

Ophiolites and global geochemical cycles: implications for the isotopic evolution of seawater

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Abstract: Isotopic profiles through ophiolite complexes provide the necessary link between the study of global geochemical cycles and plate tectonics. The hydrothermal circulation that occurs beneath the sea floor is the primary mechanism for exchange between the mantle of the Earth and the hydrosphere. The subduction of the hydrothermally altered crust and overlying sediments is the primary mechanism for crustal recycling. Oxygen and strontium isotopes of seawater track the competition between continental weathering and mid-ocean ridge hydrothermal exchange to control the composition of the oceans. Information derived from ophiolite studies on the elemental fluxes and the depth of seawater penetration into the oceanic crust provides constraints on the important rate constants associated with these competing processes. The same tectonic rates that account for the Sr isotope evolution of seawater indicate that the oxygen isotopic composition of the ocean is constrained to vary within narrow limits (per mil level). Isotopic analysis of dredge samples and ophiolite complexes demonstrates that seawater–ocean crust interactions result in an oxygen isotopic zonation of the oceanic crust with masses (concentration times volume) centred on the initial isotopic composition of the crust. This requires that the oxygen isotopic composition of the ocean resides at near steady-state conditions over Earth history. The inferences from ophiolite complexes contrast strongly with the results of measurements on carbonates from epicontinental seaways, particularly for the Palaeozoic. Ophiolites and greenstone belts track exchange processes between the ocean and the igneous crust whereas most carbonate measurements track the surface ocean on continental shelves. For oxygen isotopes, the mass of epicontinental seaways and the rates of meteoric water input suggest a resolution to the controversy that accounts for both data sets.

Isotopic studies of ophiolites (e.g. Muehlenbachs 1986, 1998; Alt & Teagle 2000) provide direct evidence of the interaction between seawater and oceanic crust and lithosphere. Mid-ocean ridges, as well as other centres of igneous activity, are heat engines that drive massive amounts of seawater throughout the oceanic crust. Black smoker hot spring vents are a direct manifestation of the geothermal energy available at mid-ocean ridges (e.g. Von Damm 1990). The chemical and isotopic composition of the seawater is dynamically maintained by the competition between the chemical weathering input to the oceans and the exchange between seawater and mantle-derived rocks at mid-ocean ridges (Muehlenbachs & Clayton 1976; Gregory & Taylor 1981; Holland 1984; Spencer & Hardie 1990; Gregory 1991; Hardie 1996, 1998; Holland *et al.* 1996; Muehlenbachs 1998).

Plate tectonic cycles provide a mechanism for chemical exchange between the mantle of the Earth and the lithosphere, hydrosphere and atmosphere (e.g. Gregor *et al.* 1988). On a planetary scale, the persistence of water in liquid, solid and

gas forms at Earth surface conditions over recorded geological time has profound implications for the distinctive evolution of the Earth when compared with other terrestrial planets.

Ophiolites, no matter where they form, are easily accessible places to study the time-integrated effect of water–rock interaction between seawater and the oceanic crust. Ophiolite sequences consisting of pillow lavas, sheeted dyke complexes and gabbroic plutonic complexes form by extension of the lithosphere producing new crust by intrusion of magma into volcanic rift zones. This may occur in several sea-floor settings, the most important of which is the mid-ocean ridge setting, where greater than 60% of the crust of the Earth forms. Ophiolites allow for the examination of complete sections through oceanic crust and upper-mantle lithosphere to assess depth of seawater penetration and time-integrated fluxes from isotopic profiles through crustal sections, and to gain information about the starting compositions of material that enters subduction zones.

The purpose of this paper is to review some of the key results of ophiolite studies as they relate

to the isotopic evolution of seawater, with particular emphasis on the isotopic profiles through the Samail ophiolite. The Samail ophiolite complex is one of the best examples of a well-preserved section of fossil oceanic lithosphere, and occurs as the structurally highest pre-Tertiary package of rocks in the 700 km long Oman Mountains. It provides a natural laboratory for studying the effects of seawater exchange with the crust including sources and sinks for important major elements and the depth of penetration of hydrothermal fluid into the crust.

Comparisons of measured profiles through ophiolitic crustal sections with concentrations preserved in fresh basalt and gabbro yield data about elemental sources and sinks for seawater. The volumes of crust and water involved in these oceanic processes have rate constants that are much shorter than the age of the Earth so that the chemical composition of seawater resides near a limited range of quasi-steady-state compositions.

Ophiolites and global cycles: seawater composition

The chemical and isotopic composition of seawater is the result of all of the interactions between fluid and rock where the resulting fluid finds its way back into the ocean reservoir that constitutes nearly all of the water present on the surface of the Earth. Seawater chemically exchanges with rocks made available for interaction by the rock cycle and therefore interacts with rocks directly derived from the mantle of the Earth, the continental crust, and with sediments, many of which are the products of previous precipitation from seawater. As such, seawater is a solution that is in chemical equilibrium with no particular rock. Each chemical species in the ocean is the result of the competition between processes that enrich its concentration in seawater and those that deplete its concentration in seawater.

The residence time of an element is its abundance in the ocean divided by its total flux into or out of the ocean. Residence times vary by several orders of magnitude, from hundreds of millions of years to thousands of years, and depend on the solubility of the element and its abundance in rocks. The failure of calculations using the salt content of the oceans to date the Earth, at the end of the nineteenth century, indicates something about the time scale for fluid–rock interaction within the crust (Barth 1962). From plate tectonics and ophiolite complexes, we now know the importance of sea-floor processes as a sink for elements delivered to the oceans through chemical

weathering. Even the longest residence time for a soluble element such as Na is short compared with the age of the Earth.

Boundary and initial conditions for hydrothermal activity

Ophiolitic studies combined with modern marine data including seismic data, samples dredged from the sea floor, and more limited data from drill holes provide the constraints on the geometry of accretion of oceanic crust. In addition to the contrast in chemical composition between seawater and basalt, for the purposes of considering fluid–rock interaction on the sea floor, the important constraints are the contrast in temperature between the ocean and the magmas emplaced on the sea floor, and the geometric constraints imposed by the extension of the lithosphere.

Temperatures of interaction

Basalts are the most abundant igneous rocks in the Solar System. Evidence from meteorites and lunar samples indicates that production of basalt has occurred throughout the history of the Solar System on the terrestrial planets, dating back to times not preserved in the Earth record. With the exception of Earth, where crustal compositions appear to be bimodal (sima > sial), basaltic crusts dominate the other terrestrial planets so that from the beginning, seawater has interacted with basaltic crusts. Experimental studies constrain the solidus temperatures of basalts to within a range of 100 °C of 1200 °C (e.g. Kushiro 2001). Initial magma temperatures for mid-ocean ridge basalt (MORB) source regions are probably higher than 1400 °C (Herzberg & O'Hara 1998), constraining, along with the latent heat content of the magma, the available heat for driving hydrothermal activity (e.g. Wolery & Sleep 1976).

The existence of pillow lavas in greenstone terranes from some of the oldest Archaean successions on the Earth indicates eruption of basalt into liquid water. The presence of liquid water on the surface of the Earth and the ability of the mantle of the Earth to consistently deliver basalt to the surface of the Earth constrain the average contrast in temperature between magma and seawater reservoirs to be similar over Earth history.

