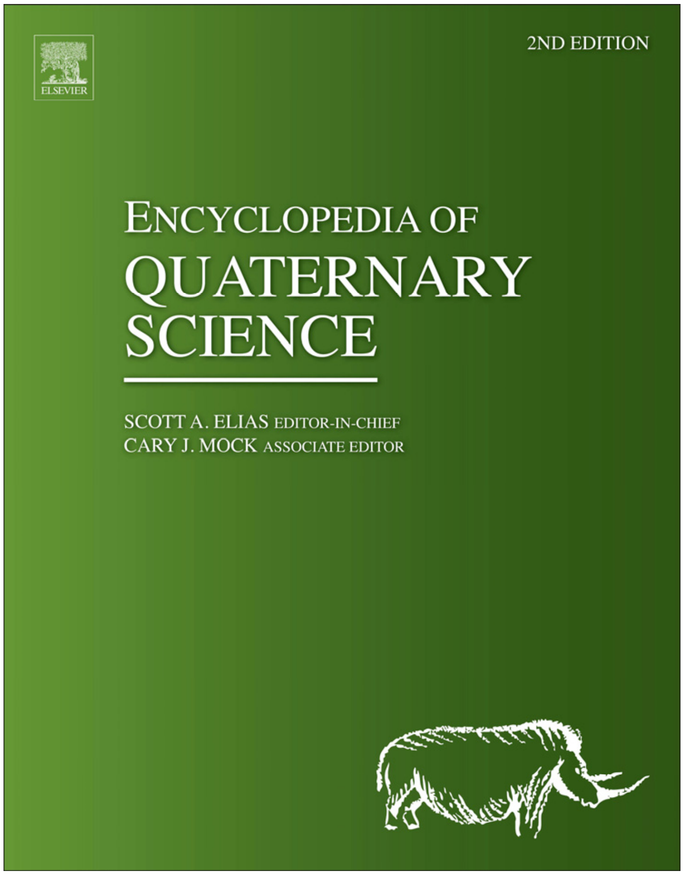

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Oxygen Isotope Composition of Seawater

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Introduction

This article deals with processes that affect the ratio of the two most common stable isotopes of oxygen in seawater and explores ways in which this has changed during the Quaternary. Both text and figures draw heavily on the water-based oxygen isotope part of a previously published essay on stable oxygen and carbon isotopes in Foraminifera (Rohling and Cooke, 1999). In contrast to the current text, which offers only the fundamental key references, the essay of Rohling and Cooke (1999) contains a very extensive set of references, and would therefore be a useful first step for further and more specialized reading.

Natural Abundance, Measurement, and Physicochemical Behavior

Oxygen exists in nature in the form of three stable isotopes: ^{16}O, ^{17}O, and ^{18}O. Their relative natural abundances are 99.76, 0.04, and 0.20%, respectively. Because of the higher abundances and the greater mass difference between ^{16}O and ^{18}O, research on oxygen isotope ratios normally concerns $^{18}O/^{16}O$ ratios.

The word isotope (Greek, meaning 'equal places') implies that the various isotopes occupy the same position in the Periodic Table. The difference between the atomic masses of the isotopic species for each element consists of a different number of neutrons in the nucleus, but isotopes have the same number of protons. The oxygen isotope $^{16}_{8}O$ contains 8 protons and 8 neutrons, giving it an atomic mass of 16. The isotope $^{18}_{8}O$ contains 8 protons and 10 neutrons, giving it an atomic mass of 18.

While the absolute abundances of minor isotopes (such as ^{18}O) cannot be determined accurately, it is still possible to get quantitative results by comparing the result given for a known external standard with that for the unknown sample. These differences in isotope ratios, known as δ values, are defined as:

$$\delta_{\mathrm{sam}} = \frac{R_{\mathrm{sam}} - R_{\mathrm{std}}}{R_{\mathrm{std}}} \times 1000$$

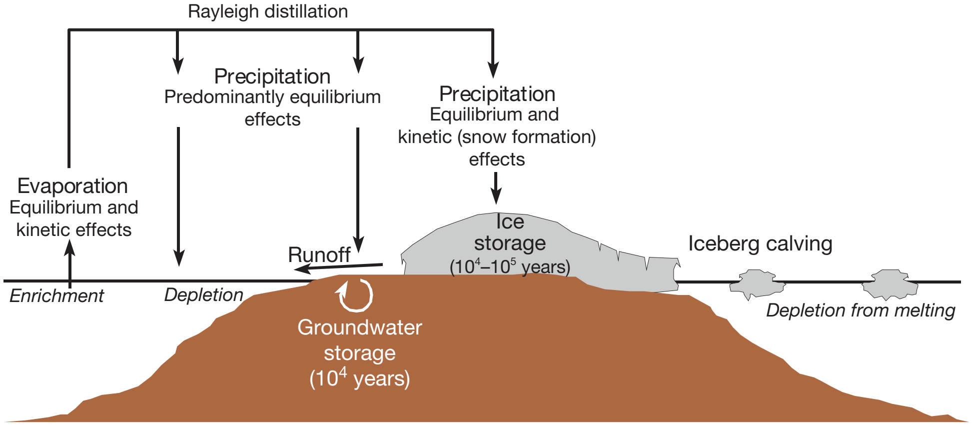
Here, sam is the sample value and std is the standard or reference value. These variations in composition are given in delta (δ) notation and are reported in parts per thousand (per mille, ‰). R stands for the heavy/light ratio between the abundances of any two isotopes (e.g., $^{18}O/^{16}O$). A positive δ value indicates enrichment in the heavy isotope, relative to the standard, and conversely, depletion is shown by a negative δ value. The standard used today in the analysis of $\delta^{18}O$ in water is the Vienna Standard Mean Ocean Water (VSMOW).

