

*Caltech technician  
using the light  
element gas  
mass spectrometer.*

## THE STABLE ISOTOPES

*by Samuel Epstein*

For the past 15 years the Division of Geological Sciences has had an active program in geochemistry dealing with studies of the natural variations of the isotopic abundances of some of the lighter elements. Such studies are of use to the geologist, geochemist, and other geoscientists in their studies of earth processes.

Most elements, as they exist in nature, are composed of non-radioactive isotopes. Isotopes of a single element have the same number of protons but a different number of neutrons in their nuclei. Chlorine consists of two stable isotopes of atomic weights 35 and 37. Calcium has six stable isotopes of atomic weights 40, 42, 43, 44, 46, and 48. The isotopes of an element are physically and chemically very similar. In compounds, the chemical and physical properties of the different combinations of Ca and Cl isotopes—various isotopic species of calcium chloride—are also similar, and calcium chloride is customarily referred to as a single chemical and not as it really exists, a mixture of such isotopic species as  $\text{Ca}^{40}\text{Cl}^{35}$ ,  $\text{Ca}^{40}\text{Cl}^{37}$ ,  $\text{Ca}^{42}\text{Cl}^{35}$ , etc.

For most practical purposes such treatment of chemical compounds is proper. Most scientists, however, are aware that they are dealing with mixtures of isotopic species of compounds when they refer to, say,  $\text{H}_2\text{O}$  or  $\text{NaCl}$ , and that the isotopic species of a single compound are chemically and physically not identical. These differences in properties are particularly relevant in cases where the lighter elements are concerned. Pure  $\text{H}_2\text{O}$  is measurably different from  $\text{H}_2^{18}\text{O}$ . Its vapor pressure, at room temperature, is lower by some 7 percent than that of  $\text{H}_2^{16}\text{O}$ ; its freezing point is  $3.8^\circ\text{C}$  higher.

The differences in chemical and physical properties of isotopic species of a chemical compound are due to the fact that the mass of an atom is a factor in the bond strengths of the atoms in a compound. Although the electronic configurations in  $\text{O}^{16}$  and  $\text{O}^{18}$  are the same, when  $\text{O}^{16}$  combines with hydrogen to form  $\text{H}_2\text{O}^{16}$  the bonds formed are less stable than the equivalent bonds in  $\text{H}_2\text{O}^{18}$ . Thus, when water is subjected to some processes, the  $\text{H}_2\text{O}^{16}$  will respond differently than will  $\text{H}_2\text{O}^{18}$ .

The process of freezing of water causes a decrease in the  $\text{H}_2\text{O}^{18}$  content in the unfrozen water because  $\text{H}_2\text{O}^{18}$  freezes preferentially relative to  $\text{H}_2\text{O}^{16}$ .

The differences in the chemical and physical properties of the isotopic species of a compound can be exploited to study a variety of processes and can be applied to many different problems. We can perhaps best illustrate the usefulness of isotopic studies by considering some investigations of the variations in the oxygen isotopic abundance, specifically with the  $\text{O}^{18}/\text{O}^{16}$  ratio in natural oxygen compounds.

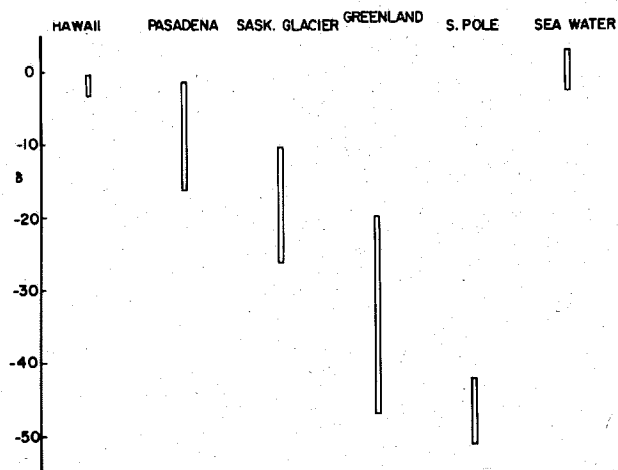
Measurements have been made of the  $\text{O}^{18}/\text{O}^{16}$  ratio in water and ice, in nearly all the common silicates, carbonates, and in a variety of oxides. These measurements, which must be made with high precision to be meaningful, were made possible by development of a mass spectrometer that can detect the addition of one  $\text{O}^{18}$  in  $2 \times 10^8$  atoms of oxygen. In other words, a change of 0.01% in the  $\text{O}^{18}/\text{O}^{16}$  ratio (normally 1/500) can be measured routinely.

