Chapter 5

THE OCEANS

Contents
5.1 Overview ................................................................. 1
5.2 Oxygen Isotope Variations in Modern Oceans ...................... 2
  5.2.1 Salinity-\(\delta^{18}O\) relations in shallow marine waters .......... 2
  5.2.2 Salinity-\(\delta^{18}O\) relations in deep ocean waters ............... 3
5.3 Depth Profiles in Modern Oceans: \(\delta^{18}O\) (\(O_2\))\(_{aq}\) and \(\delta^{13}C\) (\(\Sigma CO_2\)) .................. 6
5.4 Stable isotope ratios as monitors of productivity ................. 7
5.5 Isotopic Compositions of Ancient Oceans ....................... 9
  5.5.1 Primitive oceans ......................................................... 9
  5.5.2 Secular changes in \(\delta^{18}O\) of marine sediments ............ 10
5.6 Seawater-Basalt Interactions – buffering the \(\delta^{18}O\) value of the ocean .... 11
  5.6.1 Low-temperature alteration ........................................ 12
  5.6.2 High temperature alteration ....................................... 13
  5.6.3 Evidence from drill core material ................................. 13
  5.6.4 Evidence from obducted material ................................. 14
5.7 Buffering the \(^{18}O/^{16}O\) Ratio of Ocean Water ................. 15
  5.7.1 Summing the processes affecting the \(^{18}O/^{16}O\) ratio of seawater .... 15
  5.7.2 Unresolved controversy ............................................. 16
  5.7.3 Model calculations ..................................................... 16
  5.7.4 An alternative explanation for the early-Earth low \(\delta^{18}O\) values .... 17
References ....................................................................... 18
5.1 Overview

The $\delta^{18}O$ values of surface marine waters vary by several per mil, particularly in coastal regions at high latitudes where isotopically light glacial and stream waters feed into the ocean. Surface water variations are due to three processes: 1) evaporation, 2) influx of fresh water and 3) melting or freezing of sea ice. In contrast to the shallow waters, the oxygen isotope compositions of deep ocean waters are nearly constant, varying by less than 1%. Salinities at depth are also nearly constant at 34 to 35‰\(^1\). Nonetheless, the subtle variations in both salinity and isotopic composition of these waters can be used to provide valuable information on mass accumulations and circulation patterns in the deep oceans.

The earliest study of oxygen isotope variations in ocean waters was made by Epstein and Mayeda (1953) whose main interest at that time was focused on the extent of oxygen isotope variability of ocean water as it pertained to determining paleotemperature estimates from $\delta^{18}O$ values of carbonates (see Chapter 6). They quickly realized that failure to consider possible variations in $\delta^{18}O$ values of surface waters could lead to a disturbingly large uncertainty of up to about 10°C in temperature estimates using the carbonate-water oxygen isotope thermometer. Further uncertainty is introduced when possible and probable temporal variations in the oxygen isotope composition of the oceans are taken into consideration.

How has the oxygen isotope composition of ocean water changed over geologic time? From simple mass balance considerations involving the amount and isotopic composition of water now locked up on land in glaciers, we know that $\delta^{18}O$ values of ocean waters were about 1‰ lower in ice-free times than they are at present. But were variations in the past larger than this? Urey et al. (1951) realized that the formation of low temperature sedimentary rocks, enriched in $^{18}O$, would cause the oceans to get lighter over time. They conclude with the following: "Perhaps it is a conclusion based on little more than prejudice, but we believe that it is most likely that the major part of this change occurred before the Cambrian. Until more data are available we will make no correction for this effect." In the ensuing half century, the community is still divided on the isotopic composition of the early ocean. On the basis of oxygen isotope analyses of marine sediments deposited at different times in the geologic past, $\delta^{18}O$ values of the early ocean as low as $-15‰$ have been proposed. A change of this magnitude in the isotopic composition of the vast quantity of water in the oceans would reflect an enormous change in some major (plate tectonic?) process operating on Earth, but the evidence presented for such changes is highly controversial. On the other hand, if the isotopic composition of the ocean has remained constant, then early ocean temperatures would have been arguably too high to support life. The question of major oxygen isotope variability in ancient oceans remains one of the most important unresolved problems in earth science. We will return to this intriguing subject later in this chapter.

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\(^1\) Salinity is often reported in permil notation, where 34‰ salinity is equivalent to 3.4 wt % dissolved solids. It should not be confused with isotopic compositions.
5.2 Oxygen Isotope Variations in Modern Oceans

5.2.1 Salinity-δ¹⁸O relations in shallow marine waters

Epstein and Mayeda (1953) first recognized the almost linear correlation between salinity (S) and δ¹⁸O value of ocean waters, and the anticipated sympathetic correlation between salinity and δD was documented a few years later by Friedman et al. (1961). The correlation between salinity and stable isotope ratios of ocean waters is explained by two simple processes: evaporation and addition of fresh water. Evaporation from the ocean surface preferentially removes light isotopologues from the water and increases its salinity, so values of both δ¹⁸O and S of surface waters increase with increasing degree of evaporation. Introduction of fresh water from melting ice, river systems or rain lowers the salinity and δ¹⁸O value of the affected parcel of ocean. The δ¹⁸O and δD values of this water are lowered because meteoric waters virtually always have lower stable isotope compositions than ocean water. The magnitude of the isotopic effect is related to the water source. δ¹⁸O values of glacial waters are very low (a typical value is −30‰), while those of rivers in temperate zones are much higher (e.g. −4.9‰ for the Mississippi River). Thus, for a given dilution factor, high-latitude glacial waters will shift δ¹⁸O values to a greater extent than low-latitude river waters for the same shift in salinity. In an ice-free world, δ¹⁸O would change by about 0.2‰ per unit change in salinity (although this will vary in accordance with the δ¹⁸O value of the fresh water), so that a 5‰ fluctuation in salinity would be accompanied by a 1.0‰ fluctuation in the O¹⁸/O¹⁶ ratio of the oceans.