All isotopes of a given element contain the same number and arrangement of electrons, and so broadly display similarity in their chemical behavior. However, the mass differences of different isotopes impose subtle differences in their physicochemical properties. The mass differences are particularly important in light elements (low numbers in the Periodic Table). Molecules vibrate with a fundamental frequency which depends on the mass of the isotopes from which they are composed. The resultant differences in dissociation energy of the light and heavy isotopes imply that bonds formed by light isotopes are weaker than those formed by heavy isotopes. Hence, as a rule of thumb, molecules comprised of the light isotopes react somewhat more easily than those comprised of the heavy isotopes.

The partitioning of isotopes between substances with different isotopic compositions is called 'fractionation.' The fractionation factor (α), which quantifies isotopic fractionation between two substances A and B, is defined as $\alpha = R_A/R_B$. Here, R_A and R_B are the heavy/light ratios between the abundances of any two isotopes (e.g., $^{18}O/^{16}O$) in the exchanging chemical compounds A and B, respectively. Fractionation mainly results from: (1) isotope exchange reactions and (2) kinetic effects. Isotope exchange reactions concern partitioning of isotopes between phases that are in equilibrium, and are therefore also known as 'equilibrium isotope fractionation' processes. Processes of equilibrium fractionation are essentially temperature dependent. Kinetic effects cause deviations from the simple equilibrium processes due to different rates of reaction for the various isotopic species (due directly to vibration differences, or indirectly through differences in bonding energies). Important kinetic effects are associated with diffusion.

Processes Controlling Oxygen Isotope Ratios in Seawater

The oxygen isotope ratio of seawater is intimately linked with fractionation processes within the hydrological cycle. Schematically, this cycle is comprised of evaporation, atmospheric vapor transport, precipitation, and subsequent return of freshwater to the ocean (directly via precipitation and via runoff or iceberg melting). Long-term storage of freshwater in aquifers and especially ice sheets is also important for seawater isotope ratios (**Figure 1**). Formation and melting of seasonal sea ice imposes strong local variability. Finally, the spatial distribution of oxygen isotopes in the world's oceans depends on processes of advection and mixing of water masses from different source regions with different isotopic signatures. The various influences are discussed below, but it should be noted that this forms only a basic introduction, and specialist texts and reviews should be consulted before advanced applications. Key texts and overviews can be found in Craig and Gordon (1965), Dansgaard (1964), Garlick (1974), Gonfiantini (1986), Hoefs (1997), Hoffmann and Heimann (1997), Joussaume and Jouzel (1993), Jouzel et al. (1975), Majoube (1971), Merlivat



Storage effects 'fix' ^{16}O: cause ^{18}O enrichment throughout oceans

Figure 1 Schematic presentation of the hydrological cycle influences on oxygen isotope ratios. Effects on seawater are described in italics (reproduced from Rohling EJ and Cooke S (1999) Stable oxygen and carbon isotope ratios in foraminiferal carbonate. In: Sen Gupta BK (ed.) *Modern Foraminifera*, pp. 239–258. Dordrecht, The Netherlands: Kluwer Academic). The 'fix' comment refers to the storage of preferentially ^{16}O-enriched precipitation in ice sheets and groundwater, which constitutes a preferential removal of ^{16}O from the oceans and thus a relative ^{18}O-enrichment in the oceans.

and Jouzel (1979), Rohling and Cooke (1999), Rozanski et al. (1982, 1993), and Stewart (1975).

Evaporation

The isotopic exchange at the sea–air interface is given by:

$$\mathrm{H_2{}^{16}O_{liquid}} + \mathrm{H_2{}^{18}O_{vapor}} \Leftrightarrow \mathrm{H_2{}^{18}O_{liquid}} + \mathrm{H_2{}^{16}O_{vapor}}$$

Molecules composed of lighter isotopes have higher vapor pressures and the lighter molecular species are therefore preferentially enriched in the vapor phase. The fractionation factor for the equilibrium exchange is $\alpha_{\mathrm{l-v}} = [^{18}\mathrm{O}/^{16}\mathrm{O}]_{\mathrm{l}}/[^{18}\mathrm{O}/^{16}\mathrm{O}]_{\mathrm{v}}$. The most commonly used relationship between $\alpha_{\mathrm{l}-v}$ and temperature during evaporation is that given by Majoube (1971):

$$\alpha_{\mathrm{l-v}} = \exp\{(1.137\ T^{-2}) \times 10^3 - (0.4156\ T^{-1}) - 2.0667 \times 10^{-3}\}$$

where T is in Kelvin. This relationship illustrates a decrease in fractionation with increasing temperature. The fractionation causes a difference between δ^{18}O of seawater and δ^{18}O of vapor evaporated from that seawater equal to $\delta^{18}\mathrm{O_l} - \delta^{18}\mathrm{O_v} = 10^3 \ln(\alpha)$ ‰. At a temperature of 20 °C this difference amounts to about 9.8‰. The equilibrium enrichment factor ε is defined as $\varepsilon = \alpha - 1$, and is often reported as a ‰ value. For $\alpha = 1.010$, $\varepsilon = 10$‰.

