Reports

Oxygen-18 Content of Atmospheric Precipitation during Last 11,000 Years in the Great Lakes Region

Abstract. *Freshwater lake marl and mollusks from Indiana show variations in ratios of oxygen-18 to oxygen-16 of a few per mil during the Postglacial. For the last 9000 years these variations are about 1 per mil for properly selected lake sediments. Thus the oxygen isotope composition of atmospheric precipitation appears relatively stable over this interval, indicating stationary atmospheric circulation patterns over the Great Lakes region. A reduction in oxygen-18 content around 10,000 years ago corresponds with the climate change indicated by pollen profiles. Large systematic differences were found between carbon-13 and oxygen-18 content of marl and mollusks.*

Isotopic paleotemperatures of marine carbonates and calcareous fossils have been measured and discussed extensively since 1947 when Urey (*1*) proposed a suitable "thermometer." This method is based on the temperature dependence of fractionation of the oxygen isotopes in the carbon dioxide-water-carbonate system. During slow precipitation of the carbonate the temperature of the solution is reflected in the ratio of the oxygen isotopes in the carbonate and can be determined by measuring this ratio with a mass spectrometer of suitable precision.

The ratio of O^{18} to O^{16} isotopes in the precipitated carbonate not only depends on temperature, but also on the ratio of O^{18} to O^{16} isotopes in the water in which the carbonate is formed. The measured difference in the ratio of O^{18} to O^{16} isotopes between a carbonate fossil and a contemporaneous sample is the result of changes in both temperature and composition of water isotopes. An estimate of the change in composition of oxygen isotopes of the water is needed before any paleotemperature determination can be made.

The changes in composition of the oxygen isotopes of the water are important even in the large ocean reservoirs. During Pleistocene glacial times large amounts of O^{18}-deficient water were stored in ice caps, resulting in ratios of O^{18} to O^{16} for ocean water higher than those presently encountered. Emiliani (*2*) estimates the maximum increase in O^{18} content of ocean water at about 0.5 per mil for the glacial periods. The difference in ratio of the oxygen isotopes, between interglacial and glacial marine carbonates formed in the Caribbean and equatorial Atlantic surface waters is about 1.6 per mil, leaving a net increase of about 1.1 per mil (about 5°C) due to temperature changes of the surface ocean waters. Shackleton (*3*), on the other hand, presented evidence that the larger part of the total difference of about 1.6 per mil might be due to only the variation in composition of the water isotopes. This would indicate Pleistocene temperature fluctuations of appreciably smaller magnitude than 5°C for the Caribbean and equatorial Atlantic surface waters.

With these divergent results for the large ocean reservoirs, it is not surprising that carbonates precipitated in lakes have been considered unsuitable for determinations of paleotemperatures. Long-term variations in isotope composition of the smaller freshwater reservoirs will be larger than those in marine waters, and short-term variations are more likely. However, under certain conditions, it is possible to arrive indirectly at an estimate of paleotemperatures by considering the change in composition of oxygen isotopes of the water itself.

The relative abundance of the O^{18} and O^{16} isotopes in atmospheric precipitation is mainly determined by fractionation of oxygen isotopes during preceding evaporation and condensation events. The final fractionation of oxygen isotopes is the result of multistage processes, with the number of stages depending on the temperature drop, $T_s - T_{oc}$, between the site of evaporation (the subtropical ocean with temperature T_{oc}) and the site of precipitation (temperature T_s) (*4*). A linear relation between mean annual temperature at the earth's surface and the annual mean of the ratio of the O^{18} to O^{16} isotopes has been demonstrated for oceanic stations of the atmospheric precipitation (*4*). For each change of 1°C in average annual temperature at the earth's surface, the ratio of O^{18} to O^{16} changes, on the average, 0.70 per mil; a reduction in temperature corresponds with a reduction in O^{18} content.

Long-term climatic changes should result in similar variations in composition of oxygen isotopes of atmospheric precipitation at a fixed coastal locality. In addition to the change associated with the temperature difference $T_s - T_{oc}$, one may expect variations caused by a change in atmospheric circulation patterns. In the latter case, air masses flowing from different regions conceivably might produce precipitation with different ratios in the oxygen isotopes. For present-day conditions, the relation between mean annual temperature and the ratio of the oxygen isotopes is influenced somewhat by the various atmospheric circulation patterns, but as a first approximation one may expect during a climatic change an average change of 0.70 per mil in oxygen isotope ratio for each change of 1°C in temperature difference $T_s - T_{oc}$.