The carbonate-water paleothermometer is a function of the difference between the δ¹⁸O values of the carbonate and water. Its applicability requires that the δ¹⁸O value of the water from which the carbonates precipitated is known or can somehow be estimated. Large variations in δ¹⁸O values of surface waters resulting from evaporation and influx of meteoric waters could bear significantly on estimates of ocean paleotemperatures that are made from analyses of carbonate from the shells of planktonic organisms. The rather loose relation observed between salinity and δ¹⁸O values is called the salinity effect and implies that we can approximate one parameter from knowledge of the other. That is, if the paleosalinity can be determined by some means, then an appropriate correction for the departure of δ¹⁸O from values of normal marine waters can be made (Railsback et al., 1989). A surprising number of authors have misused this term, assuming that salinity itself affects the oxygen isotope fractionation between carbonates and ocean water, which is not the case. There is indeed a small effect on the fractionation between water in highly saline solutions and other phases (see section 3.6.4) but, at the relatively low salinities of ocean water, the effect on oxygen isotope fractionation is negligible. The salinity effect employed in paleotemperature studies is not related to salinity-fractionation effects.

Craig and Gordon (1965) measured isotopic compositions of both water vapor and surface waters along N-S and E-W transects across the Atlantic Ocean. These data, shown in Figure 4.9, reflect the non-equilibrium nature of the evaporation process and also point to relative humidity as a dominant control on vapor compositions. As one travels in a northerly direction in the Atlantic Ocean, there is little change in δ¹⁸O values of liquid water, but δ¹⁸O values of the overlying water vapors decrease with increasing latitude due to decreasing sea-surface temperatures and concomitant increases in the magnitude of the isotopic fractionation between liquid and vapor. The measured δ¹⁸O
values of the vapor are, however, about 4.5‰ more negative than those expected at equilibrium because of kinetic isotope effects. During the process of evaporation, light molecules preferentially diffuse through the near-surface layers of liquid water and into the vapor phase, with little back-exchange. Kinetic effects also favor the diffusion of the light isotopologues from the saturated layer just above the liquid into the unsaturated air layer above that. The lowest \( \delta^{18}O \) values are, as expected, found in the region of the trade winds, where evaporation is highest and relative humidity is lowest. Variations in the \( \delta^{18}O \) value of water vapor are minimal in an E-W direction.

The factors that contribute to changes in \( S \) and \( \delta^{18}O \) are summarized in Figure 5.1. Intense evaporation in the region of the trade winds causes both \( \delta^{18}O \) and \( S \) values to increase, whereas intense precipitation at equatorial latitudes lowers both \( \delta^{18}O \) and \( S \) values. At high latitudes, meltwater entering the ocean has very low \( \delta^{18}O \) values, so that oxygen isotope ratios are accordingly more strongly affected than salinity (note the steeper slope in Fig. 5.1). In contrast, the formation of sea ice, a particularly important process in the Weddell sea off Antarctica, affects salinity more strongly than oxygen isotope ratios. This is because the oxygen isotope fractionation between ice and seawater is negligible (O'Neil, 1968), but formation of ice – which essentially incorporates no salt – will strongly increase the salinity of the remaining water. The salinity of the surrounding water thus increases while its \( \delta^{18}O \) value decreases, but only very slightly. Assuming \( \Delta^{18}O_{\text{ice-water}} = 2\% \), a quantity of ice formation that changes the salinity by 2‰ will only change the \( \delta^{18}O \) value by 0.1‰.

The salinity - \( \delta^{18}O \) values of waters from the N. Atlantic surface waters plot on a nearly linear array, with low salinity - low \( \delta^{18}O \) values becoming especially pronounced towards Greenland (Fig. 5.2). The nearly perfect linear correlation is partly an artifact of the huge range of \( \delta^{18}O \) and \( S \) plotted in Fig. 5.2. When we look at the Pacific waters at a smaller scale (Fig. 5.3) it become apparent that salinity and \( \delta^{18}O \) do not correlate quite as well as suggested by Fig. 5.2. Compare the N. and S. Pacific waters in Fig. 5.3.

### 5.2.2 Salinity-\( \delta^{18}O \) relations in deep ocean waters

Craig and Gordon (1965) developed deep ocean circulation models using the combined \( \delta^{18}O-S \) data. Because the total variation in the isotopic composition of deep ocean water is only about 0.5‰, the researchers needed to be able to measure the \( \delta^{18}O \) values at an unprecedented level of precision. To meet this challenge, Craig and Gordon developed a procedure to greatly increase the precision of their \( \delta^{18}O_{\text{water}} \) determinations. It is worth detailing here because, although many researchers may quote extremely high precision, the protocol developed by Craig and Gordon illustrate just how hard it is to really achieve such a goal.
Craig and Gordon analyzed relatively large samples of water to limit the effects of vapor loss and contamination during sample manipulation. In addition, they equilibrated their water samples with CO$_2$ that had previously been isotopically equilibrated with a water of ‘normal’ marine composition. In this way, changes in the $\delta^{18}O$ value of the equilibrating CO$_2$ gas would be very small during exchange with their ‘actual’ samples, thus minimizing changes in the isotopic composition of the water sample during the equilibration process. The mass spectrometer working standard was CO$_2$ that had also been equilibrated with water of marine composition, and both reference and sample gas were introduced through the sample inlet side of the mass spectrometer, thus eliminating any fractionation effects that might arise when switching between standard and sample inlets. By adopting this protocol, they were able to reach an overall precision of better than ±0.02‰.

