

UREY AND GEOLOGICAL THERMOMETRY

In 1929, oxygen isotopes of masses 17 and 18 were discovered in atmospheric oxygen and in 1931 deuterium, the stable heavy isotope of hydrogen was detected. By 1938, the carbon dioxide/water isotopic exchange for the oxygen isotope analysis of water had been developed. And by the end of the 1930s, it was known that variations in both oxygen and hydrogen occurred in the hydrologic cycle.

After World War 2, the Nobel Laureate Professor Harold C. Urey gave up his interest in the isotope separation of uranium isotopes (Manhattan Project work) and moved from Columbia to Chicago. There he updated and expanded earlier calculations of his with Greiff on isotope exchange equilibria using an advanced method devised by J. Bigeleisen and Goeppert-Mayer at Columbia. This gave the possibility of calculating the temperature coefficient of an isotope exchange equilibrium constant in addition to the logarithm of the constant with confidence. During these calculations, Urey noted that the fractionation factor for oxygen-18/oxygen-16 exchange between CO_3^{-2} and H_2O would decrease by 1.004 between 0°C and 25°C . This showed that it is possible to use this temperature coefficient in order to measure paleotemperatures.

Isotope paleoclimatology started with Urey's researches into both the empirical and theoretical aspects of isotope chemistry which followed his award of the Nobel Prize in 1934. By that time, he had already examined oxygen isotopes in stony meteorites and terrestrial rocks and claimed that they are constant to 2.5%. Later work produced permil (‰) accuracies and, as mentioned earlier, he treated the thermodynamics of isotope equilibria and also geological and cosmological problems. In 1947, he published a seminal paper on the thermodynamic properties of isotopic substances.

In 1947, A.O. Nier constructed a mass spectrometer for measuring the isotopic variations in gas samples with high accuracy. Urey improved its precision and started taking paleotemperatures of Cretaceous belemnites using carbon dioxide in the mass spectrometer. Nier also devised the phosphoric acid technique for obtaining carbon dioxide from carbonates for analysis.

In 1950, J.M. McCrea discussed the isotopic chemistry of inorganic carbonates and a paleotemperature scale. Least-squares calculations of the relevant data obtained in the range 7 to 25°C gave slopes of 17.5 and 13.0 for series using Florida and Cape Cod water respectively. In the first carbonate/water paleotemperature scale of Samuel Epstein, Ralph Buchsbaum, Heinz Lowenstam and H.C. Urey produced in 1951, a similar slope (4.3) was obtained and essentially agreed with McCrea's values.

Urey realised that if calcium carbonate is slowly crystallized in the presence of

water at 0°C, the ratio of the oxygen isotopes should be 1.026:500 if the ratio of the oxygen isotopes in the water is 1:500. This means that the ratio of the oxygen isotopes in the water is 1:500 and hence the oxygen 18 is slightly concentrated in the calcium carbonate in relation to the water. If the temperature is 25C, the oxygen isotopes will be concentrated only to the extent of 1.022:500 compared to 1:500 in water. Clearly there is a slight temperature coefficient for the abundance of oxygen-18 in the calcium carbonate as compared with that in the water. The degree of the fractionation is so small that the atomic weight of oxygen in the calcium carbonate will be changed by only 0.0000007 atomic weight units as the temperature change by only one degree Celsius. Urey recognised the significance of this, and noted that **“I SUDDENLY FOUND MYSELF WITH A GEOLOGICAL THERMOMETER ON MY HANDS”**.

Urey went on to devise the famous PDB standard. This entailed using constant temperature water baths to grow marine animals collected from various places. These were set up at 3 Pacific Coast marine laboratories and these were stocked with calcareous organisms with notched or drilled shells. The idea was that if repair took place, the new shell should give reliable data which could be used to fix points on the temperature scale. Sedentary or attached forms living in relatively confined areas were used so that the point where they were collected would be representative of the conditions under which the animals grew their shells.