Craig and Gordon (1965) found that, in addition to equilibrium fractionation, further fractionation should have occurred to explain their observations of stronger depletions in vapor than expected from equilibrium fractionation only. This further depletion is thought to be due to kinetic effects during molecular diffusion within the boundary layer between the water–air interface and the fully turbulent region (where no further fractionation occurs). Within that boundary layer, diffusion predominates because of slow atmospheric transport. The kinetic enrichment factor ($\Delta\varepsilon$) for oxygen isotopes depends on the relative air humidity (h) in the turbulent region outside the boundary layer, giving a relationship for most natural circumstances of $\Delta\varepsilon = 14.2\ (1 - h)$ ‰, where h is presented as a fraction (i.e., 0.7 means 70% relative humidity). Since diffusion rates depend on property gradients, the final isotopic composition of newly evaporated water also depends on the isotopic composition ($\delta^{18}\mathrm{O_{atm}}$) of vapor already present in the turbulent region of the atmosphere, and on δ^{18}O of the surface water (Gonfiantini, 1986):

$$\delta^{18}\mathrm{O_E} = \frac{1}{1 - h + \Delta\varepsilon}\left(\frac{\delta^{18}\mathrm{O_{Sea\ surface}} - \varepsilon}{\alpha} - h\delta^{18}\mathrm{O_{atm}} - \Delta\varepsilon\right)$$

Here, the δ^{18}O, $\Delta\varepsilon$, and ε values, normally reported in ‰, are to be used in true form, that is, value $\times 10^{-3}$. It will be obvious that the preferential uptake of the lighter isotope during evaporation causes a shift to heavier δ^{18}O values in the remaining surface waters.

Precipitation and Atmospheric Vapor Transport

Fractionation processes during the formation of droplets are basically the same as during evaporation, but work in the opposite direction. Droplets are normally near equilibrium with atmospheric vapor, due to an absence of significant kinetic fractionation during condensation when relative humidity is 100%. The equilibrium fractionation factor for condensation is the same as that for evaporation and may therefore be determined with Majoube's (1971) equation for the appropriate temperature, and then used in $\delta^{18}\mathrm{O_l} - \delta^{18}\mathrm{O_v} = 10^3 \ln(\alpha)$ ‰ to determine the isotopic composition of the droplets for any given atmospheric vapor composition.

Since condensation preferentially removes the heavier isotope ^{18}O, the δ^{18}O of the remaining atmospheric vapor becomes progressively more depleted. Relative to an original atmospheric vapor composition that is given by the composition of evaporated water ($\delta^{18}\mathrm{O_E}$), the isotopic composition of the atmospheric vapor (AV) is approximated by $\delta^{18}\mathrm{O_{AV}} = \delta^{18}\mathrm{O_E} + 10^3(\alpha - 1)\ln f$ (Dansgaard, 1964), where α is the fractionation factor at condensation temperature and f is the fraction of atmospheric vapor remaining after rain-out (e.g., 0.7 if 70% of the evaporated water remains as atmospheric vapor due to 30% rain-out). The isotopic composition of precipitation formed in equilibrium with the atmospheric vapor is found according to $\delta^{18}O_P - \delta^{18}O_{AV} = 10^3 \ln \alpha$. From these relationships, which represent a basic Rayleigh distillation process, it is immediately obvious that the first precipitation will be of a similar isotopic composition as the original seawater, and that a longer pathway from the source region (and consequently more rain-out) causes atmospheric vapor to become more and more depleted. New precipitation from this vapor reflects this depletion (**Figure 2**). As a result, precipitation is significantly more depleted at high latitudes than in the tropics (reaching values as low as −57‰ in Antarctica).

The magnitude of rain-out is strongly temperature dependent. As atmospheric vapor is transported toward colder regions, it experiences successive condensations. This effect – rather than temperature dependence of the fractionation factor – determines a basic quasilinear relationship of $0.69‰\,°C^{-1}$ between $\delta^{18}O$ of precipitation and temperature, as has been observed for temperatures between −40 and +15 °C. Above 15 °C, this relationship with temperature breaks down. There, mainly in areas with strong convection in the atmosphere, the so-called amount effect dominates. This effect approximately determines 1.5‰ depletion in the $\delta^{18}O$ of precipitation for every 100 mm increase in rainfall.

The changes in oxygen-isotope composition of atmospheric vapor and precipitation affect surface waters in the world's oceans through addition of freshwater via precipitation directly onto the sea surface or via runoff. Arid, evaporative areas demonstrate the evaporative surface water $\delta^{18}O$ enrichment. Regions in reasonable proximity to a river mouth will be affected by the volumetrically weighted average isotopic composition of precipitation over the river's catchment area. A high-latitude river system imports freshwater with generally lower $\delta^{18}O$ values than those of a low latitude river – for example, the average (pre-Aswan dam) Nile river $\delta^{18}O$ composition was near −2‰, whereas the Arctic McKenzie river discharges waters with a composition around −20‰.