The isotopic compositions and salinities of near surface waters vary considerably with latitude as we have already seen in figures 5.2 and 5.3. But with increasing depth, there is a convergence at or below ~1000 m to values that are remarkably constant for large distinct ocean basins. Values of $\delta^{18}O$ and $S$ for ten samples of water that spanned 40° of latitude were identical to within 1σ standard deviations of 0.04 and 0.03‰, respectively. $\delta^{18}O$-S values for deep oceans basins are given in Table 5.1. Although subtle, the distinctions are significant, and can be explained completely by specific circulation patterns as discussed in the following section.

The $\delta^{18}O$-S values of North Atlantic Deep Waters (NADW) plot directly on the linear array defined by N. Atlantic surface waters (Fig. 5.2). The deep waters are thus consistent with downwelling of cold, surface-waters in the Norwegian sea, in accord with independently developed circulation models. In the South Atlantic region near the Weddell Sea (59–65°S), the slope d$\delta^{18}O$/d$S$ is close to zero (dashed line in Fig. 5.4),
consistent with the relations associated with the formation of sea ice, explained above (Fig 5.1). Salinities range from 33.4 to 34.7 per mil, while δ¹⁸O values are constant at -0.4 to -0.5 ‰ for all but the most saline waters. The δ¹⁸O-S values for the Antarctic Bottom Waters (AABW) are distinct from those of the NADW because the mechanism of their formation differs from that occurring in the North Atlantic. North Atlantic waters achieve sufficient density to sink by cooling and evaporation (increase in salinity) of Gulf Stream waters. In contrast, waters in the Weddell sea are so cold that significant freezing occurs, increasing salinity and density, but not changing δ¹⁸O values. Combining salinity and isotopic data, two distinct bodies of downwelling waters (AABW and NADW) are clearly identified (Fig. 5.4).

**Table 5.1.** Salinity and δ¹⁸O values of principal deep water ocean masses. From (Craig and Gordon, 1965).

<table>
<thead>
<tr>
<th></th>
<th>Salinity(‰)</th>
<th>δ¹⁸O(‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Atlantic Deep Water</td>
<td>34.93</td>
<td>+0.12</td>
</tr>
<tr>
<td>(NADW)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antarctic Bottom Waters</td>
<td>34.65</td>
<td>-0.45</td>
</tr>
<tr>
<td>(AABW)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indian Deep Waters (IDW)</td>
<td>34.71</td>
<td>-0.18</td>
</tr>
<tr>
<td>Pacific Deep Waters (PDW)</td>
<td>34.70</td>
<td>-0.17*</td>
</tr>
</tbody>
</table>

*Antarctic samples have a slightly lower δ¹⁸O value of -0.21‰

In contrast to the compositions of North Atlantic waters, data for the Pacific Deep Waters (PDW) do not lie on the δ¹⁸O-S line for surface Pacific waters (Fig. 5.3), implying an exotic source for the PDW. In addition, neither of the two Atlantic downwelling sources (NADW or AABW) match the combined δ¹⁸O-S values of the PDW. Instead, the
Chapter 5. The Oceans

PDW data lie intermediate to the NADW and AABW data, and are explained by simple mixing of these two deep water sources (Fig. 5.4). Such mixing is consistent with our current understanding of global ocean circulation patterns. Appreciable ocean downwelling occurs only in the North Atlantic and the Antarctic. The North Atlantic data reflect the downwelling source in the Norwegian Sea and the AABW reflect a source in the Weddell Sea associated with ice production and downwelling of cold high-salinity waters. These two downwelling waters move eastward and mix, eventually traversing both the Pacific and Indian Oceans.

5.3 Depth Profiles in Modern Oceans: $\delta^{18}O \ (O_2)_{aq}$ and $\delta^{13}C \ (\Sigma CO_2)$

Atmospheric oxygen all over the globe has a constant $\delta^{18}O$ value of 23.8±0.3‰ (Luz and Barkan, 2011). The oxygen isotope fractionation between $O_2$ dissolved in seawater and $O_2$ in the atmosphere is 0.6‰ at 25°C (note direction of this fractionation; $\delta^{18}O$ of $O_2$ dissolved in seawater is 0.6‰ higher than in air), and is reflected in measured $\delta^{18}O$ values of $O_2$ in shallow seawater. Because of the huge production of $O_2$ during photosynthesis, and the relatively low amounts of dissolved $O_2$ in the oceans, the $\delta^{18}O$ value of dissolved $O_2$ in the shallow marine environment is controlled by atmospheric oxygen and ultimately the isotopic fractionation associated with photosynthesis (see Box 5.1). With increasing depth, the abundance of dissolved oxygen in the ocean decreases from a value of ~210 μmoles/kg to a minimum of 150 μmoles/kg at about 1 km depth (Fig. 5.5). This decrease is due to oxidation of sinking organic matter. With increasing depth, the $O_2$ concentration increases again to 270 μmoles/kg because of the $O_2$ contribution of downwelling waters from the North Atlantic and Antarctic. $\delta^{18}O$ values of dissolved oxygen mirror the oxygen concentration profile. $O_2$ dissolved in surface waters has $\delta^{18}O$ values in excess of 24‰ as a result of equilibrium exchange with $O_2$ in the atmosphere. $\delta^{18}O$ values increase with depth because light oxygen is preferentially...
consumed in the oxidation of organic matter. At a depth of ~1 km, dissolved oxygen attains maximum $\delta^{18}O$ values in excess of 30‰. $\delta^{18}O$ values then decrease to a near constant value of 26‰, related to the continual contribution of fresh $O_2$ in downwelling waters.