Geometric constraints of accretion

The average temperature of interaction between circulating seawater fluid and oceanic crust depends upon the geometry of accretion. Ophiolites such as the Samail ophiolite complex with later-

ally continuous sheeted dyke complexes require nearly 100% extension in order to form. This type of extensional setting (coupled with the initial primary permeability of the volcanic crust) provides the permeability necessary to allow for the circulation of seawater into the crust. The physical properties of water drive the circulation system towards the critical point of water (Norton 1984). The existence of permeability and a fracture system connected to the surface keep the fluid–rock interaction confined to a hydrostatically pressured system. This is in contrast to the magma chambers and crystal mush systems that reside at lithostatic pressure.

Studies of layered gabbro complexes such as the Skaergaard intrusion (e.g. Taylor & Forester 1979) clearly show that there is little direct infiltration of hydrothermal fluid into the magma chamber as long as it remains above the solidus. The heat content of the magma and the permeability contrast between the magma chamber and

rocks below the solidus promote vigorous hydrothermal activity above and to the sides of the magma chamber. These magmatic centres localize along the axes of mid-ocean ridges, the foci of magmatic activity of the ocean crust accounting for over 90% of igneous activity on the surface of the Earth. The permeability contrast between impermeable magma, fractured gabbro, and much more permeable dyke complex and pillow lava sets the conditions for hydrothermal exchange over a wide range of temperatures.

Profiles through the oceanic crust: the Samail ophiolite

The Samail ophiolite was one of the first ophiolite complexes to have profiles of Sr, Nd and O isotopes (Fig. 1) measured through relatively complete sections of oceanic crust (Gregory & Taylor 1981; Lanphere *et al.* 1981; McCulloch *et*

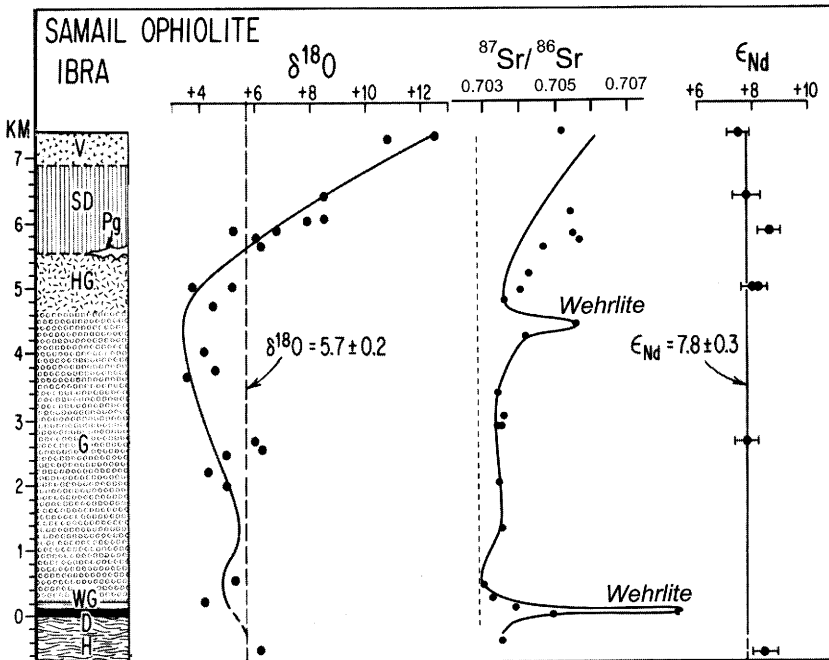


Fig. 1. Isotopic profiles through the Samail ophiolite modified after McCulloch *et al.* (1981) to include the data of Lanphere *et al.* (1981) from the Wadi Kadir traverse. Three different behaviours are illustrated: the ocean crust is a source and a sink for ^{18}O , a sink for ^{87}Sr and indifferent to ^{143}Nd exchange. The symbols V, SD and Pg correspond to oceanic layer 2 consisting of pillow lavas, sheeted dyke complex and plagiogranite, respectively. Oceanic layer 3 rocks consist of high-level non-cumulus gabbro (HG), layered cumulate gabbro (G) and wehrlite–gabbro (WG) from the composite Ibra section of the Oman Mountains. For this composite section, D represents cumulus dunite at the base of the crust and H represents tectonite harzburgite beneath the palaeo-Moho. $\delta^{18}\text{O} = [(^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{standard}} - 1] \times 10^3$ and $\epsilon_{\text{Nd}} = [(^{143}\text{Nd}/^{144}\text{Nd})_{\text{sample}} / (^{143}\text{Nd}/^{144}\text{Nd})_{\text{standard}} - 1] \times 10^4$. The standards for O and Nd are Standard Mean Ocean Water and a standard chondritic earth reservoir (CHUR), respectively.

al. 1981). The shapes of the profiles illustrate behaviours distinct for each isotopic system that relates to the particular element's abundance in the crust and in seawater. These three elements illustrate three different behaviours with respect to sea-floor hydrothermal alteration.

Neodymium: trace element with a very short residence time

Nd is an element with an extremely short residence time (300? years; e.g. Piepgras *et al.* 1979) in the ocean as a result of its insolubility in surface waters. It is present in such small concentrations because of the short residence time that the oceans are not well mixed with respect to Nd. The profile of Nd isotope ratios through the Samail ophiolite shows no effect of seawater interaction on the rocks (Fig. 1). The profile reflects the initial heterogeneity in Nd resulting from melting processes in the mantle. This is in contrast to Sr, for which the profile shows a gradient in isotopic ratios associated with sea-floor hydrothermal exchange.

Strontium isotopes: trace element with a million year residence time

Sr is an element with a residence time of the order of a few million years so that the oceans are relatively well mixed with respect to Sr isotopes. Sr isotope ratios are enriched in the upper portions of the Samail oceanic crust, reflecting the exchange with seawater that had an isotopic ratio near 0.707 during the Cretaceous. Phases such as plagioclase in the layered gabbro have enriched Sr contents relative to pyroxene and olivine so that anorthositic layers deep in crustal layer 3 still record the mantle-derived signature of 0.70295. However, even at depths near the Moho, Sr-depleted samples such as wehrlite layers exhibit a pronounced enrichment in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios indicative of exchange with seawater Sr (Fig. 1).

Seawater Sr is derived from two competing processes: input of radiogenic Sr from the weathering of Rb-enriched continental crustal rocks and input of mantle-derived Sr from Rb-depleted mantle. Because Cretaceous seawater had an isotopic ratio greater than that of the mantle, the altered oceanic crust is always enriched in $^{87}\text{Sr}/^{86}\text{Sr}$ compared with its primary initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Exchange with mantle-derived Sr at mid-ocean ridges drives the isotopic composition of Sr in seawater towards the mantle value and keeps the Sr isotopic composition of seawater from moving all the way to the average isotopic

composition of the river flux (*c.* 0.712–0.715; Goldstein & Jacobsen 1988; Palmer & Edmond 1989). Secular change curves for Sr isotopes show that the Phanerozoic Sr isotopic composition of seawater ($0.706 < ^{87}\text{Sr}/^{86}\text{Sr} < 0.709$) lies between the end-member compositions reflected by fluid in isotopic equilibrium with mantle Sr and fluids carrying Sr derived from continental weathering.

