

Figure 9.39 $\delta^{18}\text{O}$ in young, fresh basalts. Dashed line is at the mean of MORB (+5.7). From Harmon and Hoefs (1995).

ian xenoliths (Figure 9.38) have lower $\delta^{18}\text{O}$ than their equivalents from elsewhere. This suggests the possibility, at least, that part of the variability in oceanic basalts reflects mantle heterogeneity. However, additional studies will be required to establish this with certainty.

9.8.1.2 Hydrogen

Estimating the isotopic composition of mantle hydrogen, carbon, nitrogen, and sulfur is even more problematic. These are all volatile elements and are present at low concentrations

in mantle materials. They partition partially or entirely into the gas phase of magmas upon their eruption. This gas phase is lost, except in deep submarine eruptions. Furthermore, C, N, and S have several oxidation states, and isotopic fractionations occur between the various compounds these elements form (e.g., CO_2 , CO , CH_4 , H_2 , H_2O , H_2S , SO_2). This presents two problems. First, significant fractionations can occur during degassing, even at magmatic temperatures. Second, because of loss of the gas phase, the concentrations of these elements are low. Among other problems, this means their isotope ratios are subject to disturbance by contamination. Thus the isotopic compositions of these elements in igneous rocks do not necessarily reflect those of the magma or its mantle source.

Hydrogen, which is primarily present as water, but also as H_2 , H_2S , and CH_4 , can be lost from magmas during degassing. However, basalts erupted beneath a kilometer or more of ocean retain most of their dissolved water. Thus mid-ocean ridge basalts and basalts erupted on seamounts are important sources of information of the abundance and isotopic composition of hydrogen in the mantle.

As Figure 9.40 indicates, MORB has a mean $\delta\text{D}_{\text{SMOW}}$ of about -67.5‰ and a standard deviation of $\pm 14\text{‰}$. How much of this variability reflects fractionation during degassing and contamination is unclear. Kyser (1986) has argued that mantle hydrogen is isotopically homogenous with $\delta\text{D}_{\text{SMOW}}$ of -80‰ . The generally heavier isotopic composition of MORB, he argued, reflects H_2O loss and other processes. Others, for example, Poreda *et al.* (1986) and Chaussidon *et al.* (1991), have observed correlations between δD and Sr and Nd isotope ratios and have argued that these provide clear evidence that mantle hydrogen is isotopically heterogeneous. Chaussidon *et al.* (1991) have suggested a δD value for the depleted upper mantle of about -55‰ .

The first attempt to assess the hydrogen isotopic composition of the mantle materials was that of Sheppard and Epstein (1970), who analyzed hydrous minerals in xenoliths and concluded that δD varied in the mantle. Since then, many additional studies have been carried out. As Figure 9.40 shows, phlogopites ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$) have δD that is

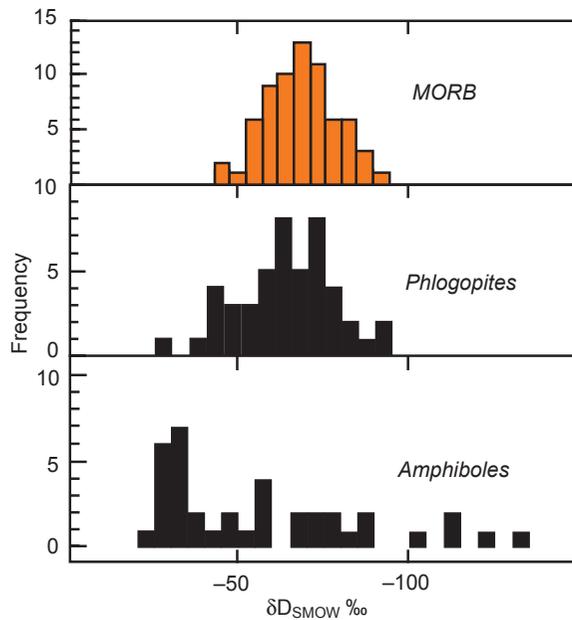


Figure 9.40 δD in MORB and in mantle phlogopites and amphiboles. The MORB and phlogopite data suggest the mantle has δD_{SMOW} of about -60 to -90 .

generally similar to that of MORB, though heavier values also occur. Amphiboles have much more variable δD and have heavier hydrogen on average. Part of this difference probably reflects equilibrium fractionation. The fractionation between water and phlogopite is close to 0‰ in the temperature range 800–1000°C, whereas the fractionation between water and amphibole is about -15 ‰. However, equilibrium fractionation alone cannot explain either the variability of amphiboles or the difference between the mean δD of phlogopites and amphiboles. Complex processes that might include Rayleigh distillation may be involved in the formation of mantle amphiboles. This would be consistent with the more variable water content of amphiboles compared with phlogopites. There are also clear regional variations in δD in xenoliths that argue for large-scale heterogeneity. For example, Deloule *et al.* (1991) found that δD in amphiboles from xenoliths in basalts in the Massif Central of France have systematically high δD (-59 to -28 ‰) while those from Hawaii can be very low (-125 ‰). At the opposite extreme, Deloule *et al.* (1991) also observed isotopic heterogeneity within single

crystals, which they attributed to incomplete equilibration with magmas or fluids.