**Text Box 5.1. The Dole Effect**

The $\delta^{18}O$ value of atmospheric $CO_2$ is $\sim$41‰, and is explained by equilibrium fractionation between (primarily) ocean water and $CO_2$ gas. The equilibrium fractionation between $CO_2$ and $H_2O$ is given by $\alpha = 1.0412$ @ 25°C. In contrast, the $\delta^{18}O$ value of atmospheric $O_2$ is 23.8‰, far higher than what would be expected based on the equilibrium isotope fractionation between $O_2$ (g) and $H_2O$ ($\sim$13‰). The high $\delta^{18}O$ value of $O_2$ gas was first measured gravimetrically by Dole (1935, 1936). The explanation for the high $\delta^{18}O$ value of $O_2$ is explained in terms of photorespiration in plants. While the conversion of $H_2O \rightarrow O_2$ occurs with minimal fractionation, the incorporation of $O_2$ during respiration preferentially incorporates $^{16}O$, leaving the remaining $O_2$ reservoir enriched in $^{18}O$ (Lane and Dole, 1956). The disequilibrium between $O_2$: $CO_2$ and $H_2O$ vapor is maintained because the exchange rates between these gaseous species are far slower than the exchange rates between $CO_2$ and liquid water and $O_2$ cycled through the photosynthesis-respiration cycle. See Keeling (1995), Welp *et al.* (2011) and Luz and Barkan (2011) for a more detailed review.

The $\delta^{13}C$ curve for total dissolved inorganic carbon ($\Sigma CO_2$) is a mirror image of the $\delta^{18}O$ curve for dissolved $O_2$. The abundance of $\Sigma CO_2$, which is primarily $HCO_3^-$, steadily increases with depth as sinking organic matter is oxidized. The concentration increases from $\sim$2000 μmoles/kg near the surface to $\sim$2160 μmoles/kg at 1 km depth, after which it remains essentially constant. The $\delta^{13}C$ values of $\Sigma CO_2$ decrease from 2‰ at the surface to 0.7‰ at ~1 km depth and then rise back up to an almost constant value of about 1‰ below 2 km ocean depth (Fig. 5.5). In the absence of biological activity, $\delta^{13}C$ of $HCO_3^-$ in surface waters would be about $\sim$1‰, a value appropriate to equilibrium exchange with atmospheric $CO_2$ (see Chapter 7 for a further explanation of this value). But isotopically light $HCO_3^-$ is preferentially used by organisms in the formation of their soft tissues, driving the $\delta^{13}C$ values of remaining $HCO_3^-$ in the upper (photic) zone to +2‰, or even higher in regions of intense biological productivity. The return to more negative $\delta^{13}C$ values at depth is caused by the addition of light carbon to these waters from the oxidation of sinking organic matter. The formation of organic matter in the productive region of shallow waters, and its systematic removal by oxidation at depth comprises the *biological carbon pump* (box 7.1). (See section 9.3.5 for nitrogen isotope variability with depth).

**5.4 Stable isotope ratios as monitors of productivity**

Stable isotopes are a powerful tool for evaluating ocean productivity and, using sedimentary materials, paleoproductivity. Carbon isotopes have long been used for this purpose. Light carbon is preferentially incorporated into organic matter, leaving the
residual HCO₃⁻ dissolved in the ocean enriched in ¹³C. Variations in the δ¹³C values of carbonates can then be used as a proxy for paleoproductivity (Chapter 7). Similarly, the δ³⁴S values of evaporitic sulfates can be used as a measure of ocean productivity (Chapter 10). This is because light sulfur is removed by bacterial sulfate reduction. The light isotope of sulfur is preferentially incorporated in the organic matter and ultimately as iron sulfide. The removal of light sulfur raises the δ³⁴S value of the remaining sulfate. Times of high organic matter burial will lead to more intense sulfate reduction and hence a higher δ³⁴S value of sulfate dissolved in the ocean.

Non-traditional isotopes have also filled this role. Silicon isotope ratios in diatom frustules have been used as a proxy for paleoproductivity (De La Rocha et al., 1998). Diatoms preferentially incorporate ²⁸Si relative to ³⁰Si by approximately 1‰ independent of temperature and diatom species (De La Rocha et al., 1997). The δ³⁰Si value of diatoms will vary depending on the conditions of formation. Four endmembers can be envisioned: 1) a small amount of diatoms are produced and their δ³⁰Si value will be 1‰ lower than the Si source (silicic acid dissolved in water). 2) The diatoms consume all of the dissolved silica. In this case, the δ³⁰Si values of the diatoms will be equal to that of the initial silicic acid. 3) In a steady state system, where Si is removed from the water column at the same rate it is being replaced from continental or upwelling sources, the δ³⁰Si value will be equal to that of the silicic acid entering the system. 4) Under conditions of closed system (finite input) Rayleigh fractionation (see 4.6.3 for a more detailed discussion of Rayleigh fractionation), the δ³⁰Si value of the diatoms will increase with increasing degree of diatom production (higher productivity). The δ³⁰Si values of diatom separates in marine sediment cores from the Southern ocean show a decrease as the last glacial period began consistent with decreased productivity. The δ³⁰Si values then increase at the
end of the last glacial as higher productivity resumed (De La Rocha et al., 1998).