Oxygen isotopes: temperature-dependent fractionation and 100 Ma residence time

The oxygen isotope profile is the most complex of all, reflecting exchange between a major element reservoir in seawater and the oceanic lithosphere (Fig. 1). Oxygen isotopes are light stable isotopes and in contrast to Sr isotopes exhibit a significant temperature-dependent fractionation between rock and water (>20‰, for plagioclase–water, O'Neil & Taylor 1967). For example, in the top parts of the section, low-temperature (e.g. 70 °C) albitization produces albite that is *c.* 20‰ enriched relative to seawater. Andesine resulting from 400 °C exchange between dyke complex rocks and circulating fluid is only a few per mil enriched relative to the seawater-derived fluid. Anorthite surviving exchange in the deeper portions of ocean layer 3 will be depleted almost 3‰ (using the exchange curve of O'Neil & Taylor 1967).

As a result, the upper parts of the oceanic crust are enriched in ^{18}O whereas the lower parts of the oceanic crust are generally depleted in ^{18}O . There is a gradient in $\delta^{18}\text{O}$ values downward in the crust, decreasing from values >+10‰ to values less than +4‰. After passing through a $\delta^{18}\text{O}$ minimum, still moving downward in the crust, the $\delta^{18}\text{O}$ curve then increases down-section back towards normal basaltic $\delta^{18}\text{O}$ values of *c.* +6‰.

Three different elements with residence times spanning approximately six orders of magnitude produce very different exchange profiles. The Nd profile is virtually unchanged when compared with a profile for pristine basalt and gabbro. This is an element that would require more than 10 000 masses of fluid to produce major isotopic change in the altered oceanic crust (McCulloch *et al.* 1981). Sr isotopes show an enrichment of the isotope ratio of the oceanic crust and a depletion of the oceans in ^{87}Sr with respect to the input of Sr isotopes from continental weathering. This is a system that clearly cannot be buffered solely by exchange with the oceanic crust, i.e. the crust is always a sink for ^{87}Sr .

For oxygen isotopes, the amount of enrichment or depletion is a function of the average temperature of exchange, the permeability of the rocks, and the time-integrated fluid flux (water/rock

ratio). With respect to seawater, the oceanic crust is both a major source and a sink for ^{18}O . Because oceanic crustal production amounts to over 90% of the total crustal growth rate of the Earth, seawater must reach a steady-state value with respect to the mantle of the Earth.

Special significance of oxygen isotope profile for seawater

When the profiles of oxygen isotopes are averaged, there are roughly complementary masses of enriched and depleted rocks that appear to balance each other so that the mean value of the altered oceanic crust is close to its primary $^{18}\text{O}/^{16}\text{O}$ ratio (Muehlenbachs & Clayton 1976; Gregory & Taylor 1981). In other words, the average bulk fractionation between seawater with a $\delta^{18}\text{O}$ value of *c.* 0 and mantle-derived rocks with $\delta^{18}\text{O}$ of *c.* 6‰ is close to the difference between the two reservoirs, i.e. +6‰. If the balance is not exact, then some other reservoir is important in controlling the oxygen isotopic composition of the oceans.

The observation that oceans near $\delta^{18}\text{O}$ *c.* 0 provide altered rocks with ^{18}O enrichments and depletions requires that the $\delta^{18}\text{O}$ value of the ocean achieve some steady state with respect to the average $\delta^{18}\text{O}$ value of the mantle. Given the time constants for exchange (100 Ma time scale), the balance need not be exact in every section that only takes a fraction of a perturbation half-life to produce. As long as the actual measured bulk Δ value ($\delta^{18}\text{O}$ of the average crust minus the $\delta^{18}\text{O}$ value of seawater) between the altered crust and seawater is near +6‰ for a long-term average, the oceans will migrate towards a $\delta^{18}\text{O}$ value of zero (Gregory 1991; Muehlenbachs 1998).

Comparison with oceanic layer 3 results

Figure 2 compares the oxygen isotope results of coexisting mineral pairs from oceanic and Samail ophiolitic realms, and shows a great similarity in the style and spread along the non-equilibrium exchange arrays (e.g. Gregory *et al.* 1989). These non-equilibrium arrays result from differing rates of isotopic exchange between seawater and plagioclase (easily exchanged) and pyroxene (more resistant to exchange). Non-equilibrium arrays are preserved only if the duration of the exchange event is short and if the exchange event is at a high enough temperature to allow pyroxene to remain stable in the presence of seawater-derived fluid. Both conditions are satisfied because the time scale for the cooling gabbroic crust is short enough, $<10^6$ years (Gregory *et al.* 1989), and

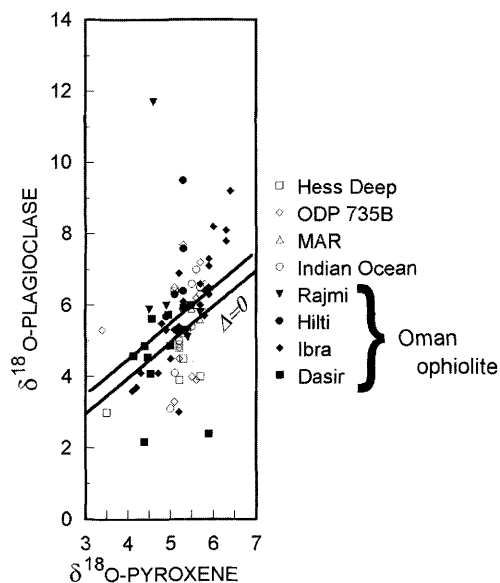


Fig. 2. Comparison between the oceanic layer 3 gabbro results (Stakes 1991; Lecuyer & Reynard 1996) and those from the Samail ophiolite complex (Gregory *et al.* 1989; Stakes & Taylor 1992; new data from the Dasir section of the ophiolite) for coexisting pyroxene and plagioclase. Both fast-spreading (Hess Deep) and slow-spreading ridges (Mid-Atlantic Ridge, MAR; Indian Ocean dredge samples, Indian Ocean Hole 735B) are represented from the modern ocean basins. Irrespective of tectonic setting, the pyroxene–plagioclase pairs display non-equilibrium fractionations (differences in the $\delta^{18}\text{O}$ values between plagioclase and coexisting pyroxene) consistent with subsolidus exchange with seawater-derived hydrothermal fluid. Under equilibrium conditions, coexisting mineral pairs are forbidden to plot below the zero fractionation ($\Delta = 0$). Similarly, more rapid exchange of plagioclase with strongly ^{18}O -shifted hydrothermal fluids results in anomalously large differences between plagioclase and pyroxene $\delta^{18}\text{O}$ values. It should be noted that the Oman traverses from Wadis Rajmi and Hilti are *c.* 50 km apart in the northern Oman Mountains. The new Dasir data are from a section that lies *c.* 100 km SE of Wadi Hilti near the Samail Gap, which separates the Jabal Akhdar dome from the Saih Hatat dome. The Ibra data are from the southeastern Oman Mountains (45 km SE of Dasir) and represent results from several profiles within a 20 km block perpendicular to the strike of the sheeted dykes.

pyroxenes in the highest grade rocks are either petrographically unaltered or exhibit incipient alteration to brown amphibole.

The results for several sections of the Samail ophiolite separated by few hundred kilometres normal (and several hundred parallel) to the spreading direction and oceanic crust are similar.

Whereas the original tectonic setting for the Oman ophiolite is controversial (e.g. Moores *et al.* 2000), both slow-spreading (Mid-Atlantic Ridge and Indian Ocean) and fast-spreading regimes (Hess Deep) are represented in the plagioclase–pyroxene pairs from modern ocean basins. Ophiolite pairs and oceanic pairs exhibit similar non-equilibrium relationships in δ – δ plots of the $\delta^{18}\text{O}$ value of pyroxene plotted against that for plagioclase.

