not. Hence a mechanism is available which may establish equilibrium between water and phosphate in animal bodies.

Sulfate is relatively rarely deposited by animals and is not an important substance for investigations of the type which we envisage immediately. Silica is often deposited by plants and animals in the form of a hydrous silica. Since the relative proportions of water and silica might change the relative abundance of the oxygen isotopes, this does not appear to be a very promising line of attack, though again experiments should be made to determine whether there is any possibility of using a silicate thermometer. Of the possible thermometers, that is, the carbonate, phosphate, sulfate and silica, it appears that the carbonate thermometer is the most likely to give satisfactory results. A combination of the carbonate and phosphate would eliminate the water and hence the isotopic variation of water always present in brackish water and fresh water would be eliminated. Dr. Martin Steinberg is investigating the possibilities of this thermometer in these laboratories.

Assuming that the shell is laid down in equilibrium with the water, the next question that becomes important is whether this composition is preserved during geological periods of time. In the first place, it can be expected that if metamorphosis of a radical kind takes place, as for example the conversion of limestone to dolomite, no satisfactory record of the isotopic abundance can be expected, for the dissolved carbonate should exchange with the water in which it is dissolved and then be redeposited with the composition partially dependent on its original composition and partially on the water which was the means of redeposition. Also, if aragonite is converted to calcite through solution in water, the record would be destroyed, but if recrystallization without the possibility of exchange occurs, the record might be preserved.

The second important method for the destruction of the temperature record is by diffusion through the solid state. Shells as usually deposited appear to be fairly compact, but examination under a microscope shows that they consist mostly of very small crystals, often with definite canals through the shell, as for example in the case of the brachiopods or the echinoderms. Thus in considering the problem of diffusion it is not the gross size of the shell which is important, but rather the small microscopic particles, since in the course of geological time it is probable that water would pass through the shell by hydrodynamic flow, or that diffusion in the liquid would bring the isotopic composition of water within the shell to that of water in which it is immersed. The diffusion problem for considering this situation exactly would be very complicated, but assuming that the initial conditions are that at the surface of the crystals the composition is that required for equilibrium with the surrounding water, and that it remains so throughout the diffusion process, and that initially the crystal had some composition different from that which would be in equilibrium with the water in which it has been immersed during the time since the shell was formed, and that it changes from this initial condition in accordance with the diffusion laws at some constant temperature, a calculation can be made which relates the size of the crystal, the time, and the coefficient of diffusion to the composition of the shell remaining. The fraction of the excess mean concentration over that in equilibrium with the surrounding water, assuming that the coefficient of diffusion is the same in all directions, is

$$\frac{Q}{Q_0} = \frac{512}{\pi^6} \left\{ \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} e^{-a(2m+1)^2} \right\}^3,$$

where $a = \frac{D\pi^2 t}{l^2}$, D is the diffusion coefficient, t the time, and l the length of the edge of the cube.

If we require that the crystal shall retain its original composition within some arbitrary percentage, the value of $\frac{D\pi^2 t}{l^2}$ can be estimated from this equation. (If one uses different values of D for different axes, the result is the same as though different lengths were used for the direction parallel to the axis and for the two directions perpendicular to this).

Table 2 gives a few values of a for a few values of Q/Q_0 .

Table 2*

$a = \frac{D\pi^2 t}{l^2}$	$\frac{Q}{Q_0}$
0.1	0.461
0.05	0.590
0.01	0.795
0.005	0.854
0.001	0.915
0.0001	0.964
0.00001	0.972

*We are indebted to Mr. L. G. Montet for the numerical results given in this table.

The coefficient of diffusion of one ion can be calculated from the electrical conductivity providing the current is carried by that ion and not by the other. Joffe (1923, p. 461) concluded that only the calcium ion carries the current but to what extent the

carbonate ion carries current was not determined except that its contribution was not detected. If we assume that the carbonate ion carries some fraction, δ , of the current, the coefficient of diffusion of the carbonate ion can be calculated from the resistivity of calcite from the equation,

$$D = \frac{RT\delta}{n^2 F^2 C \rho} ,$$

where n is the number of charges on the ion, i.e., 2, F is the faraday, 9650 EMU, C is the number of gram molecules of carbonate ions per cm^3 , ρ is the specific resistance in absolute units, and δ is the unknown fraction of the conductivity due to carbonate and assumed to be 0.01 here. If ρ is in ohms, this formula must be multiplied by 10^{-9} . Curie (1889, p. 385)* measured the specific

*See Landolt-Bornstein Tabellen II, 1062 (1923).

resistance of calcite, and his values and the values of D calculated from them are given in Table 3.

Table 3

Measured Specific Resistance of Calcite
and Calculated Coefficients of Diffusion

	$t^{\circ}\text{C}$	ρ	D_{CO_3}
to axis	20	5.5×10^{14}	4.4×10^{-23}
	100	5×10^{11}	4.8×10^{-20}
	160	3×10^{10}	8.1×10^{-19}
⊥ to axis	15	9.5×10^{15}	2.5×10^{-24}
	100	2.4×10^{12}	1.0×10^{-20}
	150	1.3×10^{11}	1.9×10^{-19}

Using the first two values of D_{CO_3} given in the table, we can estimate the time required for diffusion to destroy the record. Thus at 20°C a crystal of 1 mm. dimensions will retain 96.4% of the original concentration relative to the equilibrium concentration of a changed environment for 2.3×10^{15} seconds (7×10^8 years), while at 100°C the same crystal will retain this record only 2.1×10^{11} seconds (6.4×10^4 years). It is evident that crystals of this size will not lose the temperature record due to diffusion in times sufficiently long to be of considerable interest, and the coefficients of diffusion may be even smaller than those given in Table 3.

A shell may grow a centimeter per year or 3×10^{-3} cm. per day within an order of magnitude. For simplicity we assume that the concentration of O^{18} with distance due to daily variation of temperature varies according to a cosine law. Then the diffusion equation gives

$$C = e^{-\frac{D\pi^2 t}{l^2}} \cos \pi \frac{x}{l} ,$$

where we take the mean concentration as zero. If we can detect a concentration difference equal to 0.5 of the original difference between maximum and minimum, i.e., at $x = 0$ and $x = l$, we have

$$l \ln 2 = \frac{D\pi^2 t}{l^2} .$$

Substituting $D = 4.4 \times 10^{-23}$ and $l = 3 \times 10^{-3}$, the time becomes 1.4×10^{16} or a half billion years. If we ask for 0.75 of the original variation the time becomes fifty million years. Thus even a daily variation of temperature might be partially preserved.

There is the question as to whether the isotopic composition of the ocean has remained constant during geological times. Such a change would be produced, if igneous rocks of one isotopic composition are weathered and sedimentary rocks of another composition are produced. At high temperatures the isotopic compositions of all chemical substances should be the same and, if this temperature was that of molten lava or higher, differences in isotopic composition of water and silicates should not be large and at least they should be less than at lower temperatures. The calculations referred to above show that O^{18} concentrates preferentially in the solid phases and not in the water, and it can be expected that this will be true with respect to the silicate rocks. Thus O^{18} should enter the sedimentary rocks and its concentration in the oceans decrease with time. Assuming that the ratio of concentration in water and silicates is the same as for sulfate and water at $25^{\circ}C$, namely, 1.016, and that 600 g. of rock have been eroded for each 1000 g. of water (Goldschmidt 1933, p. 112), it is easily shown that the water should have changed its ratio of oxygen isotopes by 3.8% due to this cause. Dr. P. Baertschi has shown that there are differences between ocean water, the Disco Island Greenland basalt containing native nickel-iron and other igneous rocks and sedimentary rocks of just the kind and magnitude predicted, though the total difference between ocean water and sedimentary rocks is not 16% as predicted. These results will be published elsewhere.

It is of interest to inquire as to the time at which these changes took place. The carbonate equilibrium should have taken

place early in the earth's history, and largely since then no important change in the O^{18} content of carbonates occurred. The shales which make up much of the sedimentary rocks should exchange their oxygen with water less readily than the carbonates, but no information is available. Baertschi finds that sandstones have an increased O^{18} content relative to the Greenland basalt and thus may have exchanged their oxygen to some extent, though the difference is small enough to be explained by equilibrium differences in concentrations between the silica and other phases of igneous rocks. Perhaps it is a conclusion based on little more than prejudice, but we believe that it is most likely that the major part of this change occurred before the Cambrian, and until more data are available we will make no correction for this effect.

If the water of the oceans has been steadily produced during the earth's history from plutonic activity, as maintained by some*,

*W. Rubey, private communication.

the entire problem of the isotopic composition of the oceans must be considered from this point of view and must involve measurements on the O^{18} and D concentrations in waters which might be expected to be juvenile, as from geysers, hot springs and volcanoes. Such measurements have not been made, but are desirable from the standpoint of the work presented here as well as for the evidence they might give relative to this suggestion in regard to the origin of the earth's water.

The oxygen of the air has a higher isotopic composition than that of the sea and fresh water. The difference in isotopic

composition amounts to about 2 per cent for air oxygen as compared with the sea. All animals use atmospheric oxygen, and hence produce water that contains an increased concentration of oxygen 18. In the case of marine animals having gills which exchange water as between the sea and their blood stream, it can be expected that in spite of the oxidation processes taking place within their bodies the water content of their bodies will be very close to that of the sea. One can reason that this must be true for the water oxygen must pass through the gills approximately as readily as does the elementary oxygen, and since the amount of water present at the surface of the gills is larger than the amount of oxygen by a factor of about 10^5 , the rate of transfer of the water oxygen must be much more rapid than the transfer of elementary oxygen, and hence the isotopic composition of the blood stream must remain close to that of the sea. On the other hand, either marine or land animals that breathe air are suspect for our purposes. Land animals drink fresh water with a decreased concentration of oxygen 18, and animals of the sea eat food containing a very considerable amount of water of the composition of water of the sea, and without knowing the relative importance of these factors it is difficult to have any confidence in regard to any measurements made on air-breathing marine animals, and even more so on land animals. It would be possible to investigate the blood of marine reptiles or mammals in order to determine how nearly the oxygen 18 content of their blood agrees with that of the sea. Up to the present time this has not been done.

The question arises as to whether marine animals maintain their body temperature above that of the surrounding sea. This

question can be answered definitely in the negative. The source of heat is the combustion of food by oxygen received through the membranes of gills, usually, or of the general body surface. The membrane through which the oxygen diffuses is the same as that through which heat is lost to the surroundings. The transport of oxygen determines the rate of heat production and this must equal the rate of loss by thermal conduction. Assuming the maximum concentration of oxygen in sea water, i.e., 6 ml. per liter, and that the oxygen combines with sugar to produce 56,000 calories per gram atom of oxygen, and knowing the coefficient of diffusion of oxygen in water and the coefficient of conduction of heat in water, we can set up the following equation:

$$56,000 D \frac{\Delta C}{\Delta l} = K \frac{\Delta t}{\Delta l} ,$$

where D is the coefficient of diffusion, K the coefficient of thermal conduction, ΔC the concentration difference of oxygen between the blood stream and the water and not greater than that corresponding to 6 ml. per liter, or .0005 gram atoms per cm^3 , Δt the difference in temperature between the water and blood stream, and Δl the membrane thickness through which both diffusion and heat conduction take place. Δl is unknown, but is the same for both processes and can be canceled from the equation and the equation solved for Δt . Substituting $D = 2 \times 10^{-5} \text{ cm}^2\text{sec}^{-1}$ and $K = 1.42 \times 10^{-3} \text{ cal. cm. sec}^{-1}\text{°C}$, we find that $\Delta t = 0.38\text{°C}$. This is the maximum difference in temperature possible under normal aerobic conditions. It is possible for animals to expend energy for limited periods of time under anaerobic conditions and thus raise their temperature above

that calculated here, but such periods would seem to be negligible as compared to the average that interests us in these studies.

The preparation of carbon dioxide gas for use in the mass spectrometer has constituted one of the most difficult problems in this research. It is so intimately related to the problem of the empirical temperature scale that both of these problems and related ones will be discussed in a separate paper. Impurities in the carbon dioxide must not produce peaks at masses 44 and 46 such that the ratio of intensities of these masses is changed by more than one part in 10^4 , which means an impurity of mass 44 of less than this amount and in the case of mass 46 of less than one in 2.5×10^6 . We are fortunate in using a relatively clean part of the mass spectrum. The carbon dioxide is prepared from calcium carbonate by the action of ortho phosphoric acid to which phosphorus pentoxide is added to bring the concentration to approximately 100%. To this enough chromic oxide is added to give a slight permanent red tint and the excess oxide is reduced with hydrogen peroxide and the excess decomposed by heating. The calcium carbonate sample is first heated in a stream of carbon dioxide-free helium for fifteen minutes at approximately 475°C in order to destroy organic matter. Approximately 9 cc. of the phosphoric acid and 50 mg. of the calcium carbonate are put in separate arms of a reaction vessel, evacuated, and brought to 25°C in a thermostat. The acid is then poured onto the carbonate. A vigorous evolution of carbon dioxide results, sometimes with a little froth which breaks during a half hour in the thermostat. The gas is then transferred to sample tubes and analyzed on the mass spectrometer. All stop cocks and tapered joints are

greased with Apiezon N stop cock grease. We have never detected any effect of impurities due to this material.

With this procedure reproducible analyses are secured for both recent specimens and fossils. Using the shells of present day marine animals grown at known temperature and correcting for the variation of isotopic composition of the various sea waters, the following equation for temperature is secured (S. Epstein, R. Buchsbaum, H. Lowenstam and H.C. Urey, in press):

$$t = 11.88 - 5.91 \delta,$$

where t is measured in $^{\circ}\text{C}$ and δ is the difference in ‰ between the ratio of O^{18} to O^{16} in a standard working gas, and this ratio for the sample, i.e.,

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) 1000,$$

where R_{sample} and R_{standard} are the ratios of $\text{CO}^{16}\text{O}^{18}$ to CO_2^{16} for the sample and reference gas respectively. The reference gas is carbon dioxide prepared from *Belemnitella americana* from the Pee Dee formation of South Carolina. The slope of this curve agrees within the limits of error with that secured by McCrea (doctoral dissertation, University of Chicago, 1949; J. Chem. Phys., in press) from inorganic crystals of calcium carbonate grown at constant temperature. This equation is believed to be accurate to $\pm 1^{\circ}\text{C}$ if the calcium carbonate were deposited in sea water of the mean isotopic composition of sea water of salinity 34.8‰. If the calcium carbonate was deposited in water of other isotopic composition, appropriate corrections must be made. The maximum variation in

temperature for fully marine conditions due to the variation of isotopic composition of the oceans is $\pm 4.5^{\circ}\text{C}$.

The variation of isotopic composition of the present oceans, as discussed by Epstein, Buchsbaum, Lowenstam and Urey, presents the greatest difficulty so far encountered in the measurements of paleotemperatures. These authors point out that isotopic composition varies approximately linearly with salinity. Their data on surface waters are not very extensive, but this rough linear relation applies also to surface waters and also the isotopic composition varies in a rough linear way with the temperature of surface waters. This indicates that, if no correction for the isotopic composition were made, a temperature of 30°C would be read as about 25°C , while a temperature of 10°C would be read as 15°C . High temperatures would be read too low and low temperatures too high. However, no correction to past temperature determinations can be made by use of their curve for two reasons. In the first place a general average change in the earth's temperature would not change the average isotopic composition of the oceans and hence a measured isotopic composition could not be corrected with their curve. In the second place the slope of the curve of O^{18} composition vs. temperature is due to evaporation and condensation of water, and hence can be expected to be greater in times of high precipitation and lower in those of low precipitation. In general one would expect that high rates of evaporation and precipitation would accompany higher average temperatures of the earth's surface. However, we have the phenomena of glacial periods which somehow appear between limits of extremely low and extremely high temperatures and

these make estimates in regard to the relation of temperature to precipitation very difficult. For the present we do not attempt to estimate the correction for isotopic variations in the sea, but this problem is being studied from several angles and it is hoped that corrections can be applied in the future.

Measurements of Isotopic Composition and Temperatures of the Upper Cretaceous

In considering geological specimens for our first attempts at measuring these temperatures, we have been guided by our considerations in regard to probable diffusion of the carbonate in solid calcium carbonate and the improbability that recrystallized carbonates would retain the record. Since aragonite is unstable and commonly recrystallized, it seems likely that all recrystallized aragonitic shells will lose the record.

A study of fossil carbonate shells indicated that the belemnites would be the most likely to retain the record. These have a very compact structure with calcite crystals of a size easily visible with the unaided eye and so closely fitted together that internal reflections do not occur since the specimens have a characteristic translucent appearance. The polarizing microscope shows that the calcite crystals are arranged with their axes perpendicular to the axis of the guard. The orientation of the crystal axes and the shape and size of the crystals are evident.

On advice from several paleontologists we have investigated the possibility that various representative species of the genus Inoceramus might retain the temperature record. These fossils again show evidence of massive calcite crystals of substantial size,

though they are opaque and not translucent as are the belemnites. The calcitic layer of the shell is also present in many present day molluscs, though usually not developed to the remarkable extent that it is in this extinct group. Experiments in progress but not reported here confirm our expectation that this group as well as the belemnites retain the temperature record.

In the case of the belemnites, a particularly convincing test for the durability of the record has been made. A Jurassic belemnite* approximately 2.5 cm. in diameter, of a brownish

*Unfortunately, we do not know the species of this specimen. It was collected along with others on the Island of Skye by Dr. Cyril S. Smith, who kindly made them available to us. The specimens are of various shapes and sizes and do not appear to be a single species. As nearly as we can learn they are Jurassic, probably from the Oxford Clay.

translucent color, having very well defined growth rings, has been investigated for a seasonal effect and bilateral symmetry of isotopic constitution both with respect to carbon and oxygen. A flat disk about 3 mm. in thickness was cut from the specimen, polished and photographed in transmitted light as illustrated in Figure 1. Samples of carbonate were ground from the specimen following the growth lines from each side of the disk, as shown by the numbered rings shown in the figure. In some cases right and left samples were not taken and analyzed, either because of accident in the cutting or preparation or because the samples were combined in order to secure sufficient carbonate for our samples. In one case both the right and left samples were lost.