9.8.1.3 Carbon

Most carbon in basalts is in the form of CO_2 , which has limited solubility in basaltic liquids. As a result, basalts begin to exsolve CO_2 before they erupt. Thus virtually every basalt, including those erupted at mid-ocean ridges, has lost some carbon, and subaerial basalts have lost virtually all carbon (as well as most other volatiles). Therefore only basalts erupted beneath several km of water provide useful samples of mantle carbon, so the basaltic data-set is essentially restricted to MORB and samples recovered from seamounts and the submarine part of Kilauea's East Rift Zone. The question of the isotopic composition of mantle carbon is further complicated by fractionation and contamination. There is a roughly 4‰ fractionation between CO_2 dissolved in basaltic melts and the gas phase, with ^{13}C enriched in the gas phase. Carbonatites and diamonds provide alternative, and generally superior, samples of mantle carbon, but their occurrence is extremely restricted.

MORB has a mean $\delta^{13}C$ of -6.5 ‰ (Figure 9.41), but the most CO_2 -rich MORB samples have $\delta^{13}C$ of about -4 ‰. Since they are the least degassed, they presumably best represent the isotopic composition of the depleted mantle (Javoy and Pineau, 1991). Carbonatites also have a mean $\delta^{13}C$ close to -4 ‰. Ocean island basalts erupted under sufficient water depth to preserve some CO_2 in the vesicles and appear to have similar isotopic compositions. Gases released in subduction zone volcanoes and back-arc basin basalts, which erupt behind subduction zones and are often geochemically similar to island arc basalts, have carbon that can be distinctly lighter (lower $\delta^{13}C$), though most $\delta^{13}C$ values are in the range of -2 to -4 ‰, comparable to the most gas-rich MORB. Carbon in mantle diopsides (clinopyroxenes) appears to be isotopically lighter on average, and the significance of this is unclear.

Diamonds show a large range of carbon isotopic compositions (Figure 9.41). Most diamonds have $\delta^{13}C$ within the range of -2 to -8 ‰, hence similar to MORB. However, some diamonds have much lighter carbon. Based on the inclusions they contain, dia-

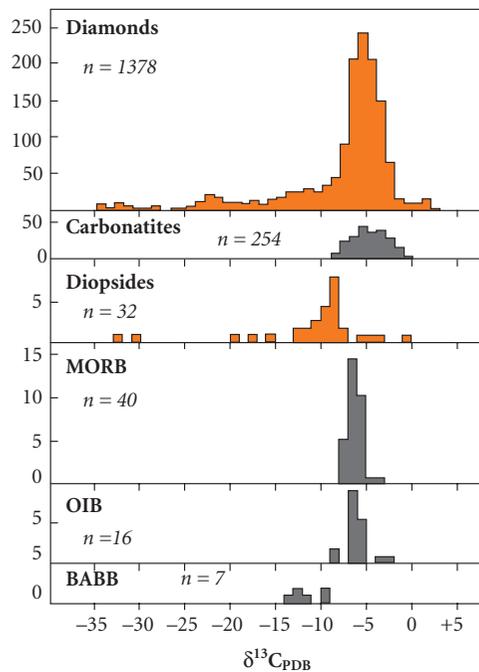


Figure 9.41 Carbon isotope ratios in mantle (red) and mantle-derived materials (gray). From Matthey (1987). Reproduced with permission.

monds can be divided between peridotitic and eclogitic. Most peridotitic diamonds have $\delta^{13}\text{C}$ close to -5‰ , while eclogitic diamonds are much more isotopically variable. Most, though not all, of the diamonds with very negative $\delta^{13}\text{C}$ are eclogitic. Many diamonds are isotopically zoned, indicating they grew in several stages.

Three hypotheses have been put forward to explain the isotopic heterogeneity in diamonds: primordial heterogeneity, fractionation effects, and recycling of organic carbon from the Earth's surface into the mantle. Primordial heterogeneity seems unlikely for a number of reasons. Among these is the absence of very negative $\delta^{13}\text{C}$ in other materials, such as MORB, and the absence of any evidence for primordial heterogeneity from the isotopic compositions of other elements. Boyd and Pillinger (1994) have argued that since diamonds are kinetically sluggish (witness their stability at the surface of the Earth, where they are thermodynamically out of equilibrium), isotopic equilibrium might not be achieved during their growth. Large fractionations might therefore occur due to kinetic

effects. However, these kinetic fractionations have not been demonstrated, and fractionations of this magnitude (20‰ or so) would be surprising at mantle temperatures.

On the other hand, several lines of evidence support the idea that isotopically light carbon in some diamonds had its origin as organic carbon at the Earth's surface. First, such diamonds are primarily of eclogitic paragenesis, and eclogite is the high-pressure equivalent of basalt. Subduction of oceanic crust continuously carries large amounts of basalt into the mantle. Oxygen isotope heterogeneity observed in some eclogite xenoliths suggests these eclogites do indeed represent subducted oceanic crust. Second, the nitrogen isotopic composition of isotopically light diamonds is anomalous relative to nitrogen in other mantle materials. Finally, Farquhar *et al.* (2002) found mass-independent fractionation ($\Delta^{33}\text{S}$ up to 0.6‰) in sulfide inclusions in eclogitic diamonds. If, as is believed, the mass-independent fractionation arises from UV photolysis in the atmosphere, then the sulfur in these diamonds must once have been at the surface of the Earth.