The similarity in alteration styles also extends to the fine-scale development of millimetre-scale vein systems in gabbroic rocks of layer 3. Manning *et al.* (2000) showed that high-temperature veins in the Samail ophiolite were similar to those found in the Hess Deep, indicating that permeability development in layer 3 rocks was similar in ophiolite and sea floor. Manning *et al.* (2000) compared the Samail ophiolite to a fast-spreading mid-ocean ridge system. The data for layer 3 gabbros complement results summarized by Alt & Teagle (2000), who compared the profiles of the upper-crustal sections of ophiolites, specifically Troodos and Oman, with profiles derived from sea-floor studies. Similarly, Banerjee & Gillis (2001) have compared suprasubduction zone rocks from the Tonga Arc with ophiolites and mid-ocean ridge rocks and found similar alteration patterns, with the exception of more epidote and trondjhemite in the forearc spreading environment.

All of the studies show that hydrothermal alteration, the effects of hot rock interacting with hot fluids, is not a very good discriminator of tectonic setting. The question is whether the distribution of $\delta^{18}\text{O}$ values observed in altered oceanic crust, and more particularly ophiolites, is sufficiently sensitive to detect isotopic variability in the global ocean over geological time (e.g. Veizer *et al.* 1999; Wallmann 2001).

Comparison with continental layered gabbro complexes

The flood basalt provinces, coastal dyke swarms and layered intrusions found in ancient rift zones share many similarities with ophiolites in terms of boundary and initial conditions for fluid–rock interaction. Continental layered gabbro complexes thus provide an answer to the question of whether ophiolites are sensitive to changes in seawater $\delta^{18}\text{O}$ values (Veizer *et al.* 1999; Wallmann 2001). The major difference in the settings is that meteoritic water is often the starting fluid instead of seawater. Over most of the Earth, meteoric fluids are on average about 4‰ depleted with respect to modern seawater. However, in some continental regions, meteoric waters (particularly

at high latitudes and at high altitudes) exhibit depletions greater than 10‰ with respect to modern seawater (e.g. Rozanski *et al.* 1993).

The studies of Taylor and coworkers have defined the isotopic exchange characteristics of meteoric hydrothermal exchange in continental layered gabbro complexes (e.g. Criss & Taylor 1986; Criss 1999). The most complete of these studies is the work on the Skaergaard layered intrusion (Taylor & Forester 1979). Figure 3 shows a comparison of the pyroxene–plagioclase pairs from the Skaergaard intrusion with those from oceanic crust and ophiolite complexes.

Mineral δ – δ diagrams can also display whole-rock data by plotting their $\delta^{18}\text{O}$ values on the zero fractionation line. This facilitates comparison of mineral pairs with whole rocks from the entire crustal section. In this case, the whole-rock values are for hydrothermally altered basalts and diabase; the results are strikingly different for continental and oceanic environments. Through the examination of shifts in the spread in $\delta^{18}\text{O}$ values of isotopically exchanged rocks, it is possible to detect differences in the isotopic composition of the starting material at the few per mil level. This clearly shows that large (5–10‰) changes in the $\delta^{18}\text{O}$ value of seawater would be easily detectable in an ophiolite section.

Whole-rock $\delta^{18}\text{O}$ values of pillow lavas through time

Figure 4 shows the whole-rock $\delta^{18}\text{O}$ values of pillow lavas through time. Pillow lavas typically exhibit zeolite- to greenschist-facies metamorphic assemblages. Bowers & Taylor (1985) were able to calculate the bulk fractionation factor for pillow basalt altered in seawater. This bulk-rock–seawater fractionation factor clusters near the value of +6‰; yet most greenstones exhibit $\delta^{18}\text{O}$ values that cluster around +9‰. For greenstones to be enriched in ^{18}O relative to seawater, there must be an initial, low-temperature partial exchange followed by subsequent growth of greenschist mineral assemblages. From a petrological viewpoint, this is most probably accomplished by an initial hydration of the groundmass glass followed by conversion to sheet silicates such as chlorite accompanied by albitization of calcic plagioclase.

A simple single-stage, hydrothermal exchange with seawater at greenschist facies should produce altered basalt or diabase with $\delta^{18}\text{O}$ values less than 6‰. Black smoker vent fluids typically exhibit $\delta^{18}\text{O} > 0$ (Shanks 2001) so that there must be a complementary ^{18}O -depleted reservoir in the recharge volume for the black smoker vent fluid.

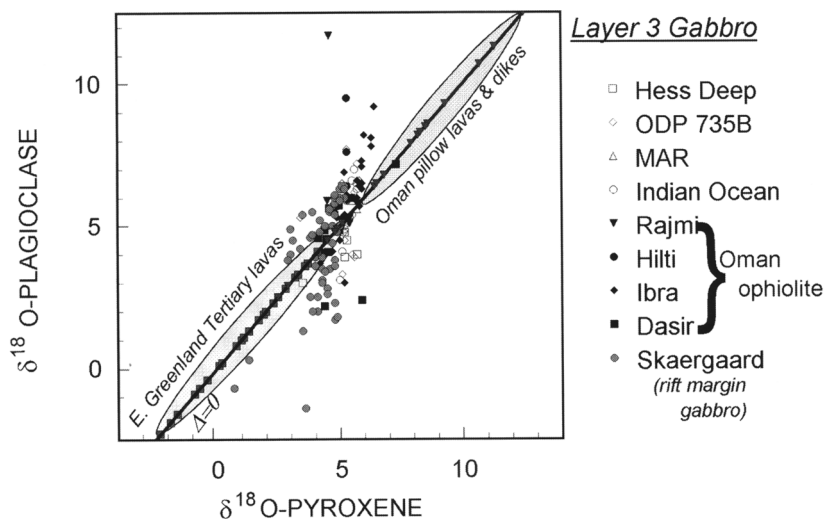


Fig. 3. Comparison of Skaergaard intrusion mineral pair data with those from oceanic layer 3 rocks along with $\delta^{18}\text{O}$ values of altered basaltic whole rocks plotted along the zero fractionation line (■, East Greenland Tertiary lava; ▼, Oman pillow lavas). The Skaergaard intrusion was altered by fluids with an initial $\delta^{18}\text{O}$ value > -11 using δD from altered rocks (Taylor & Forester 1979) that give calculated water δD *c.* -100 , and assuming a meteoric water line with a D excess of $+10\text{‰}$. The fields for Oman pillow lava and East Tertiary lavas are strikingly different, as would be expected for pillow lava sections altered by -5 to -10‰ seawater. These results are inconsistent with the forward modelling shown by Wallmann (2001), where somehow the isotopic profile of the oceanic crust is rendered insensitive to changes in starting fluid isotopic composition by parameters in the model. Data from the Skaergaard intrusion are from Taylor & Forester (1979), and pillow lava data are from Gregory & Taylor (1981) and Stakes & Taylor (1992).

A plausible explanation for the ^{18}O -enriched character of most greenstones is that there is a superposition of alteration regimes as the new crust spreads away from the ridge axis. As the crust spreads, the rocks encounter ^{18}O -shifted fluids exiting from the newly solidified sides of the magma chamber where layer 3 gabbro has become depleted in ^{18}O (e.g. Gregory & Taylor 1981).