The samples were analyzed for the C^{13} and O^{18} isotopes and the results are given in Table 4,

Fig. 1

Table 4

Analyses of a Jurassic Belemnite

Ring No.	δC^{13}			δO^{18}			t °C
	R	L	Av.	R	L	Av.	
1	3.34	2.50		-0.65	-1.84	-0.65(?)	15.7
2	3.57	3.35	3.41	-0.47	-0.95	-0.71	16.1
3	3.82	3.94	3.88	-0.46	-0.30	-0.38	14.1
4	2.65	2.88	2.76	-1.04	-0.89	-0.96	17.5
5	2.41	2.37	2.39	-1.32	-1.37	-1.35	19.9
6	3.27	3.69	3.49	-1.37	-1.15	-1.26	19.3
7	4.26	4.39	4.32	-1.21	-1.14	-1.17	18.8
8	3.52	--	3.52	-1.14	--	-1.14	18.6
9	2.65	--	2.65	-1.04	--	-1.04	18.0
10	--	2.75	2.75	--	-1.05	-1.05	18.1
11	3.46	3.62	3.54	-0.62	-0.49	-0.55	15.1
12	3.29	3.40	3.34	-1.03	-0.85	-0.94	17.4
13	3.37		3.37	-0.89		-0.89	17.1
14	--		--	--		--	--
15	3.06	3.08	3.07	-1.54	-1.31	-1.42	20.3
16	3.18		3.18	-0.71		-0.71	16.1
17	3.09	3.16	3.12	-0.83	-0.64	-0.73	16.2
18	2.75		2.75	-0.75		-0.75	16.3
19,20	2.74		2.74	-1.21		-1.21	19.0
21	2.59		2.59	-1.24		-1.24	19.2
22,23	2.66		2.66	-0.89		-0.89	17.1
24	2.65		2.65	-1.30		-1.30	19.6
Av.							17.6

It will be noted that the right and left samples of the outermost ring do not agree either with respect to the C^{13} or O^{18} , and that the check for the two samples of the second ring is rather bad for the O^{18} , but that otherwise the agreement on the two sides lies within 0.2‰. Considering probable errors of measurement, and the difficulty of cutting samples of the same thickness from the two sides, the agreement is very satisfactory indeed. It will be noted that a radial variation of isotopic composition occurs both in the carbon and oxygen isotopes. The variation of the carbon isotopes does not correlate with any other variable that we have

Fig. 2

found either in fossil or present day specimens, and the variation in this specimen is of the order found in present day specimens. The erratic variation is probably due to fractionation of the carbon isotopes by plants and the large effect that this has on the very small amount of carbon in the sea (approximately 28 mg. per liter).

In Figure 2 is a plot of the temperatures deduced from our O^{18} abundances against a radius measured along a line from the center of growth outward. The temperatures are plotted as horizontal lines over the range of the radius for which they are the mean temperature. The true temperature curve should intercept equal areas above and below these lines. Such a curve is drawn trying to take account of this requirement and the uncertainty of the data. Where analyses for both the right and left sides are available the line is the average, and points above and below represent the two data. The plot of $\delta(C^{13})$ is also given in the figure and shows no correlation with the seasons. The lack of structure at the smaller radii is probably due to the thickness of samples being too great to show the variations that may exist.

It seems difficult to believe that any possible "accidental" process of diffusion or exchange could have produced such a distribution of carbon and oxygen isotopes, and we conclude that the record has been substantially preserved for over a hundred million years by this belemnite. In our work on other belemnites, we have never had any reason to doubt the isotopic record providing the specimen had retained its translucent character.

This Jurassic belemnite records three summers and four winters after its youth, which was recorded by too small amounts of carbonate for investigation by our present methods, warmer water in its youth than in its old age, death in the spring, and an age of about four years. The maximum seasonal variation in temperature is about 6°C. The mean temperature was 17.6°C.

Dr. C. J. Stubblefield of the British Museum has very kindly given us his cooperation, in securing specimens of belemnites, oysters and brachiopods from the Upper Cretaceous Chalk of England. Thus we have in this case well-preserved specimens imbedded in a matrix which has been modified but slightly with time. Table 5 is a list of the specimens secured from him and his record of the places and zones from which they originate.

Dr. J. Troelsen of the Mineralogical and Geological Museum of Copenhagen also supplied us with three belemnites from the lower and upper Maestrichian of Denmark. The data regarding their collection are as follows:

1. Belemnitella mucronata, Upper Maestrichian,
17 m. below the top of the white chalk,
Stevns, Denmark.
2. Belemnitella mucronata, Upper Maestrichian, 30-40
m. below the top of the white chalk, Stevns, Denmark.
3. Belemnitella mucronata, Lower Maestrichian (white
chalk), Møen, Denmark.

Table 5

	Zone	Rhynchonellids	Oysters	Belemnites
Senonian	UPPER CHALK	1.Ostrea lunata	Trimingham Group of "Rh." <u>plicatilis</u> (J.Sowerby)	Trimingham <u>Belemnitella mucronata</u>
		2.Belemnitella mucronata	" 1153 <u>Ostrea semiplana</u> (J. de C. Sowerby)	1145 <u>Belemnitella mucronata</u>
		3.Actinocamax quadratus	" 1086 <u>Ostrea vesicularis</u> Lamarck	1156 <u>Actinocamax quadratus</u>
		Offaster pilula {	" 1046 <u>Ostrea incurva</u> Nilsson	1040a <u>Actinocamax sp.</u>
		5.Echinocorys scutata var. depressula	" 918 <u>Ostrea canaliculata</u> (J. Sowerby)	
		6.Marsupites testudinarius	" 838 <u>Ostrea semiplana</u> (J. de C. Sowerby)	817 <u>Actinocamax sp.</u>
		7.Uintacrinus westfalicus		
		8.Micraster coranguinum	" 322 <u>Ostrea boucheroni</u> Coquand	295 <u>Actinocamax sp.</u>
		9.Micraster cortestudinarium	" 138 <u>Ostrea vesicularis</u> Lamarck	
Turonian	MIDDLE CHALK	10.Holaster planus	" 116	
		11.Terebratulina lata	" 116	
		12.Inoceramus labiatus	80 "Rh." <u>cuvieri</u> d'Orbigny	
Cenomanian	LOWER CHALK	13.Actinocamax plenus	" 34	54 <u>Actinocamax plenus</u>
		Holaster subglobosus		
		14.Schloenbachia varians	21 "Rh." <u>mantelliana</u> (J. de C. Sowerby)	

All the localities are in Hampshire except the Ostrea lunata zone, which comes from Trimingham. The numbers of the localities refer to the Stratigraphy of the Chalk of Hants, by R. M. Brydone, Publication Dulau, London 1912.

In studying the isotopic composition of these specimens we first removed carefully the chalk from the specimen. In the case of the belemnites the surface layers and any chalky infiltrations that may have occurred in cracks of the specimen were carefully removed. When possible a complete cross section of the guard was used in order to secure a true average temperature. In any case a piece of the solid clear calcite was ground to a fine powder and carbon dioxide prepared from these samples. In the case of the brachiopods and oysters the chalk again was carefully removed and parts of the clean shells were ground to fine powder and used for the preparation of the carbon dioxide samples. Whenever the chalk was available samples of the chalk in the immediate neighborhood of each specimen were analyzed. The results of the carbon and oxygen analyses for the English samples are recorded in Tables 6 and 7. In these tables the zones have been numbered as indicated in Table 5.

Table 6

$\delta (C^{13})$ for Upper Cretaceous of England

Zone	Brachiopod		Oyster		Belemnite	
	Specimen	Chalk	Specimen	Chalk	Specimen	Chalk
1	1.39	0.94	0.79	0.71	0.46	1.64
2	2.83	1.87	2.60	1.55	2.11	1.39
3	2.58	1.61	1.80	1.76	1.12	1.32
4	2.90	--	2.26	1.72	0.92	--
5	2.40	1.80	1.68	1.19	--	--
6	2.32	1.67	1.87	1.67	1.85	--
7	--	--	--	--	--	--
8	--	1.58	1.67	1.52	--	--
9	1.53	0.75	2.09	1.04	--	--
10	1.97	1.17	1.30	0.90	--	--
11	--	--	1.22	1.22	--	--
12	--	--	--	--	--	--
13	--	--	2.84	2.81	3.20	--

Some specimens of Table 5 were not used because of bad preservation.

Table 7 $\delta(O^{18})$ for Upper Cretaceous of England

Zone	Brachiopod		Oyster		Belemnites		Belemnite Temperature
	Specimen	Chalk	Specimen	Chalk	Specimen	Chalk	
1	-1.46	-2.39	-1.85	-2.26	-0.55	-1.88	15.0°C
2	-1.93	-2.90	-2.69	-2.92	-0.42	-2.52	14.4
3	-2.40	-2.46	-2.99	-2.66	-1.24	-3.85	19.2
4	-1.95	--	-1.91	-2.66	-1.26	--	19.3
5	-2.43	-2.20	-2.73	-2.74	--	--	
6	-2.10	-2.46	-2.44	-2.56	-2.03	--	23.8
7	--	--	--	--	--	--	
8	--	-2.68	-2.89	-2.35	--	--	
9	-2.83	-2.94	-2.02	-2.59	--	--	
10	-2.60	-2.47	-3.68	-2.75	--	--	
11	--	--	-3.62	-3.16	--	--	
12	--	--	--	--	--	--	
13	--	--	-1.89	-3.54	-0.40	--	14.2
14	--	--	--	--	--	--	

It will be noted that the oysters, brachiopods and their chalks agree in O^{18} composition only very roughly, and that their C^{13} concentrations do not agree within the limits of our measurements. The belemnites do not agree in O^{18} concentrations with their chalks nor with the oysters and brachiopods. It is our conclusion that only the belemnites retain the temperature record. It is probable that the crystals of the other specimens are so small and the structure so open that diffusion has destroyed the record. In other studies now in progress we have found that a chalky belemnite, i.e., one that has lost its translucent character, agrees in isotopic composition with its surrounding chalk.

Present day specimens show marked variation in C^{13} concentrations even when they grew in the same region at the same time. Thus the samples considered here should have had identical or nearly identical O^{18} concentrations, but not identical C^{13} concentrations when first buried. If both the oxygen and carbon concentrations

changed with time we would expect that the oxygen concentrations would tend to change by comparable amounts, and hence remain somewhat the same as observed. On the other hand the carbon concentrations should show no such approximate agreement. If complete equilibrium with water and carbon of constant composition had been reached, all the analyses should be identical, and thus we conclude that this is not the case.*

*We have analyzed a few samples of ooze from the Pacific and Atlantic Oceans in cooperation with W. F. Libby and J. R. Arnold, who are working on C^{14} concentrations in such materials. We are unable to interpret the results in any consistent way as yet, and evidently more data are required.

The oxygen analyses for the Danish specimens together with derived temperatures are given in Table 8. The specimens are numbered as given previously.

Table 8

Oxygen Isotopic Analyses and Temperatures
of the Danish Belemnites

<u>Specimen</u>	<u>$\delta(O^{18})$</u>	<u>t°C</u>
1	-0.17	12.8
2	-0.43	14.3
3	-0.09	12.3

Upper Cretaceous paleotemperature data for North America were secured from the Exogyra costata zone of a number of widely scattered outcrops of the Gulf Coast and Eastern Seaboard of the United States between western Tennessee and northeastern Mississippi northeastward to New Jersey*. The specimens from Tennessee were

*The specimens from Western Tennessee, Mississippi, North and South Carolina were collected by H. C. Urey and H. A. Lowenstam. We are indebted to Dr. L. W. Stephenson for advising us on certain collecting localities in South Carolina, to Dr. Horace C. Richards who guided us to the New Jersey outcrops, and to Mr. P. A. Bethany of Macon, Mississippi, who advised us on and collected with us from the outcrops of the Macon area.

derived from the sandy marls of the basal $1/3$ of the exposure on Dave Weeks' place, $3\frac{1}{2}$ miles south of Enville, McNair County, the type locality of the Coon Creek tongue of the Ripley formation (Wade 1926). Though belemnites do not occur in these deposits, depriving us of our reliable standard for comparison, the excellent shell preservation of all the molluscan elements with originally

aragonitic shells, elsewhere in the outcrop areas examined preserved only as casts, implied exceptional favorable burial conditions suggestive of preservation of original isotopic abundances. The specimens analyzed from northeastern Mississippi were secured from the Prairie Bluff Chalk, at two localities, the glades on the Vanny Jackson farm west of the Rocky Hill Church road, 3.6 miles north-northeast of Starkville, Oktibbeha County, which is the general area of fossil locality 6846 of Stephenson and Monroe (1940, and from glades on the A. Lindley farm 4 miles southwest of Macon, Noxubee County (Stephenson and Monroe's (1940) collecting locality 17242, 17484). At both localities, the specimens secured for the analyses were found loose in the residual fossil concentrations which littered the glades, since Prairie Bluff specimens satisfactorily preserved and located in situ were unavailable. The positions marked 10 feet and 13 feet above the base of the Prairie Bluff formation in Table 9 for the specimens from the Lindley locality refer to collecting levels on the glade and not to stratigraphic positions. Despite the richness of the assemblages in the glade concentrations, only originally pure calcitic skeletal forms or the calcitic layer of calcite and aragonitic inter-layered shells are as such preserved, reducing the number of potential elements for paleotemperature determinations to crinoidal remains, echinoids, Terebratulina floridana, ostreidae and pectinidae among the pelecypods and guards of Belemnitella americana, the balance consisting of molds, prevalently in phosphatic form. Shark teeth occur associated with the invertebrate assemblages composed of carbonate skeletons, furnishing source material for a possible future check of the carbonate thermometer by the phosphate thermometer.

Table 9

Oxygen Isotopic Analyses and Temperatures
from *Belemnitella americana* from the Southeastern United States

Formation	Locality	Level	Analysis	Temp.	Ave. Temp.
Prairie Bluff	Starkville, Miss. 3.6 miles NNE on Rocky Hill Church Road	Unknown	(1)-0.53	14.9	
			(2)-0.97	17.6	
			(3)-1.23	19.1	
			(4)-1.09	18.2	
			(5)-0.11	12.5	16.4
	Macon, Miss. A. Lindler place 4 miles SW of Macon	13 feet above base of Prairie Bluff	(1) 0.00	11.9	11.9
			(1)-1.03	17.9	
			(2)-0.75	16.2	
			(3)-0.51	14.9	
			(4)-1.49	20.6	17.9
Peedee	Peedee River, S. Carolina	105" above base of formation	(1)-0.51	14.9	14.9
		57" to 68" above base of formation	(1)-0.44	14.5	
			(2)-0.30	13.6	
			(3)-0.26	13.4	
			(4)-0.31	13.7	
			(5)-0.27	13.4	
			(6)-0.67	15.8	
			(7)-0.55	15.1	
			(8)-0.46	14.6	
			(9)-0.28	13.5	
			(10)-0.66	15.8	
			(11)-0.61	15.5	14.4
Peedee	Cape Fear River	Unknown	(1)-0.54	15.1	
			(2)-0.89	17.1	16.1
Havesink	Mullica Hill, N.J.	Base of formation	(1)-1.21	19.1	
			(2)-1.18	18.8	
			(3)-0.90	17.2	
			(4)-0.81	16.7	
			(5)-1.00	18.8	
			(6)-0.98	17.6	18.0

(continued)

Table 9 (cont.)

Formation	Locality	Level	Analysis	Temp.	Ave. Temp.
	Hornerstown, N.J.	Base of formation	(1)-0.87 (2)-0.53	17.0 15.0	
	Crosswicks Creek		(3)-0.49 (4)-0.75 (5)-0.80 (6)-0.80 (7)-0.39 (8)-0.62	14.8 16.3 16.6 16.6 14.2 15.5	16.0
	Cream Ridge	Unknown	(1)-0.59 (2)-0.70	15.4 16.0	15.7

The South Carolina specimens were secured in situ from the basal section of the Pee Dee formation which is well exposed in the west bank of the Pee Dee river at Burches Ferry, $15\frac{1}{2}$ miles from Florence. This is the locality from which Stephenson (1923) described and figured a number of well preserved specimens of Belemnitella americana and described a new species. At the time of our visit, the river was low enough to expose a total of $13\frac{1}{2}$ feet of Pee Dee strata, consisting of calcareous, argillaceous, glauconitic sand above $3\frac{1}{2}$ feet of the shales of the Black Creek formation. Belemnitella americana was found to occur in small numbers through the entire local Pee Dee section, being concentrated in conspicuous numbers in a narrow 9 inch zone, 57 inches above the base of the formation. The Belemnitella guards are throughout oriented more or less horizontally, with occasional deviations ranging up to about 10° from the horizontal plane. Within the horizontal plane the belemnite rostra display random orientation as far as could be ascertained in the vertical exposure. Exogyra costata occurs sparingly distributed through the basal $7\frac{1}{2}$ feet of the section, the individuals being generally small and thin shelled. Larger, but

comparatively fragile individuals occur in greater numbers in the overlying 22 inches of the section which is conspicuously fossiliferous, consisting of a semi-coquina of pelecypod shell debris. The specimens analyzed were taken in situ.

The North Carolina specimens were collected from a 6 inch thick calcareous sandstone ledge of the Pee Dee formation, which is exposed above water level and 6 inches of soft marl below water level at the Jackson's Hole Landing, locality of Stephenson (1923, p.25), Northeast Cape Fear River. A number of large, heavy shelled Exogyra costata individuals, with strongly resorbed surfaces, and a single rostrum of Belemnitella americana were secured in situ from the water covered marly layer, which contrasts strongly with the rich mollusk assemblages of overlying calcareous sandstone ledge. Pectinidae and Belemnitella americana, originally calcitic skeletal types alone are well preserved, the originally aragonitic shells of the associated pelecypods being often represented by casts and molds. As the Pee Dee section lacks top and bottom it is not possible to determine the stratigraphic position of this section within the formational range.

The New Jersey specimens analyzed were secured from the Navesink marl at the well known fossil locality in the hillside just south of the railroad trestle at Mullica Hill (Weller, 1907, locality 169), in the cut of a tributary of Crosswicks Creek near Hornerstown, and from the dump piles of the abandoned "marl pit" on Edgar Schank's farm near Cream Ridge (Weller, 1907, locality 127). The Mullica Hill specimens were derived from a 4 inch thick shell bed, consisting of Exogyra costata, pectinidae and Belemnitella

americana in a marly glauconitic sandy matrix about 12 feet above the base of the bluff exposure. The preservation of the pelecypods and belemnites is generally poor due to leaching and partial limonitic replacement, while conspecific forms occurring in shell beds, located 10 feet lower and about 3 feet higher up in the bluff section are represented only in the form of casts and molds. The Hornerstown specimens are derived from a shell bed, composed principally of Exogyra costata, Gryphaea convexa, and Belemnitella americana. The dense packing of the pelecypod shells with the random oriented, inter-wedged Belemnitellas indicates post mortem concentrations, swept together in shallow agitated waters. Burial grounds foreign to the habitat thus strongly implied for the Belemnitella element. According to Spengler and Peterson (1950), the shell beds mark the base of the Navesink member of the Monmouth formation, previously interpreted as a formation and group respectively. A basal position for the Mullica Hill and Hornerstown specimens in the Navesink is thus indicated, while the stratigraphic position of the Cream Ridge forms, secured loose from the dump piles, cannot be determined.