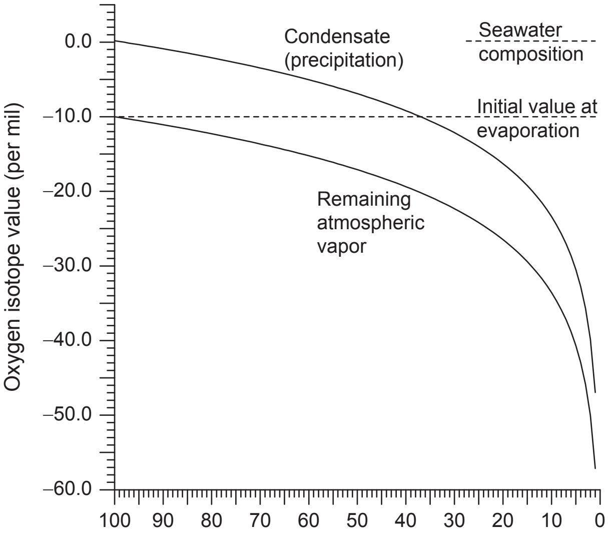


Figure 2 The relationships between isotopic composition of atmospheric vapor and precipitation relative to evaporation with an original composition of −10‰ and fractionation at a constant temperature of 15 °C. Reproduced from Rohling EJ and Cooke S (1999) Stable oxygen and carbon isotope ratios in foraminiferal carbonate. In: Sen Gupta BK (ed.) *Modern Foraminifera*, pp. 239–258. Dordrecht, The Netherlands: Kluwer Academic.

Two crucial 'delayed' responses need to be taken into account. Both result from long-term storage of precipitation. Besides runoff from rivers, icebergs calving from continental ice sheets also provide a source of 'continental' freshwater. Icebergs import into the ocean a 'fossil' isotopic signature depending on the age of the calving ice. Since ice cores in the Greenland and Antarctic Ice Sheets penetrate ice aged well over 100 000 years, and (in Antarctica) even reach 900 000 years, the isotopic signatures of bergs shed by those ice sheets should not be considered as a result of the present-day freshwater cycle. Similarly, but much less importantly, fossil waters may accumulate in aquifers and at a much later stage contribute to river discharge into the oceans, thus causing deviations from the isotopic compositions of rivers expected from precipitation in the catchment basin. Fossil ground waters may be as old as 35 000 years.

Long-Term 'Storage': Glacial Ice Volume

Apart from delayed return of 'fossil' isotopic signals back into the ocean, long-term storage systems, such as glacial ice sheets and – to a much lesser extent – major aquifers, may also affect the global $\delta^{18}O$ balance. Because the timescales of storage (on the order of 10^4–10^5 years) exceed those of ocean ventilation (on the order of 10^3 years), the modification of ocean water $\delta^{18}O$ due to these storage effects will be mixed throughout the ocean and, therefore, will be manifest both at the surface and at depth.

The main influence is related to the volume of glacial ice sheets. These are built up by high latitude precipitation (snow) at very low temperatures toward the end of the Rayleigh distillation process (**Figure 1**), and so record extremely light $\delta^{18}O$ values (**Figure 2**). This preferential sequestration of ^{16}O in ice sheets leaves the oceans relatively enriched in ^{18}O. At the same time, build-up of ice volume lowers global sea level. Research on $\delta^{18}O$ changes in fossil carbonate, complemented by accurate constraints on sea level changes from fossil coral reef studies, suggests that the relationship between sea level lowering and mean oceanic $\delta^{18}O$ enrichment approximates $0.012 \pm 0.001‰\,m^{-1}$. Work on $\delta^{18}O$ values of actual glacial waters, trapped as pore water in marine sediments, has revised this relationship to about $0.010 \pm 0.001‰\,m^{-1}$ (see the Section 'Processes Controlling Oxygen Isotope Ratios in Seawater').

The above relationships provide a sound working model for a time with a well-matured ice sheet, but it should be noted that the processes behind it may invoke a more nonlinear relationship for growing or recently matured ice sheets. Ice sheets go through a cycle of growth (young), equilibrium (mature), and decay. Mature ice sheets are mass balanced: ice accumulates at the surface, then flows from the surface to the bottom and out to the edges, where it is shed through iceberg calving and/or melting. Precipitation reaching the summit of a recently 'matured' ice sheet may therefore be significantly more depleted in $\delta^{18}O$ than that lost from the edges at the same time, which concerns ice deposited when the ice sheet was much 'younger' (smaller/lower with higher temperatures than over the mature ice sheet). Therefore, an ice sheet may be mass balanced, but not yet isotopically balanced. After a significant lag ($>10^4$ years), the ice reaching the edges will be that built up on a mature ice sheet, and the isotopic composition of accumulating and calving ice will be more or less the same; only then will the ice sheet have reached isotopic balance.

Sea Ice Freezing and Melting

The δ^{18}O of newly formed sea ice is 2.57 ± 0.10‰ enriched relative to that of seawater. Although this is a small offset compared with the massive salinity difference between seawater (S usually >30 p.s.u.) and sea ice ($S<20$ p.s.u.), the isotopic difference still imposes a major seasonal fluctuation associated with sea ice formation and melting. It is tempting to assume that such seasonal influences would cancel out in the long term, but increases in surface water salinity due to salt (brine) rejection when sea ice is formed may lead to convection and transport of existing surface waters into the ocean interior. The removed surface waters would be replaced by surface waters that were not (as much) affected by freezing processes, and when the sea ice subsequently melts the isotopic effect would not cancel out. The 'brine rejection' influence of sea ice formation can thus lead to significant regional vertical and horizontal δ^{18}O anomalies.