Two mechanisms are capable of producing greenschist-facies meta-basalt and diabase with $\delta^{18}\text{O}$ values greater than $+6\text{‰}$ that involve superposition of exchange regimes in an evolving crust. Whatever the mechanism of the increase in $\delta^{18}\text{O}$ values of altered pillow lavas and diabase dykes, it is clear that if the $\delta^{18}\text{O}$ value of the starting seawater fluid was shifted downward by 5 – 6‰ , the measured values in Figure 4 would be very different. The mean greenstone $\delta^{18}\text{O}$ value of *c.* $+8$ – 9‰ would be shifted downward to values less than 6‰ . The data from the Skaergaard intrusion and other continental volcanic provinces clearly show depleted volcanic rocks when fluids are ^{18}O -depleted relative to seawater.

Even though it is not possible to demonstrate complementary depleted and enriched ^{18}O reservoirs in the ancient past for entire profiles through

the oceanic crust, the most common submarine rock type in the ancient rock record, greenstones (altered pillow lavas), exhibit $\delta^{18}\text{O}$ values consistent with seawater $\delta^{18}\text{O}$ values near zero over Earth history. The result is inconsistent with inferences from the carbonate record (e.g. Wallmann 2001) that require that the $\delta^{18}\text{O}$ value of the global ocean changed rapidly by as much as 6‰ over certain intervals of Phanerozoic history.

The rate constant problem

Attempts to explain the discrepancy between the greenstone–ophiolite isotopic record and the carbonate record group into three types of interpretations. The first is that the $\delta^{18}\text{O}$ value of seawater changes by as much as 5 – 10‰ over geological time. This is a larger increase for a major constituent of water and rock than that observed for the trace element Sr. This interpretation is in clear conflict with the ophiolite record. Second, the surface temperature of the Earth as recorded by carbonates and cherts varies by several tens of degrees and, in general, surface temperatures were tens of degrees higher than today's if seawater maintains its $\delta^{18}\text{O}$ value near zero. This interpretation seems to run counter to global temperature

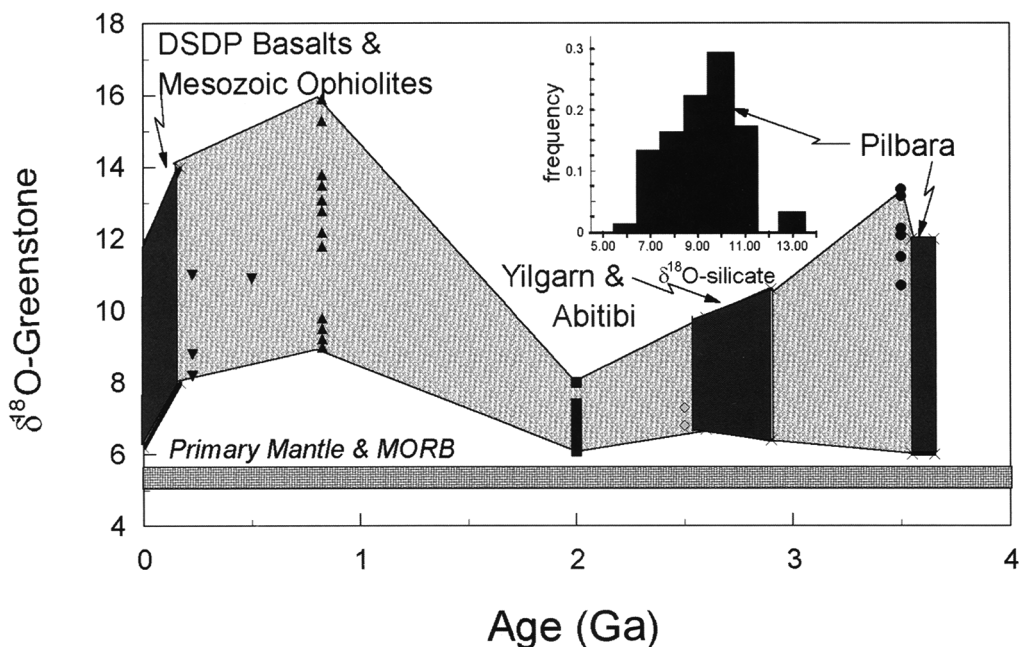


Fig. 4. $\delta^{18}\text{O}$ values of greenstones through geological time. Greenstones with $\delta^{18}\text{O}$ values $>+6\%$ are common throughout Earth history and are inconsistent with exchange and alteration by fluids strongly depleted in ^{18}O . ∇ , Canyon Mountain (Permian) and Bay of Islands (Ordovician) ophiolite; \blacktriangle , Darb Zubaydah Ophiolite, Saudi Arabia, an accreted arc terrane; \blacksquare , Purtuniqu ophiolite; \diamond , Fortescue pillow lavas basement for the Hamersley Iron Formation; \bullet , Barberton Mountain Belt; figure modified from Gregory (1991; references therein). The Purtuniqu ophiolite data are from Holmden & Muchlenbachs (1993). The frequency distribution in the inset shows the results for over 100 greenstone silicate analyses from the Pilbara block, mainly from the North Pole Dome, Western Australia. DSDP, Deep Sea Drilling Project.

change estimates from sedimentology and climate modelling, and from astrophysical inferences that suggest a faint young Sun (e.g. Sagen & Mullen 1972; Hoffman *et al.* 1998). If anything, inferences about the snowball Earth suggest that mean global temperatures may have been lower than isotopic estimates, which have them double or triple back into the past (e.g. Knauth & Epstein 1976). Third, one of the records, either the ophiolite or the carbonate record, is irrelevant to the isotopic composition of the oceans.

The major contributions of ophiolite studies to the seawater oxygen isotope controversy are two-fold. First, ophiolite studies confirmed inferences from dredge sample work summarized by Muehlenbachs & Clayton (1976) that hypothesized the existence of complementary reservoirs of ^{18}O -depleted and ^{18}O -enriched rocks in the altered oceanic crust. Second, the demonstration of the depth of penetration of seawater in a more complete geological context allows the estimation of the rate constants of exchange. Table 1 shows

rate constant calculations for Sr and O isotopes using the same assumptions of oceanic crustal production rates and continental weathering rates translated into numbers that make sense tectonically following the analysis of Gregory (1991; references therein) on the profiles shown in Figure 1.

A global spreading rate of $3 \text{ km}^2 \text{ a}^{-1}$ yields a characteristic age of oceanic crust of about 100 Ma assuming an oceanic crustal area of $3 \times 10^8 \text{ km}^2$. A chemical weathering rate of $3 \text{ km}^3 \text{ a}^{-1}$ yields a mean age of continental crust of about 2500 Ma for a constant crustal volume of $7.5 \times 10^9 \text{ km}^3$ (e.g. Armstrong 1991). Tectonic rates significantly different from these rates are not geologically sustainable, otherwise the rock record would change dramatically. The age distributions on the continents and in the ocean basins would be substantially different from the current distribution with young ocean basins ($<150 \text{ Ma}$) and middle-aged continents (mean age of 1.8–2.6 Ga). Interpretations of measured iso-

topic ratios on carbonate rocks that require huge changes in the tectonic rates for the Earth suggest that there must be another explanation for these carbonate data sets.

Table 1 shows that the same spreading rates and chemical weathering rates applied to the Sr and O isotopic systems yield dramatically different results consistent with observations on the isotopic composition of the oceans. The rates take into account the depth of penetration of seawater into the crust for each isotopic system, the integrated fluid and the elemental concentrations in fluid and rocks. The target steady-state values are calculated from reasonable choices for the isotopic composition of the reservoirs for the continental and oceanic crust (e.g. Goldstein & Jacobsen 1988; Palmer & Edmond 1989). For Sr, this is straightforward because there are minimal temperature effects. Weathering is more dominant (63:37) in controlling the Sr isotopic composition of seawater, which can change rapidly on geological time scales (<5 Ma).