All of the North American specimens included in the present study of paleotemperatures fall within the range of the Exogyra costata zone, as shown by the correlation of the formations from which they were derived (Figure 3). In comparing the stratigraphic positions of the specimens secured from Tennessee, Mississippi and South Carolina, and the Mullica Hill and Hornerstown localities in New Jersey within their respective formations and in relation to the formational ranges and their correlation, it will be seen that

FIG. 3

the Coon Creek forms from southwestern Tennessee occupy a lower, those from the Peedee formation of South Carolina and from the Navesink localities of New Jersey an intermediate, and the Prairie Bluff forms from northeastern Mississippi a higher position within the zonal range. Their stratigraphic relations to the North Carolina and Cream Ridge locality of New Jersey cannot be determined because of the unknown stratigraphic positions of the latter within their respective formations. To judge from the narrow range of the Navesink marl, the New Jersey specimens may occupy a position anywhere between the top of the Coon Creek formation of southwestern Tennessee and the base of the Prairie Bluff chalk in northeastern Mississippi, those from the Peedee formation of North Carolina a considerably wider interval.

The North American forms serve for an initial survey of the special paleotemperature range within the time interval occupied by the Exogyra costata zone, even though in some cases our specimens came from different levels within that zone and in other cases the relationships within the zone are uncertain.

Discussion of the North American Temperatures

The Exogyra costata zone is correlated with the Maestrichtian of the European standard section (Stephenson and Reeside 1938, p. 1637; Stephenson et al. 1942, Chart No. 9). Belemnitella mucronata which occupies in the Upper Senonian of northern and central Europe a similar stratigraphic position as Belemnitella americana in southeastern North America, has been considered closely related to the North American species (Stephenson 1923, p. 56). Approximate time equivalency of their enclosing strata is further indicated by

other faunal and floral similarities (Stephenson 1923, pp. 56-57). Keeping in mind the as yet existing uncertainties in intercontinental correlation, particularly with reference to details in time equivalency and length of time intervals compared, it is nevertheless permissible to compare in general terms the Maestrichian paleotemperature data from both sides of the Atlantic, that is, of the Gulf Coastal area in North America and of southern England and Denmark in northwestern Europe. There is surprisingly little difference in the temperatures recorded by the reliable forms from either side of the Atlantic despite the latitudinal range of the collecting localities, which extend from 33° to about 41°N in North America to between about 52° and 56°N in England and Denmark.

In surveying the meaning of the temperature records only those of the belemnites can be at present considered with some reliance. As the temperatures recorded constitute at best mean temperatures of skeletal growth periods, they do not necessarily represent annual mean temperatures of the waters in which they lived. This is clearly indicated by the temperature range recorded by the shell of a recent Chama macerophylla from the Bermuda inshore waters, which has been analyzed for seasonal effects. Shell material is laid down only after the surface waters reach 24°C and extends through the warm part of the year, which reaches a maximum at 29°C , while the yearly temperature range of the inshore waters covers a range from 18°C to 29°C . The mean temperature of $26\frac{1}{2}^{\circ}\text{C}$ recorded by the Chama macerophylla shell is thus $2\frac{1}{2}^{\circ}\text{C}$ higher than that of the waters. Organisms with a narrow temperature range for skeletal growth, particularly with a growth period largely off the

average with reference to the yearly range of their waters, would constitute unreliable data for climatic records unless forms from identical habitat with wider or overlapping skeletal growth periods are available for comparison. The Inoceramus lineage now under investigation may furnish a comparative element for correction at a future date.

Returning to the belemnites, preference for cooler waters is strongly implied by their geographic distribution. Dacque (1915, pp. 423-426) in discussing the paleo-climatology of the Cretaceous, pointed out that starting with the beginning of the Cretaceous broad climatic zoning is introduced, becoming sharply established by Upper Cretaceous time. Differentiation into a boreal and Mediterranean-aquaetorial zones is fairly well documented, the aquaetorial zone being characterized by prominent carbonate sediments, reef forming corals and rudistids, large foraminifera and heavy shelled Nerineidae and Actaeonellids. Most convincing is the dwarfed and crippled appearance of rudistids found in the bordering boreal zones both to the north and south, as shown by Dacque's distribution map for the rudistids. Belemnitella was shown to be confined to the northern boreal zone of the Upper Cretaceous seas. In comparing the size ranges of the collections of Belemnitella americana secured from the various localities of the Gulf Coastal area, an increase in maximum sizes attained is clearly noticeable / from Mississippi northeastward to New Jersey. The Mississippi localities were apparently located in the southern border area, as Stephenson and Monroe record representatives of the rudistid genus Durania from the Exogyra cancellata subzone of the upper Selma Chalk in which Belemnitella americana makes its first appearance.

The northeastward trend of increasing sizes in Belemnitella americana could be correlated with cooler water preference, but their mean temperature records do not seem to support this view. Refinement in the sampling procedure contemplated for studies of seasonal variations may decide this question. Throughout our discussion we have neglected the possibility and even probability of some variation of the isotopic composition of the waters, and this may explain the nearly identical temperatures of the Carolina and Mississippi region as contrasted to New Jersey.

The depth range is another factor yet to be considered in the evaluation of the temperatures recorded by nectonic elements such as belemnites. The sediment character and the burial assemblages of the American representatives in the locations examined indicate that though the bottoms were largely below effective wave base (except for New Jersey examples, which occur in wave concentrated shell beds), the abundant and varied mollusk forms point to comparatively shallow bottoms, well within the euphotic zone. This is in agreement with Naef's (1922) conclusions of prevalent shallow water habitat for the belemnites in general as implied by functional morphology. Thus the temperature variation should be characteristic of a limited depth range. That Belemnitella lived in shallow cooler waters is further indicated by the absence of stray individuals in the southern Tethys waters.

The narrow gradient indicated by the mean temperatures of the Belemnitellas across the latitudinal width from Mississippi to Denmark is surprising. Unless the temperature tolerance of skeletal growth of the European and American species happens to coincide, rather uniform climatic conditions are suggested over the greater

part of the boreal zone during the Maestrichian. Gradual lowering of the temperatures through Upper Cretaceous times toward the Maestrichian are indicated in England and in agreement with the establishing of the climatic zones noted by Dacqué. Increased mixing of the oceans due to stronger current development should have resulted. North and South America were probably separated by the circum-equatorial Tethys, and the waters from the pole area previously connected with it via the western interior strait became separated at about the critical time that the lowering of the late Cretaceous temperatures is indicated to have taken place. Free mixing of the northern waters due to lack of the present existing north-south land barriers should have tended to equalize the temperatures toward the pole. Subtropical climatic conditions could have thus been maintained on the northern land masses where the dinosaurs continued to flourish.

Cowles (1939, 1940, 1945) has suggested extinction of the dinosaurs at the closing interval of the Cretaceous due to increased temperatures. On the other hand continued lowering of the temperatures as suggested by the English downward trend would have equally caused their extinction. We do not wish to emphasize this apparent downward trend since our temperatures depend on single samples in each zone and our experience indicates that a variation between a number of specimens of the same locality of as much as 5°C is possible. The investigation of more specimens from these zones and seasonal variations of such specimens may enable us to reach a definite conclusion. Longitudinal paleotemperature traverses

for the entire Upper Cretaceous extending into early Tertiary, based on a large number of associated faunal elements and including benthonic forms should furnish a clearer trend of paleo-climatologic conditions as well as aid in quantitatively evaluating the temperature niches of the marine organisms.

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The Carbonate-Water Isotopic Temperature Scale

Samuel Epstein, Ralph Buchsbaum,
Heinz Lowenstam and Harold C. Urey

In the preceding paper¹ a method for measuring paleotempera-

¹H. C. Urey, H. Lowenstam, S. Epstein and C. J. McKinney, This Journal, in press.

tures has been discussed. This method depends on a variation in the oxygen-18 abundances in calcium carbonate deposited in the sea. McCrea² investigated the isotopic composition of calcium carbonate

²J. M. McCrea, J. Chem. Phys., in press.

precipitated inorganically from water and determined the temperature coefficient for the abundance of O^{18} in calcium carbonate relative to water as a function of temperature, and found a value of $-5.4^{\circ}C$ per mil increase in the ratio of O^{18} to O^{16} in the calcium carbonate. McCrea gave a calculation for this quantity including estimates of the effect of the translational and hindered rotational degrees of freedom in the solid state on the distribution functions, and arrived at a value of 5.1. Assuming free rotation in the solid state Urey³ calculated a value of 5.7 for the same quantity. It is

³Harold C. Urey, J. Chem. Soc. 562, 1947.

the purpose of this research to determine this quantity and to set up an equation relating temperature to the difference in isotopic composition of samples of carbon dioxide prepared from organically precipitated calcium carbonate and an arbitrarily selected reference sample of carbon dioxide.

The determination of a relationship between temperature and O^{18} abundance in calcium carbonate from marine shells and from inorganic calcium carbonate precipitates is similar. But there are a number of special considerations to be taken into account in the case of marine shells to find the temperature of the sea water in which the marine animals lived. These factors are (a) the isotopic composition of the oxygen of the oceans, (b) the collection of marine shell-bearing animals which grew in water of constant and known temperatures, and (c) the problem of impurities in the carbon dioxide prepared from marine shells.

(a) Isotopic composition of marine waters

Since the ratios of vapor pressures of H_2O^{16} to H_2O^{18} are 1.008 and 1.011 at $25^\circ C$ and $0^\circ C$ respectively⁴, evaporation and

⁴E. H. Reisenfeld^a and T. L. Chang, Z. phys. chem. B33, 127 (1936).

condensation continuously change the O^{18} contents of bodies of water. The magnitude of the variation of O^{18} in the oceans is of importance to the determination of a valid temperature scale and to the general problem of the determination of temperature of unknown samples, because this thermometer depends essentially on the magnitude of the difference between the O^{18} contents of the calcium carbonate and the water in which it was precipitated. Consequently a series of O^{18} determinations were made on samples of sea water, most of which were made available to us by H. Pottersson, who collected them on the Albatross expedition⁵. The method of

⁵H. Pottersson, Endeavour 8, No. 32, 182-187 (1949).

determining the relative O^{18} content of water samples involves the equilibration of carbon dioxide with the water at $25^{\circ}C$ and analysis of an aliquot of the gas. The carbon dioxide so equilibrated is compared with our standard working sample of carbon dioxide prepared from the calcium carbonate of belemnites of the Feedee formation¹ using a high precision mass spectrometer⁶. The analyses are relative

⁶C. J. McKinney, J. M. McCrea, S. Epstein and H. C. Urey, Rev. Sci. Instr., in press.

only, but are correct within a probable error of about 0.2‰ of the isotope ratio. The results of these analyses are given in Table 1, together with the point of collection, temperature, and salinity. The unit used in this table and referred to previously is defined by the following equation:

$$\delta(O^{18}) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) 1000,$$

where R_{sample} and R_{standard} are the ratios of $CO^{16}O^{18}$ to CO_2^{16} for the sample and standard reference gas respectively.

Apparently, the isotopic composition of oxygen is not homogeneous throughout the oceans. Deviations from the mean isotopic composition of the oceans occur in the waters close to the mouth of a river, as is the case for the President Channel location. If water of fully marine composition is considered, then the maximum variation of O^{18} in ocean water is 1.4‰, which would represent about $7^{\circ}C$ variation in temperature determination. Clearly, it is necessary to determine the O^{18} content of the water in which a marine shell grows if this particular shell is to be used in correlation of temperature with the O^{18} content of organically precipitated shell.

Table 1

Relative O^{18} Content of Marine Waters

<u>Location</u>	<u>Depth of point of collection Meters</u>	<u>Temperature °C</u>	<u>Salinity ‰</u>	<u>$\delta(O^{18})$ ‰</u>
30°47'N	10	---	37.44	-0.01
25°25'W	1000	---	35.43	-0.59
26°25'N	5000	---	34.9	-0.21
34°00'W				
14°27'N	5000	42	34.9	-0.74
66°13'W				
14°15'N	0	27.7	36.0	0.42
71°02'W				
02°52'S	20	18.8	34.4	-0.36
88°20'W	500	7.5	34.6	-0.50
	1000	45	34.6	-0.55
13°25'S	0	27.7	35.8	-0.23
149°30'W	1000	4.3	34.6	-0.93
	4000	1.4	34.7	-0.65
07°45'S	10	29.5	34.5	0.57
120°30'E				
10°06'N	20	29.3	35.5	0.06
52°45'E	500	10.7	35.0	-0.25
	2000	2.9	34.8	-0.90
35°41'N	50	16.5	38.8	0.69
21°50'E	2000	13.6	38.7	0.84
00°13'S	25	22.6	35.6	0.04
18°26'W	500	7.1	34.7	-0.50
	2500	3.0	34.9	-0.38
	7500	1.4	34.8	-0.44
28°05'N	25	28.5	36.8	0.38
60°49'W	500	16.3	36.3	-0.18
	2000	3.7	35.0	-0.59
43°04'N	2000	3.6	35.0	-0.67
19°40'W				

(continued)

Table 1 (cont.)

<u>Location</u>	<u>Depth of point of collection Meters</u>	<u>Temperature °C</u>	<u>Salinity ‰</u>	<u>$\delta(O^{18})$ ‰</u>
President Channel, Puget Sound	171	9.4	31.4	-0.94
Middle Channel, Puget Sound	157	7.4	33.1	-0.91
Encenada, Mexico	~ 0	19	33.5	-0.81
St. Tomas, Mexico	~ 0	15	33	-0.77
Monterey Bay, California	~ 0	11	33.8	-0.85
La Jolla, California	~ 0	15	34.0	-0.76
Bermuda	~ 0	18-29	---	0.64

On further examination of the data an attempt was made to establish a correlation between the O^{18} content and the salinity of the water. Such a correlation is possible because processes which tend to increase or decrease the O^{18} of the water also tend to increase or decrease the salinity. The plot of salinity against relative O^{18} content is shown in Figure 1. The points scatter badly, but a regular trend is evident and a straight-line relationship is assumed between salinity and O^{18} content of the water. The relationship is only approximate as was to be expected. Extrapolation of the line to zero salinity gives -13.5‰ as the relative O^{18} content of fresh water.

Fig. 1

The approximate linear relationship between salinity and O^{18} abundances suggests that it might be more rigorously followed if limited to surface waters. And since surface salinity and surface temperature show some indication of being related linearly, we have plotted in Figures 2 and 3 salinity vs. O^{18} content and temperature vs. O^{18} content respectively for the waters of Table 1 coming from a depth of 25 meters or less. The plots indicate rather definite linear relations but the data are too meagre to justify any definite conclusion. We shall continue this investigation as we secure more water samples, particularly from higher latitudes.

The mean isotopic composition of the oceans will be close to that of the water of mean salinity, and we have selected this as having -0.47‰ relative to our standard gas and corresponding to 34.8‰ salinity. This gives -13.0‰ as the isotopic composition of fresh water relative to that of sea water of 34.8‰ mean salinity. This difference is larger than that expected for a fractionation equal to the ratio of vapor pressures, and substantially greater than that for any fresh water samples investigated by us. Lake Michigan is representative, and analyzes as -6.2‰ relative to our mean sea water.

This large variation of isotopic composition of sea water decreases the reliability of temperature measurements by this method unless a sample of water is analyzed at the same time and a correction for the isotopic composition of the water is made on the carbon dioxide analyses. This error, some 2.5 times as large as expected, is disappointing, especially when paleotemperatures are considered. It must be that the melting ice of high latitudes has a lower O^{18}

Fig. 2

Fig. 3

content than has fresh water of the temperate zone. The whole problem of water evaporation from the oceans and its precipitation over the land and oceans is very complex, and our data are not sufficiently extensive to justify a more detailed discussion at present.

A correlation between salinity and O^{18} content is useful in that salinity data which are quite readily available for present-day oceans can give an approximate correction for the isotopic abundance if water samples are not available for mass spectrometric analyses. We hope the distribution of O^{18} between phosphate and water will give another thermometer with a different temperature coefficient, thus making possible the elimination of the water phase*.

*M. Steinberg is developing this possibility in our laboratory.

(b) The isotopic temperature scale

One of the problems in establishing a temperature scale using marine calcareous-shelled animals was to get snells which grew at known temperatures. To grow certain marine animals under controlled temperatures in the laboratory is a lengthy and difficult project. Nevertheless, constant-temperature baths were set up at three Pacific Coast marine laboratories** and these were stocked

**Oceanographic Laboratory, University of Washington, Friday Harbor, Washington. We are indebted to Dr. Thomas G. Thompson and Dr. Emory Swan for assisting in this work, and also to Dr. C. Barnes for help in locating suitable areas for collecting. At the Hopkins Marine Station we are indebted to Dr. Rolf Bolin for help in looking after one of the experimental tanks. At Scripps Oceanographic Laboratory, La Jolla, California, we are indebted to Dr. Carl Hubbs who assisted us in setting up one of the experimental tanks and in making collections in lower California.

with calcareous organisms with notched or drilled shells. It was thought that if repair occurred, the new shell, when analyzed, would yield reliable data which could be used to fix points on the temperature scale. Not all of the material is in, and some of the attempts were unsuccessful. However, at this writing one of the experimental batches of animals has been analyzed and the results are given on page 17. Consequently, shell-bearing marine animals were collected from locations which have a minimum annual variation of temperature. The species of animals chosen were attached or sedentary forms which live in relatively confined areas so that the point at which collection was made would be representative of the condition under which the animals grow their shells. Animals were collected from marine locations which had records of maximum constancy and which had a minimum of contamination with fresh water drainage. Collections were made in the cooler waters of Puget Sound, intermediate conditions of Monterey Bay, and the warmer waters of certain areas along the coast of lower California in Mexico. In addition, shells from the still warmer waters of Bormuda were analyzed.

Particular care was taken to make a good estimate of the temperature at which the particular fragment of shell used for analyses grew. For example, the samples analyzed from Santa Tomas, Mexico, included one large red abalone, *Haliotis rufescens*, and one large black abalone, *Haliotis cracherodii*, and two giant keyhole limpets, *Megathura crenulata*. The *Haliotis* were collected August 25, 1949, and thus the outer few millimeters of the rim of the shell grew within the months May to August. Dr. C. L. Hubbs measured temperatures at several stations in this region during September

1948, May, July and August 1949, and also observed the daily variation on August 18, 1949. From these measurements we conclude that 15°C is a reasonable average temperature. The variations in temperature during these months is about the same as the daily variation from 14.4°C to 17.0°C . Thus a probable error of $\pm 1^{\circ}\text{C}$ seems a reasonable estimate. In the case of the giant keyhole limpets a complete cross section of the shell was taken so that it was necessary to estimate the average annual temperature. The temperature in this location goes down as low as 11°C and as high as 17°C . The average temperature of this sample of the shell was thus estimated to be 14°C within an error of less than 3°C and perhaps as close as 1°C . Similar considerations led to the assignment of other temperatures and similar uncertainties exist in the estimates.

Table 2 gives a description of the location at which the marine animals were found, the estimated temperature of the fragment of shell used for analyses, and the relative O^{18} of the water collected in conjunction with the sample.

The carbon dioxide was prepared from the marine shells by reacting the calcium carbonate with approximately 100% ortho phosphoric acid in an evacuated vessel. The carbon dioxide was trapped in a liquid nitrogen cooled trap and pumped free of the more volatile impurities, then passed through traps covered by a solid CO_2 -acetone bath to freeze out the less volatile impurities like water.