Advection and Diffusion

Advection and mixing of water masses from different source areas strongly affect the basic δ^{18}O composition observed at any site. Each 'source area' concerns a basin or region – which may be very remote from the study site – where surface waters are 'imprinted' with a certain δ^{18}O composition, through action of the freshwater cycle, freezing/melting of sea ice, etc. This 'preset' isotopic composition may be considered as a virtually conservative property for the newly formed water mass, as long as this water mass does not come into contact with other sinks or sources of δ^{18}O, notably the freshwater cycle. In practice, therefore, δ^{18}O may be used as a conservative tracer for transport (advection) and mixing of water masses in the subsurface ocean.

A mixing end product receives a δ^{18}O composition resulting from the volumetrically weighted averaged δ^{18}O compositions of its components: $\delta^{18}\mathrm{O}_{\mathrm{end\ product}} = (A\ \delta^{18}\mathrm{O}_A + B\ \delta^{18}\mathrm{O}_B + C\ \delta^{18}\mathrm{O}_C)/(A+B+C)$ where A, B, and C are the volumes of three mixing components and $\delta^{18}\mathrm{O}_A$, $\delta^{18}\mathrm{O}_B$, and $\delta^{18}\mathrm{O}_C$ are their isotopic compositions, respectively. Any change in relative proportions or the individual 'preset' isotopic compositions of the various mixing components would, therefore, affect the isotopic composition of the mixing end product. Any change in isotopic composition must therefore be viewed within the broader context of water mass formation and mixing on ocean-wide scales, and should not be purely ascribed to local changes in surface forcing (e.g., freshwater budget). It has been found that these hitherto 'ignored' processes may be particularly important for the global δ^{18}O distribution during times with comprehensively rearranged ocean circulation (e.g., glacial periods).

Global Seawater δ^{18}O Distribution

The combined processes listed above result in a global seawater δ^{18}O distribution. A current collection exists of over 20 000 seawater δ^{18}O measurements made since about 1950 (Schmidt et al., 1999). The date of that reference refers to the original appearance date, based on compilations made for two publications (Bigg and Rohling, 2000; Schmidt et al., 1999), but the database is current up to the present. From that database, **Figure 3** shows the integrated surface ocean (top 50 m) δ^{18}O field interpolated onto a $4° \times 5°$ grid. Data are registered from all depths and are accompanied by a variety of other oceanographic measurements, most notably salinity. A diverse series of search modes allows extraction of data from the database according to specific research needs.

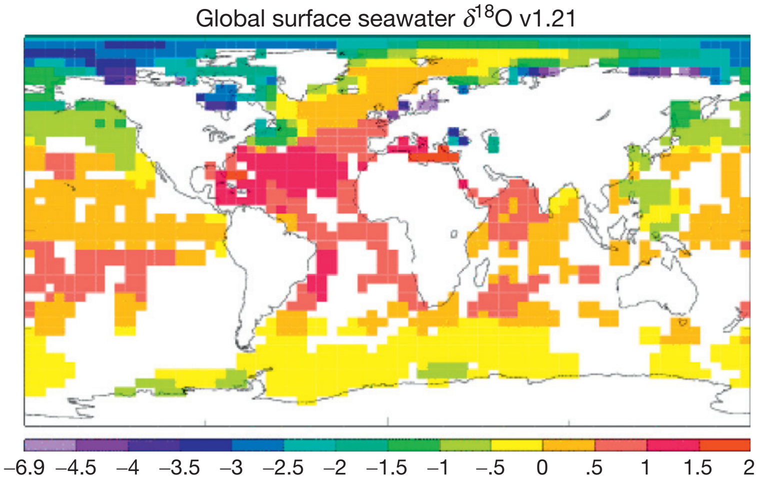


Figure 3 Example of output from the Schmidt et al. (1999) global sea water δ^{18}O database (extracted 13 January 2012). The image shows surface water δ^{18}O integrated over the top 50 m on a $4 \times 5°$ grid.

Oxygen Isotope Ratios in Seawaters of the Quaternary

Oxygen isotope ratios in seawater have changed considerably in the geological past. Apart from regional and short-term temporal variability, there have been fluctuations on global scales and of long ($\geq 10^4$ years) duration. These global-scale and long-duration fluctuations were mostly associated with changes in continental ice volume. In this section, it is discussed how we know of such past δ^{18}O variations.

Seawater δ^{18}O Inferred from Measurements on Fossil Carbonates

By far the most common manner to evaluate past changes in seawater δ^{18}O is via an indirect method, which starts with the analysis of δ^{18}O in fossil carbonates – mostly the shells of unicellular zooplankton (Foraminifera). The stable isotopes of oxygen (and carbon) in carbonates are analyzed by mass spectrometric determination of the mass ratios of carbon dioxide (CO_2) obtained from the sample, with reference to a standard carbon dioxide of known composition. The CO_2 is produced by reaction of the carbonate with phosphoric acid: $CaCO_3 + H_3PO_4 \Leftrightarrow CaHPO_4 + CO_2 + H_2O$. The δ^{18}O of carbonates is not measured against the VSMOW standard but against the Vienna Pee Dee Belemnite (VPDB) standard. The VPDB and VSMOW scales relate to one another according to $\delta^{18}O_{VSMOW} = 1.03092\ \delta^{18}O_{VPDB} + 30.92$.

