GEOCHEMISTRY OF THE STABLE ISOTOPES

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A review is given of geologic investigations using stable isotopes and changes in their abundance. Many natural processes tend to concentrate particular isotopes by a factor of several percent. Four creationist applications arising from this natural isotopic enrichment are considered. First discussed are large scale errors in C^{14} radiometric dating of fresh water Mollusk shells due to C^{12} isotope exchange. It is shown that this age-determination uncertainty may also affect all other radiometric dating methods. Popular concepts of evaporite deposition and continental drift, that are dependent upon long geologic ages, are discussed. Recent stable isotope data which can be used to contradict these ideas is interpreted. The final application concerns information from extraterrestrial isotopes. Looking ahead, future research with stable isotopes will concentrate on paleotemperatures which may provide additional evidence for a preflood vapor canopy.

I. Introduction

The controversial use of radioactive isotopes for radiometric dating has continued to increase since they were discovered by J. J. Thomson in 1913.

A similar but less familiar study involves the *stable* isotopes. The absolute abundances of stable isotopes do not change with time as a consequence of radioactive decay. Distribution of these isotopes provides important geologic information; their study is termed stable isotope geochemistry.

In this report the notation and techniques of stable isotope measurements will be described in order to elucidate the current surge of geochemical literature. Experiments to be reviewed involve precise measurement of variations in isotopic abundances.

Insight into the conditions and importance of chemical, physical, and biological processes that have been operative in various geological environments is gained from these experiments. Emphasis will be given to current literature, especially regarding the validity of data interpretation and future trends in stable isotope research, which apply to scientific creationism.

II. Techniques

Components of the same chemical element with different masses are called isotopes. An element with atomic number (Z) may have several isotopes, depending on the number of neutrons (N) in the nucleus.

There are 273 naturally occurring stable isotopes associated with 81 elements. The abundance of stable isotopes for the elements hydrogen, carbon, and oxygen are listed in Table 1. The listed values are the average relative abundances as determined from wide sampling.

On a local scale, however, isotopes of these elements and the isotopes of the other light elements often exhibit measureable variations in abundance from one environment to another. The variation results from unequal partitioning of the isotopes of an element between two or more phases during natural processes due to differences of mass, vapor pressure, etc.

Hence in catalogs of isotopic abundances the warning is given that particular samples may have unusual isotope concentrations due to fractionation effects:

> The isotopic abundances listed are the current best estimate for the naturally occurring elements. However, samples have been observed for which the measured values differ significantly from those listed.[1]

This natural separation of isotopes is imitated in technology such as gaseous diffusion, where nuclear fuel is U^{235}-enriched.

As an example of natural isotope fractionation, consider the molecular constituents of water as listed in Table 2. The relative abundances are derived from Table 1. During evaporation of water the lighter molecules escape preferentially, so the water vapor is depleted in O^{18} and H^2 relative to the reservoir.

A comparative measurement, the isotope ratio normally reported is that of the heavier less abundant isotope to the lighter more abundant isotope such as O^{18}/O^{16}. The difference in the measured ratios between a sample and a standard then determines the extent of isotope fractionation that has occurred in the sample. In the literature this difference is conventionally expressed as a delta (δ) deviation between the sample and standard in parts per thousand (ppt),

$$\delta(O^{18}/O^{16})\ (\text{ppt}) = \left[\frac{\frac{O^{18}}{O^{16}}\ \text{sample}}{\frac{O^{18}}{O^{16}}\ \text{standard}} - 1\right] \cdot 10^3$$

Oxygen isotope deviations for a number of sources are summarized in Figure 1. The chosen standard with zero $\delta(O^{18}/O^{16})$ value is ocean water. Atmospheric water vapor usually has a δ value between –15 → 0 ppt, with values as low as –50 ppt (5% O^{18} depletion) in polar regions. The negative sign implies that evaporated water is depleted in O^{18} relative to sea water; the vapor is 0.0 → 1.5% lighter in O^{18} than the sea.

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Figure 1. Oxygen isotopic composition ranges for various samples. (References are shown by means of superscript numbers.)