9.8.1.4 Nitrogen

The solubility of N_2 in magmas is very limited, hence of volcanic rocks, once again only submarine basalts provide useful samples of mantle N. There are both contamination and analytical problems with determining nitrogen isotope ratios in basalts, which, combined with its low abundance (generally less than 1 ppm), mean that accurate measurements are difficult to make. Nitrogen substitutes readily for carbon in diamonds, which can contain up to 2000 ppm N, making diamonds important samples of mantle N. Nitrogen may be present as the ammonium ion in many kinds of rocks. NH_4^+ substitutes readily for K in many minerals; consequently N concentrations in sediments and metasediments may reach several hundred ppm. In all, a fair amount of data is now available for a variety of mantle and crustal materials, and these data are summarized in Figure 9.42. Measurements of $\delta^{15}\text{N}_{\text{ATM}}$ in MORB range from about -10 to $+8\text{‰}$, with a mean value of about -3 to -5‰ . Peridotitic diamonds show a similar range, but are a little lighter on average. Eclogitic diamonds show considerably greater

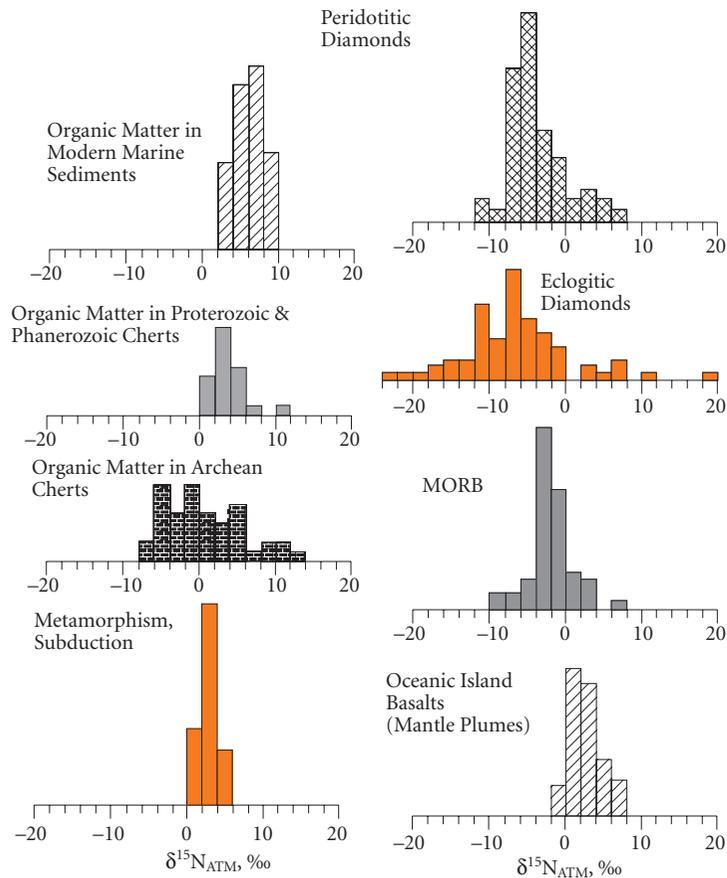


Figure 9.42 Isotopic composition of nitrogen in rocks and minerals of the crust and mantle. Modified from Marty and Dauphas (2003). With permission from Elsevier.

scatter in $\delta^{15}\text{N}_{\text{ATM}}$, with the most common values in the range of -12 to -6% . Interestingly, ocean island basalts, which presumably sample mantle plumes, have distinctly more positive $\delta^{15}\text{N}_{\text{ATM}}$, with a mean in the range of $+3$ to $+4\%$. The N isotopic composition of mantle plumes thus appears to match well with that of organic matter in post-Archean sediments, metamorphic rocks, and subduction-related volcanic rocks. This observation led Marty and Dauphas (2003) to propose that nitrogen in mantle plumes is largely recycled from the surface of the Earth. They argue that because nitrogen can be bound in minerals as ammonium, it is more readily subducted and recycling into the mantle than other gases.

Figure 9.42 also illustrates an interesting shift in $\delta^{15}\text{N}$ in organic matter in sediments in the late Archean. Marty and Dauphas (2003) suggest two possible causes. First, the absence

of atmospheric oxygen in the Archean meant that there was no nitrate, and hence no dissimilatory denitrification and consequently no fractionation associated with that process. Second, chemosynthetic life may have dominated the Archean. Modern chemosynthetic bacteria from hydrothermal vent ecosystems have a lower $\delta^{15}\text{N}$ than most plants, meaning the N isotopic composition of organic matter in Archean sediments would have been lighter than in post-Archean sediments.