There are several processes that determine the oxygen isotope composition of newly formed foraminiferal carbonate. Firstly, equilibrium fractionations between water and the various carbonate species ($CaCO_3$, H_2CO_3, $HCO_3{}^-$, $CO_3{}^{2-}$) determine an important temperature influence on the δ^{18}O of foraminiferal carbonate. Secondly, there are considerable kinetic effects, notably as the shell growth-rate changes through the organism's life cycle. To minimize the influence of kinetic effects, often grouped under the name 'vital effects,' analytical strategies have been designed that focus on time series of single species (to avoid vital effect differences between species), and that use very narrow size windows from which specimens are picked for analysis (to minimize changes in the vital effects with growth). There are other, currently less well-constrained influences, such as the concentration of the carbonate ion ($CO_3{}^{2-}$). Stable isotope ratios in carbonate are discussed in a separate chapter, and the present discussion is restricted to equilibrium fractionation between water and carbonate, which holds important clues regarding the way we can determine past seawater δ^{18}O changes.

The overall reaction involved in the precipitation of carbonate is: $Ca^{2+} + 2HCO_3{}^- \Leftrightarrow CaCO_3 + CO_2 + H_2O$. Where oxygen is concerned, the various carbonate species in seawater, including the predominant bicarbonate ($HCO_3{}^-$) ion, are isotopically equilibrated with the water (H_2O) molecules. The overall equilibrium fractionation between calcite and water is a function of temperature. For the range of 0–500 °C, O'Neil et al. (1969) determined that the equilibrium fractionation factor α_{c-w} between calcite and water (α_{c-w}) changes with temperature according to: $\alpha_{c-w} = \exp\{(2.78\ T^{-2}) \times 10^3 – 3.39 \times 10^{-3}\}$ where T is in Kelvin. Other workers have reported slightly different equations, for example, with the last coefficient at 2.89×10^{-3} rather than 3.39×10^{-3}. The summary effect of equilibrium fractionation is a roughly 0.2‰ depletion in carbonate δ^{18}O for every 1 °C temperature increase, although Kim and O'Neil (1997) presented a more detailed relationship where the δ^{18}O change with temperature is more pronounced at low temperatures (up to 0.25‰ $°C^{-1}$) than at higher temperatures (around 0.2‰ $°C^{-1}$).

A first observation to be made regarding planktonic Foraminifera is that several species may inhabit different depths at different stages of their life cycle. Since temperature decreases with increasing depth in the surface oceans, vertical migrations influence equilibrium fractionation. This again is a problem that can be circumvented by analytical strategy; time series of data are considered for single species in very narrow size windows, so the habitat-depth effect should be similar for all and thus will not affect the inferred variability sea water δ^{18}O over time.

Simplified, therefore, a time series of δ^{18}O analyzed from fossil planktonic Foraminifera in a sediment core is dominated by two main variables: temperature variability and seawater δ^{18}O variability. The temperature changes can be 'corrected for' using other methods for estimating past seawater temperatures (e.g., Mg/Ca ratios in the foraminiferal carbonate, organic geochemical biomarker ratios, or statistical transforms of microfossil abundance variations). This then allows the estimation of past changes in seawater δ^{18}O.

Time series of foraminiferal δ^{18}O and – by implication – seawater δ^{18}O illustrate that glacial ice volume has varied strongly over the last 2 million years, a period known on the geological timescale to fall within the Quaternary. During the last 400 000 years, the main variability can be seen as a rough sawtooth pattern with a 100 000-year rhythm of glacial–interglacial cycles, which is mainly related to global ice volume fluctuations (**Figure 4**). Ice sheets grew spasmodically over periods of roughly 90 000 years, reaching a maximum extent that was followed by a very abrupt ice volume reduction heralding the onset of an interglacial maximum with a typical mean duration of some 10 000 years. Between 0.4 and 1 million years ago, there was a less well-defined state, with a complex interplay between main periods of 100 000 and 41 000 years for the glacial cycles. Prior to 1 million years ago (especially in the interval between 2.5 and 1 million years ago), the glacial cycles followed a well-developed 41 000-year period, and in that period the glacial cycles did not have a conspicuously sawtoothed temporal structure (**Figure 4**). Following calibration with dated fossil coral reefs, the past δ^{18}O fluctuations were found to indicate that global ice volume has waxed and waned so much that global sea level variations occurred between 140 m below and 5–10 m above the present-day level. For the last glacial cycle, such studies suggested a relationship between sea level lowering and mean oceanic δ^{18}O enrichment in the region of 0.012 ± 0.001‰ m^{-1}.

Other Uses of Foraminifer-Based δ^{18}O in Paleoceanography

There have been recent forays into alternative uses of foraminiferal carbonate-based δ^{18}O that avoid the complications involved in deconvolving the carbonate δ^{18}O data in terms of past temperature and seawater δ^{18}O. These studies have focused instead on the fact that, in specific settings, carbonate