For oxygen isotopes, the target value for seawater is chosen by assuming an average value of rocks (δ_i) dissolved minus a bulk-rock–fluid fractionation factor (Δ_{iw}) of +20 for continental weathering. This target value reflects all of the geological time that has passed so that the rock cycle has produced sediments with a memory of their previous interactions with the oceans, i.e. the bulk $\delta^{18}\text{O}$ value is no longer dominated by a normal igneous rock signature ($\delta^{18}\text{O} < +8\text{‰}$; Taylor 1968). A frequency distribution diagram of sandstone whole-rock $\delta^{18}\text{O}$ values illustrates the shift upwards in isotopic composition from first cycle sediments such as the Archaean Lalla Rookh

Sandstone to the Phanerozoic Lachlan and Ouachita fold belt sandstones (Fig. 5). The net effect is that the target for the $\delta^{18}\text{O}$ value of the ocean driven by the weathering flux changes from a minimum value of -14 to -4‰ .

The target value for oxygen isotopes for the ridge crest interaction is based upon the difference in the $\delta^{18}\text{O}$ values between the ocean and the mantle reservoir that partially melts to produce the oceanic crust. The ridge crest interaction is more dominant for O isotopes; the roles are reversed when compared with Sr isotopes and the time constant for the simple cycle is *c.* 100 Ma instead of *c.* 2 Ma for Sr isotopes. Other workers have concentrated on estimating the relative amounts of high- and low-temperature alteration and ^{18}O exchange that will depend on the relative portions of oceanic layer 2 and 3 rocks (e.g. Holland 1984; Muehlenbachs 1986; Wallmann 2001). In analysis of Table 1, this variability is buried in the value of Δ between the crust and seawater.

The fluctuations in the value Δ can be gauged by examining the variability in thickness of the oceanic layers deduced from seismic refraction surveys (e.g. Shor & Raitt 1969). These surveys sample much more of the oceanic crust than has been possible by drilling and dredging. The possible perturbations in the value of Δ induced by changes in the relative proportions of high- and low-temperature exchange must scale like the variability in the thickness of oceanic layers 2 and 3. Considering the mean age of the oceanic crust and the symmetry of spreading processes, these perturbations to the value of Δ are likely to be short compared with the half-life of a perturbation to the global ocean $\delta^{18}\text{O}$ value.

Table 1. Tectonic rates transformed into cycle rates, characteristic times, weighting factors and steady-state target isotopic ratios (after Gregory 1991)

	Tectonic rate	Rate (Ma^{-1})*	Time (Ma) [†]	f^{\ddagger}	Target [§]
<i>Ridge crest</i>					
Oxygen	$3 \text{ km}^2 \text{ a}^{-1}$	0.008	125	0.73	0
Strontium	$3 \text{ km}^2 \text{ a}^{-1}$	0.160	6.3	0.37	0.703
<i>Weathering</i>					
Oxygen	$3 \text{ km}^3 \text{ a}^{-1}$	0.003	350	0.27	-4
Strontium	$3 \text{ km}^3 \text{ a}^{-1}$	0.278	3.6	0.63	0.712
<i>Total</i>					
Oxygen		0.011	91		-1
Strontium		0.438	2.3		0.709

*The rate constant is the coefficient (k) for the damping factor (e^{-kt}) for transient perturbations.

[†]Characteristic time is $1/k$. The process with the shortest time constant usually dominates.

[‡] $f_i = k_i / \sum k_i$.

[§]Near steady state, the target $\delta^{18}\text{O}$ value for seawater after its exchange with the i th reservoir is $(\delta_i - \Delta_{iw})$. Near steady state, the seawater $\delta^{18}\text{O} = \sum f_i(\delta_i - \Delta_{iw})$, where $f_i = k_i / \sum k_i$. Because of the rock cycle, particularly for the continents, the δ_i can vary faster than the system can respond.

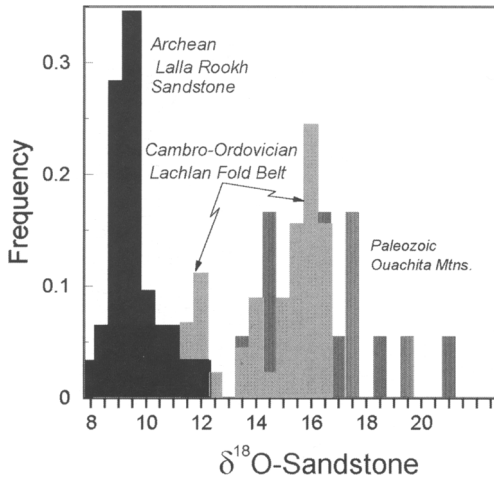


Fig. 5. A comparison between the $\delta^{18}\text{O}$ values of sandstones from an Archean sandstone succession (new measurements from the Lalla Rookh Sandstone, Pilbara block, Western Australia) and Palaeozoic fold belts (the Lachlan fold belt, Australia, Gray *et al.* 1991; and the Ouachita Mountains, USA, Richards *et al.* 2002). As a result of the rock cycle and the recycling of crustal quartz enriched in ^{18}O owing to low-temperature interactions with surface fluids, the $\delta^{18}\text{O}$ values of Phanerozoic sandstones are higher than those from first cycle sands sourced from Archean quartz-bearing igneous rocks. The effect of all of the recycling of crustal materials is to shift the target value of seawater resulting from continental weathering upward from $<-10\%$ to values closer to -4% .

Figure 6 shows calculations for oxygen isotopes using a fixed $3 \text{ km}^3 \text{ a}^{-1}$ chemical weathering rate (e.g. $26 \text{ tons km}^{-2} \text{ a}^{-1}$ actual rock dissolution, Berner & Berner 1996) with variable spreading rates from 1 to $5 \text{ km}^2 \text{ a}^{-1}$. The area filled by the pattern represents the best estimate based upon spreading rates for the last 150 Ma. The inset shows the half-life of a perturbation for different choices of tectonic weathering rates and spreading rates. For nearly all combinations of spreading and weathering rates that produce the dichotomy in the ages between ocean basins and continents, the ridge interaction should dominate the oxygen isotopic composition of the oceans.

Global weathering rates

Large changes in weathering rates ($60\text{--}150 \text{ km}^3 \text{ a}^{-1}$) are required to shift the $\delta^{18}\text{O}$ value of seawater by the magnitude (the absolute change and the time scale for the change) required by interpretations of the carbonate record (e.g. Walker & Lohmann 1989; Gregory 1991; Wallmann 2001). Chemical denudation rates measured from

today's rivers (see the review by Berner & Berner 1996), when extrapolated into global weathering rates, range from $c. 50 \text{ km}^3 \text{ a}^{-1}$ for dissolution of evaporites to $11 \text{ km}^3 \text{ a}^{-1}$ for carbonate rocks and down to about $2\text{--}3 \text{ km}^3 \text{ a}^{-1}$ for silicate rocks. Clearly, there are not enough evaporite rocks in the crust of the Earth to sustain such high dissolution rates.