5.5 Isotopic Compositions of Ancient Oceans

How much has the isotopic composition of the global oceans changed through time? Why does present day seawater have the isotopic composition that it does? What exchange mechanisms or buffering capacity exist in the oceans to cause $^{18}\text{O}/^{16}\text{O}$ and D/H ratios to change or remain the same through time? These questions are important for a number of reasons, the most compelling being that ancient ocean temperature estimates using stable isotope fractionations are remarkably high if the oxygen isotope composition of the ocean has remained unchanged.

5.5.1 Primitive oceans

If the earliest oceans had equilibrated with hot primitive mantle-derived igneous rocks, they would have had $\delta^{18}\text{O}$ and $\delta\text{D}$ values of $\approx 7 \pm 1\%_\circ$ and $\approx -60 \pm 20\%_\circ$, respectively (Silverman, 1951). As primitive Earth cooled, interactions between ocean water and basalt would have led to the formation of hydrous minerals. At this stage of development, the $\delta\text{D}$ value of the ocean may have raised the $\delta\text{D}$ of the primitive waters to a small extent, but the effect of this process on $\delta^{18}\text{O}$ would have been negligible.

Marine sediments and alteration minerals formed by low temperature weathering of terrestrial rocks have D/H ratios that are considerably lower than the D/H ratio of ocean water, so formation of hydrous minerals at low temperatures is a very efficient way to raise the D/H ratio of the world oceans. The effect is somewhat lessened by the fact that marine sediments are subducted into the mantle and some fraction of the water entrained within them is returned to the surface in volcanic emanations.

In contrast to hydrogen, oxygen isotope ratios of the ocean will be lowered significantly by formation of marine sediments and minerals from weathering of igneous rocks. Oxygen isotope fractionations between sedimentary materials (carbonates, silica, phosphates, clays) and water are so large at low temperatures (~20-30‰) that locking up $^{18}\text{O}$ in weathering minerals and in marine sediments should have played a major role in lowering the $\delta^{18}\text{O}$ value of the initial oceans from the putative high initial values to those near 0‰. The degree to which $^{18}\text{O}/^{16}\text{O}$ ratios were lowered and D/H ratios were raised by weathering and sedimentary processes depends once again on material balance considerations and how much sedimentary material was reworked over time.

The hydrogen isotope history of primitive oceans is seldom addressed and, for the most part, remains unresolved. Limited hydrogen isotope analyses of rocks that formed in ancient oceans (greenstones and ophiolites) are similar to those of modern equivalents (Sheppard and Epstein, 1970; Yui et al., 1990; Lécuyer et al., 1996) suggesting that D/H values of the ocean have remained fairly constant throughout geologic time, except during glacial times when light water is locked up in continental ice sheets. Modeling of hydrogen fluxes into and out of the ocean led Lécuyer et al (1996) to conclude that the $\delta\text{D}$ of the Archean ocean may have been several tens of per mil lower than the modern value. A similar conclusion was reached by Pope et al. (2012) based on the $\delta\text{D}$ values of Archean serpentinites.

The oxygen isotope history of ancient oceans, on the other hand, has received considerable attention using a number of approaches. In the early years of stable isotope geochemistry, much attention was devoted to the carbonate-water isotope thermometer,
and the lack of knowledge regarding the $\delta^{18}O$ values of ancient oceans was a major concern. The oxygen isotope composition of ancient oceans has relevance not only to ocean paleotemperatures, but to understanding ocean hydrothermal systems, models of ocean growth, plate tectonic histories, and reconstruction of environmental conditions in the past.

5.5.2 Secular changes in $\delta^{18}O$ of marine sediments

Marine sediments have been used to address the question of oxygen isotope compositions of ancient oceans. The $\delta^{18}O$ values of cherts, iron formations, phosphorites, and limestones provide information on how $\delta^{18}O$ values of ancient oceans may have differed from those of the modern oceans. In every suite of samples examined to date, measured $\delta^{18}O$ values of marine sediments decrease with increasing age (Fig. 5.6).

![Fig. 5.6. Schematic variation in the $\delta^{18}O$ values of cherts and carbonates. Carbonate compilation from (Kasting et al., 2006) based on compilation from Ján Veizer. Chert data from references in Figure caption 8.8. The length of the lines refers to the range of analyses ($y$ axis) and the range of potential age ($x$ axis). The lower $\delta^{18}O$ values of ancient sediments may be due to lower $\delta^{18}O_{\text{ocean}}$ values in the past, higher ocean temperatures in the past or more intense diagenesis of the older samples.]