Variations in the  $\text{O}^{18}/\text{O}^{16}$  ratio are described in terms of delta values, where delta is the permil change of the  $\text{O}^{18}/\text{O}^{16}$  ratio relative to the  $\text{O}^{18}/\text{O}^{16}$  of a given standard. The standard is usually mean ocean water. Thus, an oxygen sample with a delta value of +10 has an  $\text{O}^{18}/\text{O}^{16}$  ratio of 1 percent or 10 permil greater than that of mean ocean water. A delta value of -10 denotes a ratio of 1 percent or 10 permil lower than that of mean ocean water. We use this notation because we are interested primarily in how the various natural materials differ in the  $\text{O}^{18}/\text{O}^{16}$  ratio, rather than in the absolute value of the ratio.

#### $\text{O}^{18}/\text{O}^{16}$ RATIOS AND WATER STUDIES

As an illustration of this isotopic effect, consider the implications of the fact that at room temperature the vapor pressure of  $\text{H}_2\text{O}^{16}$  is greater than that of  $\text{H}_2\text{O}^{18}$  by some 1 percent. The transfer of water in the meteorological cycle of the world is due to the processes of evaporation and condensation. If we keep in mind that, with each partial evaporation of a water body and with every partial condensation of water vapor in the atmosphere, there is an accompanying isotopic change in the resulting liquids and vapor, then we can readily understand that different rains, lakes, ocean waters, glaciers, and rivers have acquired an  $\text{O}^{18}/\text{O}^{16}$  ratio that is related to the detailed history of these waters in terms of the evaporation and condensation cycles.

The  $\text{O}^{18}/\text{O}^{16}$  ratios of the oceans are the least variable of these natural waters. Yet systematic differences in the isotopic composition of the oceans are measurable. Surface ocean waters in the warmer areas of the world are usually enriched in  $\text{H}_2\text{O}^{18}$



The range of the  $\text{O}^{18}/\text{O}^{16}$  ratios of precipitation at localities from different latitudes. The lengths of the bars represent about the maximum range in the  $\delta$  values in the designated locality.

because these waters suffer evaporation and are the main source of water vapor for the atmosphere. The cold ocean surfaces in the northern and southern areas are usually slightly enriched in  $\text{H}_2\text{O}^{16}$  because there is a resultant addition of fresh waters from rains, snow, and continental runoff.

An additional factor governing the  $\text{O}^{18}/\text{O}^{16}$  ratio of the ocean waters is the  $\text{O}^{18}/\text{O}^{16}$  ratio of the fresh water which is added or depleted from the surface of the oceans. For example, an ocean water sample collected at a depth of about 7,500 meters near the equatorial regions in the Atlantic Ocean showed a relatively normal salinity value, yet its  $\text{O}^{18}/\text{O}^{16}$  ratio was somewhat lower than might be expected for deep ocean water.

It was apparent that this sample could only have acquired its isotopic composition by being exposed to the surface at the polar areas and by receiving some melt water of unusually low  $\text{O}^{18}/\text{O}^{16}$  ratio and then becoming part of the sinking cold waters that reached as far as the equatorial latitudes.