Collections were made in Puget Sound, Monterey Bay and areas along the coast of lower California in Mexico. Mussels and brachiopods from Puget Sound (Middle Channel and President Channel), abalones and keyhole limpets from Pacific Grove, California (Hopkins Marine Station), abalones and limpets from Lower California, Mexico (Santo Tomas also between Encenada and Morro Points, Mexico) and a snail *Strombus gigas* – from Bermuda (Laboratory tank) were analysed.

Interestingly, in 1969, T. Tarutani, R.N. Clayton and T.K. Mayeda showed that the inorganic precipitation of minerals also yielded temperature equations for paleotemperatures. Their paper dealt with the effect of polymorphism and magnesium substitution on oxygen isotope fractionation between calcium carbonate and water.

The resulting PDB standard was based on measurements of oxygen in carbonates in a belemite, *Belemnitella Americana*, collected from the Peedee Formation of the North American Cretaceous.

A carbonate/water paleotemperature scale was devised based on the fact that the isotopic composition of oxygen from calcium carbonate (for instance from belemnites) differs from that in water and depends upon the temperature when the carbonate is precipitated under equilibrium conditions. The calcareous-shelled abundance of carbonates in the geological record was optimal. However much work had to be done to create such a scale and so it is not surprising that Urey called it

“THE TOUGHEST CHEMICAL PROBLEM I EVER FACED”.

The ratios of vapour pressures of H_2^{16}O to H_2^{18}O are 1.008 and 1.011 at 25°C and 0°C, respectively. Evaporation and condensation continuously alter the oxygen-18 isotope contents of bodies of water. The size of such variation is important in determining a valid temperature scale and also to the general problem of the determination of temperatures of unknown samples. This is because the carbonate-water temperature scale depends on the magnitude of the differences between the oxygen-18 contents of the calcium carbonate and the water in which it was precipitated.

FIRST CARBONATE/WATER PALEOTEMPERATURE SCALE

In 1951, S. Epstein, R. Buchsbaum, H. Lowenstam and H.C. Urey reported determination of an isotopic temperature scale for measuring temperatures at which a marine shell-bearing animal grows its shell by determining the oxygen-18/oxygen-16 ratio in the calcium carbonate of the shell. Initially extraneous oxygen was introduced into the calcium carbonate during one of the stages of processing of the shell and this introduced an error in the temperature scale. Consequently, the whole problem was examined and a modified method for preparing samples of carbon dioxide from the calcium carbonate of the shell was devised.

At the end of the paper, the authors stated that “we have delayed publication of this paper while it was in galley proof because we discovered disturbing variations in our temperature determinations, We traced this to the use of heated copper oxide to remove impurities from the helium gas passed over samples during the heating process. Small amounts of oxygen from the copper oxide were present in the helium, and the carbon dioxide formed apparently exchanged in some cases with the calcium carbonate of the samples. Removal of all oxygen by means of a charcoal trap at liquid nitrogen temperature corrected these difficulties. Our tentative corrected temperature becomes $t = 14.8 - 5.14\delta$. The slope now agrees with McCrea’s value.”

FIRST PROCEDURE

Previously purification of the calcareous shell consisted of heating 50 mg of the powdered sample in a slow stream of helium at 470°C. The helium was purified from organic compounds by passing it over cupric oxide heated to 700°C and through a liquid nitrogen cooled trap. Contamination with oxygen gas originating from the cupric oxide and from back diffusion through the furnace opening occurred. The oxygen oxidised the organic material of the powdered shell to form carbon dioxide which in turn exchanged with the calcium carbonate of the shell. Since carbon dioxide formed with atmospheric oxygen analyses about -20 per mil relative to carbon dioxide extracted from calcium carbonate of a normal marine shell, the isotopic exchange lowered the oxygen-18/oxygen-16 ratio of the calcium

carbonate of the shells. Samples used for the temperature scale were treated similarly and an almost constant error result. Additional work showed that there existed a large discrepancy between the oxygen-18/oxygen-16 analysis of the calcium carbonate in the prismatic and pearly layers from the same shell fragment. This led to detection of the error.