The long-term variations in composition of oxygen isotopes of freshwater lakes are reflected in the ratios of O^{18} to O^{16} of carbonates precipitated in those lakes. The isotope ratio of the water comes into play through exchange of oxygen isotopes between dissolved carbon dioxide, bicarbonate, carbonate ion, and the larger water reservoir; this exchange is relatively fast, and isotope equilibrium between those components is nearly always attained for natural waters. The resulting isotope composition of precipitated carbonate is not entirely identical to the composition of the water isotopes because the exchange equilibriums tend to enrich bicarbonate and carbonate ion in O^{18} with respect to water. Slowly precipitated carbonate, in turn, is enriched in O^{18} with respect to carbonate ion. The temperature dependence of the fractionation of the oxygen isotope in this water-carbonate system is the basis of the Urey method of measurement of paleotemperatures. For complete isotope equilibrium the ratio of O^{18} to O^{16} of the formed carbonate increases with 0.24 per mil (*5*) for each decrease of 1°C in temperature of the solution. For a certain locality where a climatic change reduces the temperature T_s, the ratios of O^{18} to O^{16} of the formed carbonate will therefore increase through this chemical effect.

The increase in O^{18} content (ΔO^{18}_{oc}) of the oceans during glacial periods should also be reflected in the O^{18} content of atmospheric precipitation. With the above defined quantities the resulting change in O^{18} content of the freshwater carbonates (ΔO^{18}) can be given as

$$\Delta O^{18} = \Delta O^{18}_{OC} - 0.70\Delta(T_S - T_{OC}) + 0.24\ T_S$$

If the changes in ocean temperature and O^{18} content are known, this equation can be used to determine the change in paleotemperature T_s at coastal localities. It should be emphasized that this relation can only be used to obtain estimates and is not intended for very precise determinations (*5a*).

Unfortunately, the first core used for the study of isotopic variations in coastal areas (Logan Lake, Maine) gave incomplete results, because the time span covered was too short. Therefore I now report results for the Great Lakes area where the situation is more complicated. The exact change in ratio of oxygen isotopes of atmospheric precipitation as a function of mean annual temperature is not known for the Great Lakes region, but an estimate can be made by considering the seasonal variations in precipitation of the ratio of oxygen isotopes. These variations amount to 8.6 per mil for Chicago (*4*), where mean temperature differences for July to January are 28°C. This indicates a smaller gradient of 0.3 per mil per 1°C and results in the equation:

$$\Delta O^{18} = \Delta O^{18}_{OC} - 0.30\Delta(T_S - T_{OC}) + 0.24\ \Delta T_S$$

or

$$\Delta O^{18} \approx \Delta O^{18}_{OC} + 0.30\ \Delta T_{OC}$$

This estimate is not very precise due to the uncertainty in the gradient discussed above, yet it is clear that for long-term changes in climate, the expected variations are mainly determined by changes in the ocean. These variations are small, and any large variation in isotope ratio of freshwater carbonates during the Postglacial has to be attributed to other causes, that is, a change in atmospheric circulation or a change in evaporation rate.

An additional complication encountered for the analyzed core (Pretty Lake, Indiana) is the possibility of evaporation of water in the lake, resulting in high content of C^{13} and O^{18} in the remaining lake water. The C^{13} and O^{18} contents of the mollusks in the Pretty Lake core are larger than those found in a group of freshwater mollusks from the Great Lakes region as analyzed by Keith *et al.* (*6*). Pretty Lake is small, more or less square, with sides of approximately 1 km. Local runoff seems to be the major source of water, because there is no apparent inlet. The outlet during the summer months is a trickle of water whereas surface temperatures in the lake easily reach 25°C during hot spells in the summer months. Enrichment in C^{13} and O^{18} through evaporation of part of the lake water seems likely, and a series of water samples from a large number of lakes and ponds has been collected in order to investigate the evaporation effects in this area in more detail.

The effects of evaporation are such that a reduction in temperature results in a smaller enrichment of O^{18} in the lake water, and consequently lower O^{18} contents can be expected during the early Postglacial. However, the absolute magnitude of this effect is not known.