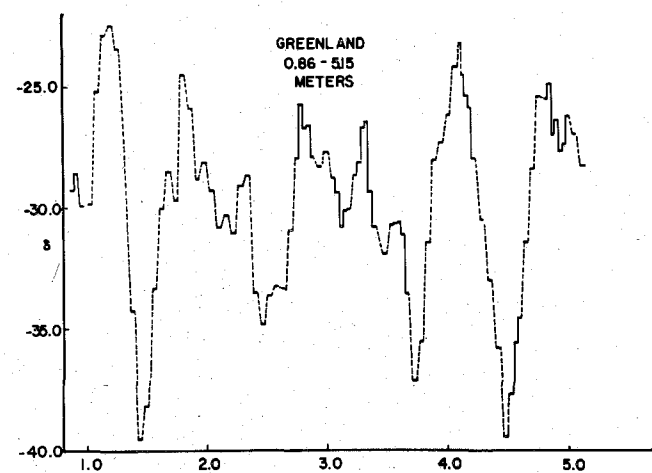
In summary, the isotopic composition of the ocean water represents a natural label which permits the tracing of horizontal and vertical ocean currents. Since the understanding of the movements of ocean water is of concern to physical oceanographers, isotopic surveys of ocean currents are important to the field of oceanography.

The isotopic compositions of water vapor in air masses and of precipitation are extremely variable, and are dependent upon the cooling and warming history of the air masses. Studies of the isotopic composition of water vapor in air samples and of the isotopic composition of rain and snow samples can give important and unique information about the movement of air masses and the history of moisture in the

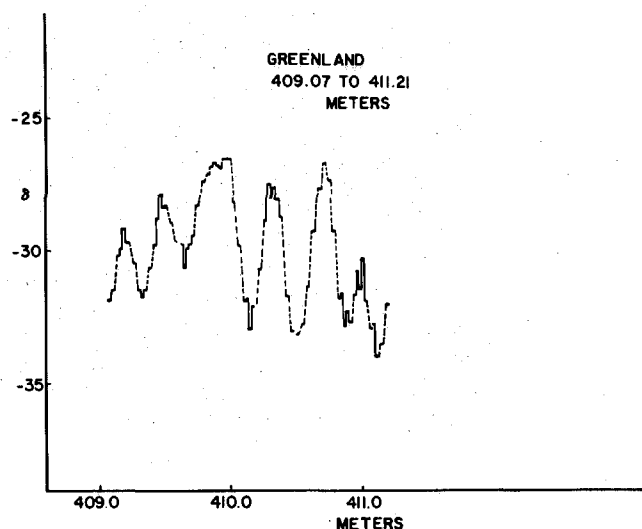
meteorological cycles. On a worldwide basis the  $O^{18}/O^{16}$  ratio of precipitation changes with latitude (left). Generally, the colder an area the less  $H_2O^{18}$  in the precipitation. In addition, the  $O^{18}/O^{16}$  ratio of precipitation falling on a single area such as Pasadena or Greenland displays a seasonal variation, and winter precipitation has less  $H_2O^{18}$  than summer precipitation. Because a mass of water vapor will preferentially lose  $H_2O^{18}$  during precipitation, a tropical air mass, as it cools on its complicated journey northwards, will continuously suffer preferential loss of  $H_2O^{18}$ . By the time such an air mass reaches Greenland, it will have lost a large fraction of its water vapor and suffered considerable depletion of  $H_2O^{18}$ . It is therefore understandable why Greenland's snow contains less  $H_2O^{18}$  than precipitation in more southerly areas.

This simplified picture also explains the seasonal variation observed in precipitation in a single area (below). It can be expected that an air mass arriving in Greenland will have been cooled to a lesser degree in summer than in winter, and thus will have suffered a lower loss in  $H_2O^{18}$  during the summer. The differences in the  $H_2O^{18}$  in summer and winter snow in Greenland are, in some cases, 150 times as great as the experimental precision.

These seasonal variations in the isotopic compositions of snows in Greenland and in the Antarctic have interesting implications in the studies of glaciology. Natural labels depicting summer and winter layers permit correlation of stratigraphic layers extending over many kilometers. The isotopic layering persists in Greenland to depths of at least 400 meters. The ability to identify layers in snow and ice assists glaciologists in studies of rates of snow accumulation, flow patterns, and the general



Seasonal effect observed in the  $O^{18}/O^{16}$  ratios in Greenland snow. The less negative values of  $\delta$  are for summer precipitation, and the most negative values are for the midwinter precipitation. The numbers on the abscissa represent the depth at which the samples are taken.