The samples of the shells described in Table 2 were then cleaned of obvious impurities and the carbon dioxide prepared.

Table 2

Description of Shell Samples Used
for Determination of Temperature Scale

Location	Specimen No.	Name	Part of specimen used	Est.Temp. °C	Water analysis
Middle Channel, Puget Sound 48°22'30"N 122°53'45"W 130-157 meters July 22, 1949	1	Mussel <u>VolSELLA</u> <u>modiolus</u>	Cross section of complete half shell	7.4 Annual variation ± 1°C	-0.91
	2	Brachiopod <u>Terebratu-</u> <u>lina trans-</u> <u>versa</u>	Complete half shell		
President Channel, Puget Sound 48°41'50"N 122°59'30"W 171 meters July 16, 1949	3	Mussel <u>VolSELLA</u> <u>modiolus</u>	Cross section of complete half shell	9.4 Annual variation ± 2.0°C	-1.94
	4	Brachiopod <u>Terebratu-</u> <u>lina trans-</u> <u>versa</u>	"		
Hopkins Marine Station, Pacific Grove, Calif.	5	Red abalone <u>Haliotis</u> <u>rufescens</u> . At low tide level May 14, 1949	At least a year's growth of shell	12.6	-0.85
	6	Giant key- hole limpet <u>Megathura</u> <u>crenulate</u> 1/2 mile off- shore, 3 m. Aug. 15, 1949	Cross section of complete shell	11.5	
Santa Tomas, Lower California, Mexico Aug. 27, 1949 3-6 meters	7	Red abalone <u>Haliotis</u> <u>rufescens</u>	Last 2 cm of large shell	15	-0.77
	8	Black abalone <u>Haliotis</u> <u>cracherodii</u>	"	15	
	9 10	Limpets <u>Fissurella</u> <u>volcano</u>	Cross section of 2 complete shells	14	
Between Encenada and Morro Points, Lower California, Mexico. 3 meters Aug. 25, 1949	11	Red abalone <u>Haliotis</u> <u>rufescens</u>	Edge of shell	20	-0.81
Bermuda, Tank in laboratory	12	Snail (conch) <u>Strombus</u> <u>gigas</u>	Regenerated shell	31	0.64
	13	Bivalve, <u>Pinna</u> sp.	" (part)	29	

Table 3 gives the results of analyses when this method of preparation of carbon dioxide is used. The specimen is indicated by number in column 1, the observed temperature in column 2, the isotopic analysis in per mils in column 3, the correction for the isotopic composition of the water in column 5, and the corrected analysis in column 6. The results of the sixth column are plotted in Figure 4.

The data show that a correlation exists between temperature at which the marine animals grew and the relative abundance of O^{18} in the carbon dioxide prepared from the shells. But the deviations from a linear or nearly linear relationship are much larger than the expected experimental error. The difference in analyses for shells collected simultaneously from the same location eliminated the possibility that the poor correlation between temperature and relative O^{18} content was due to incorrect estimation of the temperature at which the animals grew.

The possibility that the animals did not lay down their shells in equilibrium with the surrounding water seemed to be an unlikely explanation because the relative O^{18} contents of calcium carbonate were not randomly distributed but showed a definite correlation to temperature. Some preliminary results were obtained during the course of this investigation which indicate that perhaps the Echinoderms and corals fractionate the oxygen isotopes of the calcium carbonate during their deposition in their complex shell structure. But not enough information has as yet been obtained to justify this conclusion regarding these groups of invertebrates. In any case, the shells here used in the determination of the temperature scale were those which are deposited external to the animals' soft parts.

Table 3Isotopic Analyses of Organic Calcium Carbonate Samples

Number of specimen (Table 2)	Observed Temp. °C	Analysis (No heat treatment)	Analysis (With heat treatment)	Water correction	Corrected analysis (No heat treatment)	Corrected analysis (With heat treatment)
1	7.4	1.43	0.36	0.44	1.87	0.80
2	7.4	1.34	0.13	0.44	1.78	0.57
3	9.4	0.54	-1.27	1.47	2.01	0.20
4	9.4	-0.21	-1.14	1.47	1.26	0.33
5	12.6	0.50	-0.51	0.38	0.88	-0.13
6	11.5	1.06	-0.31	0.38	1.45	0.07
7	15	0.92	-0.97	0.30	1.22	-0.67
8	15	0.95	-0.81	0.30	1.25	-0.51
9	14	0.60	-0.43	0.30	0.90	-0.13
10	14	0.46	-0.50	0.30	0.76	-0.20
11	20	0.27	-1.80	0.34	0.61	-1.46
12	31	-0.58	-2.27	-1.11	-1.69	-3.38
13	29	---	-1.75	-1.11	---	-2.86

Fig. 4

Comparison of results of McGree with those of Table 3 indicated that the possible errors in the present work were of the order of magnitude of 1% of the mass 46 to mass 44 ratio. Since impurities of mass 46 present to the extent of three parts per million would introduce an error equivalent to 1% in the ratio, the usual chemical methods for analysis of impurities would be impractical in this case. Therefore, the criterion for valid analyses became the consistent correlation between temperature at which the shells were laid down and the measured change in relative abundance of mass 46 in the carbon dioxide.

(c) Methods of purification

The method of collecting the ion currents in the mass spectrometer gave measurements of the abundance ratio of mass 46 to the sum of masses 43, 44, 45, and 47. Consequently, although the ratio of mass 46 to mass 44 would be relatively insensitive to small concentrations of impurities of masses 43, 45, and 47, these had to be considered. Purification of samples could then either decrease or increase the value of the 46 to 44 ratio depending on whether purification eliminated impurities of mass 46 or of masses 43, 44, 45, and 47.

Many molecules or radicals formed in the ionizing chamber of the mass spectrometer, both organic and inorganic in nature, can contribute to the ions of mass 43 to 47. Some of these can be C_2H_5OH , CS , CH_3COOH , BCl , NO_2 , N_2O and propane. The first attempts were focussed on the possible impurities in the carbon dioxide gas. Several carbon dioxide samples from different marine shells were mixed with small volumes of bromine gas and irradiated by strong

light, with the hope that bromination would shift the mass range of the impurities beyond the 43 to 47 range. Some samples of carbon dioxide were mixed with Van Slyke's⁷ oxidizing solution or passed

⁷D. D. Van Slyke, J. Folch and J. Plazin, J. Biol. Chem. 136, 509 (1940).

over hot CuO. Organic impurities would then be converted to carbon dioxide, and if present in trace amounts should not affect the 46 to 44 ratio of the carbon dioxide sample as a whole. Samples were also mixed with traces of ammonia and water to hydrolyze compounds like boron trichloride, and over hot copper to reduce possible traces of nitrogen oxides.

In all the above mentioned cases no appreciable effect on the isotopic analyses was observed.

Samples of carbon dioxide from the shells were also mixed with fluorine. Only in cases where there was evidence of incomplete separation of the carbon dioxide and fluorine and subsequent contact with glass was there a change in O¹⁸ analysis. These changes were erratic for any one source of gas samples and varied from -0.3‰ to -200‰ of the 46 to 44 ratio. This was obviously due to Si²⁸ of mass 47 adding to ion beam 44 and thus showing a decrease in the ratio of 46 to 44.

A more successful approach to the purification problem involved treatment of the powdered calcium carbonate before preparation of the carbon dioxide. The powder was heated at 400°C for 60 minutes with a slow stream of helium passing over the powder. The helium was first purified by passing it over copper oxide at 750°C and then through a liquid nitrogen cooled trap. With this treatment

the relative O^{18} contents of the calcium carbonate from shells was decreased in most cases, and in a reproducible manner.

Experiments to determine the length of time necessary for heating the calcium carbonate powder to attain constancy of O^{18} analysis with further heating showed that 15-30 minutes heating at $400^{\circ}C$ was necessary to "purify" the samples tried. A safety factor of two was adopted, and the samples were heated for one hour. Since the equilibrium pressure of carbon dioxide over calcium carbonate is 10^{-6} atmospheres at $400^{\circ}C$, it was necessary to test this treatment for possible loss of carbon dioxide and fractionation of the oxygen isotopes. Two samples of calcium carbonate, one normal in O^{18} and the other enriched by 100 ‰, were precipitated inorganically (using sodium carbonate and calcium chloride). Samples of each were analyzed without the heat treatment and with heat treatment. The analyses of each variety of calcium carbonate checked, showing that heat treatment did not change the analyses of such samples. Clearly, it was the organically precipitated calcium carbonate alone which was affected by the heat treatment. To shorten the length of time for the experiments the powdered samples were heated for 15 minutes at $475^{\circ}C$ with the attainment of the identical results observed for the longer heating times. We do not understand the mechanism of purification of the marine shell samples by the heating process. In most cases it is obvious that charring of organic matter occurs.

Calcium carbonate samples from specimens listed in Table 2 were heated before the carbon dioxide was prepared, and then analyzed. The results are given in Table 3, column 4, uncorrected, and in the

last column after correction for the isotopic composition of the water. These results are plotted in Figure 5.

Comparisons of data plotted in Figure 4 with those of Figure 5 indicates that the heat treatment of the organically precipitated calcium carbonate lowered the apparent O^{18} contents of the carbon dioxide prepared from all these samples. Apparently the marine shells contained variable amounts of some impurity, causing the inconsistency in the relationship between temperature and O^{18} content when unheated samples were used.

Least squares calculations of the data in Table 3 gave a straight line relationship

$$t = 11.88 - 5.91 \delta(O^{18}),$$

where t equals the temperature in $^{\circ}C$, $\delta(O^{18})$ is the per mil difference between the ratios of masses 46 and 44 for the sample and standard gas. The constant 11.88 is characteristic of our standard gas, while the constant 5.91 should be independent of this gas.

Discussion

Our constant, 5.91, for the slope of the curve differs from that secured by McCrea, namely, 5.4. The deviation is in the direction expected for incomplete equilibrium between solid calcium carbonate and dissolved carbonate ion as found by him. We do not believe that this is the cause of the disagreement since a considerable variety of organisms all give analyses lying so closely

Fig. 5

on our curve*. The measurements of these small quantities are very

*

In fact, as this is written an analysis of a sample of regenerated shell from *Haliotis cracherodii* grown in a bath at a controlled temperature of $18.9 \pm 0.1^{\circ}\text{C}$ shows agreement with our curve within 0.3°C .

difficult and though we do not understand the reasons for the disagreement, we may note that it is only 10% in the slope of the curve. Rather than regarding this as disagreement, we believe that it shows that these living organisms approximate equilibrium conditions rather closely. Analyses at present are more reproducible than they were at the time that McCrea completed his work, and this may have significance in regard to the discrepancy.

The possible effects of the difference in crystal structure of calcite and aragonite have not been explored. It is hardly to be expected that any large effects will be present, but as our techniques improve, they should be investigated. Not only is it possible that the isotopic composition of aragonite and calcite crystals grown under similar conditions may be different, but our heating procedure may convert aragonite to calcite and thus modify fractionation effects in the liberation of carbon dioxide by phosphoric acid.

The presence of a physiological effect in the case of certain groups of animals such as the echinoderms and corals, and plants such as the coralline algae has seemed probable at some points in our work, but we do not feel that it is certainly established. These specimens are difficult to investigate because of the large amounts of organic matter present, but having established a rather secure

basis for our work on the mollusks and brachiopods, it now seems feasible to investigate these groups. The echinoderms and corals are not particularly useful in relation to the paleotemperature scale because of extensive infiltration of the fossils. The Foraminifera should be investigated; for, even if not useful over long periods of time, they may be of interest for the investigation of more recent temperatures.

The variation of O^{18} content in marine and fresh waters, together with precise methods of measurement of the small quantities involved, makes possible an investigation of meteorological effects of considerable interest. The fractionation of the oxygen isotopes in evaporation and precipitation of water should give some information in regard to these processes as they occur in nature. We intend to continue our studies on the isotopic composition of water since the problem bears so directly on the measurements of paleotemperatures.

Conclusion

The variation in isotopic composition of marine waters has been investigated and found to be appreciable in terms of the isotopic temperature scale. When corrections are made for the isotopic composition of sea water in which mollusks and brachiopods have lived, it has been shown that a linear relationship between temperature and the O^{18} concentration exists. The slope of the curve agrees approximately with calculated values and with that secured when inorganically precipitated calcium carbonate samples crystallized at known temperatures are used. It is found that organically precipitated calcium carbonate gives reproducible analyses if it is first heated to 475°C for 15 minutes and then reacted with phosphoric acid to prepare carbon dioxide, the gas used in the mass spectrometer

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A Mass Spectrometer for the Measurement
of Small Differences in Natural Abundances

C. R. McKinney, J. M. McCrea, S. Epstein,
H. A. Allen, and H. C. Urey

During recent years great progress has been made in developing mass spectrometers for the measurement of the relative abundance of isotopes. Particularly sensitive instruments have been developed by Nier, Thode and others¹. Basically, the mass

¹A. O. Nier, Rev. Sci. Inst. 18, 398 (1947).

H. G. Thode, R. L. Graham, J. A. Ziegler, Can. J. Res. B23, 40 (1945).

For an excellent review of this subject, see M. G. Inghram, Advances in Electronics 1, 219 (1948).

spectrometer and electronic units in our research were those described by Nier. We report only the changes we made in these that assisted us in being able to measure small differences in the abundance of the rarer isotopes in gaseous compounds. The method has been applied to carbon and oxygen in carbon dioxide and to oxygen in oxygen gas. Our success in securing this greater sensitivity depends both upon increasing the intensity of the ion beam and upon increasing the absolute sensitivity of detection. In doing this, it has been necessary to improve the stability of the beam intensity and output from the amplifiers by the use of more stable power supplies, more reliable amplification systems, and an improved emission regulator. Also, it has been necessary to use a method for rapid change of samples in order to decrease errors due to general variability of the instrument with time, and it has proved essential that a recording potentiometer be used to detect and record the state

of balance of the simultaneously collected ion beams. The instrument has been constructed with the objective of measuring small differences in isotopic abundances of the oxygen isotopes as a means of measuring paleotemperatures, but the instrument and our procedures may be useful in other researches.

Power Supply for Electromagnet

Figure 1 shows the circuit diagram of the power supply used to furnish the current for the magnet windings and to supply some of the power requirements for the high voltage electronic unit.

Several measures are used to achieve good stability of the output of this power supply. The voltage to the screen of the 6L6 tubes (1V4 and 1V5) and the plate supply of the 12AU6 (1V13) amplifier tube is obtained from a separate power supply regulated by using OA2 (1V6 to 1V9) miniature voltage regulator tubes. A 5651 voltage regulator tube (1V11) is used to obtain a reference voltage. The ripple of the output is minimized by adjusting potentiometer 1P2. This adjustment controls the amount of ripple fed by means of a cathode follower amplifier tube (1V10) in a degenerative manner to the screen of amplifier tube (1V13). To further increase the stability of the power supply, the current for the heaters of the critical amplifier tubes (1V10, 1V12, and 1V13) is supplied by the output of the power supply itself. By using switch 1S3, the unit is allowed to warm up under reduced output voltage. Relay 1S2 protects the circuit from excessive voltage rise during operation. A properly adjusted power supply unit has an output of 250 volts with a current of about 200 milliamperes. The ripple is 1.5 millivolts, peak to peak, with a noise level of about 0.6 millivolts. The internal resistance for direct current

conditions is 0.35 ohms and for 60 cycle load variation about 0.6 ohms. A 1.1 volt (1 per cent) variation in the alternating current input appears as a 0.000184 per cent, or a 5 millivolt, variation in the output. The 115 volt power line is regulated by a Sola Constant Voltage Transformer.

The magnet current can be varied by varying the resistance in series with windings by means of controls 1P4 and 1P5 and switches 1S4 and 1S5. A helipot 1P5, connected to a motor by a clutch mechanism allows automatic magnetic scanning for the desired mass range.

High Voltage Supply

The high voltage supply shown in Figure 2 furnishes a continuously variable regulated voltage in the range 600 to 2200 volts for accelerating the ions in the mass spectrometer. The voltage of the output is varied by means of decades 2D1 to 2D4, which are ganged with 2D1A and 2D2A to keep the load across the rectifier and transformer nearly constant. Condenser 2C4 and resistor 2P2 are included to eliminate tendencies for oscillation. Tube 2V3 performs the function of supplying part of the output ripple in a degenerative manner to the grid of 2V2 which in turn acts to reduce the ripple of the output.

The reference voltage of 250 volts, the heater current for control tubes 2V1, 2V2 and 2V3, ^{and} the other necessary voltages are obtained from the appropriate places in the magnet power supply. The thermal time delay relay 2S3 protects the cathodes of 2V4 and 2V5.

The Electron Emission Regulator

The emission regulator circuit as shown in Figure 3 consists of two parts. One part is a power supply similar to the one used in the magnet circuit. Since the requirements for this power supply are less critical than the one used for furnishing current to the magnet windings, the plate supply voltage for the amplifier tube (3V12) is obtained from the unregulated direct current from the rectifiers. This power supply provides the electron accelerating voltage and the trap voltage in the ion source.

Regulation of electron emission of the filament in the source is accomplished by the second part of the emission regulator. Electron emission currents from the filament in the ion source flows through resistors 3R10 and 3P2 and the resulting voltage drop is amplified and applied to the grid of a series control tube (3V14) which controls the current flowing through the primary of transformers 3T4 and 3T5. The secondaries of these transformers supply the current to the filament in the mass spectrometer. Tube 3V13 serves to maintain proper wave form of the primary current. The controlled range of electron emission from the filament in the mass spectrometer extends from 100 to 500 microamperes depending upon the setting of 3P2. Switch 3S5 is a three-position switch which allows meter 3M2 to read either trap current, total emission current or to indicate the zero adjustment of 3P6 so that meter 3M1 reads electron accelerating voltage.

Ion Current Amplification

Essentially the same amplifier design as described by Nier was used initially in this research. A stable D.C. amplifier is

obtained by using our previously described power supply and by using the tubes described in circuit diagram 4. To allow collection of currents of approximately 3.7×10^{-9} and 1.5×10^{-11} amperes for masses 44 and 46 respectively, and to get sensitivity of 0.2% in determining the ratio of mass 46 to mass 44, the respective sizes of the resistors $4R_1$ of the two amplifiers must be approximately 1.5×10^{10} and 1.5×10^{11} ohms, respectively.

A null method for determining the mass 46 to 44 ratio has been described by Nier, Ney and Inghram². We have found that the

²A. O. Nier, E. P. Ney and M. G. Inghram, Rev. Sci. Inst. 18, 294 (1947).

substitution of a vibrating reed electrometer and an A.C. amplifier for the F.P. 54 electrometer tube gives more satisfactory operation than the method described above, and we have adopted this latter method of operation.

A schematic diagram of this system is given in Figure 5.

