b25 Oxygen isotopes measurements

< oxygen-18 / oxygen-16; delta ^{18}O >

We never said it would be easy. —Richard Felder.[1]

The vapor pressure of $H_2{}^{18}O$ is one percent lower than that of $H_2{}^{16}O$.

Harold Clayton Urey in 1947 explained that the equilibrium and kinetic properties of chemical systems involving hydrogen, carbon, nitrogen, and oxygen, in the range of natural environmental fluctuations, are linearly dependant on isotopic masses.[2] For example, when water evaporates from the sea, more $^1H_2{}^{16}O$ water (which contains the light isotope of oxygen,^{16}O) proportionately leaves than does the heavier water $^1H_2{}^{18}O$. *Note*: $^1H_2{}^{18}O$ is not "heavy water," which is specifically deuterium oxide, $D_2{}^{16}O$ or $^2H_2{}^{16}O$, although with two extra neutrons per molecule, both $^1H_2{}^{18}O$ and $^2H_2{}^{16}O$ are equally about 11% heavier than ordinary water $^1H_2{}^{16}O$.

By natural fractional distillation on a grand scale, seawater evaporates $^1H_2{}^{16}O$ water (molecules with ^{18}O are preferentially left behind). When this evaporate (condensed as snow) accumulates as glacial ice on the land, the ratio of $^{18}O/^{16}O$ increases in volumetric proportion in the world's marine water. Marine organisms construct their shells from the elements in the water about them. The isotopic reaction equilibria between ^{18}O and ^{16}O in the water and solid carbonate results in an enrichment of the heavier oxygen isotope ^{18}O in calcareous shell as the water becomes colder. In 1953, **Samuel (Sam) Epstein** (1919-2001),[3] guided by Urey, measured a 0.1 percent increase in the $^{18}O/^{16}O$ ratio in carbonate crystals for each 4.3 °C decrease in water temperature in which they grew.[4] This result is not sensitive to water salinity, pressure, or whether the $CaCO_3$ shell is calcite or aragonite (but see below).

Precision is affected by the ocean being stirred on the order of once every thousand years (implying, as water molecules in a glass of water far exceed the number of glassfuls of water in the ocean, that in each glass of water you now drink is a water molecule that passed though say Cromwell's bladder).[5]

Environmental temperatures can be derived from calcareous shells. What does effect the result is the beginning value of $^{18}O/^{16}O$ ratio. This is known to vary according to the volume of water in the sea (which is tied to the amount of ice on the land). Also the pH has an affect.

In $CaCO_3$ shells, paleotemperatures recorded by oxygen isotope variations which are a combined proxy of ice sheet's growth and shrinkage (that respectively increases and decreases the $^{18}O/^{16}O$ ratio in seawater) ***and*** the sea's temperature (the calcification temperature) ***and*** the alkalinity of the sea ($^{18}O/^{16}O$ ratio of calcite shells decreases with increasing seawater $CO_3{}^{2-}$ ion concentration).

A once "paradox in palaeoclimatology" was the apparent existence recorded by sedimented shells of planktonic foraminifera of a cool sea-surface in the tropics under conditions of high CO^2 in the atmosphere.[6] Now it is understood that the shells of planktonic foraminifera in tropical waters that settle below the thermocline can recrystallize on or below the seafloor to have an isotopic composition that records the 10–30 °C cooler temperatures there.

A sensitive measure of glacial ice accumulations is in the $CaCO_3$ tests of benthic foraminifera that live in deep and *constantly near freezing* abyssal water.

Initial results of the Deep Sea Drilling Project (begun in 1968 with funds from the National Science Foundation)[7] are that ice volume accounts for two thirds of the deep-ocean water records of $\delta^{18}O$

(delta^{18}O is the ratio of $^{18}O/^{16}O$ relative to a standard in parts per thousand; see ***Footnote b25.1***) and global climate the remainder. (The DSDP wound down in 1980, as its research vessel *Glomar Challenger* reached the end of its sea life. Beginning in 1985 is the very active Ocean Drilling Program, an international program that employs a retrofitted drill ship named *JOIDES Resolution*.)[8]

Environmental temperatures can also be derived from precipitation. The Rayleigh condensation model is that as an air mass cools and condensation proceeds, its remaining vapor is progressively depleted in the heavy isotope. Likewise, the heavy isotope will be less in the precipitate (mist, rain, snow) which can then form. At high latitudes, the oxygen isotope composition of precipitation closely follows this expectation (***Figure b25.1***).

A prime journal to consult is *Paleoceanography*. ❑

Footnote b25.1 A measure of isotope composition deviations

In nature, the heavy oxygen-18 isotope (written ^{18}O) is much less abundant than lighter in weight, ordinary, oxygen-16 isotope (^{16}O). The ratio of ^{18}O / ^{16}O in a sample is what can be readily measured using a mass spectrometer. The *deviation* (written as δ, which is the lower case Greek letter delta) of this ratio from an agreed-to-baseline standard ratio can be conveniently expressed as

$$\delta\,^{18}O \;=\; \frac{^{18}O\,/\,^{16}O \text{ of the sample}}{^{18}O\,/\,^{16}O \text{ of the standard}} \;-\; 1$$

The oxygen-18 isotope deviation ($\delta\,^{18}O$) from zero is usually expressed as a permillage (‰) and not a percentage (%).

Figure b25.1 [9] High altitude glaciers can have basal ice that has not moved since the end of the Ice Age. This ice is frozen to the bed rock and is stagnant because the glacier is now thin above it (the overlying Holocene glacial ice does not apply enough pressure to cause it to flow out of pockets where it is caught). This hypothesis has been tested by Lonnie Thompson and found to be true of a tropical glacier (Huascaran) at an elevation of 6,050 meters in the Peruvian Andes. In 1993, he drilled two 160-meter long ice cores and obtained such Pleistocene ice which is recognizable because of its dustiness (indicative of a drier upwind Amazonia). The dusty ice has an oxygen isotope compositions (triangular data points) which indicate that the Pleistocene climate was at least 11°C colder than is the Holocene climate. A plot showing that oxygen isotope compositions of precipitation-means are proxies for annual temperature-means of high latitude regions (filled circles). The straight line is the theoretical prediction of the Rayleigh condensation model.[10]