The most extensive and least interrupted carbonate deposits in lakes consist of marl, a finely divided crystalline carbonate occasionally interspersed with fragments of mollusks, ostracodes, and charophytes. These deposits are often in the form of mounds (bioherms) rising from the bottom of the lake to within 1 or 2 m of the lake surface. The Pretty Lake core discussed here is from such a shallow water environment. The precipitation of marl in lake waters is governed by the CO_2-bicarbonate-carbonate system and is best illustrated by the equation:

$$CaCO_3 + CO_2 + H_2O = Ca^{++} + 2\ HCO_3^-$$

Through photosynthesis the CO_2 in the water is depleted, resulting in a shift of equilibrium toward the left. Half of the carbon in the bicarbonate, which reassociates, will provide a new CO_2 supply; the other half will be precipitated as calcium carbonate. The tops of marl mounds are normally in the photic zone and the production of the "photosynthetic" carbonate seems to be the major factor in their growth. Temperature, CO_2 partial pressure, *p*H, and the contents of other dissolved substances all seem to play a part, next to photosynthesis, in the precipitation of calcium carbonate (*7*).

Fifty milligrams of crystalline material, obtained through microscopical sorting, was used for analysis of oxygen isotopes. Whenever possible, shell fragments were obtained from the same samples. Sorting with regard to species was not possible because of the scarcity of mollusks in the core. The organic material in the carbonate was charred for about 30 minutes under vacuum at a temperature of 420°C. A Nuclide mass spectrometer (R.M.S.-2) was used for the analysis of oxygen and carbon isotopes (Fig. 1). All C^{14} ages in Fig. 1 have been corrected for the C^{14} deficiency of the lake water by deducting the approximate age of organic material deposited in the center of the lake a few decades ago. The correction is only approximate because the C^{14} deficiency in a lake is not necessarily constant with time. However, age errors exceeding a few hundred years seem unlikely (*8*).

A striking feature of Fig. 1 is the small spread in ratios of the oxygen isotopes amounting to about 1 per mil between 2500 and 9000 years ago. This raises the issue of recrystallization of the carbonate and the associated reequilibration with water, resulting in a homogeneous distribution of the oxygen isotopes reflecting the composition of water isotopes at the time of reequilibration. This mechanism seems unlikely however. The mollusk fragments are predominantly aragonite, and recrystallization should convert the carbonate to the more stable calcite form. Thus the mollusks evidently still reflect the original isotope ratio. The parallelism of the curves in Fig. 1 for the precipitated carbonate, which is nearly all calcite, and the mollusk fragments implies that reequilibration of the marl fraction is also unlikely. In addition, mollusks in a core from Lake Chichancanab, Yucatan, Mexico, exhibit variations in ratio of O^{18} to O^{16} of at least 8 per mil, clearly demonstrating that for this core reequilibration did not occur under comparable conditions over a 6000-year interval.

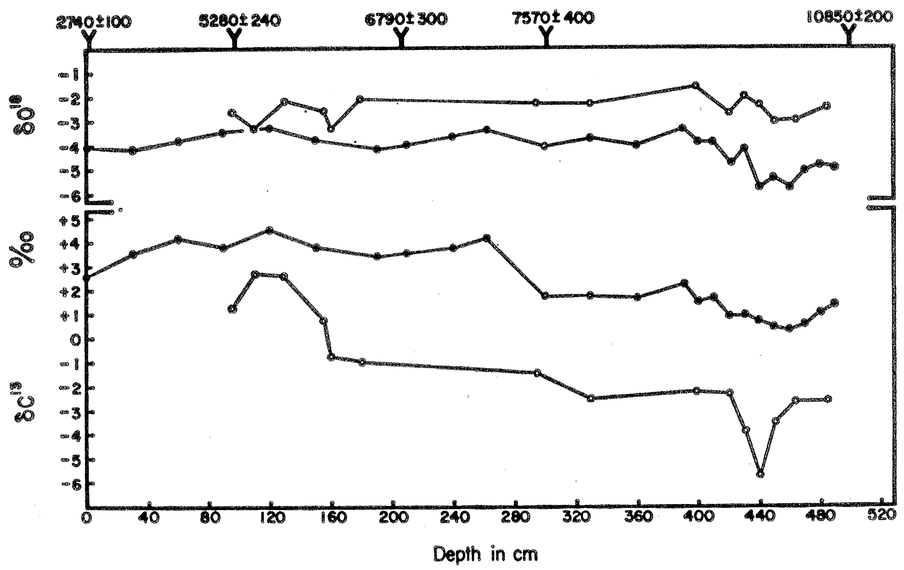

Fig. 1. Relative O^{18} and C^{13} content of marl and mollusks as a function of depth for Pretty Lake, Indiana; δO^{18} and δC^{13} represent the per mil deviation from the PDB standard. Solid points are for marl; open circles for mollusk data. Carbon-14 ages for the organic fractions are given in top row.