The variations with depth of the  $O^{18}/O^{16}$  ratios of Greenland ice taken from a depth ranging from 409.07 to 411.21 meters.

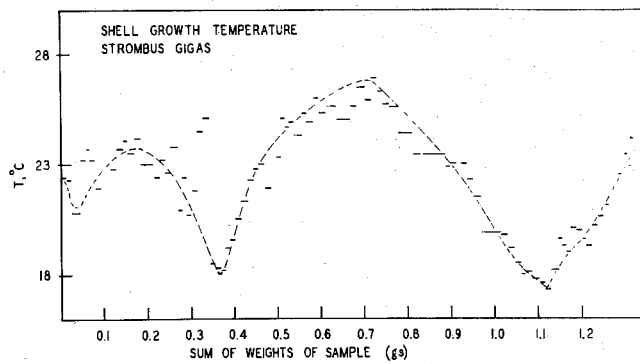
history of an ice cap.

Thus, a single difference in isotopic properties of water—the difference in vapor pressure of  $H_2O^{18}$  and  $H_2O^{16}$ —contributes to at least three different scientific fields, and more applications are possible.

#### TEMPERATURE STUDIES USING $O^{18}/O^{16}$ VARIATION

When two or more oxygen compounds are formed in isotopic equilibrium with one another, the  $O^{18}/O^{16}$  ratios of the oxygen in the compounds are usually different. The partition of the isotopes of oxygen is temperature-dependent. It is therefore possible to use the partition coefficient or the isotopic fractionation factor between two oxygen compounds as temperature indicators. Because it is difficult to change the oxygen isotopic composition in crystalline minerals, silicate minerals of common rocks and fossil carbonate skeletons are capable of preserving their isotopic composition of oxygen over millions of years. Thus, in many of these rocks and shells there are very old isotopic records of the temperatures of formation of the rocks and minerals or of the temperature of the ocean in which the animals laid their carbonate skeletons.

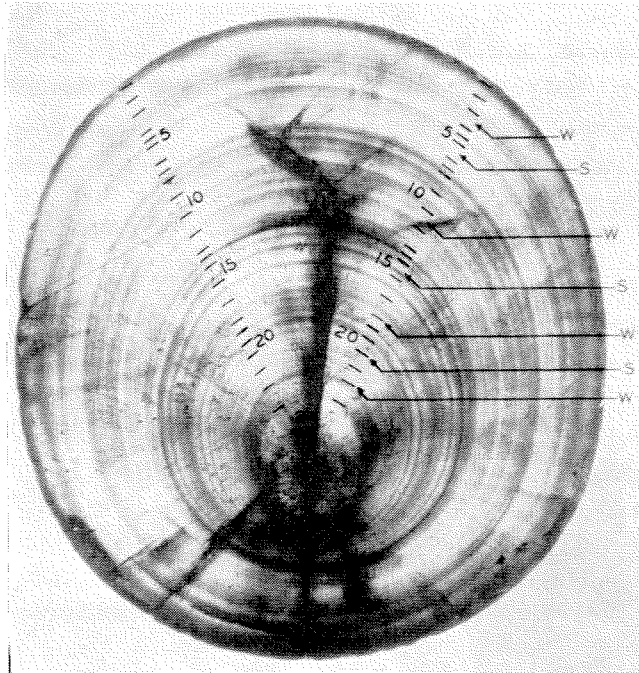
For example, the carbonate shell of a marine mussel, snail, or brachiopod has an  $O^{18}/O^{16}$  ratio 3 percent greater than does the water in which the animal grew. The  $O^{18}$  enrichment in the shell relative to that of the water decreases as the temperature increases. The precision of the mass spectrometer is such that we can measure a change in the  $O^{18}/O^{16}$  ratio equivalent to  $0.5^\circ\text{C}$  in growth temperature of a shell. By carefully grinding off the growth increments of a shell perpendicular to the growth lines,



The oxygen isotopic temperature record of increments of carbonate shell as sampled perpendicular to the growth lines. The length of each bar represents the weight of a sample ground off for several duplicate analyses. The average time interval represented by each bar could be a little over a week. (In collaboration with H. A. Lowenstam.)

we can get a series of samples representing growth periods of a few weeks.