Gas Feed and Recording Potentiometer

Since the amplifiers always drift with time and have a noise level as high as or higher than the sensitivity required, it is necessary to have a record of the state of balance of the potentials produced by the two peaks being compared, and it is necessary to be able to change from one sample to another very rapidly.

Two complete feed systems with gas volumes, mercury leveling reservoirs, and capillary leaks of the type previously described by Nier were attached to the mass spectrometer through a magnetically operated valve which delivered one sample to the mass spectrometer and the other to a waste vacuum line. In this way the flow of the

two samples could be reversed rapidly. Since the valve is on the high vacuum side of the leaks there is a very small lag in changing from one sample to the other. The tube leading from the valve to the mass spectrometer must be fairly large in order that the hold up in this region is small. In our instrument the volume of the valve and connecting tube is about 10 cc. and the internal diameter and length of the feed tube within the mass spectrometer head are 3 mm. and 12 cm. respectively. The greater resistance of a 2 mm. I.D. tube considerably increased the time lag. The gases replace each other in a few seconds. The construction of the valve is shown in Figure 6. The memory effect of each gas is small and hence when samples of nearly identical composition (differing by, say, 5% in the ratio) are compared, this effect is insignificant. However, if samples of substantially different isotopic composition are used differing by a few per cent, then some minutes must elapse before steady conditions are established. If carbon dioxide containing oxygen of double the normal concentration or higher is used, the feed system that contained the concentrated gas will contaminate succeeding samples so that analysis to high precision, i.e., differences of the order of 0.02% in the ratio, cannot be made until the apparatus has been pumped and swept out for many days.

It is not possible to judge the steadiness of the balance of the two potentials by watching a galvanometer when it is desired to detect differences of the order of the unsteadiness of the potentials being observed. The galvanometer fluctuates unsteadily, and whether the mean has any reliable meaning cannot be judged. The recording potentiometer makes a trace which can be averaged over a satisfactory period of time.

We have used recording potentiometers to observe the balance between the potentials of the two peaks. The recorder draws an irregular line down the chart with negligible drift (if the instrument is in proper adjustment). If erratic fluctuations occur the instrument is unreliable. Of course, if the small but statistically regular fluctuations are too great the precision desired cannot be secured. By observing the record for some time it is possible to judge the stability of the amplifier circuits particularly as well as the mass spectrometer as a whole, and thus decide whether analyses can be made. The use of the recording potentiometers is essential to securing differences to a precision of 0.2% of the oxygen isotope ratio.

The type of traces obtained are shown in Figure 7, where trace 2 represents the null point of the standard and trace 1 represents the deviation from the null point by an increase of 0.63% in the intensity of ion beam of mass 46. If the deviation from the null point was large, part of the increase or decrease in mass 46 was taken up by changing the setting on the decade resistor system. Straight lines are drawn through the irregular curves and extended to the point where the samples were changed and the differences are read at these points. The displacement on the chart is easily calibrated in terms of the dial settings in the resistance panel. The average of some five or seven readings is then used to correct the ratio read from the resistances.

Conclusion

Two instruments of this type have been constructed and operated, one for 18 months, the other for 6 months. At present electronics technicians can keep the instruments in operation from

50 to 75% of the time. The analyses are made by laboratory technicians. Altogether some two thousand high precision comparisons of oxygen isotopic abundances in carbon dioxide, some hundreds of carbon abundances in the same gas, and perhaps a hundred comparisons of oxygen isotopes in oxygen gas have been made with these instruments. Examples of check analyses are given in Table 1. The recorded figures are the differences in per mils of the normal ratios between the sample and the standard working gas, i.e.,

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) 1000,$$

where R_{sample} and R_{standard} are the ratios of $\text{CO}_2^{16}\text{O}^{18}$ to CO_2^{16} for the unknown sample and reference gas respectively. These examples of analysis on carbon dioxide are taken from our working notebooks and are a group of consecutive duplicate analyses selected at random and with no omission of any results. These duplicate analyses are on different preparations of the gas from the same samples of calcium carbonate and hence the fluctuations include any variations due to the chemical preparation of the gas. (The calcium carbonate is heated to 475°C for 15 minutes in a stream of pure helium gas and the carbon dioxide liberated by reaction of the carbonate with 100% orthophosphoric acid). Thus the operation of the instrument is at least as reproducible as indicated by these results. On the basis of analyses made before the vibrating reed amplifier was adapted to the instrument, we believe that variations greater than 0.2% are due to variations introduced by the method of preparing the gas, a subject which will be discussed elsewhere.

The first example of the oxygen gas analyses is for two preparations from a silicate rock. The last three examples are all for tank oxygen. The most recent of our analyses are given here since they represent the precision we have been able to attain in our most recent work. It is expected that this precision will be maintained and in fact improved in the future as we acquire more experience in these analyses.

Table 1

Sample	¹³ C ₂ gas		¹³ C ₂ gas		Sample	¹⁸ O ₂ gas	
	δ (0 ¹³)	Date	δ (C ¹³)	Date		δ (0 ¹⁸)	Date
1	-0.53	12/13/49	0.42	12/13/49	1	17.11	12/7/49
	-0.59	1/4/50	0.50	1/4/50		16.77	12/8/49
2	-2.98	12/20/49	1.95	12/20/49	2	0.23	2/10/50
	-2.99	1/3/50	1.75	1/3/50		-0.10	2/13/50
	-3.00	1/3/50	1.58	1/3/50			
3	-3.87	12/12/49	1.30	12/12/49	3	0.00	2/10/50
	-3.83	1/3/50	1.35	1/3/50		0.00	2/11/50
						-0.20	2/13/50
4	-2.30	12/13/49	2.30	12/13/49	4	0.44	2/10/50
	-2.56	1/4/50	2.46	1/4/50		-0.02	2/11/50
						-0.14	2/13/50
5	-2.18	12/22/49	1.73	12/22/49			
	-2.22	1/4/50	1.90	1/4/50			

Power Supply (Regulated)

1R1	13,500 Ohms, 10 Watt, Wire Wound
1R2	5,000 Ohms, 10 Watt, Wire Wound
1R3	68,000 Ohms, 1 Watt
1R4	39,000 Ohms, 1 Watt
1R5	22 Megohms, 1 Watt
1R6	50,000 Ohms, Precision Wire Wound
1R7	75,000 Ohms, Precision Wire Wound
1R8	35,000 Ohms, Precision Wire Wound
1R9, 1R10	470 Ohms, 1 Watt
1R11, 1R12	47,000 Ohms, 1 Watt
1R13	60,000 Ohms, 1 Watt
1R14	470,000 Ohms, 1 Watt
1R15	15,000 Ohms, Precision Wire Wound
1R16	1 Megohm, Precision Wire Wound
1R17	50,000 Ohms, Precision Wire Wound
1R18	25,000 Ohms, Precision Wire Wound
1R19	Sufficiently small to cause relay to close in case of excessive voltage rise during operation.
1R20	680,000 Ohms, 1 Watt
1R21 to 1R30	750 Ohms, 10 Watt
1R31	.65 Ohm (Wound with Nichrome Wire)
1C1	8 MFD. 600 V.
1C2	12 MFD. 600 V.
1C3	20 MFD. 600 V.
1C4, 1C5	.01 MFD. 400 V.
1C6	250 micro-microfard

(continued)

Power Supply (Regulated) - 2

1V1	5Y3
1V2, 1V3	5U4G
1V4, 1V5	6L6
1V6, 1V7, 1V8, 1V9	0A2
1V10, 1V12, 1V13	12AU6
1V11	5651
1L1	5 Henry 100 Milliamps Filter Choke
1T1	Stancor Power Transformer Type P6143
1T2	Westinghouse Power Transformer (Navy Type No. CAY-301164)
1P1	15,000 Ohms Wire Wound Potentiometer
1P2	500,000 Ohms Carbon Potentiometer
1P3	10,000 Ohms Wire Wound Potentiometer
1P4	800 Ohms 25 Watt Rheostat
1P5	800 Ohms 15 Turn Helipot
1M1	0-200 Milliampere meter
1S1	S.P.S.T. Toggle Switch
1S2	Single Pole Relay, normally open
1S3	S.P.S.T. Toggle Switch
1S4	Single Pole// Position Rotary Switch
1S5	D.P.D.T. Toggle Switch

Fig. 1

Parts List for High Voltage Supply

2R1	250,000 Ohms, Precision Wire Wound
2R2, 2R6, 2R8	75,000 Ohms, Precision Wire Wound
2R3	1 Megohm, Precision Wire Wound
2R4	25,000 Ohms, Precision Wire Wound
2R5	50,000 Ohms, Precision Wire Wound
2R7	35,000 Ohms, Precision Wire Wound
2R9	30,000 Ohms, Precision Wire Wound
2R10	40,000 Ohms, Precision Wire Wound
2R11	2.2 Megohms Carbon 1 Watt
2R12	50,000 Ohms, 100 Watt
2R13, 2R14	2 Megohms, Precision Wire Wound
2R16	Reduces 10 V. to 6 V. required by 2S3 Relay
2R17, 2R18, 2R19	10 Megohms, 2 Watt
2D1A	10 Steps, 5,000 Ohms per step (10 Watt each)
2D2A	10 Steps, 470 Ohms per step (2 Watt each)
2D1	10 Steps, 100,000 Ohms per step Precision Wire Wound
2D2	10 Steps, 10,000 Ohms per step Precision Wire Wound
2D3	General Radio Decade Type 510E 1,000 Ohms per step
2D4	General Radio Decade Type 510D 100 Ohms per step
2P1	100 Ohms, Wire Wound Potentiometer
2P2	3 Megohms, Carbon Potentiometer
2P3	800 Ohms, 25 W. Potentiometer
2V1, 2V2, 2V3	12AU6

(continued)

Parts List for High Voltage Supply - 2

2V4	Type 813 Transmitting Tube
2V5	Type 8020 High Voltage Rectifier
2C1	.01 MFD. 600 V.
2C2	.25 MFD. 400 V.
2C3	2 MFD. 600 V.
2C4	.1 MFD. 600 V.
2C5	4 MFD. 3000 V.
2C6	4 MFD. 4000 V.
2T1	Stancor Filament Transformer Type P-4086, 5V C.T. 14 amp. 10,000 V. insulation
2T2	Maloney Elect. Co. High Voltage Transformer Part No. 5503 (Army Surplus) 5600 V. at .1 amp. (Reduced to 3700 V. with 1 KVA. Variac)
2T3	Stancor Filament Transformer Type 6139 10 V. C.T. 8 amp.
2T4	General Radio Variac $7\frac{1}{2}$ amp. Capacity
2M1	0-1 Milliamp. meter
2S1	S.P.S.T. Toggle Switch
2S2	S.P.S.T. Toggle Switch - High Voltage On-Off
2S3	Amperite Thermostatic Delay Relay Type 6N045
2S4	S.P.S.T. High Voltage Rotary Switch For Beam On-Off

Parts List for Emission Regulator

3R1	300 Ohms, 10 Watt	
3R2	35,000 Ohms, 20 Watt	
3R3	7,500 Ohms, 10 Watt	
3R4	5,000 Ohms, 10 Watt	
3R5	25,000 Ohms,	Precision Wire Wound
3R6	.5 Megohm	Precision Wire Wound
3R7	15,000 Ohms	Precision Wire Wound
3R8, 3R13	15,000 Ohms, 2 Watt	
3R9, 3R11, 3R14	82,000 Ohms, 1 Watt	
3R10	150,000 Ohms, 1 Watt	
3R12	50 Ohms, 5 Watt	
3R15, 3R19, 3R20, 3R22	68,000 Ohms, 1 Watt	
3R16	27,000 Ohms, 1 Watt	
3R17	470 Ohms, 2 Watt	
3R18	47,000 Ohms, 1 Watt	
3R25	2.2 Megohms, 1 Watt	
3R26	75,000 Ohms	Precision Wire Wound
3R27	50,000 Ohms	Precision Wire Wound
3R24, 3R28	35,000 Ohms	Precision Wire Wound
3R29	250 Ohms	Precision Wire Wound, Shunts meter 3M2 to read 500 microamperes full scale.
3R30	1,000 Ohms	Precision Wire Wound. Shunts meter 3M2 to read 200 microamperes full scale.
3R21, 3R23, 3R31 to 3R38	0.47 Megohms, 1 Watt	

(continued)

Parts List for Emission Regulator - 2

3R39, 3R40, 3R41	10 Megohms, 1 Watt
3R42, 3R43	2.2 Megohms, 1 Watt
3P1	800 Ohms, 25 Watt rheostat
3P2	250,000 Ohms, Carbon Potentiometer
3P3	15,000 Ohms, Wire Wound Potentiometer
3P4	.5 Megohm, Carbon Potentiometer
3P5	5,000 Ohms, Wire Wound
3P6	10,000 Ohms, Wire Wound
3P7	5,000 Ohms, Wire Wound
3P8	3 Megohm, Carbon Potentiometer
3T1	Thordarson No. T18V01 1:1 Isolation Transformer (Changes made so secondary is insulated for 3500 V) 250 Volt-Ampere Capacity.
3T2	Acme No. T4822 Power Transformer
3T3	Stancor No. P6143 Power Transformer
3T4, 3T5	6.3 Volt, 5 amperes Filament Transformers
3T6, 3T7	6.3 Volt, 2 amperes Filament Transformers
3C1, 3C3	16 MFD. 600 V.
3C2, 3C4	8 MFD. 600 V.
3C5	.05 MFD. 600 V.
3C6, 3C7	.01 MFD. 400 V.
3M1	0-100 Volts D.C. Voltmeter
3M2	0-100 Microampere D.C. - 1000 Ohms resistance
3M3	0-10 A.C. amperes
3V1	6X4
3V2, 3V3	5Y3
3V4	6L6

(continued)

Parts List for Emission Regulator - 3

3V5, 3V8, 3V9, 3V12	6AU6	
3V6, 3V7	0A2	Miniature voltage regulator tube
3V10	5651	Miniature voltage regulator tube
3V11	6AG5	
3V13, 3V14	807	
3S1	S.P.S.T.	Toggle ON-OFF Switch
3S2	D.P.D.T.	High Voltage Relay
3S3		Push Switch Normally Closed
3S4		Push Switch Normally Open
3S5		2 Pole Three Position Switch
3S6		2 Pole Seven Position Switch

Parts List for D.C. Amplifier

4R1 1.5 x 10¹⁰ ohm Victoreen Hi-Megohm obtained from
Victoreen Instrument Co., Cleveland, O.

4R2 30 ohm Wire Wound Potentiometer

4R3 20,000 ohms Helipot 10 turns, obtained from Helipot Corp.
South Pasadena, California.

4R4 250,000 ohms - Precision Wire Wound

4R5 100,000 ohms Helipot 15 turns

4R6 20,000 ohms - Precision Wire Wound

4R7 35,000 ohms - Precision Wire Wound

4R8, 4R9 500,000 ohms - Precision Wire Wound

4R10 75,000 ohms, - Precision Wire Wound

4R11, 4R12 1 Megohm - Precision Wire Wound

4R13 300,000 ohms - Precision Wire Wound

4R14 1,000 ohms, 50 watt

4R15 25,000 ohms - Precision Wire Wound

4R16 80 ohm Special Wire Wound

4R17 40 ohm Special Wire Wound

4R18 12 steps of 26 ohms each Special Wire Wound

4V1 - VX-41A obtained from Victoreen Instrument Co., Cleveland, O.

4V2 - 12SL7-GT

4V3 - 12SL7-GT

4V4 - 12J5 -GT

4C1 - 100 Micro-Microfarad Variable Air Dielectric Condenser

4C2 - .002 MFD. Condenser 400 V.

Fig. 4

Parts List for Ion Beam Balancing Circuit

- 5R1 - 1.5×10^{11} ohms, Victoreen Hi-Megohm resistor. Obtained from Victoreen Instrument Company, Cleveland, Ohio.
- 5R2 - 1.5×10^{10} ohms, Victoreen Hi-Megohm resistor.
- 5R3 - Put and take decade resistance potentiometer, made up of General Radio decade resistance units 510A, 510B, 510C, 510D and 510E.
- Vibrating reed electrometer - Obtained from The Applied Physics Corporation, 30 West Green Street, Pasadena, California.
- D. C. feedback amplifier - as shown in Figure 4.

NP-1472
- 95 -

Fig. 5

Fig. 6

NP-1472
- 97 -

Fig. 7

ON THE ISOTOPIC CHEMISTRY OF CARBONATES
AND A PALEOTEMPERATURE SCALE*

J. M. McCrea**

Kent Chemical Laboratory, University of Chicago, Chicago, Illinois

The Temperature variation of the fractionation of oxygen in exchange reactions between dissolved carbonate and water and between calcite and water are calculated on theoretical grounds, and checked experimentally. In the course of the experiments it was necessary to investigate several methods of decomposing calcium carbonate to carbon dioxide for mass spectrometer analysis. A method was developed for growing calcium carbonate from solution with the same isotopic composition as the carbonate shells of organisms produced at the same temperature from water of the same isotopic composition, and the results of these experiments at various temperatures are expressed in an equation relating the temperature of formation with the isotopic composition of the calcium carbonate and of the water.

*A portion of a dissertation submitted to the Department of Chemistry, University of Chicago, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1949.

**Present address Experimental Station, Ralston, Alberta, Canada.

ON THE ISOTOPIC CHEMISTRY
OF CARBONATES

Introduction

In recent years the slight separation of isotopes in exchange equilibria between chemical species has been studied both theoretically and experimentally. On the theoretical side, this separation or fractionation turns out to be temperature dependent.¹ Experimentally, measurements of the fractionation have usually been made at one temperature only, but the hydrogen-water exchange of protium and tritium has been studied over a considerable temperature range.² Because of the intriguing possibilities of studying marine climatology in the geologic past by an investigation of oxygen isotopic composition of carbonate fossils, the present studies of the temperature variation of the oxygen isotope fractionation in exchanges between water and carbonate ion in solution and between water and calcium carbonate were undertaken.³ The conditions under which the results obtained may be related to paleotemperature determinations have been discussed elsewhere,⁴ but in a number of instances these are strictly parallel to those of the laboratory experiments described here.

Theoretical Considerations

The methods of calculation of the fractionation factor for an exchange between two chemical species in the gaseous or dissolved state from spectroscopic data have

¹H. C. Urey, J. Chem. Soc., 1947, 592.

²J. Black and H. Taylor, J. Chem. Phys., 11, 395 (1943).

³H. C. Urey, loc. cit.