The mean value of the dissolved load is closer to $5 \text{ km}^3 \text{ a}^{-1}$, which then is corrected down to about $3 \text{ km}^3 \text{ a}^{-1}$ ($26 \text{ tons km}^{-2} \text{ a}^{-1}$, Berner & Berner 1996). These rates scaled to the volume of continental crust yield crustal residence times that range from 150 to 3750 Ma. Hercod *et al.* (1998) estimated a chemical denudation rate of $4 \text{ km}^3 \text{ a}^{-1}$ (residence time 1.9 Ga) in a carbonate rock dominated watershed where serial measurements were made over a period of 1 year to take into account seasonal changes in solute export. This estimate is a factor of two lower than the average carbonate rate reported above.

Clearly, geological rates that yield residence times significantly different from the mean age of the continental crust are not sustainable. Recycling of rocks already formed in the presence of seawater with a $\delta^{18}\text{O}$ value close to zero has little effect on the oxygen isotopic composition of the oceans, so that it is the processing of mantle-derived silicate that has the biggest impact on the $\delta^{18}\text{O}$ value of seawater. The rates inferred for silicate rocks are in general less than $3 \text{ km}^3 \text{ a}^{-1}$; this is particularly so if the continental crust has grown slightly with time (e.g. Albarede 1989).

In Figure 6, the quasi-steady-state $\delta^{18}\text{O}$ value of seawater is less than the present-day value of the ocean because of the presence of ice sheets today that result in a $c. 1\%$ enrichment in the $\delta^{18}\text{O}$ value of seawater. During our global ice-house conditions (Fischer 1982) significant volumes of ^{18}O -depleted ice are stored in the Antarctic and Greenland ice sheets (e.g. Gregory & Taylor 1981). Because most of the pre-Cretaceous carbonate ^{18}O measurements are on continental shelf rocks, it is instructive to look at the water balance for the Earth.

Short-term water cycle effects on the $\delta^{18}\text{O}$ of seawater

Waxing and waning of ice sheets produces an oxygen isotope ice volume effect that shows up in ice cores (Petit *et al.* 1999) and deep-sea cores (Emiliani 1978). Because the processes involving ice sheet advance or retreat involve time constants less than 10^5 years and are reversible, the net effect of the glacial advance and retreat is to add 'noise' to the long-term signal (Gregory & Taylor

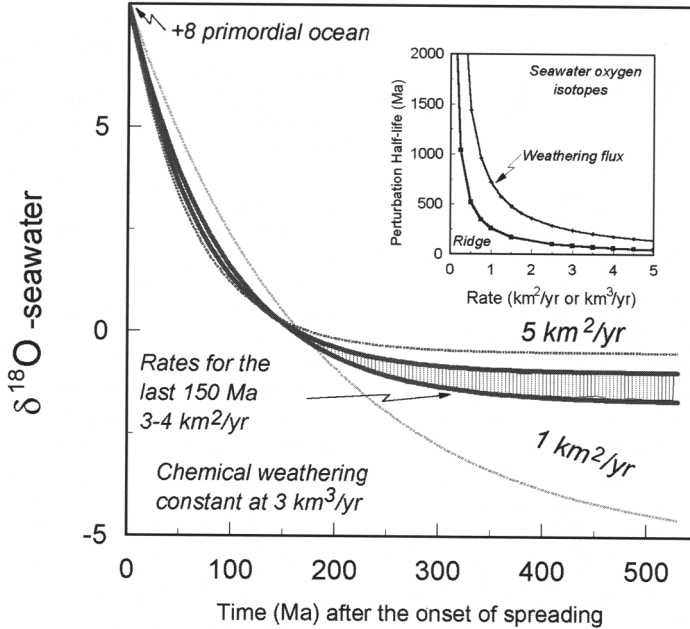


Fig. 6. $\delta^{18}\text{O}$ evolution of seawater for plausible choices of spreading rates and chemical weathering rates, assuming a starting ocean outgassed from the mantle during early Earth history. It should be noted that the +8‰ starting composition could just as easily been -8‰ and the shape of the curve would be similar to the curve shown by Wallmann (2001) for the change in seawater $\delta^{18}\text{O}$ during the Phanerozoic. This curve and the curve of Wallmann (2001) are smoother than the actual curves inferred from carbonate data. The global cycle for oxygen isotopes in seawater cannot accommodate rapid changes (several per mil per 10 Ma) through fluid-rock interaction that occurs at any plausible geological rate (Walker & Lohmann 1989; Gregory 1991). The question is: why would the isotopic composition of the global ocean ever have moved to -8‰ in the first place? The system is damped for any reasonable combination of spreading and weathering rates (inset) so that the global ocean obtains $\delta^{18}\text{O}$ values near 0‰ early in Earth history, probably by the beginning of the Archaean. The ^{18}O -depleted rocks that must have resulted from high-temperature exchange in the crust are very difficult to find in the rock record. In particular, the lack of ^{18}O -depleted greenstones and gabbros is troubling for global seawater changes inferred solely from carbonate, phosphate and chert (e.g. Muehlenbachs 1998). The inset shows perturbation half-life v. weathering and spreading rates cast as tectonic rates amenable to dimensional analysis. Any plausible combination of weathering and spreading rates must be consistent with the dichotomy of young ocean basins and middle-aged continental crust relative to the age of the Earth. Permissible combinations of tectonic rates drive the $\delta^{18}\text{O}$ value of seawater towards its current value.

1981). Long-term storage of ^{18}O -depleted ice will shift the $\delta^{18}\text{O}$ value of the ocean towards more positive values. The long-term global cycle will work to reverse the increase in $\delta^{18}\text{O}$, provided the ice caps can persist for significant portions of perturbation half lives, about the time scale of an era like the Cenozoic.

Table 2 illustrates a mass balance calculation for the hydrosphere. Any perturbation to the ocean by partitioning water between the ocean and other reservoirs is simply its mole fraction times its $\delta^{18}\text{O}$ value. Ice volume changes have clearly imparted per mil level changes in the oxygen isotopic composition of the oceans; if only because the $\delta^{18}\text{O}$ value of ice is strongly ^{18}O depleted with respect to seawater. The meteoric

water cycle provides a mechanism to produce masses of ^{18}O -depleted water.

Epicontinental seaways

In the geological past, particularly during times of inferred global greenhouse conditions, sea level was higher than it is today. Epicontinental seaways are much more extensive during times of more rapid sea-floor spreading. Land-locked epicontinental seas or very large shallow seaways could conceivably have significantly lower $\delta^{18}\text{O}$ values than the global ocean. The last row in Table 2 shows the impact of a large epicontinental sea (the surface area of all continents, 100 m deep, that has a $\delta^{18}\text{O}$ value of -5‰ close to the average of

Table 2. *Water balance*

Reservoir	Volume*	%	$\delta^{18}\text{O}$	$X \cdot ^{18}\text{O}$
Oceans	1400	96	0	0
Ice caps and glaciers	43.4	2.97	<i>c.</i> -35	-1.04
Ground water	15.3	1.0	-4	-0.04
Meteoric waters	0.2	0.01	-4	-0.00
Total	1459	100	-1.1	-1.08
Maximum epicontinental sea [†]	30	2.05	-5	-0.1

*Volumes from Berner & Berner (1996).

[†]For this purpose, a maximum epicontinental sea is a hypothetical 100 m deep sea covering $3 \times 10^8 \text{ km}^2$; this is larger than any conceivable seaway. It should be noted that -0.1 is the change in seawater if the reservoir was instantaneously mixed back into seawater. X is the volume %, \approx the mole fraction of the reservoir.

modern meteoric water) on the $\delta^{18}\text{O}$ value of seawater. Such a hypothetical seaway would affect the $\delta^{18}\text{O}$ value of the global ocean by enriching it by only +0.1‰.