Oxygen isotopic analysis of this series of increments provides a relatively detailed temperature record of the marine environment in which the shell grew. Such an isotopic temperature record can be observed in a recent snail, *Strombus gigas*, which grew off Bermuda in waters varying in temperature from a winter low of 18°C to a summer high of about 28°C. (Note above that the temperatures calculated from  $O^{18}/O^{16}$  ratio of the carbonate samples from the snail give a nice seasonal fluctuation.)



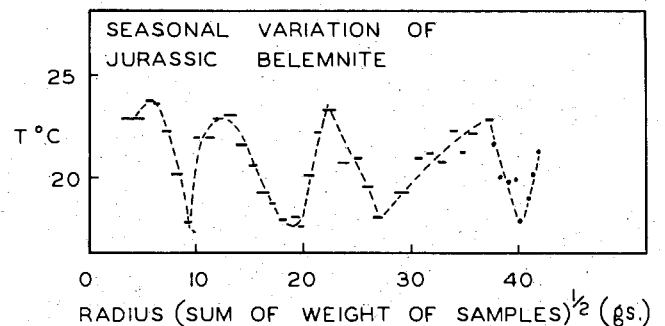
A cross section of a Jurassic Belemnite showing the growth rings and the sequence of cutting. The w's and s's designate the positions of the winter and summer calcium carbonate growth increments.

While there are many complications associated with shell growth, the isotopic data can be used to determine what time of the year animals lay down their shells, whether their growth habits change with age, and other factors.

If we go back in time about 120 million years and repeat the sampling procedure in a Jurassic Belemnite fossil (below), we can also observe a seasonal variation. The oxygen isotopic composition of this very old fossil tells us that the animal grew a shell over a four-year period. Incidentally, the presence of such a seasonal variation represents good evidence that the fossil carbonate that we analyzed is the original carbonate laid down by the animal, since it is not probable that the carbonate of a recrystallized shell would have such systematic variations. This method of measuring paleotemperatures was first developed by Harold Urey and his co-workers at the University of Chicago some 15 years ago and has been used for measuring Upper Cretaceous (60-90 million years ago) temperatures as well as temperatures of the oceans during the glacial periods in the Pleistocene.

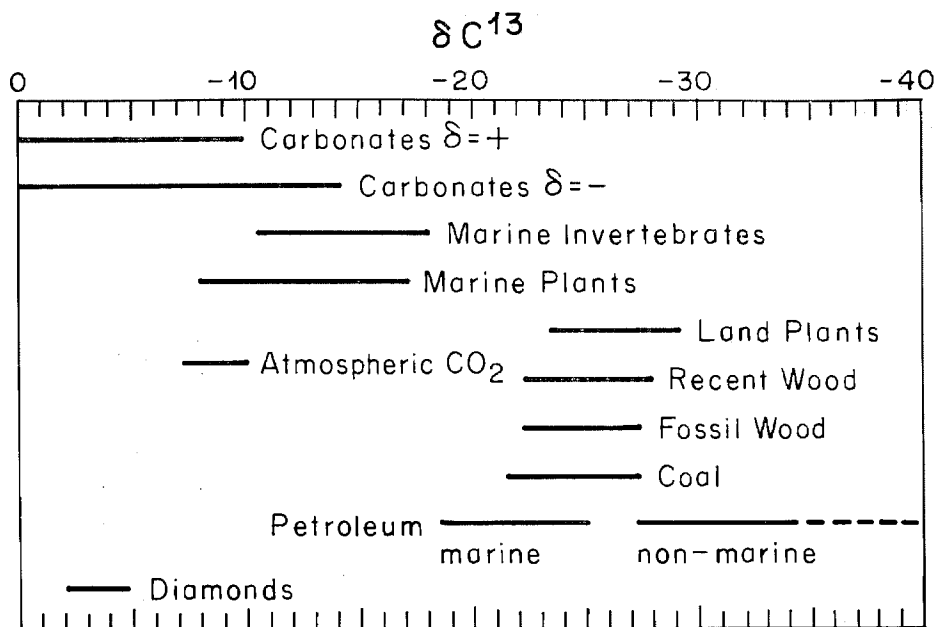
Since, in principle, any fractionation factor representing the partition of the  $O^{18}/O^{16}$  ratio between two oxygen compounds can give us a temperature, then the  $O^{18}/O^{16}$  ratio of coexisting silicates, oxides, and carbonates in rock samples can also serve this purpose. Indeed, the isotopic composition of coexisting minerals in common rocks has been used to determine a temperature of crystallization or of metamorphism of various rock types. The relationship between the fractionation factor and temperature is usually determined in the laboratory by equilibrating various minerals with water at different temperatures.