9.8.1.5 Sulfur

There are also relatively few sulfur isotope measurements on basalts, in part because sulfur is lost during degassing, except for those basalts erupted deeper than 1 km below sea-level. In the mantle, sulfur is probably predominantly or exclusively in the form of sulfide, but in basalts, which tend to be some-

what more oxidized, some of it may be present as SO₂ or sulfate. Equilibrium fractionation should lead to SO₂ being a few per mil lighter than sulfate. If H₂S is lost during degassing, the remaining sulfur would become heavier; if SO₂ or SO₄ is lost, the remaining sulfur would become lighter. Total sulfur in MORB has δ³⁴S_{CDT} in the range of +1.3 to -1‰, with most values in the range 0 to +1‰. Sakai *et al.* (1984) found that sulfate in MORB, which constitutes 10–20% of total sulfur, was 3.5 to 9‰ heavier than sulfide. Basalts from Kilauea's East Rift Zone have a very restricted range of δ³⁴S of +0.5 to +0.8 (Sakai *et al.*, 1984).

Chaussidon *et al.* (1989) analyzed sulfides present as inclusions in minerals, both in basalts and in xenoliths, and found a wide range of δ³⁴S (-5 to +8‰). Low-Ni sulfides in oceanic island basalts, kimberlites, and pyroxenites had more variable δ³⁴S than sulfides in peridotites and peridotite minerals. They argued there is a fractionation of +3‰ between sulfide liquid and sulfide dissolved in silicate melt. Carbonatites have δ³⁴S between +1 and -3‰ (Hoefs, 1987; Kyser, 1986). Overall, it appears the mantle has a mean δ³⁴S in the range of 0 to +1‰, which is very similar to meteorites, which average about +0.1‰.

Chaussidon *et al.* (1987) found that sulfide inclusions in diamonds of peridotitic paragenesis (δ¹³C ~ -4‰) had δ³⁴S of about +1‰ while eclogitic diamonds had higher and much more variable δ³⁴S (+2 to +10‰). Eldridge *et al.* (1991) found that δ³⁴S in diamond inclusions was related to the Ni content of the sulfide. High-Ni sulfide inclusions, which they argued were of peridotitic paragenesis, had δ³⁴S between +4‰ and -4‰. Low-Ni sulfides, which are presumably of eclogitic paragenesis, had much more variable δ³⁴S (+14‰ to -10). These results are consistent with the idea that eclogitic diamonds are derived from subducted crustal material.

9.8.2 Stable isotopes in crystallizing magmas

The variation in stable isotope composition produced by crystallization of a magma depends upon the manner in which crystallization proceeds. The simplest, and most unlikely, case is *equilibrium* crystallization. In this situation, the crystallizing minerals remain in isotopic equilibrium with the melt until

crystallization is complete. At any stage during crystallization, the isotopic composition of a mineral and the melt will be related by the fractionation factor, α. Upon complete crystallization, the rock will have precisely the same isotopic composition as the melt initially had. At any time during the crystallization, the isotope ratio in the remaining melt will be related to the original isotope ratio as:

$$\frac{R_\ell}{R_0} = \frac{1}{f + \alpha(1-f)}; \quad \alpha \equiv \frac{R_s}{R_\ell} \quad (9.67)$$

where R_l is the ratio in the liquid, R_s is the isotope ratio of the solid, R₀ is the isotope ratio of the original magma, and *f* is the fraction of melt remaining. This equation is readily derived from mass balance, the definition of α, and the assumption that the element concentration in the magma is equal to that in the crystals; an assumption valid to within about 10%. It is more convenient to express eqn. 9.67, in terms of δ:

$$\Delta = \delta_{melt} - \delta_0 \equiv \left[\frac{1}{f + \alpha(1-f)} \right] * 1000 \quad (9.68)$$

where δ_{melt} is the value of the magma after a fraction *f* - 1 has crystallized and δ₀ is the value of the original magma. For silicates, α is not likely to be much less than 0.998 (i.e., Δ = δ¹⁸O_{xtals} - δ¹⁸O_{melt} ≥ -2). For α = 0.999, even after 99% crystallization, the isotope ratio in the remaining melt will change by only 1 per mil.

The treatment of *fractional crystallization* is analogous to Rayleigh distillation. Indeed, it is governed by the same equation:

$$\Delta = 1000(f^{\alpha-1} - 1) \quad (9.46)$$

The key to the operation of either of these processes is that the product of the reaction (vapor in the case of distillation, crystals in the case of crystallization) is only instantaneously in equilibrium with the original phase. Once it is produced, it is removed from further opportunity to attain equilibrium with the original phase. This process is more efficient at producing isotopic variations in igneous rocks, but its effect remains limited because α is generally not greatly different from 1. Figure 9.43 shows the calculated change in the oxygen isotopic composition of melt