Using oxygen isotope ratios of marine sediments to reconstruct conditions in ancient oceans is plagued with uncertainty. Consider that the $\delta^{18}O$ value of a chemical sediment in the ocean is a function of both temperature and $\delta^{18}O$ value of the water – two variables and only one analysis (the $\delta^{18}O$ value of the sediment). To complicate matters even further, the sediments examined may not have retained their original isotopic ratios through time. There are three ways to explain the observed secular trends for marine sediments seen in Fig. 5.6:

- $\delta^{18}O$ values of the oceans were more negative in the past
- Temperatures of ancient oceans were higher in the past
- Sediments become lighter with time through diagenetic reactions.
If explanation 1 is correct, mammoth and, for the most part unidirectional, changes occurred in the way the Earth operates, specifically in plate tectonic processes including cessation of activity for very long periods. Explanation 2 is attractive because temperatures were quite likely higher in the very old oceans. Some data, however, require marine organisms to have thrived at temperatures as high as about 70°C, a temperature most biologists would find unacceptable. Many workers in the field favor (at least in part) explanation 3 – diagenesis – but it too is fraught with uncertainty. Most importantly, certain sedimentary minerals are grossly more resistant to oxygen isotope exchange with diagenetic fluids than others. As a consequence, rates of diagenetic alteration are expected to be different as well. Nonetheless, the same secular trend is seen in the oxygen isotope compositions of all sedimentary rocks. It is well to point out that there are rare but important exceptions to these systematics documented in the literature. That is, there are reported cases of ancient sedimentary minerals whose oxygen isotope compositions are similar to those of modern equivalents.

Some combination of all three processes might explain the trends, but assigning relative contributions of each process is not possible with the data at hand. Understanding these secular trends and the exceptions, bears importantly on our understanding of how the Earth worked in the past and poses an exciting challenge to earth scientists.

5.6 Seawater-Basalt Interactions – buffering the $\delta^{18}$O value of the ocean

Muehlenbachs and Clayton (1976) forever changed the ‘ocean composition’ landscape with their landmark paper on interactions between seawater and oceanic crust. These authors measured oxygen isotope compositions of samples dredged from the ocean floor as well as samples from Deep Sea Drilling Project (DSDP) boreholes. Confirming early measurements of Garlick and Dymond (1970), they reported that $\delta^{18}$O values of ocean crust covered a broad range, from $<4\%_o$ to $>25\%_o$. The variability was explained by seawater alteration of oceanic crust at both low and high temperatures. Combining the two alteration regimes, Muehlenbachs and Clayton devised a model of ocean-crust interaction that effectively buffers the $\delta^{18}$O value of the ocean to its present steady-state value of 0‰. Further investigations of this model (Gregory, 1991) indicate that drastic and long-term (many tens of millions of years) changes in plate tectonic activity would be required to cause significant changes of several per mil in the $^{18}$O/$^{16}$O ratio of the ocean. Kasting et al. (2006) suggested that changes in ocean depth and rate of pelagic sediment accumulation since the beginning of the Paleozoic Era (~550 Ma) may explain the changing oxygen isotope composition of the ocean in the deep past. Their idea is discussed in section 5.7.4.

The buffering of the $\delta^{18}$O values of the ocean work in the following way. Pristine Mid Ocean Ridge Basalt (MORB) has a very uniform $\delta^{18}$O value of 5.7‰. Oceanic basalts with lower and higher values than this contain hydrous alteration phases. Muehlenbachs and Clayton recognized two types of alteration of oceanic crust – a low temperature alteration with $\delta^{18}$O values that are higher than the source mid-ocean ridge

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2 However, recent discovery of thermophilic bacteria thriving in near-boiling waters lessens the force of this argument.
basalts (MORB) and a high-temperature alteration with δ¹⁸O values that are lower than MORB. Each of these alteration mechanisms affects the δ¹⁸O value of the ocean. Alteration of continental crust by meteoric water will also affect the oxygen isotope composition of the ocean. The combined effects of these three alteration processes results in a buffering of the δ¹⁸O value of the ocean to its present-day value of 0‰ (Muehlenbachs, 1998).

5.6.1 Low-temperature alteration

The vast majority of oceanic basalts are altered to some extent at low temperature and have δ¹⁸O values that are more positive than 5.7‰. Only the youngest glassy MORB preserves its primary δ¹⁸O value of 5.7±0.2‰ (Ito et al., 1987). Most alteration of this type occurs between 0 and 15°C but some occurs at temperatures as high as 50°C. The δ¹⁸O values of basalts that were intensely altered at the lowest temperatures near 0°C can be as high as 25‰. This is because equilibrium fractionations between clay minerals and water are very large at low temperature. The altered rock has a high δ¹⁸O value, which has the effect of lowering the δ¹⁸O value of the ocean. The positive correlation between δ¹⁸O values and H₂O⁺ contents of the rock illustrates this point (Fig. 5.7). The high δ¹⁸O values are unambiguously explained by the presence of hydrous phases that form during low-temperature alteration of anhydrous basalt on the ocean floor. In most cases, measurements are made of mixtures, hereafter written as basalt, of pristine MORB and alteration phases. In the initial stages of alteration, the alteration phases may only be incipient precursors to smectite minerals and are not visible under the microscope. But even minor degrees of alteration can be easily determined by a measurement of H₂O⁺ (water given off by heating).

Low-temperature alteration starts almost immediately after extrusion of the basalt and is a very heterogeneous process that normally affects about 10% of the rock to depths of about 600 meters in the crust. After several million years the basalts reach a relatively constant δ¹⁸O value of 8 to 10‰. Lack of further change with time indicates effective cessation of circulation of low-temperature seawater through the rocks. The low-T interaction between basalt

![Graph](image-url)

**Fig. 5.7.** Variation in the δ¹⁸O values and wt% water of ocean basalts. The increase in both parameters is related to low temperature interaction with seawater. After Muehlenbachs and Clayton, (1972).
and seawater causes an increase in the $\delta^{18}$O value of the rock and a corresponding decrease in the $\delta^{18}$O value of the water, the magnitudes of which are determined by the ratios of water to rock, or W/R ratio. Stakes and O’Neil (1982) suggested that these low-T systems are water dominated with W/R > 50/1.