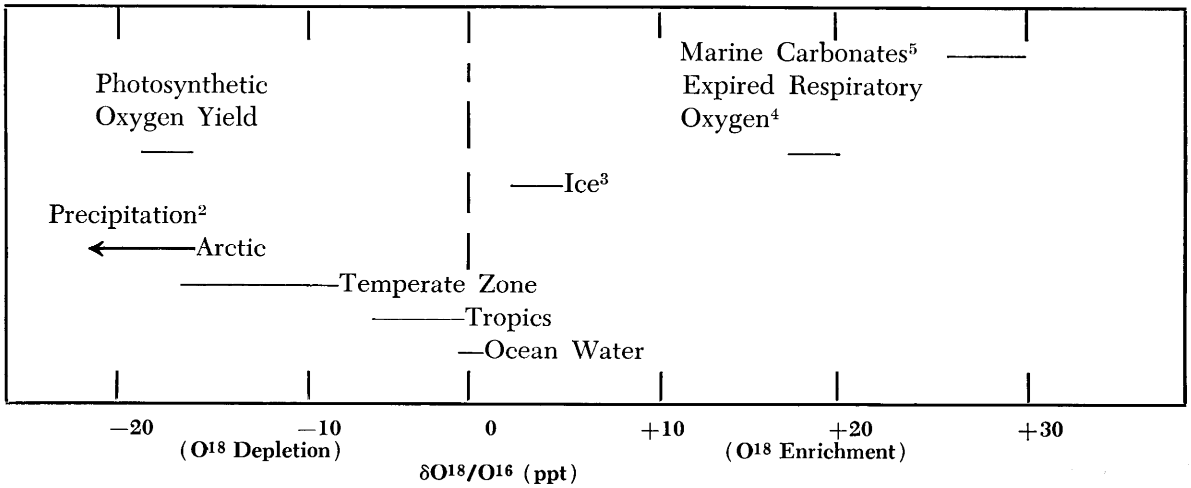

Table 1. Stable isotopes of hydrogen, carbon, and oxygen. Mass is given in atomic mass units.

Element	Z	N	Z + N	Atomic Mass (amu)	Atomic Percent Natural Abundance
H	1	0	1	1.007825	99.985
		1	2	2.01410	0.015
C	6	6	12	12.00000	98.89
		7	13	13.00335	1.11
O	8	8	16	15.99491	99.759
		9	17	16.99914	0.037
		10	18	17.99916	0.204

Table 2. Nine varieties of molecules present in water.

Molecule	Molecular Mass (amu)	Approximate Relative Abundance
$H^1{}_2O^{16}$	18.01056	10^6
$H^1{}_2O^{17}$	19.01479	370
$H^1H^2O^{16}$	19.01684	300
$H^1{}_2O^{18}$	20.01481	2040
Trace molecules with small relative abundance: $H^2{}_2O^{16}$, $H^2{}_2O^{17}$, $H^2{}_2O^{18}$ $H^1H^2O^{17}$, $H^1H^2O^{18}$		

The heavy isotope content of water vapor is additionally depleted by precipitation as the water vapor is carried North by atmospheric circulation, as is shown in Figure 1. Other complex details can be studied in this way: the range of values for atmospheric water also results from seasonal, altitude, and temperature effects.[2] Other interesting examples of isotope fractionation appear in Figure 1:

1. Ice preferentially holds heavy O^{18} atoms, relative to local water.[3]

2. Plants prefer to fix and use O^{18} rather than O^{16} or O^{17} during photosynthesis. This is balanced by respiration, which consumes oxygen containing a lower O^{18}/O^{16} ratio than that of the atmosphere. The O^{18}/O^{16} ratio of the atmosphere has dropped to a point such that the ratios for photosynthetic oxygen delivered to the air and the oxygen extracted from the air by respiration are equal.[4]

3. Carbonates precipitated in oceans become enriched in heavy O^{18} relative to sea water. The O^{18} content increases with the strength of the oxygen-cation bond. Therefore O^{18} is concentrated in quartz and dolomite relative to other silicates and carbonates.[5]

These isotope effects are widespread and not limited to oxygen. During photosynthesis, plants[6] also fix C^{12} rather than C^{13} or C^{14}. Relative to atmospheric CO_2 plants are enriched in C^{12} by 1 → 1.8%. These land plants eventually give rise to isotopically light humus in rivers and lakes (Section III A).

Actual delta δ determinations are made with a high precision isotope mass spectrometer. Quantitative analysis of the isotopic content relative to the standard is determined for each sample. The difficult experiment requires 100% conversion of the sample into a gas followed by ionization, mass separation, and detection. Present methods resolve δ variations as small as ±0.0001 ppt, or $10^{-5}\%$.

As can be seen from Table 2, absolute isotopic abundances are not nearly as well known as the comparative ratios, a common situation in physical measurements. Isotope fractionation can be predicted and calculated, as shown in a classic 1954 reference in which the basis of stable isotope geochemistry was given.[7]

III. Application

A. Radiocarbon Dating Errors

Many applications may be made of light isotope fractionation. There is presently an active effort to improve instrument resolution and solve a variety of geologic problems. Four typical geochemistry experiments that involve creation research will be discussed, beginning with age measurements.