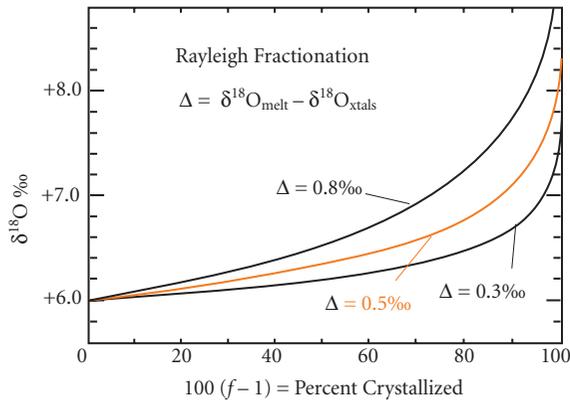


Figure 9.43 Plot of $\delta^{18}\text{O}$ versus fraction of magma solidified during Rayleigh fractionation, assuming the original $\delta^{18}\text{O}$ of the magma was +6. After Taylor and Sheppard (1986).

undergoing fractional crystallization for various values of Δ ($\approx 1000(\alpha - 1)$). In reality, Δ will change during crystallization because of (1) changes in temperature, (2) changes in the minerals crystallizing, and (3) changes in the liquid composition. The changes will generally mean that the effective Δ will increase as crystallization proceeds. We would expect the greatest isotopic fractionation in melts crystallizing non-silicates such as magnetite, and melts crystallizing at low temperature, such as rhyolites, and the least fractionation for melts crystallizing at highest temperature, such as basalts.

Figure 9.44 shows observed $\delta^{18}\text{O}$ as a function of temperature in two suites: one from a propagating rift on the Galapagos Spreading Center, the other from the island of Ascension. There is a net change in $\delta^{18}\text{O}$ between the most and least differentiated rocks in the Galapagos of about 1.3‰; the change in the Ascension suite is only about 0.5‰. These, and other suites, indicate the effective Δ is generally small, of the order of 0.1–0.3‰. Consistent with this is the similarity of $\delta^{18}\text{O}$ in peridotites and MORB, which suggests a typical fractionation during melting of 0.2‰ or less.

We can generalize the temperature dependence of oxygen isotope fractionations by saying that at low temperature (i.e., Earth surface temperatures up to the temperature of

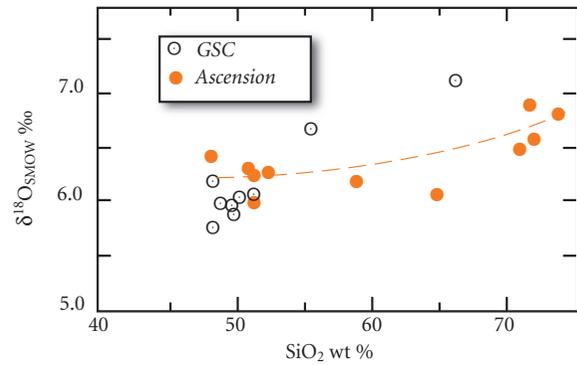


Figure 9.44 $\delta^{18}\text{O}$ as a function of SiO_2 in a tholeiitic suite from the Galapagos Spreading Center (GSC) (Muehlenbachs and Byerly, 1982) and an alkaline suite from Ascension Island (Sheppard and Harris, 1985). Dashed line shows model calculation for the Ascension suite.

hydrothermal systems, 300–400°C), oxygen isotope ratios are changed by chemical processes. The amount of change can be used as an indication of the nature of the process involved, and, under equilibrium conditions, of the temperature at which the process occurred. *At high temperatures (temperatures of the interior of the Earth or magmatic temperatures), oxygen isotope ratios are minimally affected by chemical processes and can be used as tracers much as radiogenic isotope ratios are.*

These generalizations lead to an axiom: *igneous rocks whose oxygen isotopic compositions show significant variations from the primordial value (+6) must either have been affected by low-temperature processes, or must contain a component that was at one time at the surface of the Earth* (Taylor and Sheppard, 1986).

9.8.3 Combined fractional crystallization and assimilation

Because oxygen isotope ratios of mantle-derived magmas are reasonably uniform ($\pm 1\%$ of 5.6‰) and generally different from rocks that have equilibrated with water at the surface of the Earth, oxygen isotopes are a useful tool in identifying and studying the assimilation of country rock by intruding

magma. We might think of this process as simple mixing between two components: magma and country rock. In reality, it is always at least a three-component problem, involving country rock, magma, and minerals crystallizing from the magma. Magmas are essentially never superheated; hence the heat required to melt and assimilate surrounding rock can only come from the latent heat of crystallization of the magma. Approximately 1 kJ/g would be required to heat rock from 150°C to 1150°C and another 300 J/g would be required to melt it. If the latent heat of crystallization is 400 J/g, crystallization of 3.25 g of magma would be required to assimilate 1 g of country rock. Since some heat will be lost by simple conduction to the surface, we can conclude that the amount of crystallization will inevitably be greater than the amount of assimilation (the limiting case where mass crystallized equals mass assimilated could occur only at great depth in the crust where the rock is at its melting point to begin with). The change in isotopic composition of a melt undergoing the combined process of assimilation and fractional crystallization (AFC) is given by:

$$\delta_m - \delta_0 = [(\delta_a - \delta_0) - \Delta \times R] \{1 - f^{1/(R-1)}\} \quad (9.69)$$