5.6.2 High temperature alteration

Low temperature alteration represents one half of the picture. Heat flow measurements at mid-ocean ridges show that newly formed crust is rapidly cooled by extensive penetration of vast quantities of water into the rock. The geophysical predictions were confirmed with the discovery of black smokers, ephemeral plumes of superheated water near mid ocean ridges. Petrographic evidence for high-temperature alteration is provided by greenschist-facies rocks that are found on the seafloor. $\delta^{18}$O values of these submarine greenstones or spilites are lower (down to ~1.8‰) than those of unaltered MORB, in contrast to what is observed for the vast majority of seafloor basalts that were altered at much lower temperatures. The low $\delta^{18}$O values of the basalt are consistent with high-temperature reactions and isotopic exchange between basalt and seawater, where $\Delta^{18}$O(basalt-water) values are very small. Above 300 to 350°C, equilibrium oxygen isotope fractionations between basalt and water are less than the 5.7‰ difference between unaltered MORB and ocean water. Therefore, seawater-basalt interactions at high temperatures decrease the $\delta^{18}$O value of the basalt and increase the $\delta^{18}$O value of the water. These high-T systems extend to crustal depths in excess of 1 km and tend to be rock dominated with W/R ratios ranging from extreme highs of about 50/1 to values as low as about 1/1.

Together these two alteration mechanisms along with continental weathering and other minor contributors buffer the $\delta^{18}$O value of the ocean to a value close to 0‰ (section 5.7). Perturbations from the near-zero value of the modern ocean are countered by the buffering effects of rock alteration, so that a constant value is expected over time.

5.6.3 Evidence from drill core material

Preliminary conclusions about the oxygen isotope systematics of seawater-basalt interactions in the modern oceanic crust were made on the basis of analyses of samples dredged from the ocean floor. Further work has shown that alteration processes in the crust are extremely heterogeneous and can be seen on millimeter scales in tiny veinlets and on kilometer scales along extensive fracture zones. Our understanding of the vertical distribution of $\delta^{18}$O values in seafloor basalts was greatly improved by the recovery of deep sea drillcores. Unfortunately, the cores are often incomplete, especially lacking extremely altered material. Accepting these constraints, Alt et al. (1986) measured an oxygen isotope depth profile of samples from DSDP borehole 504B. They presented evidence for low-temperature alteration in the upper 600 meters of core, followed by an abrupt change in mineralogy and isotopic composition that is consistent with high-temperature metamorphism (Fig. 5.8). The sharp division between styles of alteration at this site can be explained by a model whereby hot seawater migrated up through the relatively impermeable dike section and cold seawater descended through the more permeable upper layers.
Chapter 5. The Oceans

5.6.4 Evidence from obducted material

Obducted equivalents of oceanic crust, the ophiolites, pose no problem of sampling and offer a way of studying the problem of seawater-crust interaction in ancient materials. Because the nature of both high-T and low-T alteration on the seafloor is almost certainly time-invariant, the patterns and $\delta^{18}O$ values of seafloor alteration should be the same in ancient ophiolites as they are in the modern crust, and indeed, this is the case (Muehlenbachs, 1986). The ophiolitic sequence from the 3.5 Ga Onverwacht Group has $\delta^{18}O$ values whose ranges are indistinguishable from modern ocean samples (Hoffman et al., 1986) and similar patterns are seen in other ancient ophiolites and hydrothermal deposits (e.g., Holmden and Muehlenbachs, 1993). The most complete and best exposed section of obducted oceanic crust is provided by the Samail ophiolite in Oman (Fig. 5.9). Gregory and Taylor (1981) found that $\delta^{18}O$ variations in this ophiolite are consistent with the seafloor interactions proposed by Muehlenbachs and Clayton. Pillow basalts and the diabase dike complex have $\delta^{18}O$ values that are higher than 5.7‰ and gabbros deeper down in the section have $\delta^{18}O$ values that are lower than 5.7‰. The amount of $^{18}O$ depletion by high-T alteration appears to be balanced by the amount of $^{18}O$

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3 Ophiolites are not exactly analogous to mid ocean ridge spreading centers, but they are all that is available.

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Fig. 5.8. $\delta^{18}O$ values of DSDP Hole 504B. There is an abrupt change from values higher than to values lower than the $\delta^{18}O$ value of normal MORB at 624m, a depth that marks an interface between hot upwelling waters and cold downwelling waters. $\delta^{13}C$ values of carbonate in the rocks below 624 m have a mantle signature. The grey region reflects the majority of values measured. After Alt et al. (1986).
enrichment by low-T alteration in the Samail rocks providing strong evidence for the buffering capacity of these alteration processes.

Analyses of altered seafloor material, represented by ophiolites, suggest that the oxygen isotope composition of the ocean has been invariant through time, with the exception of transient shifts due to accumulation of glacial ice on the continents.

5.7 Buffering the $^{18}\text{O}/^{16}\text{O}$ Ratio of Ocean Water

The two competing types of seawater-basalt interactions known to occur in the oceanic crust are not coincidental and are natural consequences of basaltic magmatism occurring on the seafloor.