Marine shells (*9*), and most likely also freshwater mollusks, are formed in isotope equilibrium with the surrounding water. When isotope equilibrium is achieved, the results presented in Fig. 1 can be converted to the SMOW standard usually employed for waters. A relatively simple comparison can be made by using the results of Epstein *et al.* (*9*). Carbonate formed at 17°C in equilibrium with ocean water averaging 0.0 per mil with regard to SMOW have a δO^{18} value of 0.0 per mil with regard to PDB (*10*). For the mollusks formed in Pretty Lake in the last 9000 years the δO^{18} value is around -2 per mil on the PDB scale with estimated summer water temperatures somewhat higher. This indicates δO^{18} values for the water of about 0 per mil with regard to SMOW. Summer conditions should be reflected as mollusks and marl are formed predominantly during the summer. Dansgaard (*4*) determined a value of -4 per mil with regard to SMOW for atmospheric precipitation observed during one summer in the Chicago area. The value of 0 per mil derived from the measurements of mollusks indicate an enrichment in O^{18} content through evaporation of at least 4 per mil and probably more as the water entering the lake is not representative of summer precipitation only.

The mode of precipitation of carbonate from an aqueous carbonate-bicarbonate solution strongly influences the oxygen isotope composition of the precipitated carbonate. For rapidly forming precipitates McGrea (*5*) found that the isotope composition equals the average of the oxygen present in the carbonate ions and bicarbonate at the time of precipitation. Under these conditions the isotope composition of the carbonate depends on the proportion of carbonate in the carbonate and bicarbonate of the aqueous solution. For slowly forming precipitates there is time for each layer of calcium carbonate formed to reach equilibrium between the solid state and the solution, and isotope fractionation between carbonate ion in solution and carbonate occurs.

This mechanism could be responsible for the systematic difference of about 2 per mil in ratio of O^{18} to O^{16} between mollusks and crystalline carbonate if the marl precipitation is accomplished in a few seconds. Under those circumstances the rapidly precipitated marl attains incomplete isotope equlibrium and reflects the oxygen isotope composition of the carbonate and bicarbonate more directly. Whether such rapid precipitation actually occurs in nature is questionable and the difference in O^{18} content of both components remains somewhat puzzling. Postdepositional exchange between marl carbonate and water is considered unlikely but cannot be disregarded completely. It is also possible that the mollusks were formed at lower temperatures (during the spring) and the marl at higher temperatures (during the summer).

Whereas the crystalline carbonate fraction is systematically depleted by about 2 per mil in O^{18} content with regard to the mollusks, it is enriched by about 4 per mil in C^{13} (Fig. 1). This enrichment is perhaps associated with photosynthesis (*11*). The aquatic plants preferentially extract isotopically light carbon during photosynthesis, and the precipitated crystalline carbonate consequently may be enriched in C^{13} with regard to the average C^{13} content of the bicarbonate in the lake water. If the solution from which the marl precipitates is protected from rapid mixing with the lake water, the marl will be enriched in C^{13} with regard to the mollusks. However, incorporation in the shell of carbon dioxide obtained from C^{13}-deficient food seems also possible (*6*).

The ratios of C^{13} to C^{12} and O^{18} to O^{16} of the crystalline carbonate in Fig. 1 are correlated such that for the smaller variations low C^{13} content generally is associated with low O^{18} content. A more pronounced correlation has been found for two other lakes (*12*). Evaporation effects may be responsible for this correlation, although a similar relation between ratios of the carbon and oxygen isotopes has been found by Keith and Weber for carbonates deposited by modern algae in marine waters (*13*), and by Labeyrie *et al.* for carbonates deposited in caves (*14*). The basic mechanism causing this correlation is not clear.

The long term trend for the ratio of C^{13} to C^{12} indicates an increase in C^{13} content of the lake bicarbonate of about 4 per mil over the last 11,000 years. This long-term increase may reflect an increase in photosynthesis, a reduction in oxidation of organic matter which is depleted in C^{13}, or a change in equilibrium between lake-water bicarbonate and atmospheric CO_2.

The top part of the Pretty Lake core is evidently missing. However, results for Green Lake, New York, indicate variations in ratio of O^{18} to O^{16} of less than 1 per mil for the last 2500 years (*12*). These results and those for Pretty Lake suggest that variations in average isotope ratio of the lake water have been smaller than 1 per mil for this region during the past 9000 years. The O^{18} content of the water, and thus atmospheric precipitation, evidently fluctuated between narrow limits, and factors that could induce important additional variations have obviously been small.