where R is the mass ratio of material crystallized to material assimilated, Δ is the difference in isotope ratio between the crystals and the magma ($\delta_{\text{crystal}} - \delta_{\text{magma}}$), f is the fraction of liquid remaining, δ_m is the $\delta^{18}\text{O}$ of the magma, δ_0 is the initial $\delta^{18}\text{O}$ of the magma, and δ_a is the $\delta^{18}\text{O}$ of the material being assimilated (Taylor and Sheppard, 1986). The assumption is made that the concentration of oxygen is the same in the crystals, magma and assimilant, which is a reasonable assumption. This equation breaks down at $R = 1$, but, as discussed earlier, R is generally significantly greater than 1. Figure 9.45 shows the variation of $\delta^{18}\text{O}$ of a magma with an initial $\delta^{18}\text{O} = 5.7$ as crystallization and assimilation proceed.

9.9 ISOTOPES OF BORON AND LITHIUM

Although there are a few earlier works in the literature, there was little interest in the isotopic composition of boron and lithium until

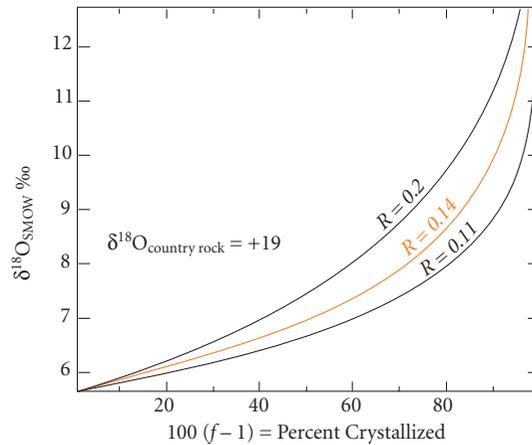


Figure 9.45 Variation in $\delta^{18}\text{O}$ of a magma undergoing AFC versus amount crystallized. Initial $\delta^{18}\text{O}$ of the magma is +5.7. After Taylor (1980).

about 20 years ago. This is perhaps because both elements have low abundances in the Earth compared with the other elements we have discussed thus far. It is perhaps also because of the analytical problems: neither B nor Li form gaseous species that can be analyzed in the gas-source mass spectrometers used for analysis of other stable isotopes, and the fractionation produced in thermal ionization mass spectrometers, which are used for elements such as Sr, Nd, and Pb, would exceed the natural ones. Since the development of new analytical techniques that overcame this latter problem in the 1980s, the field of boron isotope geochemistry has developed rapidly, and a range of about 9% in the $^{11}\text{B}/^{10}\text{B}$ ratio in terrestrial materials has been observed. Boron isotope geochemistry has been used to address a wide variety of geochemical problems. Most notable among these are: hydrothermal processes, the nature and origin of ore-forming fluids, the origin of evaporites and brines, pH of ancient oceans, the origin of subduction-related magmas, and geochemical evolution of the mantle.

Though both lithium and boron can occur as stoichiometric components of minerals, these minerals have limited occurrence, and these elements generally substitute for other elements in silicates. Boron is relatively abundant in seawater, with a concentration of 4.5 ppm. Lithium is somewhat less abundant,

with a concentration of 0.17 ppm. In silicate rocks, the concentration of boron ranges from a few tenths of a ppm or less in fresh basalts and peridotites, to several tens of ppm in clays. Lithium concentrations in these materials typically range from a few ppm to a few tens of ppm. The $^{11}\text{B}/^{10}\text{B}$ is reported as per mil variations, $\delta^{11}\text{B}$, from the NIST SRM* 951 standard. The $^7\text{Li}/^6\text{Li}$ ratio is reported as per mil variation, $\delta^7\text{Li}$, from the NIST SRM 8545 Li_2CO_3 (L-SVEC) standard (see Table 9.1). Prior to 1996, Li isotope ratios were often reported as $\delta^6\text{Li}$, that is, deviations from the $^6\text{Li}/^7\text{Li}$ ratio. However, the standard used was the same, so that for variations of less than about 10, $\delta^7\text{Li} \approx -\delta^6\text{Li}$; at higher deviations, a more exact conversion is necessary, e.g., $-38.5\text{‰} \delta^6\text{Li} = 40\text{‰} \delta^7\text{Li}$. The analytical precision for most of the Li isotope data now in the literature is about 1‰, but recent advances, particularly the use of multiple-collector inductively coupled plasma mass spectrometers, promises to reduce uncertainty to as little as 0.2‰.

9.9.1 Boron isotopes

In nature, boron has a valence of +3 and is almost always bound to oxygen or hydroxyl groups in either trigonal (e.g., BO_3) or tetrahedral (e.g., $\text{B}(\text{OH})_4^-$) coordination (the only exception is boron bound to fluorine, BF_3). Since the bond strengths and vibrational frequencies of trigonal and tetrahedral forms differ, we can expect that isotopic fractionation will occur between these two forms. This is confirmed by experiments which show a roughly 20‰ fractionation between $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$, with ^{11}B preferentially found in the $\text{B}(\text{OH})_3$ form.