5.7.1 Summing the processes affecting the $^{18}\text{O}/^{16}\text{O}$ ratio of seawater

There are five natural processes that affect the oxygen isotope composition of seawater:

1. Continental weathering – lowers $\delta^{18}\text{O}_{\text{ocean}}$
2. Seafloor weathering (a misnomer meaning low-T alteration) – lowers $\delta^{18}\text{O}_{\text{ocean}}$
3. Hydrothermal alteration of ocean basalt (high-T alteration) – raises $\delta^{18}\text{O}_{\text{ocean}}$
4. Water cycling associated with subduction and magmatism
5. Continental growth (minor – long term)
6. Glaciation – raises $\delta^{18}\text{O}_{\text{ocean}}$ (short term fluctuations)

Glaciation is different in kind from the other processes. Removal of light water vapor to continental ice sheets results in unidirectional (positive) changes of 1-2 permil in the $\delta^{18}\text{O}$ value of seawater, and occurs on a relatively short time scale of $10^3$ years.

The first four processes enumerated above comprise the backbone of the buffering hypothesis. These different processes operate in such a way that the $\delta^{18}\text{O}$ value of the oceans is maintained at a value near 0‰ (Fig. 5.10). In fact the buffering model is quite robust because the $\delta^{18}\text{O}$ value of MORB is fixed and the temperatures of both low-T and high-T alteration are also fixed within narrow limits and cannot change with time. If the
\( \delta^{18}O \) value of seawater could be shifted to either higher or lower values by some unknown process, basalt-seawater interactions would force it back to a value near 0‰ in ~250 million years. The buffering rate is therefore on the order of ~100 Ma.

5.7.2 Unresolved controversy

From the very onset of stable isotope geochemistry, there have been strong proponents for and against the existence of major changes in oxygen isotope ratios of the ocean over geologic time. At this point in time, the arguments are centered on evidence for changes in \( \delta^{18}O \) of only about 3-6 per mil over relatively short geologic periods of tens of millions of years. Most of the strong evidence comes from oxygen isotope variations in carefully selected brachiopod shells and inorganic cements deposited in Devonian times (see Chapter 6). The arguments are cogent and yet model calculations, discussed below, indicate that such changes are unlikely. Biogenic phosphate is much more resistant to diagenetic changes of oxygen isotope ratios and isotopic analyses of conodonts and fossil fish remains may provide penetrating evidence on this important question, one way or the other.

5.7.3. Model calculations

Gregory (1991) presented the following material balance equation relating the rate of change \( \delta^{18}O \) of seawater to exchange processes between the lithosphere and hydrosphere

\[
d\delta W/dt = \Sigma k_i(\delta W + \Delta_i - \delta^o) \tag{5.1}
\]

![Fig. 5.10. Buffering effects of different alteration mechanisms to the \( \delta^{18}O \) value of the ocean. Plotted are the effect of each flux and how it changes the ocean isotopic composition on the billion year time scale. The sum of all the alteration mechanisms is shown by the curve 'total', which buffers the \( \delta^{18}O \) value of the ocean to a value of 0‰ See Muehlenbachs (1998) for details.](image)
where $\delta W$ is the instantaneous $\delta^{18}O$ value of seawater, $\delta_i^o$ are the initial $\delta^{18}O$ values of the different rock reservoirs ($i$), $\Delta$ are bulk fractionation factors between the $i$ reservoirs and water, and $k_i$ are the rate constants in units of 1/t.

From the definition of $\Delta$, it follows that $\delta_i^o - \Delta$ is the $\delta^{18}O$ value of seawater ($\delta W$) when steady state conditions are reached with the $i$th reservoir and

$$
\delta W_{\text{steady state}} = \frac{\sum k_i (\delta_i^o - \Delta)}{\sum k_i}
$$

In both simple and more refined models developed to address the fluxes of $^{18}O$ in and out of the ocean, relative rates of continental weathering and sea floor spreading are key parameters. There are obvious constraints on these rates, one being that the rate of continental weathering must be less than that of continental growth. Rates of seafloor spreading have very little effect on the overall buffering process as long as the average global spreading rate is greater than 1 km$^2$/yr. Present global spreading rates are 3-4 km$^2$/yr and were probably higher in the past. If seafloor spreading rates were doubled, the time required for the $\delta^{18}O$ of the ocean to return to zero from a perturbed value would be on the order of 60 million years. $\delta^{18}O$ values of the oceans could change only if seafloor spreading effectively ceased and continental weathering continued. The rate of change would be on the scale of billions of years, however. If seafloor spreading really did stop, there would be a reduction in global tectonic activity as well, and the effect of continental weathering would diminish accordingly.

### 5.7.4. An alternative explanation for the early-Earth low $\delta^{18}O$ values

An alternative view on the effect of plate tectonic-related buffering of the ocean by rock alteration was presented by Kasting et al. (2006). They suggested that conditions in the ocean have not been constant through time. In particular, they proposed that the depths of the oceans may have been shallower in the past, and as a result, the confining pressure at the mid ocean ridges from the overlying ocean would have been less than today. This would result in a significantly reduced depth of fluid penetration and reduced high temperature hydrothermal alteration at the ridges. The high temperature hydrothermal activity would have been less in the distant past and the overall $\delta^{18}O$ value of the oceans would have been lower. This idea in part explains the low $\delta^{18}O$ values measured in ancient sediments. This idea is predicated on a significant reduction in heat flow from the mantle since the Phanerozoic, an idea which is not well supported by geophysical models. Overall, the paleoclimate community remains divided over which mechanism – higher temperatures, lower $\delta^{18}O$ values of the ancient ocean, or diagenesis – are responsible for the secular variations in sediments through time.
Chapter 5. The Oceans

References