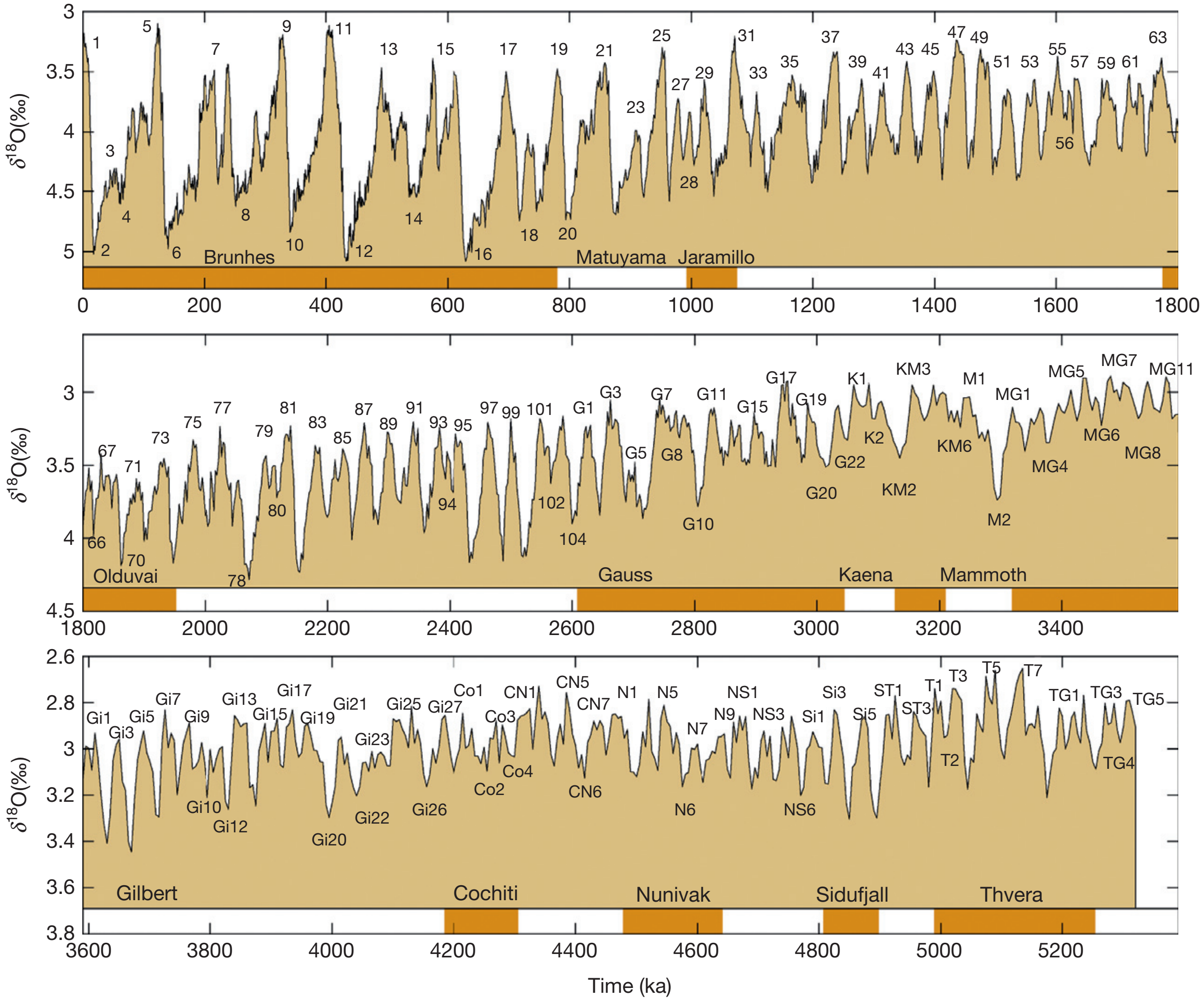


Figure 4 A stacked record of stable oxygen isotope variations for the last 5.3 million years, constructed from 57 globally distributed deep-sea (benthic foraminiferal) records. Numbers indicate glacial (down = heavy δ^{18}O values) and interglacial (up = light δ^{18}O values) intervals. The dark/light bar at the bottom of each panel indicates (named) intervals of normal (dark) and reversed (light) geomagnetic polarity. Time is indicated in units of 1000 years (ka). Reproduced from Lisiecki LE and Rayme ME (2005) A Pliocene-Pleistocene stack of 57 globally distributed benthic δ^{18}O records. *Paleoceanography* 20: PA1003, http://dx.doi.org/10.1029/2004PA001071.

δ^{18}O offers a very useful approximation of past seawater density, because it is a function of temperature and the hydrological budget (as is density). Thus the carbonate δ^{18}O data can be used as a dynamic proxy for the reconstruction of density gradients with depth or in a spatial sense. Lynch-Stieglitz et al. (1999) used depth transects of benthic foraminiferal δ^{18}O data on both sides of Florida Straits in geostrophic (where the horizontal pressure gradient is balanced by the Coriolis force) current intensity reconstructions of the Florida Current during glacial times. Billups and Schrag (2000) argued that, in tropical and subtropical regions, the δ^{18}O data obtained from various planktonic foraminiferal species may be used to reconstruct past changes in spatial surface–water density gradients, on a global scale.