These simple examples illustrate our ability to use natural abundances of the isotopes of oxygen for labeling waters and measuring temperatures; however, we can safely state that the  $O^{18}/O^{16}$  ratio



The variations of the oxygen isotope temperature given by calcium carbonate increments with distance from the core of the Jurassic Belemnite. (In collaboration with H. C. Urey, H. A. Lowenstam, and C. R. McKinney.)

$\delta C^{13}$  values or  $C^{13}/C^{12}$  variations of carbon from various natural sources. (From Harmon Craig, UCSD.)



of any oxygen found in its natural habitat will give us some information about its origin and history. Atmospheric oxygen, for instance, has an  $O^{18}/O^{16}$  ratio unlike natural waters and unlike the oxygen given off by photosynthesizing plants. It is clear that the amount and isotopic composition of atmospheric oxygen depends on the amount of photosynthesis, respiration, oxidation of fuels, reaction with rocks, photochemical reactions, and volcanic emanation.

Associated with all these processes are accompanying isotopic fractionations, the studies of which will help us more fully understand the processes responsible for our atmospheric oxygen. Some work on this problem has already been done by Malcolm Dole of Northwestern University, but there is much promise of significant results in the continuation of this isotopic research.

Other common light elements, like hydrogen, carbon, and sulphur, have been studied isotopically, although less extensively than oxygen. Isotopic analysis of the  $C^{13}/C^{12}$  ratio in natural materials, as done by H. Craig of the University of California at San Diego (shown above), summarizes some of the isotopic geochemical studies. For example, the  $C^{13}/C^{12}$  ratio in terrestrial plants is low in relation to that of atmospheric  $CO_2$  because the photosynthetic process prefers to fix  $C^{12}O_2$  relative to  $C^{13}O_2$ . The  $C^{13}/C^{12}$  of the atmospheric  $CO_2$  is mainly determined by its equilibrium with the large amount of bicarbonate dissolved in the ocean.

The reason for the low  $C^{13}/C^{12}$  ratio for petroleum is not quite clear, but some speculations have been put forth. One is that petroleum originates from lipids, which are found in most marine and

non-marine plants. Lipids have a low  $C^{13}/C^{12}$  ratio relative to that of the rest of the plant, and are thus isotopically most similar to petroleum. If one is interested in processes involving carbon, there is a good likelihood that the understanding of the process can be enhanced by studying the isotopic fractionations associated with this process.

The isotopic variations in the  $S^{34}/S^{32}$  ratios in naturally occurring sulphides, sulphates, and sulphur have been measured in several laboratories, and this work has contributed significantly to the understanding of the origin of sulphur and sulphide ore deposits.

The  $H^2/H^1$  ratios in waters and minerals have also been studied, and the research should contribute significantly to studies of geochemical processes involving water and organic matter. The  $H^2/H^1$  and  $O^{18}/O^{16}$  ratios in waters usually vary in a parallel manner. When the isotopic variations deviate from this parallel behavior we obtain information about non-equilibrium evaporation and condensation and about the nature of waters that have interacted with rocks and minerals at depth and elevated temperatures.

There are many potential uses for earth scientists in measurements of isotopic abundance variations in the light elements. That such measurements have been useful in many other branches of science becomes obvious if we consider that many chemical and physical processes may have an associated isotopic fractionation and that the study of this isotopic fractionation can enhance the understanding of these processes. The little that has been done in the stable isotope field shows a promise for an expanded effort in the future.