Where $\delta = (R_{\text{sample}}/R_{\text{standard}} - 1)1000$ and R_{sample} and R_{standard} are $C^{16}O^{18}O$ to $C^{16}O_2$ for the sample and standard reference gas (CO_2) respectively, δ is the difference between the oxygen-18 content of the sample and that of the reference gas. Erroneous data were obtained from a carbon dioxide sample from different layers of a fragment from *Haliotis rufescens*.

REVISED PROCEDURE

The revised purification process uses helium gas flowing at 0.4 ml/second passing through a copper-filled furnace at about 500°C through and activated charcoal-filled trap cooled with liquid nitrogen and into the roasting furnace. The continuous flow of helium sweeps the volatile decomposition products of the heated organic compounds away from the calcium carbonate and simultaneously provides an inert atmosphere over the sample. The sample, in a platinum boat, is inserted into the furnace while the temperature of the furnace is low (<200°C) to permit sweeping out of all air from the furnace before heating of the sample begins. The opening of the furnace is covered by a cap containing a capillary opening to prevent back diffusion of air.

Sweeping with helium continues for 20 minutes before the heater of the furnace is turned on. This is enough to sweep out the furnace about six times. The sample roasts in the furnace at least 30 minutes after the temperature of the furnace reaches 470°C. The resulting calcium carbonate is grey and it is then reacted with phosphoric acid to release the carbon dioxide for mass spectrometric analysis.

The relevant isotopic exchange reaction is given by: $\frac{1}{3}CaC^{16}O_3 + H_2^{18}O = \frac{1}{3}CaC^{18}O_3 + H_2^{16}O$. Only two thirds of the oxygen reacts to yield carbon dioxide when carbonate is treated with phosphoric acid.

The equilibrium constant for this is given by :

$$K = \frac{(CaC^{18}O_3)^{1/3}(H_2^{16}O)}{(CaC^{16}O_3)^{1/3}(H_2^{18}O)} = \frac{\{CaC^{18}O_3\}/\{CaC^{16}O_3\}^{1/3}}{[H_2^{18}O]/H_{216}O}$$

K yields the fractionation factor, α , the quotient of the ratios R_c and R_w . These are the oxygen-18/oxygen-16 ratios of carbonate and water respectively in the system

calcite-water. The fractionation factor is $\alpha = R_c/R_w$, where R_c and R_w are the oxygen-18/oxygen-16 ratios of carbonate and water respectively. In the calcite/water system, the fractionation factor is 1.0286 at 25C so that the calcite precipitated in equilibrium will be enriched in oxygen-18 by 2.86‰ (28.6‰). The fractionation is temperature-dependent with values near unity and carbonate can be either enriched or depleted in heavy oxygen isotopes.

THIS SPANS A WIDE RANGE OF DISCIPLINES FROM BIOLOGY THROUGH ISOTOPIC FRACTIONATION TO THE HISTORY OF THE EARTH.

DELTA , δ

Measurements of CO₂ (ratio 44/46 – the first containing carbon and two oxygen-16s, the second containing carbon and one oxygen-18) in the mass spectrometer are expressed in units of δ . $\delta = \text{sample to standard} = R_{\text{sample}} - R_{\text{standard}} / R_{\text{standard}} \times 1000$. The ratio R can be ¹⁸O/¹⁶O or D/H, ¹³C/¹²C, etc.