⁴H.C. Urey, Science, 108, 489 (1949).

been reviewed, and a large number of numerical results given.⁵ As it is of interest in connection with experimental results to follow, the case of the carbonate-water exchange will be considered in some detail. The fractionation factor, α , is the ratio of the two isotopes in one phase divided by the corresponding ratio for the other phase, and in the same case of carbonate ion and water

$$\alpha = \frac{3 [\text{CO}_3^{18}] + 2 [\text{CO}^{16}\text{O}_2^{18}] + [\text{CO}_2^{16}\text{O}^{18}]}{3 [\text{CO}_3^{16}] + 2 [\text{CO}^{16}\text{O}_2^{18}] + [\text{CO}^{16}\text{O}_2^{18}]} \cdot \frac{[\text{H}_2\text{O}^{18}]}{[\text{H}_2\text{O}^{16}]}$$

Provided that the equilibrium constants for the exchange reactions between the various carbonate ions are those given by the symmetry numbers, this expression for α reduces to the expression for the equilibrium constant for the reaction

This equality of fractionation factor and equilibrium constant appears to be a very good approximation except in the case of hydrogen isotopes, and in view of the lack of knowledge of the vibration frequencies of the mixed type of ion and the great complexity of any method of calculating these frequencies, the equality will be assumed in the present case.

In extending the calculation of fractionation to the crystalline case, effects due to the lattice motion must be considered, as well as the internal motion of polyatomic ions. Several not too satisfactory assumptions are made in order to obtain relations which may be used to calculate numerical results. The degree of freedom necessary for CaCO_3 may be grouped as six of internal vibration in the carbonate, six of lattice vibration, and three of a type of lattice vibration corresponding to rotation of the carbonate ion. As the spectroscopic data from which

⁵H. C. Urey, J. Chem. Soc., 1947, 592.

the calculations will be made show that the carbonate ion in calcite has the same symmetry as in aqueous solution, the isotope shift of a given ion frequency is taken as the same fraction of the frequency for either state. The contribution to the fractionation between states due to any given mode of vibration, wave number ω , may be found by forming

$$\frac{Q_{\omega}^*}{Q_{\omega}} = \exp \frac{hc(\omega - \omega^*)}{2kT} \cdot \frac{1 - \exp -hc\omega/kT}{1 - \exp -hc\omega^*/kT}$$

for both states, and evaluating

$$\left(\pi \left(\frac{Q_{\omega}^*}{Q_{\omega}} \right)_{\text{crystal}} / \pi \left(\frac{Q_{\omega}^*}{Q_{\omega}} \right)_{\text{solution}} \right)^{1/n}$$

where n is the number of atoms exchanging to produce CO_3^{*2-} from CO_3^{2-} , 1 for carbon and 3 for oxygen.

Using a representation of the lattice motion in terms of Debye and Einstein relations with θ as the Debye temperature corresponding to three degrees of freedom and ϕ_t , ϕ_r as characteristic temperatures referring to the remaining degrees of freedom and with $D(x) = \frac{3}{x} \int_0^x \frac{x'^3 dx'}{\exp x' - 1}$ as the Debye energy function,

$$\begin{aligned} -\ln Q^*/Q &= \frac{F^* - F}{RT} \\ &= \frac{3}{8} (\theta^* - \theta)/T + 3 \ln \frac{1 - \exp -\theta^*/T}{1 - \exp -\theta/T} + D(\theta/T) - D(\theta^*/T) \\ &+ \frac{3}{2} (\phi_t^* - \phi_t)/T + 3 \ln \frac{1 - \exp -\phi_t^*/T}{1 - \exp -\phi_t/T} \\ &+ \frac{3}{2} (\phi_r^* - \phi_r)/T + 3 \ln \frac{1 - \exp -\phi_r^*/T}{1 - \exp -\phi_r/T} . \end{aligned}$$

If it is assumed that $\theta^*/\theta = \phi_t^*/\phi_t$, then the relations

$$\theta^*/\theta = (M_{\text{Ca}} \cdot M_{\text{CO}_3} / M_{\text{Ca}^*} \cdot M_{\text{CO}_3^*})^{1/4} \quad \text{and} \quad \phi_r^*/\phi_r = (I_{\text{CO}_3} / I_{\text{CO}_3^*})^{1/2} \quad \text{cause } Q^*/Q \text{ for}$$

the crystal to approach Q^*/Q for the solution as T approaches infinity, and give the desired vanishing fractionation between the crystal and solution at high

temperatures.

The above treatment is quite crude, particularly in regard to the treatment of rotation as an Einstein function of characteristic temperature ϕ_r . In numerical calculation, the rotational contribution to fractionation made in this way turns out to be entirely too great compared with translation and vibration. This may be due to the neglect of the zero point energy term arising from the 'caging' effect of adjacent molecules in the solution. For the oxygen exchange, the rotational contribution is assumed to be the same as the translational. For the carbon exchange, with the moment of inertia of the ion unaltered by the exchange, the rotational contribution must be zero.

Numerical values for the vibration frequencies are available for carbonate, both in aqueous solution and in calcite.^{6,7} The temperatures ϕ_t and ϕ_r will be taken to correspond to the Raman frequencies assigned to lattice motions of the translational and rotational type. From heat capacity measurements at low temperatures, θ is known.⁸ This information and the results of the calculation of the fractionation between aqueous carbonate and calcite are given in Table 1. In this table and later, it is usually convenient to adopt an abbreviating notation for expressing differences in isotopic composition and fractionating effect.⁹ Thus if the isotope ratio in one sample is $(1 + .001x)$ times that in a given sample, the two are said to differ in isotopic composition by $x\text{‰}$, and if the fractionation factor for an exchange between two compounds is $(1 - .001a)$, the fractionation

⁶G. Herzberg, Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand Co., New York, 1945, p. 178.

⁷R. S. Krishnan, Proc. Indian Acad. Sci., 22A, 182 (1945).

⁸T. C. Anderson, J. Amer. Chem. Soc., 56, 340 (1934).

⁹H. C. Urey, Science, 108, 489 (1948).

between the two compounds is said to be a‰. The fractionation between aqueous carbonate and calcite given in Table 1 is used to obtain the value for the fractionation factor between calcite and water listed in Table 2. The other results listed in Table 2 were calculated by the usual methods.

TABLE 2
CERTAIN FRACTIONATION FACTORS AT VARIOUS TEMPERATURES

Exchange of O^{16} and O^{18} between	Temperature, °C			
	0.0	8.0	17.0	25.0
$CO_3^{=}$ (aq.) - O	1.1046 ₃	1.0998 ₄	1.0948 ₃	1.0907 ₂
H_2O (g.) - O	1.0741 ₃	1.0716 ₂	1.0689 ₈	1.0667 ₇
H_2O (l.) - H_2O (g.)	1.0103 ₆	1.0095 ₉	1.0089 ₉	1.0083 ₀
$CO_3^{=}$ (aq.) - H_2O (l.)	1.0176 ₁	1.0162 ₆	1.0148 ₆	1.0137 ₆
Calcite - H_2O (l.)	1.0254 ₈	1.0237 ₈	1.0210 ₁	1.0205 ₈

Over the temperature range of these tables, the fractionation factors for the exchanges between carbonate and water and between calcite and water are very well expressed by relations linear in the absolute temperature with coefficients of $1/T$ of 12.6 and 15.9 respectively. Differentiating, the temperature coefficients of the fractionation factors for these exchanges are $-12.6/T^2$ and $-15.9/T^2$, or in the ‰ notation, $-1.26 \times 10^4 / T^2$ and $-1.59 \times 10^4 / T^2$.

Remarks on Natural Abundances

Aside from one case, the isotopic compositions met with in the following experimental work lie within the range of those found in naturally occurring substances, but this is so merely because the various exchange reactions were studied at the natural abundance level. In the theoretical discussion just given, an assumption

regarding the distribution of isotopes among the various carbonate ions was made. As a consequence of this assumption, the fractionation factor α reduced to the equilibrium constant for a reaction, and as a result became independent of actual isotope abundance in the system. Although the problem of measurement would be somewhat simplified if the $O^{18} : O^{16}$ ratio were closer to unity, the same final results would be expected. The methods adopted are such that it would be inconvenient at the present time to work at other than the natural abundance level where large quantities of water are available. As a matter of orientation, it is noted that surveys of isotopic abundances indicate a spread of about 50% around average natural abundances of 1.1% O^{13} , .039% O^{17} and .204% O^{18} ¹⁰⁻¹². In order that the results might be used in connection with the investigation of paleotemperatures, the water used for a large number of the experiments was of marine origin.

Measurement of Isotopic Differences

The determinations of differences in isotopic compositions were made by a double collecting Nier type mass spectrometer tube with gas handling and electronic systems designed for the measurement of small differences.^{13,14} The probable error of the difference determination of O^{18} in CO_2 was usually less than .05% for differences less than 15% during stable operation of the instrument as given by the recorder chart, but the reproducibility of a repeated analysis after the gas sample had been completely removed from the gas reservoir on the mass spectrometer and then

¹⁰G. T. Seaborg and I. Perlman, Rev. Mod. Phys., 20, 585 (1948).

¹¹A.O. Nier and E. A. Gulbranson, J. Amer. Chem. Soc., 61, 697 (1939).

¹²M. Dole and R. L. Slobod, Ibid., 62, 471 (1940).

¹³A. O. Nier, Rev. Sci. Inst., 18, (1947).

¹⁴Details of the mass spectrometers will be reported by C. R. McKinney, J. M. McCrea, S. Epstein, H. A. Allen and H. C. Urey.

reintroduced was about .15%, as other effects are introduced in transferring the gas.

Preparation of Carbon Dioxide

Considerable difficulty was experienced in obtaining a carbon dioxide from a given calcium carbonate as reproducibly as the mass spectrometer analyzed a given gas sample. For a method to be satisfactory, there may be no exchange of oxygen with reagents or vessels. If one-third of the carbonate oxygen is left out of the gas sample, the splitting must occur reproducibly. The gas produced should contain no impurity which could contribute ion beams of the same m/e as carbon dioxide. For this reason ethanol, acetone and hydrocarbon solvents were kept out of contact with apparatus, and chloroform and carbon tetrachloride were used as grease solvents. The Apiezon Products' grease 'N' and wax 'W' were found satisfactory for use with the gas handling systems. It is difficult to obtain a carbon dioxide which is free of ion beams derived from trace impurities in the mass range 40 - 55, even after the background of the mass spectrometer is allowed for. The ideal case for a given isotopic composition may be recognized when the relative intensities of the ion beams are those calculated for the theoretical distribution of the isotopes among the possible molecular species. An example of such a distribution is shown in Table 3.

Thermal Decomposition of Carbonate

Since thermal decomposition involves no reagents, several samples of carbon dioxide were prepared by inductively heating a platinum crucible containing calcium carbonate inside a cooled glass chamber. Although essentially quantitative decomposition was found to occur, the isotopic composition of gas obtained from a given carbonate sample showed a large variation. As far as could be seen, this variation was not caused by changes in decomposition temperature or rate of heating. An

TABLE 3

MASS DISTRIBUTION IN NATURAL CARBON DIOXIDE*

Mass	Contributing Species	Individual Abundance	Relative Abundance of Given Mass**
44.....	$C^{12}_2O^{16}_2$	.9842	.9842
45.....	$C^{13}_2O^{16}_2$	1.095×10^{-2}	.01172
	$C^{12}_2O^{16}_1O^{17}_1$	7.7×10^{-4}	
46.....	$C^{12}_2O^{16}_1O^{18}_1$	4.025×10^{-3}	.00403
	$C^{13}_2O^{16}_1O^{17}_1$	8.6×10^{-6}	
	$C^{12}_2O^{17}_2$	1.5×10^{-7}	
47.....	$C^{13}_2O^{16}_1O^{18}_1$	4.48×10^{-5}	4.63×10^{-5}
	$C^{12}_2O^{17}_1O^{18}_1$	1.6×10^{-6}	
	$C^{13}_2O^{17}_2$	1.7×10^{-9}	
48.....	$C^{12}_2O^{18}_2$	4.12×10^{-6}	4.13×10^{-6}
	$C^{13}_2O^{17}_1O^{18}_1$	1.8×10^{-8}	
49.....	$C^{13}_2O^{18}_2$	4.6×10^{-8}	4.6×10^{-8}
All....	All	1.0000	1.0000

* Taken to contain 1.10% C^{13} , .039% O^{17} , and .204% O^{18} .

**Slight differences between the relative abundances of the masses and the relative intensities of the ion beams may be expected, but the isotope effect in ionization without bond rupture should be much less than that with bond rupture discussed for the case of propane by J. Bigeleisen, J. Chem. Phys., 17, 334 (1949).

effect due to the state of division was noted. The gas obtained by decomposition of fragments of a calcite crystal weighing about .1 g each gave differences in isotopic composition from a reference gas in the range -25.5 to -27.3% with an average for five samples of -26.5, while powdered samples of the same material gave

gas of composition -23.5 to -24.2‰, with an average for six samples of -23.9. In the face of this effect, efforts were made to exchange the oxygen of calcium oxide and carbon dioxide at temperatures around 1000°C, and then to mix up the isotopes by a repeated decomposition and reformation of calcium carbonate. The result of either of these procedures was to effect about 50% of the possible exchange in ten minutes, and little more after that. This behavior in isotopic exchange is strikingly parallel to the way in which calcium oxide absorbs carbon dioxide rapidly up to about 50% of theoretical, and only very slowly after that. Thus the kinetics of the decomposition of calcium carbonate thermally are such that carbon dioxide can not be obtained with the desired reproducibility of isotopic composition.

Acid Decomposition of Carbonate

Several general conditions must be met by an acid solution which is used to prepare carbon dioxide for mass spectrometer analysis from an alkaline earth carbonate. The salts produced in the decomposition reaction should be soluble in the solution, or a protective coating on the carbonate will slow or stop the reaction. Nitric acid, by decomposition to nitrogen dioxide, yields an intolerable impurity of molecular mass 46, and formic acid must be rejected for similar reasons. In view of the known exchange between water and carbon dioxide, a solution with a low concentration of water is desirable. Of the non-oxy acids, 47% reagent hydrobromic acid seems best suited, while the concentrated oxy-acids perchloric, sulphuric and phosphoric, when present in excess, dissolve calcium carbonate completely. With an oxy-acid there is the possibility of exchange between the anion and carbon dioxide, and if there is, the acid is unsuited for this purpose. Using portions of three arbitrary calcium carbonates, A, B, C, decomposition using various acids was performed to find out experimentally which were suitable.

The system used for carrying out the decomposition is shown in Figure 1. The

NP-1472
- 109 -

GAS PREPARATION APPARATUS
FIGURE I

reaction vessel containing the powdered carbonate (40 to 100 mg) in the main tube and acid (5 to 10 cc) in the side arm can be evacuated, and then tipped to pour the acid on the carbonate. After the gas is generated (this may take some thirty minutes in the case of phosphoric acid), the carbon dioxide is expanded into the rest of the evacuated system, and then condensed into the U-trap with liquid nitrogen cooling. The system is pumped to remove any residue of non-condensable gas. The carbon dioxide is measured in the manometer, and then transferred to a sample tube to be used on the mass spectrometer manifold. By means of the thermocouple gauge, the pressure in the system may be followed, and unless the pressure falls below 10^{-2} mm of Hg on the first condensation and below 10^{-3} on the later ones, the preparation is not considered satisfactory.

The results of the analysis of carbon dioxide samples obtained from the three carbonates mentioned above and four decomposing acids are shown in Table 4. The greater scatter and the reduced differences in the last two columns of the table in the case of sulphuric acid would seem to indicate that an exchange process is taking place. The other acids show a greater reproducibility, and the differences are much the same for all three, although not statistically so. There can be no doubt that different acids give a different product gas from the same carbonate sample. The gas is satisfactorily pure in the required mass range for all four acids. As a matter of interest, some early results using the thermal decomposition method are compared in Table 5 with those using phosphoric acid decomposition. Again there is a difference in the gas produced from the same carbonate. A difference of about 6% has been noticed between the carbon dioxide produced by the action of aqueous hydrochloric acid and that produced by the thermal decomposition method in another case.¹⁵

¹⁵M. Dole and R. L. Slobod, loc. cit.

TABLE 4

Preparing Acid	Oxygen Isotopic Composition, ‰				
	Difference from Standard			Mean Difference between Preparations	
	CaCO ₃ Sample				
	A	B	C	A and B	B and C
H ₃ PO ₄ (ca 100%)....	- 3.07 - 3.27	-10.42 -10.63	-21.15 -21.47	7.3 ₆	10.7 ₆
HClO ₄ (ca 71%)....	- 8.69 - 9.87	-14.33 -15.44	-25.13 -26.74	5.8 ₁	10.5 ₄
HBr aq. (ca 47%)....	- 4.59 - 4.91	-12.27 -12.32	-24.15 -24.23	7.5 ₄	11.9 ₀
H ₂ SO ₄ (ca 98%)....	-12.19 -14.16 -15.19	-18.70 -19.51	-26.90 -27.65	5.2 ₅	8.2 ₇

Because of its very low vapour pressure, phosphoric acid is rather more readily handled in the vacuum system, and the activity of water in its concentrated solutions is less than that for the other acids mentioned, a state of affairs which is likely to lead to a low exchange rate between the solution and carbon dioxide. To verify that the exchange is small, a tracer 100% phosphoric acid was made by dropping water of composition 1.5% ¹⁸O on the appropriate amount of phosphorus pentoxide chilled to liquid nitrogen temperatures. This acid, with an isotopic composition of .50% ¹⁸O or 3,400‰ greater than normal oxygen, produced a carbon dioxide only 8.5‰ richer in ¹⁸O than that produced using normal acid. The amount of isotope mixing is then .0025 of the maximum possible, and any exchange effects are negligible in the decomposition of natural carbonates with an unenriched phosphoric acid.

There was no observed evolution of heat in the decomposition, and the composition of the gas is only slightly, perhaps not even significantly, altered by the

TABLE 5

COMPARISON OF THERMAL AND ACID DECOMPOSITION

Sample of CaCO_3	Oxygen Isotopic Composition of CO_2 , ‰		
	Difference from Standard		Difference between Methods
	Thermal	Acid (H_3PO_4)	
16/A02-3	- 8.7	- 2.7	6.0
25/A02-3	-10.3	- 3.9	6.4
32/A02-3	-11.5	- 4.8	6.7
57/A02-3	-14.0	- 8.8	5.2
Average			6.1

temperature at the start of reaction. Using samples of a given powdering of a calcium carbonate shell, gas samples gave check analyses of 1.09 and 1.01‰ in the case of decomposition at 14°C , 1.00 and .95‰ at 25°C , and .43 and .43‰ at 37°C . A variation of concentration of the phosphoric acid between 85 and 100% is accompanied by a similar slight variation in the isotopic composition of the gas produced. The acid decompositions in the following investigation were performed at 25°C with a phosphoric acid of specific gravity 1.80 (95% H_3PO_4), made by adding phosphorus pentoxide to the usual 85% acid. As a result of impurities which characterize commercially available grades of phosphorus pentoxide, the resulting solution has a brownish tinge, but it performs the decomposition of the carbonates reproducibly to .1‰ as is illustrated by the three sets of duplicate determinations just mentioned.