Mollusk shells generally yield radiocarbon ages which are anomalously large. Especially true of fresh water shells, one study of *living* fluvial mollusks gave an average radiocarbon age of 1733 years.[6] This discrepancy is now understood to be the result of an extreme shell deficiency in radioactive C^{14} due to carbon isotope fractionation effects.

Modern mollusk shells have a C^{14}/C^{13} ratio as much as 2.5% smaller than the same ratio for modern wood. The reason for the lack of C^{14} is the incorporation of inactive (C^{14}-- deficient) carbon from humus through the food web as well as carbon dioxide from humus decay. Present attempts to correct for this source of error in radiocarbon shell dating are very uncertain.

Troubles arise from other possible sources of carbon for shells including dissolved atmospheric CO_2 and dissolved limestone. A similar fractionation correction must be made for all C^{14} dating, including that of wood.

In wood analysis the situation is somewhat better since the soil and atmospheric sources of carbon are better known. The question of possible atmospheric carbon variation in the past is a separate problem.

Do Rb^{87}, U^{235}, or K^{40} fractionation effects invalidate other radiometric dating methods? Consider one possibility:

> A potassium-rich magma crystallizes to form an ingneous rock. Gaseous Ar^{40} begins to accumulate as a stable decay product of K^{40}. The K^{40}/Ar^{40} ratio is therefore a basic measure of the time interval since crystallization. But isotope exchange may also occur. Suppose that the rocks adjoining the sample have a preference for light isotopes of a given element. Gaseous diffusion exchange can then occur whereby the sample loses intrinsic Ar^{36} and gains additional Ar^{40} from the geological environment. This and other non-decay contributions of Ar^{40} would lead to a long and incorrect sample age by K^{40}/Ar^{40} dating, just as with the Mollusk shells.

Whether or not $Ar^{40} \longleftrightarrow Ar^{36}$ exchange really occurs in nature is not known. Exchange is difficult to detect for the heavy elements. The delta values are too small to be studied by present spectrometry.

Nevertheless such slight effects would strongly control the radiometric age of samples. Improved technology which resolves heavy element isotope fractionation will likely lead to important dating corrections for the heavy isotope radiometric methods.

B. Origin of Evaporites

Oxygen isotope effects have been used to support the conclusion that the Mediterranean Sea has repeatedly evaporated to a desert basin during the span of geologic "history." Samples of evaporite mineral deposits beneath the sea have been obtained by means of the deep sea drilling vessel, Glomar Challenger:

> The ratio of oxygen 18 to oxygen 16 in a sample can reveal its genesis. Evaporites precipitated from evaporated sea water have a narrow range of isotopic compositions. In contrast, those deposited on playas, or desert lakes, have a wide range of values. Analysis of Glomar Challenger Mediterranean samples shows a high variability of isotopic composition and thus provides additional confirmation of their playa origin.[8]

The reasoning here is that $H^1{}_2O^{16}$ escapes preferentially during sea evaporation, and the remaining surface waters should be isotopically homogeneous because of mixing currents.

Contrarily, in desert lakes, there is a lack of water movement and therefore little mixing. Large isotopic differences might build up between regions of the lake depending on patterns of evaporation and precipitation.

However these conclusions are not in agreement with those of Lloyd,[9] who found no isotopic differences in evaporation from seas, ponds, and small vessels during his experiments. Isotopic variability in evaporation has been obtained in results of other experimenters.[10]

Thus the interpretation of isotope concentrations found in Mediterranean evaporites is uncertain. The fractionation may well have some explanation other than the drying up of the Mediterranean Sea.

The article by Hsü contains many other interesting geological finds and conclusions. Like the isotope results, however, the facts must be carefully interpreted. No doubt the Deep Sea Drilling Project will prove to be a continuing and exciting source of data for examination in the light of biblical creation.

Now the assumption that seas containing evaporites have dried up repeatedly should be considered. Evaporite salt domes on the Gulf Coast have been analyzed isotopically for caprock sulfur which occurs atop the domes. The same S^{32}/S^{34} ratio is found throughout the region:

> It thus seems likely that all domes come from a single evaporite sequence rather than from a series of evaporation beds of widely different ages.[11]

Thus even if large scale evaporation is assumed in the Gulf Coast area, there is no isotopic evidence for a *repetition* of the event.