Appropriate standards have to be applied. For oxygen in carbonates Belemnite Americana from the Peedee Formation, Cretaceous North America (PDB) and Vienna Peedee Belemnite V-PDB) are used. For oxygen-16 and oxygen-18, the normal abundance variation is 100:1 and standard mean ocean water (SMOW) or V-SMOW or standard light Antarctic precipitation (SLAP) are used. SMOW is long exhausted and was originally defined as SMOW relative to NBS standard water. He collected water at the equator zero longitude (water from no place and no time). It was a large sample later distilled into fractions. Measurements for deuterium and oxygen-18 were made. Then the fractions were recombined and amounts adjusted until the $\delta^{18}\text{O}$ of 0‰ relative to the original defined SMOW relative to NBS standard water was obtained. The oxygen-18 value was exactly 0‰ to ± 0.02 , but the δ D/H was not zero. Craig added heavy water until the D/H δ was brought to zero ± 0.02 .

Of V-SMOW, Craig stated that “I don’t know why it should be called V-SMOW, except for the IAEA people to pretend that they made it”. The IAEA said that people would confuse it with SMOW and would not accept the name. SMOW is a distilled water and Craig’s calibrations showed that it is 0.0 against original NBS standard water. He added that “I do not believe that anyone can see a significant difference from the values I gave relative to the NBS standard”.

INTERPRETATIONS

One of several equations is : $T = 16.0 - 4.14(\delta_c - \delta_w) + 0.13(\delta_c - \delta_w)$. Later revised so

that 16 became 16.9 and 4.14 became 4.2.

ISOTOPIC COMPOSITION OF OCEANS NOW AND IN THE PAST

For simplicity, the isotopic composition of oceans both now and through the geological was taken to be zero. Therefore, the factor δw was given as zero because it represents the corrected oxygen-18 of carbon dioxide equilibrated isotopically at the same temperature with the water from which the carbonate was precipitated measured against the same mass spectrometer working gas (carbon dioxide).

Attempts were made to gauge the isotopic compositions of paleo-oceans. The slope of the oxygen-18/salinity relationships for the Red Sea implies that a change of salinity of one per mil is associated with a difference of 0.29 per mil in oxygen-18, thus altering the isotopic temperature by about one degree Celsius.

During Pleistocene glaciations, N.J. Shackleton believed that the oxygen-18 value altered by 1.0-1.4 ‰ during the glacial and interglacial stages of this epoch. As early as 1955, Cesare Emiliani had outlined the most important features of Quaternary glacial to interglacial variations from oxygen isotope determinations on planktonic foraminifera for Caribbean and equatorial deep-sea cores.

UREY'S "PLUMBING"

In 1958 Urey relocated from the Enrico Fermi Institute in Chicago to the School of Chemistry at the Scripps Institution of Oceanography (University of California San Diego at La Jolla). He and the group's seminal activities there were described collectively and somewhat mockingly as "Urey's plumbing" by some physicists.

Heinz Lowenstam and Samuel Epstein examined Mesozoic belemnites supporting Urey's paleotemperature scale which was later modified by Harmon Craig. M. Steinberg had tried to develop this idea in Chicago by taking into account the possibility that the distribution of oxygen-18 between phosphate and water might provide another thermometer with a different temperature coefficient and thus make it possible to eliminate the water phase. Another mineral phase, biogenic silicate/water, was also considered.

Unfortunately, subsequent work in Pisa by R. Bowen and A. Longinelli showed that the differences in values of carbonate, silicate and phosphate in equilibrium with water are almost constant. However, the phosphate-water temperature scale was revised by Longinelli and S. Nuti in 1973, but it is rarely used because of its very minuscule deviation from the carbonate one. Consequently, it is not practical to use

either silicate or phosphate to assess temperature and isotopic composition in pairs of biogenic carbonate, silicate and phosphate.

Temperatures can be calculated using a quadratic equation describing an almost linear relation of δ oxygen-18 values and temperatures within a restricted temperature interval. In 1985, G. Wefer published a list of different paleotemperature equations for carbonates, e.g. for molluscan aragonite, the relevant equation is $T = 21.8 - 4.69 (\delta_{\text{aragonite}} - \delta_w)$.