Precipitation of Carbonate and Bicarbonate

In all but highly alkaline solutions, tracer experiments have shown that

carbonate and water exchange by a hydrolysis of carbonate to bicarbonate, carbonic acid and dissolved carbon dioxide. The exchanging steps take place among carbonic acid, water and carbon dioxide and among carbon dioxide, bicarbonate and hydroxide. At 25°C, the half time of the reaction is 28 hours at pH 11, and decreases with decreasing pH.¹⁶ If there is no exchange between solid calcium carbonate and water, a brief consideration of the ionization relationships in an aqueous carbonate-bicarbonate system shows that the rapid precipitation of calcium carbonate from such a solution and subsequent examination of carbon dioxide produced from the carbonate gives a means of studying the oxygen isotopic equilibria in the system. Using the rough values of $10^{-6.5}$ and $10^{-10.5}$ for the first and second ionization constants of carbonic acid and 10^{-8} for the solubility product of calcium carbonate, the concentrations of carbonate, bicarbonate and carbon dioxide are given by $[\text{CO}_3^{=}] = 10^{-5}$, $[\text{HCO}_3^-] = 10^{5.5} [\text{H}^+]$ and $[\text{H}_2\text{CO}_3 + \text{CO}_2.\text{Aq}] = 10^{12} [\text{H}^+]^2$ when the calcium concentration is 10^{-3} M. If the pH of the solution is maintained greater than 9 during precipitation, less than one percent of the carbon of a carbonate-bicarbonate solution of greater than .1 M concentration will escape precipitation. As a result of the marked increase in solubility of calcium carbonate with ionic strength, a somewhat larger excess of calcium is required to effect the same completeness of precipitation in a solution of marine salinity.¹⁷

Calcium carbonate samples were prepared from aqueous carbonate-bicarbonate solutions by precipitation. When the precipitation was carried out in the temperature range 15 to 60°C, rapidly coagulating precipitates were obtained, while outside that range gelatinous ones were formed. It was found that the isotopic composition of

¹⁶G. A. Mills and H. C. Urey, J. Amer. Chem. Soc., 62, 1019 (1940).

¹⁷H.U. Sverdrup, M. W. Johnson and R. H. Fleming, The Oceans, Their Physics, Chemistry and General Biology, Prentice-Hall, Inc., New York, 1946, pp. 192-210.

the coagulating precipitates formed under the same concentration and equilibration temperature conditions differed at the most by .5‰, while variations of 5‰ were met with in the case of the gelatinous form. The solutions from which the carbonate and bicarbonate were precipitated were made up in natural waters treated to remove alkaline earth ions without changing the oxygen isotopic composition. This was usually done by precipitating these ions as carbonates, as a complete distillation of marine waters from the salt residue is less convenient. The details of concentration and time of thermostating before precipitation of carbonate and bicarbonate in the form of calcium carbonate on the addition of excess 3M calcium chloride solution are given in subsequent tables. The precipitate was separated by filtration, washed, dried in air or in a vacuum dessicator. As no variation in isotopic composition was observed as a result of variation in the time of filtration, washing, and drying, the coagulated precipitate does not exchange rapidly with air or water.

The method of removing the alkaline earth ions from water by precipitation usually leaves the carbonate-bicarbonate solution made up in the water supersaturated with respect to calcium carbonate, and this may be slowly deposited during the thermostating period as a thin white encrustation on the walls of the containing vessel. In one case there was sufficient deposit to compare the isotopic composition of this crust with the precipitate from the calcium chloride addition, and the former was 2.9‰ richer in C^{13} and 5.8‰ richer in O^{18} . At 32°C, this is of the order of the estimate of the fractionation between carbonate ion in solution and calcium carbonate, and offers immediate explanation of the wide variability of the gelatinous precipitates. When first formed, the calcium carbonate has the same isotopic composition as the ion in solution, but if the solid is built up very slowly, there is time for each layer to reach the equilibrium between the solid state and the solution. With coagulating precipitates, the build up of solid is so fast that the composition of the solution is maintained, with the encrustation it is so slow that the bulk has

an isotopic composition which is in equilibrium with the water, and with the gelatinous precipitate it is slow enough to allow partial exchange, giving an erratic isotopic composition. As is shown by the results of Table 6, if calcium, strontium and barium carbonates are precipitated in coagulating form under the same conditions of temperature and concentration, all yield a carbon dioxide of the same isotopic composition. By far the most likely set of conditions to give these results is that the isotopic composition of the three carbonates is the same, and that there is no difference in the acid decomposition process with a change of metal ion in the carbonate.

TABLE 6

PRECIPITATED CARBONATES OF THE CALCIUM GROUP (25°C)*

Precipitating Ion	Oxygen Isotopic Composition %o Difference from Standard	
	In Florida Coast Water	In Lake Michigan Water
Ca ⁺⁺	-3.1 ₇	-10.5 ₃
Sr ⁺⁺	-3.0 ₅	-10.3 ₁
Ba ⁺⁺	-3.4 ₁	-10.6 ₂

*Rapidly precipitated from solution .049 M in Na₂CO₃ and .00034 M in NaHCO₃.

Although the results listed in Table 7 and graphed in Figure 2 are not as consistent as might be desired, they show a linear variation of the isotopic composition of the precipitate with the proportion of carbonate in the carbonate and bicarbonate of the aqueous solution, and establish that the isotopic composition of the fast formed precipitate is the average of the oxygen present in the carbonate at the time of precipitation.

TABLE 7

ISOTOPIE VARIATION OF PRECIPITATED CALCIUM CARBONATE WITH
CARBONATE-BICARBONATE COMPOSITION OF SOLUTION

Synthetic Concentration*		$\% \text{CO}_3^{=}$ in Solution	Precipitation		Oxygen Isotopic Analysis, ‰ Diff. from Standard
NaHCO_3	Na_2CO_3		Time in Thermostat before	pH kept above 8.5 during?	
.30CM	.000M	0.0	7 days	No	- 5.8 ₅
			12	Yes	- 7.2 ₈
.262	.0125	4.5	7	No	- 6.4 ₁
.225	.025	10.0	7	No	- 6.0 ₁
			12	Yes	- 6.7 ₇
.150	.050	25.0	5	Yes	- 6.5 ₉
.075	.075	50.0	5	Yes	- 8.7 ₂
.0375	.0875	69.8	5	No	- 9.8 ₇
			5	Yes	- 9.8 ₈
.000	.100	95.6	7	No	-11.7 ₉
			12	Yes	-10.8 ₈

*Lake Michigan Water was used as solvent.

In the calculation of the ionic composition of the solutions from their stoichiometry, it is necessary to use the infinite dilution values of the ionization constants of water and bicarbonate, as activity data are lacking at these concentrations.¹⁸ The least squares solution of the results gives 5.7₄ ‰ as the fractionation between carbonate and bicarbonate at 25°C, and a different series of precipitations gave 6.3₇‰. The value of 5.9‰ is used to make hydrolysis corrections to

¹⁸ H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, Reinhold, New York, 1943, p. 492

Figure 2 Isotopic Variation of CaCO_3 Precipitate with Solution Composition at 25°C

later date on the carbonate-water exchange.

The results on the temperature variation of the bicarbonate-water fractionation shown in Table 8 and Figure 3 are not extensive enough to justify any but a linear composition-temperature relationship, and the least squares value of the temperature coefficient is $-.19_7$ ‰ per °C.

TABLE 8

TEMPERATURE VARIATION OF THE FRACTIONATION OF
OXYGEN BETWEEN BICARBONATE AND WATER

Temperature, °C	Oxygen Analysis, ‰ Difference from Standard	Variation in Fractionation, ‰ of 25° Value*
12 ± .5	-2.5 ₁	+2.4 ₀
25.1	-5.7 ₀	+ .2 ₀
36.0	-7.8 ₃	-1.9 ₄
42.9	-9.6 ₈	-3.8 ₀

*25° value as found by least squares.

The water used for these solutions was laboratory distilled water, no particular significance can be attached to the constant term in the equation.

Two series of experiments showing the temperature variation of the carbonate-water fractionation are listed in Table 9. A correction for the varying hydrolysis of carbonate with temperature has been made using the results for the bicarbonate just mentioned and the carbonate-bicarbonate fractionation data. By expressing the results relative to 25°C, both series of experiments may be shown in a single graphical representation as in Figure 4. A least squares analysis linear in the temperature gives slopes of $-.142_0$ ‰ per °C and $-.143_1$ ‰ per °C, and a difference of 7.1₉ ‰ in O¹⁸ content between the samples of water from Monterey Bay and Lake Michigan.

Figure 3 Temperature Variation of Oxygen Fractionation, $\text{HCO}_3^- - \text{H}_2\text{O}$

TABLE 9

TEMPERATURE VARIATION OF ISOTOPIC COMPOSITION
OF CARBONATE DISSOLVED IN WATER

Temp. °C	Days in Thermostat	Oxygen Analysis % Difference from Standard	$\delta =$ CO ₃	Hydrolysis Correction ‰	Variation ‰ of 25° Value
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Precipitation of CO₃⁼ as CaCO₃ from a Solution in
Water from South District Waterworks, Chicago, Ill., Aug., 1948
.0485 M in Na₂CO₃ and .00034 M in NaHCO₃

14	8	- 9.5 ₄	95.0	-.3 ₂	+1.5 ₁
25.1	8	-10.9 ₃	93.2	-.4 ₀	+ .0 ₃
36.2	7	-12.4 ₆	91.0	-.4 ₇	-1.5 ₈
44.4	7	-13.6 ₆	89.2	-.5 ₂	-2.8 ₄

Precipitation of CO₃⁼ as CaCO₃ from a Solution in
Monterey Bay Water Collected at Pacific Grove, Calif., June, 1947
.0738 M in Na₂CO₃ and .00074 M in NaHCO₃

16.2	6.5	- 3.1 ₂	95.4	-.2 ₉	+ .9 ₅
16.2	8.5	- 2.7 ₅)			
25.9	6.5	- 3.3 ₅	94.2	-.3 ₄	+ .1 ₇
25.9	8.5	- 3.9 ₆)			
31.8	6.5	- 4.4 ₇	93.2	-.3 ₇	- .8 ₈
31.8	8.5	- 4.8 ₈)			
57.0	6.5	- 7.8 ₆)	87.8	-.5 ₀	-4.7 ₀
57.0	8.5	- 8.8 ₄)			

Expressing the slopes in terms of ‰ of the 25°C value, -.143₆ and -.143₈ are

Figure 4 Temperature Variation of Oxygen Fractionation, $\text{CO}_3^{2-} - \text{H}_2\text{O}$
 (x Lake Michigan Water Series, o Monterey Bay Water Series)

obtained. This agreement is much better than is statistically called for, and the uncertainty of the degree of hydrolysis renders the value $-.144$ ‰ per $^{\circ}\text{C}$ less reliable than would be indicated statistically. The calculated value at 31.5°C , the mean temperature of the experiments, is $-.135$ ‰ per $^{\circ}\text{C}$, and the agreement between the two numbers is considered good.

Slow Formation of Carbonate Solids

The way in which an encrustation of an alkaline earth carbonate can be slowly laid down on the walls of a vessel containing the appropriate bicarbonate solution as carbon dioxide is gradually removed is much more comparable to the manner of growth of a carbonate shell than is the precipitation process just discussed. As will be found experimentally, the temperature coefficient for this type of deposit, which represents solid state equilibrium conditions, should be different to that for the ion. A suitable bicarbonate solution may be made by taking a slight excess of the carbonate powder (1.5 g/l of water for calcium, strontium or barium, 15 g/l for magnesium) and adding the desired water; then, if a partial pressure of an atmosphere of carbon dioxide is maintained over the solution while the latter is well shaken, a large part of the powder will be dissolved, and after filtration, the solution may be stored in bulk for long periods if cool and well stoppered.

About 200 cc of this solution is placed in a round bottom flask maintained at constant temperature and the carbon dioxide is gradually removed, either by diffusion alone, or by a finely dispersed stream of nitrogen previously saturated by passage through water of the same isotopic composition as the solution. In from five to twenty-four hours a white encrustation forms on the walls of the vessel and, in the case of nitrogen sweeping, on the dispersing jet also. If the structure of the deposit is to be determined by X-ray, a powder may be obtained by scraping the walls. Otherwise a flask with a ground joint and acid holding side arm is used.

The deposit on the disperser may be examined microscopically, and if dense enough can provide a gas sample as well.

The X-ray analyses of the samples showed either nearly pure aragonite or an approximately equal mixture of calcite and aragonite. Microscopically, the deposits were confused aggregates of crystalline matter, occasionally showing isolated crystals of good geometry. There was a tendency to form smaller crystals at lower temperatures.

Two waters were used for the bulk of the encrustation experiments, one collected near Palm Beach, Florida, in Sept., 1948, and the other near East Orleans, Mass., on the Atlantic side of Cape Cod, during a rainy period in Dec., 1948. The respective salinities of 36.7 ‰ and 32.2 ‰ make it not surprising that there is a difference in the oxygen composition of the calcium carbonate obtained from the two waters at the same temperature. The average difference of the carbonates is 1.1₄ ‰ and a few subsidiary experiments measuring this difference in composition by allowing carbon dioxide to come to equilibrium directly with excess of the waters gave a larger value of 1.6₀.

As successive calcium carbonate deposits formed from the same stock solution at the same temperature showed a spread of as much as 1 ‰, considerable attention was focussed on possible variations in the deposition process. No relationship was observed between composition and crystal structure, seeded or spontaneous crystallization, or the method of removing carbon dioxide from the bicarbonate solution. Only the coarsest estimate of the rate of deposition can be made under these conditions, but it appears that the variation is not correlated to this either. The situation is unsatisfactory, in that a set of four determinations may show a spread of only .3 ‰ while another set yields a spread of 1 ‰ or more, and the variability inherent in the chemical manipulations as performed is somewhat more than four times that arising from the mass spectrometer determinations. The other calcium group carbonates

precipitated by this method gave results not significantly different from those for calcium carbonate at 25°C. Ionic strength also gave no significant effect on the composition of the carbonate in solutions up to 3 M in sodium chloride.

The results showing the variation of the isotopic composition with temperature are listed in Table 10. As may be seen in Figure 5, the variation is well expressed by a relation linear in the solute temperature. Least squares relations for the Florida and Cape Cod waters respectively are

$$\begin{aligned} \Delta 0^{18} &= 1.51_7 \times 10^4 / T - 54.2_7 \quad \text{and} \\ \Delta 0^{18} &= 1.04_5 \times 10^4 / T - 57.6_4 \end{aligned}$$

If the values given by these relations are compared in the middle of the temperature range of the experiments, say at 295°K, the figure 1.1₄ ‰ is obtained as the difference in isotopic composition of the waters. This may then be subtracted from the Florida results, and a repetition of the least squares process gives

$$\Delta 0^{18} = 1.62 \times 10^4 / T - 56.75$$

as the relation embodying all data and giving the composition of the carbon dioxide produced by phosphoric acid decomposition of calcium carbonate laid down from Cape Cod water in terms of the deposition temperature. The average deviation of an individual result from the relation is .38 ‰. Where both a wall and a disperser sample from the same preparation were available, each was given a weight of two-thirds as compared to unity for a single sample for a given preparation. The value 1.62×10^4 is the coefficient of $1/T$ in the relation for the variation of the fractionation when the fractionation is expressed in ‰ of the fractionation at 286.5°K, the temperature at which $\Delta 0^{18} = 0$. The corresponding calculated value is 1.56×10^4 , and the agreement is considered to be as good or better than the theoretical soundness of the calculation.

TABLE 10

TEMPERATURE VARIATION OF THE COMPOSITION OF SLOWLY FORMED
CALCIUM CARBONATE

Temperature	¹⁸ O Analysis, ‰ Difference from Standard					
	Various Preparations					Average
	Formed from a Bicarbonate Solution in Florida Water					
- 1.2	4.1 ₇	3.6 ₃				3.9 ₀
+ 6.0	1.7 ₃	2.0	1.2 ₂			1.8 ₉
13.6	1.1 ₇	1.6 ₅	.3	.5 ₇		.9 ₂
19.9	- .3 ₇	- .1 ₀	- .5 ₉	- .4 ₆		- .3 ₃
25.1	- 1.9 ₅	- 1.2 ₄	- 1.5 ₈			- 1.5 ₉
31.8	- 1.6 ₈	- 2.8 ₂	- 2.5 ₇	- 2.6 ₄		- 2.4 ₃
	Formed from a Bicarbonate Solution in Cape Cod Water					
+ 3.8	1.5 ₀	2.1 ₉				1.8 ₄
7.3	.9 ₉	1.9 ₁	1.4 ₈	.6 ₀	1.2 ₆	1.4 ₂
	(1.8 ₇	1.8 ₆				
13.6	.0 ₈	.4 ₈	- .1 ₀	- .5 ₆	- .5 ₉	- .3 ₂
18.0	- 1.3 ₁	- .8 ₅	- .7 ₆	- 1.3 ₂	- 1.2 ₀	- 1.0 ₉
	(- 1.1 ₁					
	- 2.2 ₈	- 2.9 ₄	- 3.5 ₆	- 3.3 ₅	- 2.9 ₁	
25.0	(- 3.2 ₃	- 2.9 ₁	- 2.7 ₇	- 2.5 ₃	- 2.6 ₇	- 3.0 ₂
	(- 2.7 ₈	- 2.2 ₄	- 3.4 ₆	- 3.5 ₉	- 3.5 ₆	
31.2	- 3.9 ₈	- 4.1 ₀				- 4.0 ₄
45.8	- 5.1 ₀	- 5.8 ₉	- 5.7 ₆			- 5.7 ₉
59.8	- 8.1 ₀	- 8.2 ₁	- 7.7 ₀			- 8.0 ₀
79.8	- 11.1 ₈	- 11.1 ₁	- 11.0 ₈	- 10.9 ₂		- 11.0 ₇

Figure 5 Variation of Isotopic Composition of CaCO_3 (s) with Reciprocal of Deposition Temperature from H_2O (o Florida Water Series, x Cape Cod Series)

The Carbonate Paleotemperature Scale

If a value .75 ‰ heavier in O^{18} than Cape Cod water is tentatively taken for the mean ocean, the temperature-composition relationship for the slowly formed carbonate may be given as

$$t = 16.0 - 5.17 \Delta O^{18} + .092 (\Delta O^{18})^2,$$

where t is the temperature in $^{\circ}C$.¹⁹ This result may be compared with the line drawn on the plot of preliminary data for natural samples of biological origin.²⁰ When it is taken into account that the reference gas in use at that time was -.95 ‰ different from the standard, the line corresponds to a linear equation

$$t = 18 - 5.44 \Delta O^{18}.$$

Both these equations give the same result for the temperature difference between two marine carbonates in terms of O^{18} content to better than one degree in the range 0 to $35^{\circ}C$. Individual temperatures, dependent on local isotopic composition, are uncertain until the latter has been determined, and if it is ($a + .75$) ‰ greater than that of Cape Cod water, then

$$t = 16.0 - 5.17 (\Delta O^{18} - A) + .092 (\Delta O^{18} - A)^2.$$

The average deviation of an individual experimental result from this relation is $^{\circ}C$ in the series of slow precipitations just described.