In natural aqueous solutions boron occurs as both boric acid, $\text{B}(\text{OH})_3$, and the borate ion, $\text{B}(\text{OH})_4^-$, the dominant species being determined by pH. At pH of around 9 and above, $\text{B}(\text{OH})_4^-$ dominates, while at lower pH $\text{B}(\text{OH})_3$ dominates. In seawater, which has a pH in the range of 7.6 to 8.1, about 80–90% of boron will be in the $\text{B}(\text{OH})_3$ form. Most fresh waters are a little more acidic so $\text{B}(\text{OH})_3$ will be more dominant; only in highly alkaline

solutions, such as saline lakes, will $\text{B}(\text{OH})_4^-$ be dominant. The most common boron mineral in the crust is tourmaline ($\text{Na}(\text{Mg,Fe,Li,Al})_3\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH,F})_4$), in which boron is present in BO_3 groups. In clays, boron appears to occur primarily as $\text{B}(\text{OH})_4^-$, most likely substituting for silica in tetrahedral layers. The coordination of boron in common igneous minerals is uncertain, possibly substituting for Si in tetrahedral sites. As we noted in Chapter 7, boron is an incompatible element in igneous rocks and is very mobile. It is also readily adsorbed on to the surfaces of clays. There is an isotopic fractionation between dissolved and adsorbed B of -20 to -30‰ (i.e., adsorbed B is ^{11}B poor), depending on pH and temperature (Palmer *et al.*, 1987).

Figure 9.46 illustrates the variation in B isotopic composition in a variety of geologic materials. Spivack and Edmond (1987) found the $\delta^{11}\text{B}$ of seawater to be $+39.5\text{‰}$, and uniform within analytical error ($\pm 0.25\text{‰}$). Fresh mid-ocean ridge basalts typically have $\delta^{11}\text{B}$ of about $-4.25 \pm 2\text{‰}$ (White and Klein, 2013). Oceanic island basalts (OIB) have slightly lighter $\delta^{11}\text{B}$ (e.g., Chaussidon and Jambon, 1994). The average B isotopic composition of the continental crust probably lies between -13‰ and -8‰ (Chaussidon and Albarède, 1992).

Perhaps the most remarkable aspect of B isotope geochemistry is the very large fractionation of B isotopes between the oceans and the silicate Earth. It was recognized very early that this difference reflected the fractionation that occurred during adsorption of boron on clays (e.g., Schwarcz *et al.*, 1969). However, as we noted earlier, this fractionation is only about 30‰ or less, whereas the difference between the continental crust and seawater is close to 50‰. Furthermore, the net effect of hydrothermal exchange between the oceanic crust and seawater is to decrease the $\delta^{11}\text{B}$ of seawater (Spivack and Edmond, 1987). The discrepancy reflects the fact that the ocean is not a simple equilibrium system, but rather a kinetically controlled open one. Since all processes operating in the ocean appear to preferentially remove ^{10}B from the ocean, seawater is driven to an extremely

* NIST stands for the US National Institute of Standards and Technology and was formerly known as the National Bureau of Standards (NBS). SRM stands for standard reference material.

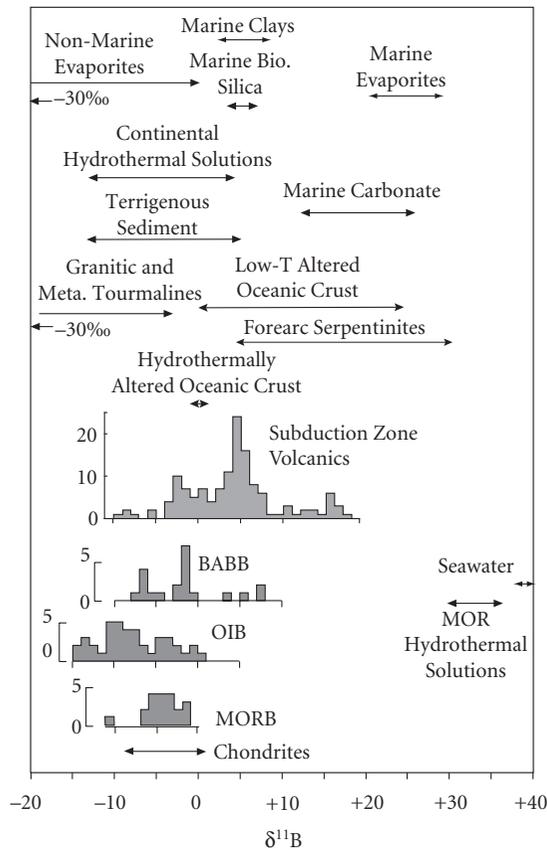


Figure 9.46 Boron isotopic composition in crystalline rocks (MORB: mid-ocean ridge basalts; OIB: oceanic island basalts; BABB: back-arc basin basalts), sediments, ground water, fresh water, salt lakes, seawater, and mid-ocean ridge (MOR) hydrothermal solutions.

^{11}B -rich composition. In addition, it is possible that fractionation of boron isotopes occurs during diagenesis. Ishikawa and Nakamura (1993) noted that ancient limestones and cherts have more negative $\delta^{11}\text{B}$ than their modern equivalents, calcareous and siliceous oozes, and suggested that further fractionation occurred during diagenesis.