THE QUATERNARY PERIOD

Quaternary paleoclimatology is the study of past climates throughout geologic and historic times and why they vary. It includes paleoceanography, the study of oceans in the geologic past. The Quaternary period is the most recent geological time interval in the history of the Earth and covers the last 1.8 million years up to the present day. It includes a series of very extensive environmental changes which have affected and shaped the landscapes and life on Earth.

During the Quaternary, major continental ice sheets and mountain ice caps have accumulated from time to time during long glacial stages. These were interspersed with warm periods each lasting a shorter time during which the temperature was similar to or higher than those of today. But for long periods of the climatic cycles of the Quaternary which were roughly 40 in number, the temperatures were cold.

Knowing and understanding how the climate has altered over the past is essential is critical for predicting future climate changes more reliably. Identifying glacial-interglacial changes, the role of carbon dioxide and changes in the Earth's orbit which may be responsible for such changes was mandatory. A method has been devised for analysing more accurately the fluctuations in the size of ice sheets that often developed during the Quaternary.

If human emissions into the atmosphere of gases causing global warming into the atmosphere significantly increase, this could trigger a rapid change in the future climate similar to those which happened in the past. So serious efforts must be made to control the release of greenhouse gases.

Scientific understanding of processes in the oceans has accelerated since Shackleton developed new methods for analysing very small samples using a mass spectrometer. This device was modified to permit analyses of microfossils found in the cylindrically shaped cores drilled out of the sediments on the ocean floors.

Using samples from the Pacific Ocean, he compared the oxygen isotopes in shells of species living near the ocean surface and those that lived at great depths. Results

showed that changes in the global ice volume were far more important than changes in water temperatures. This concluded a long-running and occasionally acrimonious debate about which of the two factors dominated. This is reminiscent of the long running dispute in geological circles about whether continents move (continental drift) or stay put (the fixist position). Plate tectonics demolished the fixist position.

In 1973, Shackleton analysed a sediment core from the western tropical Pacific that contained evidence of the most recent reversal of the Earth's magnetic field which occurred about 780,000 years ago. From time to time, the Earth's magnetic field reverses or "flips". When this happens, the North Pole becomes a South Pole and the South Pole becomes a North Pole. In the past ten millions years, there have been on average four or five reversals per million years. A complete reversal may take between one and several thousand years to complete.

Ocean drilling was done on the Glomar Challenger, a specially built ship and used for scientific exploration between August 11 1968 and November 11 1983. A length up to 6.24 km long was suspended from the ship down to the bottom of the sea. A depth below that up to 1.3 km could be penetrated through the ocean bottom.

Reconstruction of the history of global ice volume through the succession of the Ice Ages made it clear that ice volume cycles occurred approximately every 100,000 years. Clearly when ocean sediment cores are analysed, each successively older Ice Age cycle could be correlated with the corresponding cycle in the first core. This formed the basis of a method for assigning an age scale based on the 100,000 year cycles in the first core.

These results supported the Milankovich hypothesis about the collective effect of changes on its climate. Milutin Milankovich was a Serbian mathematician and physicist from the University of Belgrade. He made important studies on solar radiation, concluding that there were periodic changes in the amount of radiation received on Earth caused by eccentricities in the Earth's orbit. The eccentricity (shape of the Earth's orbit), axial tilt (tilt of the Earth's axis as the Earth wobbles) and precession (the change in the direction of Earth's axis of rotation relative to the Sun) of the Earth's orbit all vary in several patterns, resulting in roughly 100,000-year ice age cycles of the Quaternary.

J.D. Hayes, J. Imbrie and Shackleton in Science 1976 included Shackleton's analysis of deep sea sediments to validate Milankovich's idea. They were able to detect periodicities of 19,000 and 23,000 years due to precessional changes, 40,000 years due to axial tilt and 100,000 years due to eccentricity. This was very important since it provided a precise way to construct an age scale for sediment cores using all three of the Earth's orbital periodicities together. So accurate dates were obtained for the reversals of the Earth's magnetic field as well as the evolution and extinction of marine organisms.