Summary for the Fractionations Considered

In these experiments, only the temperature variation of the fractionation between the carbonates and water has been measured, while the fractionation has not been. The heat of reaction may be calculated readily by expressing the fractionation

¹⁹ An investigation of the isotopic composition of the ocean is being carried out by S. Epstein, L. Dean and H. C. Urey, and the value .75‰ is only an estimate based on the Cape Cod and Florida Waters and a possible linear relation between salinity and composition.

²⁰ H. C. Urey, Science, 108, 489 (1948).

factor in the form

$$= K = K_t [1 + .001 f(T)]$$

as $RT^2 \frac{d \ln K}{dT}$ becomes $\frac{.001 RT^2}{1 + .001 f(T)} \cdot \frac{d f(T)}{dT}$.

Numerical values are given in Table 11.

TABLE 11
CALCULATED AND EXPERIMENTAL RESULTS AT 25°C

Exchange of O^{18} between	Calculated Fractionation Factor	Temperature Coefficient ‰ per °C		Heat of Reaction cal. per g. atom Exchange
		Calc.	Expt.	
$CO_3^{--}(aq) - H_2O$ (1)	1.014	-.140	-.144	25.4
Calcite - H_2O (1)	1.021	-.175	-.183	32.4
$HCO_3^-(aq) - H_2O$ (1)			-.197	34.8

The fractionation between aqueous carbonate and bicarbonate at 25°C was found to be 5.9 ‰.

Conclusion

In the experiments just described, the temperature dependence of the fractionation of oxygen in carbonate-water systems has been studied in considerable detail. The results have compared on the whole satisfactorily with theoretical calculations. The isotopic composition of calcium carbonate slowly formed from aqueous solution has been noted to be usually the same as that produced by organisms at the same temperature. As a result a relation giving the growth temperature in terms of isotopic composition has been obtained, and with certain restrictions it may be used to determine paleotemperatures. In the course of the work, further interesting features of the chemistry of oxygen isotopes in reactions involving carbonates have been observed.

The writer is indebted to Dr. L. R. Blinks of the Hopkins Marine Station, Pacific Grove, Calif., for the Monterey Bay water, and to Dr. H. A. Lowenstam of the Department of Geology, University of Chicago, for the water from Florida. The X-ray determinations were made through the kindness of Mr. D. F. Clifton of the Institute for the Study of Metals, University of Chicago. As a result of a discussion with Dr. J. E. Mayer, the preliminary treatment of the solution-crystal fractionation was much improved. The development of the mass spectrometers for this work was made possible through aid in the form of a grant from the Geological Society of America. The writer is very fortunate in having had available the facilities of the Institute for Nuclear Studies, and thanks the Institute and the University of Chicago for fellowship aid. Deepest appreciation goes to his laboratory companions, Mr. C. R. McKinney and Dr. S. Epstein, for co-operation and helpful suggestions throughout the course of the work. This interesting problem fundamental to the study of paleoclimatology was suggested by Dr. H. C. Urey, whose deep and continued interest in its progress was a determining factor in its successful completion.

Appendix

At the time this work was done, it appeared that there was an inconsistency between the reports of loss of C^{14} activity in precipitated barium carbonate and the lack of any appreciable exchange of carbonate oxygen observed, as any mechanism which leads to the exchange of carbon must also lead to oxygen exchange, although the converse is not necessarily true. An article published during the preparation of the manuscript reporting in rather more detail experiments on the carbon exchange gives a picture which is quite in accord with the results on oxygen exchange.²¹ The nature of the carbonate precipitate in filtration was directly correlated to the C^{14} exchange with carbon dioxide in a moist atmosphere, and it was also noted that barium carbonate and aqueous carbonate did not show any carbon exchange in one week.

The lack of phosphorus exchange between phosphate and phosphite likewise is a necessary but not a sufficient condition for the lack of oxygen exchange in the phosphoric acid decomposition process.²²

²¹G. Samos, Science, 110, 663 (1949)

²²V. D. Ionin, A. F. Lukovnikov, M. B. Neimen and A. N. Nesmeyanov, Doklady Akad. Nauk, USSR, 67, 463 (1949), abstracted in Chem. Abstr., 43, 7815a (1949).

Progress Report on the
Isotopic Phosphate Thermometer
Martin Steinberg

An investigation is in progress to establish a "phosphate-carbonate thermometer" based on the distribution of the oxygen isotopes (16 and 18) between inorganic phosphate and carbonate fossil deposits. Such a thermometer would supplement the "carbonate-water thermometer" which is based on the temperature dependence of the equilibrium constant for the exchange reaction between the carbonate of an inorganic deposit and water,

for which the equilibrium expression is

$$\frac{(\text{CO}_3^{16}) (\text{H}_2\text{O}^{18})}{(\text{CO}_2^{16}\text{O}^{18}) (\text{H}_2\text{O}^{16})} = K_c. \quad (2)$$

Similarly, the distribution of the oxygen isotopes between marine phosphate deposits and water may be governed by an equilibrium such as

for which the corresponding equilibrium expression is

$$\frac{(\text{PO}_4^{16}) (\text{H}_2\text{O}^{18})}{(\text{PO}_3^{16}\text{O}^{18}) (\text{H}_2\text{O}^{16})} = K_p. \quad (4)$$

Division of Equation (2) by Equation (4) yields

$$\frac{(\text{CO}_3^{16}) (\text{PO}_3^{16} \text{O}^{18})}{(\text{CO}_2^{16} \text{O}^{18}) (\text{PO}_4^{16})} = \frac{K_c}{K_p} \doteq K. \quad (5)$$

If both the carbonate and phosphate equilibria are established with the water, at the same time and place, the temperature dependence of the constant, K, in Equation (5) may be used as a thermometer which is independent of the isotopic composition of the water which may have varied with time and location in past geological ages.

The techniques for the determination of oxygen isotopic abundances in fossil carbonate deposits have been developed. This report is concerned with the development of a method for the establishment of the phosphate half of the thermometer; i.e., the determination of the isotopic abundances of phosphate oxygen in phosphate bearing marine deposits and the temperature dependence of these abundances. The phosphate oxygen must be removed for mass spectrometer measurements without isotopic fractionation and preferably in quantitative yield. The general procedure then involves the separation of phosphate from other oxygen bearing substances, namely carbonate, in fossil deposits, and the subsequent removal of the oxygen from the phosphate.

The most difficult step in the analytical procedure appears to be the removal of oxygen from the phosphate, and it is currently under investigation. We are liberating oxygen from inorganic calcium phosphate by the treatment of approximately 50-70 mg. samples with a 25% excess of fluorine at an initial pressure of

1.5 atmospheres at 200°C for 3 hours according to the reaction

Under these conditions the reaction is essentially quantitative (between 90 and 100%).

The experimental procedure which appears to yield satisfactory results is as follows. Empty stainless steel reactor tubes are filled with fluorine at one atmosphere, sealed, and are then heated at 200°C for 3 hours to coat the walls with a fluoride deposit so as to inhibit the removal of oxygen as iron oxides in the subsequent sample fluorination. The fluorine is pumped off and dissipated in a sodium bromide tower and the tubes are filled with dry nitrogen. Weighed, powdered calcium phosphate samples are quickly inserted in the reaction tubes, which are resealed and heated under vacuum at 400°C for 14 to 16 hours to dry the sample. The tubes are cooled to liquid nitrogen temperature and 50 cc (S.T.P.) fluorine are admitted to each tube, followed by the 3 hour reaction period at 200°C. After the reaction is complete, the tubes are held at liquid nitrogen temperatures and oxygen produced in the reaction and excess fluorine are passed into an evacuated nickel tube filled with about 100 grams of sodium bromide maintained at 200°C. The excess fluorine is reduced to sodium fluoride yielding bromine which is removed on passage through a liquid nitrogen trap. The oxygen at this point is carried by a Töpler pump into a gas measuring burette and then is transferred into gas sample tubes for subsequent $\text{O}^{18}/\text{O}^{16}$ measurement with the mass spectrometer.

The tank fluorine used contains about 1.2 volume per cent of approximately a 50:50 mix of oxygen and nitrogen. A correction must be made for the effect which the tank fluorine oxygen has on the apparent O^{18}/O^{16} ratio of the phosphate oxygen. A measured volume of tank fluorine is passed through the sodium bromide and cold trap to remove the fluorine, and the oxygen-nitrogen mix is measured and its O^{18}/O^{16} ratio is determined in the spectrometer. With this information the abundance correction can be calculated for each sample.

Using the above described procedure early results were rather erratic. It is believed that these variations were caused by the production of oxygen in the sodium bromide tower through the reaction of fluorine with water trapped in the crystals. Repeated fluorinations apparently eliminated this source of difficulty. Below are listed some of the most recent results for corrected values of the O^{18}/O^{16} ratios of oxygen from calcium phosphate relative to an arbitrary standard oxygen sample.

O^{18}/O^{16} , ‰ vs. standard

Series 1	-0.22	} Av. 0.35 ± 0.50
	+0.59	
	+0.68	
Series 2	-0.07	} Av. -0.01 ± 0.12
	+0.16	
	-0.13	

The last series has the desired precision and tests are in progress to determine the reproducibility with samples prepared at different times. Work will now be done on the separation of phosphates from carbonates, which are the most likely oxygen bearing impurities in fossil phosphate deposits, followed by removal and abundance measurements of the phosphate oxygen. When these objectives are attained it should be possible to apply the methods to phosphate bearing samples of animal origin grown at known temperatures and determine the relation, if any, between phosphate oxygen abundances and temperature of deposition.

Progress Report on
a Continuous Method for Recording
Seasonal Variations in Paleotemperatures

L. B. Dean

The present method of measuring paleotemperatures by oxygen isotope analysis of the shells of fossil marine animals has certain limitations. Because of the relatively large amount of calcium carbonate - at least 10 milligrams - required for an analysis, only the mean temperature of an animal over a period of months or more is obtained. During this time the water may have changed significantly in temperature, or the animal may have moved to a different part of the ocean. In the case of animals living in shallow water, there is the further possibility that during the time over which the mean temperature has been measured the isotopic composition of the water was changed briefly on numerous occasions by rain water. Thus a method of analysis which would give isotopic analyses at more closely spaced intervals would give considerably more information. Such a method would also be of interest in the study of the habits of present day organisms. This report contains a proposed scheme for measuring short-time temperature fluctuations, and the progress that has thus far been made in developing the technique.

Sea shells grow by the successive deposition of layer upon layer of calcium carbonate. A rapidly growing animal deposits a monomolecular layer about once a second. These layers are, in general, curved surfaces since growth takes place radially outward. In all of the shells which have been found suitable for paleotemperature analysis, a section cut through the shell shows definite

growth lines, or lines of constant age. These probably arise from the inclusion of small amounts of impurities into the calcium carbonate. Since these striations make visible the directions of the growth planes, it is possible to cut from a shell a thin pencil whose axis is perpendicular to the growth planes. Then one end of such a strip will be composed of calcium carbonate which was deposited during the early stages of growth of the animal, while the material at the other end will have been deposited just before the animal's death. Shell sections obtained in this manner have been cut into about ten or twelve parts, and the parts analyzed separately for the oxygen isotopic ratio. This has given a rough measure of the seasonal variation in temperature of the animals thus studied.

The plan of the present work is to grind the calcium carbonate pencil into a fine powder and onto a long strip of tape in such a way that the material at a given position on the tape will correspond with a given position in the pencil, and hence with a definite time in the growth of the animal. This can be accomplished by grinding the pencil from one end to the other while the tape is passing underneath to catch the falling powder. A watchmaker's lathe is now available for accurate grinding.

An all-glass apparatus has been built for the generation of carbon dioxide from the carbonate on the tape. The tape is inserted into the apparatus, which is then evacuated. The tape is slowly drawn from one portion of the system to another by winding it onto a spool driven from the outside through a ground glass joint. Along the way the tape goes through phosphoric acid. The carbon dioxide thus formed is constantly pumped away through a

trap cooled with solid toluene to remove water vapor and phosphoric acid. A portion of the gas will be allowed to pass through a mass spectrometer for isotopic analysis. It may be found necessary to use an automatically variable leak at this point, in order to assure a constant rate of flow into the spectrometer. This method is in principle capable of giving a continuous record of an animal's temperature. The "resolving time" is limited, however, by

- (1) mixing of the calcium carbonate when it is put on the tape;
- (2) simultaneous generation of gas from a finite length of tape as it is passed through the acid; and
- (3) mixing of the carbon dioxide gas after it has been generated.

These limitations can be minimized, respectively, by

- (1) very careful grinding;
- (2) reducing the effective path length with a sharp cut-off; and
- (3) choosing tube diameters in accordance with pressures used.

As yet there have been no attempts at testing the method with a mass spectrometer. Various tapes have been examined for their strength, resistance to phosphoric acid, vapor pressure, and similar properties concerning their suitability for this work. Although none of the tapes is ideal in all respects, there are some that appear to be usable with slight modifications in technique.

The next phase of the program will be the determining of the conditions necessary for obtaining a steady source of carbon

dioxide for the spectrometer. When this is done the method can be tested with the spectrometer, using calcium carbonate of known isotopic composition. The resolving time of the apparatus can be determined by putting two different compositions of carbonate alternately on the same tape. If everything is satisfactory, the technique can then be applied to unknown samples.

Progress Report on
the Oxygen Isotopic Abundances
in Igneous and Sedimentary Rocks

S. Silverman

The purpose of this investigation is to determine the isotopic abundances of oxygen in silicate rocks. Since oxides of silicon are believed to make up about 60% of the content of the hypothetical 10-mile crust on the earth, any attempt at a full understanding of the geochemistry of oxygen, without considering the oxygen in silicate rocks, must necessarily be inadequate. Many processes may have been instrumental in changing the relative abundances of the oxygen isotopes in the earth's crust (deformation, erosion, solution, sedimentation, diffusion, and possibly by fractionation during crystallization in the initial formation of the crust). The interrelationships between the rocks of the earth's crust, the changes during erosion and sedimentation, and the selective enrichment of oxygen isotopes in the cycle of evaporation from and drainage of water into the oceans must also be known for a fuller understanding of the history of oxygen on the earth. Thus a program was instigated to investigate the O^{18}/O^{16} ratios of representative samples from each of the major rock classifications. In addition, the O^{18}/O^{16} ratio in meteorites may be determined and compared with the abundances on earth.

The most apparent procedure, upon immediate consideration, was the liberation of oxygen through reaction with fluorine and hydrofluoric acid:

As a result of numerous trials, the most productive procedure using the above reactants was found to be as follows:

The reaction between a 50 mg. sample of rock specimen (finely ground to c.a. 100-200 mesh) and about a 30% excess of reactants ($\text{HF} + \text{F}_2$) was carried out in a specially designed nickel reaction tube. Quantitative yields of oxygen gas were realized when the sample and reactants were heated to about 135°C for 24 hours. After the reaction was completed, the excess HF and F_2 gases were separated from the oxygen by passing the mixture through a potassium bromide absorption tower, where the F_2 and HF were removed by reaction with the KBr and bromine gas liberated. The Br_2 and SiF_4 were separated from the oxygen by passing the mixture through a trap immersed in liquid nitrogen.

The oxygen is collected in a sample tube and is now ready for mass spectrometric analysis.

This initial method was found to have several disadvantages. The tank fluorine was found to contain as much as 1.7% of inert gas (mixture of oxygen and nitrogen). The KBr absorber, due to adsorption of the oxygen, slowed down the collection procedure considerably and necessitated hours of heating under high vacuum before yields larger than 90% could be accumulated. This phenomenon may also have introduced the possibility of fractionation through preferential adsorption of one of the oxygen isotopes.

With this procedure, samples of Quartz, Labradorite, and Tektite (stoney meteorite) were run and the mass spectrometer

analyses yielded values of the O^{18}/O^{16} ratios which were reproducible to within 5%. Since the sensitivity of the instrument was of the order of 0.3%, a program was undertaken to improve the reproducibility of the results. After more than 150 determinations on a large variety of specimens, the most promising procedure is, at present, as follows:

The use of chlorine trifluoride and hydrofluoric acid instead of fluorine and hydrofluoric acid has the advantage in that ClF_3 has a relatively high boiling point (+ 11.3°C) and a negligible vapor pressure (10^{-9} mm. Hg) at liquid nitrogen temperatures and therefore can easily be separated from oxygen. This also serves to eliminate the inconvenience arising from the inert gases present in the tank fluorine. Following a series of controlled investigations on the silicate-chlorine trifluoride reaction, an optimum procedure has been developed in which quantitative yields of oxygen (over 95%) were obtained by use of c.a. 40 mg. platinum as a catalyst with a 50 mg. sample with excess ClF_3 and HF and reacting at a temperature of 400°C for 24 hours.

The 50 mg. sample and 40 mg. of platinum are ground together in an agate mortar to insure thorough mixing and intimate contact between rock specimen and catalyst. The mixture is then kept in a dessicator until the reaction tube is ready for charging.

A dry box was designed and constructed such that the reaction tubes could be opened and charged with the sample in an atmosphere of dry nitrogen, thus completely preventing exposure of the inside of the reaction tube to atmospheric oxygen or moisture. The sample is introduced into the reaction tube in the dry box by means of

a long-handled, remote-controlled spoon through an opening in the top of the dry box, and the reaction tube is then sealed, the entire operation being performed under a constant stream of dry nitrogen.

Prior to charging, the empty reaction tubes are filled with fluorine at one atmosphere and heated to about 450°C for about 15-30 minutes to insure complete removal of adsorbed moisture on inner walls of the tubes. The fluorine is then withdrawn and the evacuated tube is heated for another 15 minutes under a vacuum of 10^{-4} mm. Hg, after which the tube is filled with one atmosphere of dry nitrogen, closed and transferred to the dry box where it is opened and charged with the sample.

After the sample is introduced into the reaction tube and before the reactants are added, the tube is heated to 400°C under high vacuum to drive off any moisture or occluded oxygen.

As a general procedure, four successive runs are made with each specimen, and all four determinations made in the same reaction tube. In this way, the reaction tube need not be cleaned (throughout the four runs on one specimen), and is only opened in the dry box.

Use of this method has made possible the attainment of a 1% reproducibility. Samples of some recent results are indicated in the following table:

<u>Sample</u>	<u>Run #</u>	<u>$^{18}\text{O}/^{16}\text{O}$ ratio (with reference to an arbitrary standard)</u>
Olivine Basalt	65	-1.37 ₆₀
	66	-0.8
	67	-1.9
	75	-1.5
Cheshire Orthoquartzite	76	+2.3
	84	+2.4
	92	+2.3
Kimberlite	107	+2.9
	99	+2.8
	95	+4.1
Arkose	104	+3.4
	112	+4.1
	120	+2.9
Nepheline Syenite	115	+0.4
	116	+0.4

This procedure is now being applied in a survey of igneous, metamorphic, and sedimentary rocks, and at the same time steps are continually being taken with the goal of improving the method and perfecting the reliability of the results.

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