At this time the formation of evaporites in the Mediterranean Sea and elsewhere around the world is little understood, with a variety of possible explanations. Some believe these seas were once shallow and continental in character and have since sunk. On the other hand, according to geophysical data the structure beneath these seas is oceanic rather than continental.[12]

A second interesting view of evaporite formation is based on a wind model by which salt precipitation is predicted without large-scale evaporation of water.[13] A third interpretation is that natural floodgates opened and closed on these seas in the past, leading to periodic evaporation.[14]

Of course evaporite basins are rare today; evaporite deposits are forming at a rate much slower than the necessary rate assumed throughout geological ages.[15] This has led some to consider a catastrophic origin of evaporites, perhaps connected with the appearance of glaciers.[16]

C. *Continental Drift*

A test of the concept of continental drift may be based on the distribution of stable isotopes. Continental drift involves ideas that the Americas, over geologic time, have relatively drifted away from Europe and Africa. The isotope application is given the name paleothermometry, the study of ancient temperatures.[17]

Isotope effects are temperature dependent. For example rocks crystallized at higher temperatures have relatively lower $\delta O^{18}/O^{16}$ values and a narrower range of δ variability.[16] Thus rock samples from continental coast lines contain a possible record of local climates in the past.

Comparative results for samples from many coasts thus far have indicated that continental climates have been very different historically. There is no climatological evidence that land masses now separated were once joined.[18] Additional worldwide paleoclimate data is being collected in the search for possible drift correlations.

In spite of wide acceptance of the continental drift model, even the much-publicized sea floor paleomagnetic data is evaluated as containing uncertain results. Interpretations of the magnetic data depend on the postulate that the earth's field has always been axial, a suspect assumption.

A better interpretation of data may be based on a quadrupole field concept.[19] In addition, the geographic distribution of evaporite deposits (Section III B) has been used to argue that continents have not changed position since earliest geologic time.[18] Thus the interesting proposal of continental drift (global tectonics) remains open to further evidence.

D. *Isotopes of the Moon and Meteorites*

The great interest in the isotopic composition of rocks from the moon has been a major impetus for returning lunar samples to earth for analysis. The search for organic material has not been successful: only traces of carbon (less than 0.001%) have been found. Water remains totally undetected.

Completed isotope studies show the creative similarity of the earth and moon. Fractionation δ values for a variety of lunar rocks and minerals are remarkably constant and identical with terrestrial values.[20]

Comets are of special interest since the age of the solar system can be dated according to the decay of the comet population.[21] Based on the accepted geologic time scale, astronomers still have difficulty postulating a continuing source of comets to replenish the supply:

> Sad to say, few theories of cometary origin exist, and fewer still are even partially convincing.[22]

Thus the presence of comets remains a strong challenge to popular long estimates of our solar system's age.

Isotope measurements have been made on meteorites, some of which may be debris from disintegrating comets. Thus far a large range of δ values has been found for meteorites and tektites.

The δ values are unlike those of earth or moon; therefore, the deduction suggested by some scientists, that the moon is not the source of meteorites, is quite logical. If the investigated meteorites are really comet debris, then comet material also is unlike the earth or moon. The significance of this is not known.

IV. Future Geochemical Research

Stable isotope geochemistry is a field which is increasing rapidly in popularity and data. Paleothermometry, a technique receiving current emphasis, has already been mentioned with respect to the continental drift model (Section III C).

Studies have been made of earth temperature fluctuations dating back to the earth's origin. A typical finding is that the earth's average temperature was warmer "80 million years ago" than it is today.[17]

When temperature history is checked by such stable isotope methods, rocks are dated according to the supposed sequence in which specific fossils lived. This is the usual unjustified circular reasoning assumption.

Thus the actual time dependence of the temperature data is very questionable. In fact some scientists reject the validity of paleothermometers because of complicating factors in isotope fractionation.[19]

However, the measureable δ factor for a given sample is dependent on the temperature at time of formation. This may be a useful tool for the creationist.

If the worldwide study of rocks results in more data to support the concept of a warm earth in the past, as initially suggested, then a vapor canopy is one valid explanation. The preflood existence of a water vapor shield surrounding the earth could be a very useful interpretation of Genesis passages and other geological data.[23]

Geochemistry will continue to be a source of checks on radiometric dating, as in the case of the Mollusk shells. One final example in this area involves comparative isotope measurements for limestones of recent origin and of assumed Precambrian (1 billion years) vintage.[24] The measured δ values are the same, much to the puzzlement of those who had predicted large δ differences arising during the time span. The validity of the geologic time scale may be challenged again on the basis of these results.

The stable isotope fractionation method presented here is one of many new and powerful research techniques. Efforts must be made to understand these experiments in order to realize their weaknesses and their valid applications to scientific creationism.

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