The results of these mass balance calculations indicate that it is possible that ophiolites and greenstones could be recording seawater isotopic signatures much different from those recorded by carbonates from epicontinental shelf regions from supercontinental masses. This suggests that there may be a wealth of palaeoenvironmental information present in the isotope and trace element signatures of pristine carbonate rocks that needs to be tested against plate reconstructions and global circulation models for the atmosphere and oceans. The carbonate record is at least a four-dimensional record that includes two spatial coordinates as well as $\delta^{18}\text{O}$ and time.

Two documented examples exist for interior seaways in the Cretaceous, when most workers would agree that the global oceans were not less than -1‰. The first is the Late Cretaceous interior seaway of North America, where portions of the water mass may have been as low as -6‰ (e.g. Tourtelot & Rye 1969; Wright 1987). The second example is the Late Aptian Eromanga Basin (Fig. 7), where DeLurio & Frakes (1999) found glendonite pseudomorphs after ikaite. Ikaite is a hydrated carbonate that only forms in water near freezing. Using the transformation of ikaite to glendonite (calcite), the measured oxygen isotopic composition glendonite shifts the oxygen isotope composition of the seaway downward to *c.* -3‰. As a result, calculated belemnite palaeotemperatures shifted downward by 10 °C to become more consistent with the presence of dropstones in the Bulldog Shale and terrestrial palaeotemperatures near freezing (Ferguson *et al.* 1999) from southeastern Australia determined from fluvial sediments with cryoturbation structures.



Fig. 7. A palaeoreconstruction of the Eromanga epicontinental sea during the Aptian–Albian for Australia showing the palaeolatitude and the position of the glendonite locality (DeLurio & Frakes 1999) of the Australian interior epicontinental seaway. Terrestrial outcrops are represented by the shaded areas and the localities where low- $\delta^{18}\text{O}$ meteoric waters are inferred from analyses of syndepositional calcite concretions in fluvial sediments from the Otways and Strzelecki Ranges, southeastern Australia (two dots; Ferguson *et al.* 1999). Waters calculated using the transition temperature from ikaite to calcite yield seaway water compositions of *c.* -3‰, which put belemnite palaeotemperatures into better agreement with the presence of ice-rafted dropstones and cryoturbation structures in southeastern Australia.

Significance of ophiolite studies

Ophiolites by their very nature, as pieces of ancient oceanic lithosphere that have escaped recycling that occurs at subduction zones, may

form in anomalous tectonic settings when compared with the normal ridge systems that extend for over 40 000 km over the surface of the Earth. For obduction to occur, ophiolite complexes must form in regions where plate interactions must be changing on a regional scale (100–1000 km). However, the physical and chemical processes that occur when hot rock interacts with seawater (10 km scale) in a zone of magmatic intrusion and extension are similar whether they occur at mid-ocean ridges, back-arc basins or in suprasubduction zone spreading centres.

Alteration patterns seen in ophiolite complexes are similar to those found in dredge samples and drill cores from the sea floor. Geometric constraints from ophiolites have shaped interpretations of the structure of the sea floor. Importantly, ophiolite studies provide the three-dimensional information on the deeper levels of the oceanic crust and upper mantle difficult to obtain from sea-floor studies.

Ophiolites with sheeted dyke complexes formed in ocean basins at water depths where seawater is likely to be the agent for fluid–rock interaction. All ophiolite and greenstone studies show similar patterns of fluid–rock interaction in terms of oxygen isotopes. If the global ocean ever was as depleted as interpretations of the carbonate record require (e.g. Veizer *et al.* 1999), there would be more ^{18}O -depleted greenstones observed in the rock record. Figure 8 shows Bay of Islands ophiolite whole-rock data as a function of depth. The Cambro-Ordovician Bay of Islands ophiolite was hydrothermally altered during a time when the global oceans were presumably very strongly depleted in ^{18}O (e.g. Veizer *et al.* 1999). The ophiolite simply does not confirm the existence of oceans with low $\delta^{18}\text{O}$ values, i.e. the rocks are not depleted as they should be (dashed curve on Fig. 8) if the oceans had the $\delta^{18}\text{O}$ value inferred by Veizer *et al.* (1999). There should be abundant oceanic layer 3 rocks from ophiolites that have $\delta^{18}\text{O}$ values <0 (Fig. 8). So far, these rocks have not been found; indicating that there must be another explanation for the carbonate oxygen isotope record.

Conclusions

Ophiolites provide a critical link between plate tectonics and global geochemical cycles because these rocks are important for understanding the most dominant crust-forming process for the Earth and for understanding its transformation from pristine mantle-derived rocks to the rocks that eventually are subducted at convergent margins. These processes enable the crust and hydrosphere to exchange elements with the mantle of the

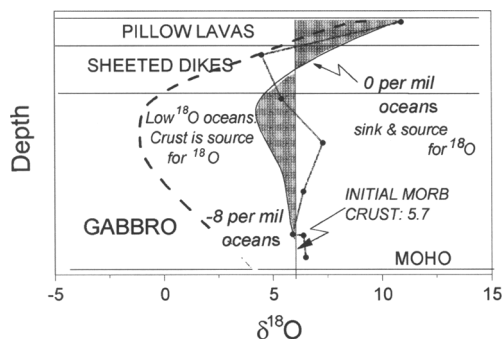


Fig. 8. Schematic profile showing a $\delta^{18}\text{O}$ profile typical for near steady-state conditions, i.e. the crust is both depleted and enriched in ^{18}O . The steady-state condition is typical of the Earth when the $\delta^{18}\text{O}$ value of seawater is close to zero. This is compared with a hypothetical profile (bold dashed line) calculated using mass balance and temperature constraints from the Samail ophiolite with the seawater fluid shifted downward to -8% . In this scenario, the crust becomes a major source for ^{18}O so that the ocean would be in a transient state with a perturbation time scale of *c.* 100 Ma. Shown for comparison are Bay of Islands ophiolite data (dots with tie lines) cited by Gregory & Taylor (1981). This ophiolite is late Cambrian and dates from a time when the global oceans according to the carbonate record, if interpreted literally, were sufficiently depleted in ^{18}O to produce the calculated dashed line profile. k, mainly from the North Pole Dome, Western Australia. DSDP, Deep Sea Drilling Project.

Earth. The behaviour of every element must be examined separately.

Profiles through the Samail ophiolite show that different elements behave very differently during hydrothermal exchange at the spreading centre. Yet, through measurement and analysis, a common set of tectonic rates (rates of material exchange) can account for the apparently different controls on the isotopic abundances. An element such as Sr can exhibit concentrations indicative of river fluxes and continental weathering inputs as the dominant control on the Sr isotopic composition of the seawater. The same global material exchange rates explain the buffering of the $\delta^{18}\text{O}$ value of the ocean by ridge crest processes.

Material balance calculations suggest that there is no reason to assume that epicontinental seaways faithfully record the isotopic composition, at least for oxygen isotopes, of the global ocean. Large changes in the isotopic composition of the interior seaways can be explained by processes related to cycling and storage of meteoric waters without affecting the oxygen isotopic composition of the global ocean. Pristine oxygen isotopic data from epicontinental seaways may record a wealth of palaeoenvironmental information.

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