The small change in isotope ratio of the carbonates encountered for the past

9000 years indicates rather stable atmospheric circulation patterns for this part of North America. If there had been any significant change during this period one would not expect a nearly constant oxygen isotope ratio. There remains the possibility that two or more variables cancel each other, but such a mechanism seems unlikely.

A drop in O^{18} and O^{16} content of about 1.8 per mil for the precipitated carbonate (somewhat less for the mollusks) is encountered between depth of 390 and 440 cm. The reduction in O^{18} content indicates colder conditions, that is, if one assumes the most likely cause to be a change in evaporation rate associated with a change in average summer temperature. A change in temperature around this time is also indicated by pollen studies of the same Pretty Lake core (*15*). This core, as well as other published pollen profiles for Indiana localities, shows a disappearance of spruce pollen (A-zone) followed by a sharp pine maximum (B-zone), which in turn is replaced by an oak and elm maximum (C-zone). The replacement of conifers by deciduous trees in the Great Lakes region is generally associated with a change in climate. For the Pretty Lake core the only possible important change in climate indicated by the oxygen ratios is between 440 and 390 cm of depth. The pine maximum in this core is between 470 and 400 cm, and the subsequent decline in pine and replacement by oak between depth of 400 and 350 cm seems to be a response to the change in climate, as indicated by the oxygen isotope ratios. In this instance, evidently about 500 years were needed by the forest vegetation to establish a new equilibrium.

The replacement of spruce by pine at around 480 cm depth does not seem to be correlative with any important change in ratio of O^{18} to O^{16}. There remains the possibility that such a change would be noticeable in a longer core.

In view of the many factors causing possible oxygen isotope composition changes in small freshwater reservoirs, it is not feasible to attach much significance to the small variations encountered in the Pretty Lake core over the last 11,000 years. However, the variations are surprisingly small and restrict the extent of possible atmospheric circulation pattern changes.

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Uranium Disequilibrium in Groundwater: An Isotope Dilution Approach in Hydrologic Investigations

Abstract. *The distribution and environmental disequilibrium patterns of naturally occurring uranium isotopes (U^{234} and U^{238}) in waters of the Floridan aquifer suggest that variations in the ratios of isotopic activity and concentrations can be used quantitatively to evaluate mixing proportions of waters from differing sources. Uranium is probably unique in its potential for this approach, which seems to have general usefulness in hydrologic investigations.*

In closed geological systems older than about 10^6 years, U^{234} will have achieved radioactive equilibrium with its parent, U^{238}; that is, their alpha activity ratio is 1.00. However, in open systems exposed to weathering and the circulation of groundwater, separation of these two isotopes can occur, giving rise to a state of radioactive disequilibrium (*1–3*).

The observed U^{234}/U^{238} disequilibrium is the result of the formation of U^{234} from the alpha and beta decay of U^{238}. Suggested physicochemical mechanisms include nuclear recoil-induced bond breakage, displacement of the U^{234} daughter within the crystal structure, and preferential attainment of the +6 valence for U^{234}, resulting in the increased mobility and preferential leaching of U^{234} with respect to U^{238} (*1, 4*). The ratio of U^{234} to U^{238} in many natural waters, including most rivers, is greater than 1.00, with the oceans having a 15 percent excess of U^{234} (*3, 5*). However, waters with an activity ratio less than 1.00 may occur when the source of the uranium is previously weathered rock.

A water-saturated, slightly oxidizing environment appears to be the primary medium for this observed disequilibrium (*4, 6*). As a consequence, the hydrologic system exerts a major control on disequilibrium patterns; frequently the result is that the waters of a region have differing activity ratios and concentrations. Such differences have been used to estimate the absolute ages of closed drainage basins (*7*).

The idea of applying isotope dilution analysis to the natural variations in uranium disequilibrium arose from an investigation of uranium isotopes in the Floridan aquifer and related natural waters of north Florida (*8, 9*). The artesian Floridan aquifer is part of the principal aquifer system in the southeastern United States consisting of tertiary limestone. This aquifer is the major source of groundwater and the most important hydrologic unit within the area of study (Fig. 1) (*10*). The karstic nature of the topography results in a well-developed, subterranean drainage system and, toward the south, several springs of the first magnitude. Wakulla Spring, one of the largest in Florida, has an average discharge of 10.3 m^3/sec (365 ft^3/sec) (*11*). Hydrologic data, including large seasonal fluctuations of spring discharge correlated with local precipitation, suggest that the source of water is local recharge in the karst area (*8*). An alternative explanation is that the source of part of the water is to the north, with flow down the gradient of the piezometric surface.