Another line of work has focused on the sea-level-dependent concentration effect on δ^{18}O in evaporative marginal seas with limited connection to the open ocean. A key study along these lines concerns the Red Sea, a highly evaporative basin with a very shallow (137 m) connection to the open ocean. As sea level varied on glacial–interglacial timescales between about 130 m below the present and about 5 m above the present, the broadly triangular strait profile imposed very serious limitations on the amount of water exchange between the Red Sea and the open ocean. With lowering sea level, the exchange is progressively inhibited, which increases the residence time of waters inside the highly evaporative Red Sea. As a consequence of this sea level effect, the glacial–interglacial δ^{18}O contrast in the Red Sea is amplified about five times relative to the open ocean. By quantifying the relationship between sea level and Red Sea δ^{18}O change, Siddall et al. (2003) developed a new technique for reconstruction of global sea level variability, using foraminiferal δ^{18}O records from central Red Sea sediment cores. Records employing this method have been further developed in detail through the last 520 000 years (Rohling et al., 2009, 2010; Figure 5). This technique relies on a physically defined

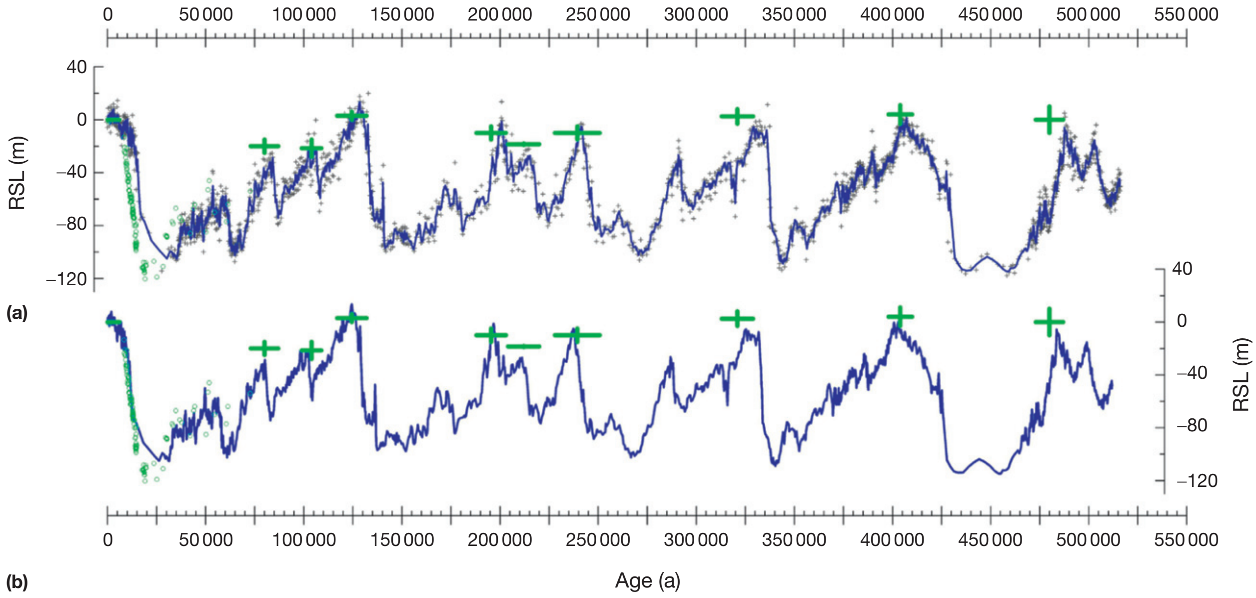


Figure 5 Sea level reconstruction from the Red Sea method (Rohling et al., 2009). Gray dots are individual values; blue line is a smoothing function so that individual data are spread around it a normal distribution with $1\sigma = 6$ m, which is the method's realistic uncertainty (Siddall et al., 2003). Green symbols denote benchmark data from U–Th dated corals and submerged speleothems. Panel (a) shows the record on its initial chronology, based on graphical correlation with the Antarctic EPICA Dome C temperature anomaly record (Jouzel et al., 2007). Panel (b) shows the record after a systematic adjustment of -4 ka, based on the offset seen in (a) between the Red Sea sea level record and the radiometrically dated points during the last deglaciation (19–8 ka) (Rohling et al., 2010). This brought midpoint ages for interglacials in the Red Sea record within 1.5% of the midpoint ages from radiometric datings (Rohling et al., 2010). Although a good match was obtained on glacial–interglacial timescales, further improvements to the chronology remain needed on shorter timescales. Data available from the DATA link with Rohling et al. (2010) at http://www.highstand.org/erohling/ejrhome.htm.

relationship between Red Sea δ^{18}O and sea level in the strait and is therefore fundamentally different in approach and sensitivity to the global deep-sea δ^{18}O records shown in **Figure 4**.

'Direct' Measurement of Past Seawater

Recent work has introduced significant new insight into the history of seawater δ^{18}O. Adkins et al. (2002) measured δ^{18}O profiles for pore waters extracted from marine sediment cores. The pore water profile reflects the past bottom water δ^{18}O conditions, subject to advective and diffusive processes within the sediment, and the Last Glacial Maximum (~20 000 years ago) stands out as the interval with highest δ^{18}O values (i.e., maximum ice volume). Hence the actual Last Glacial Maximum bottom water δ^{18}O was determined from sediment cores for a variety of sites around the world, from a range of different water depths. The sea level difference between the Last Glacial Maximum and the present was taken from other analyses, and overall, this study suggests that the actual relationship between sea level lowering and mean oceanic δ^{18}O enrichment is closer to $0.010 \pm 0.001‰\,\mathrm{m}^{-1}$. This indicates that the steeper relationship previously derived from carbonate-based δ^{18}O changes likely contained some residual temperature effects (i.e., glacial deep-water temperatures were colder than was assumed).

See also: K/Ar and ^{40}Ar/^{39}Ar Dating. **Paleoceanography, Physical and Chemical Proxies:** Oxygen-Isotope Stratigraphy of the Oceans. **Quaternary Stratigraphy:** Overview.

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