Spivack and Edmond (1987) investigated the exchange of boron between seawater and oceanic crust. Boron is readily incorporated into the alteration products of basalt, so that even slightly altered basalts show a dramatic increase in B concentration and an increase in $\delta^{11}\text{B}$, with altered oceanic crust having $\delta^{11}\text{B}$ in the range of 0 to +25%. Smith *et al.* (1995)

estimated that average altered oceanic crust contains 5 ppm B and $\delta^{11}\text{B}$ of +3.4%. During high-temperature interaction between seawater and oceanic crust, Spivack and Edmond (1987) concluded that boron was quantitatively extracted from the oceanic crust by hydrothermal fluids. The isotopic composition of these fluids is slightly lower than that of seawater. They inferred that the B in these fluids is a simple mixture of seawater- and basalt-derived B, and that little or no isotopic fractionation was involved. Analysis of hydrothermally altered basalts recovered by the Ocean Drilling Project generally confirm these inferences, as they are boron-poor and have $\delta^{11}\text{B}$ close to 0 (Ishikawa and Nakamura, 1992).

Island arc volcanics (IAV) show a wide range of B isotopic compositions, overlapping the MORB range but on average have more positive $\delta^{11}\text{B}$ (mean $+4.02 \pm 5\%$). Palmer (1991) concluded that these positive values in part reflect the incorporation of subducted marine sediment and altered oceanic crust into the sources of island arc magmas. Chaussidon and Jambon (1994) suggested that the positive $\delta^{11}\text{B}$ values in IAV might also reflect assimilation of sediment or altered oceanic crust during magma ascent. More recent work suggests that B isotopic fractionation between solids and fluids during dehydration of the subducting slab may be an important, and perhaps dominant, effect. As oceanic lithosphere warms during the initial phases of subduction, B will be both desorbed from mineral surfaces (particularly sediment) into pore fluid and liberated into the fluid phase during dehydration. In this process, ^{11}B will partition preferentially into fluid. Benton *et al.* (2001) suggested this process accounts for the high $\delta^{11}\text{B}$ observed in serpentine mud in mud volcanoes in the Marianas forearc. Progressive dehydration of subducted oceanic lithosphere and associated B isotopic fractionation may also explain cross-arc isotopic variations in which $\delta^{11}\text{B}$ of IAV decreases with distance from the trench (e.g., Ishikawa *et al.*, 2001). Volcanic rocks from the South Sandwich arc have particularly high $\delta^{11}\text{B}$, averaging +15. Tonarini *et al.* (2011) argue that these high values reflect incorporation of forearc serpentinites into arc magma source regions through the process of subduction erosion.

The differences in $\delta^{11}\text{B}$ between oceanic island basalts (OIB) and MORB is perhaps more problematic. Though no experimental or theoretical studies have been carried out, it seems unlikely that significant fractionation of boron isotopes will occur during melting of the mantle, both because the temperatures are high, and because the atomic environment of B in silicate melts is probably similar to that in silicate solids. Thus, as we found was the case for O isotopes, B isotope fractionation probably occurs only at the surface of the Earth, and the difference between OIB and MORB must somehow reflect surface processes. Chaussidon and Marty (1995) argued that the boron isotopic composition of the mantle is that of OIB (-10‰) and that the higher $\delta^{11}\text{B}$ of MORB reflects contamination of MORB magmas by altered oceanic crust. This seems unlikely for several reasons. First, although there are still relatively few data available, MORB appears to be relatively homogenous in boron isotopic composition. This means assimilation would have to be systematic and pervasive and that all MORB magmas would have to assimilate roughly the same amount of material. Both of these seem highly improbable. Second, there is little or no other evidence for assimilation of oceanic crust by MORB magmas. Third, oceanic island basalts have an opportunity to assimilate not only altered oceanic crust, but also overlying sediment. Yet, according to the Chaussidon and Marty (1995) hypothesis, they are not systematically contaminated. Although they are not *systematically* contaminated, there is evidence of occasional assimilation of oceanic crust and/or sediment by oceanic island basalt magmas from both B and Os isotope geochemistry. This may explain some of the lower $\delta^{11}\text{B}$ values in OIB seen in Figure 9.45 (Chaussidon and Jambon, 1994).

The alternative explanation for the lower $\delta^{11}\text{B}$ in OIB is that they contain a component of material recycled into the mantle, through subduction, from the surface of the Earth. The idea that mantle plumes, and the OIB magmas they produce, contain material recycled from the surface of the Earth has been suggested on other grounds (Hofmann and White, 1982), and we shall discuss it further in Chapter 11. You (1994) pointed out that significant fractionation of B isotopes will

occur during sediment dewatering at moderate temperatures during the initial stages of subduction. The fluid produced will be enriched in ^{11}B , leaving the sediment depleted in ^{11}B . Thus the effect of subduction zone processes will be to lower the $\delta^{11}\text{B}$ of oceanic crust and sediment carried into the deep mantle. Deciding between this view and that of Chaussidon and Marty (1995) will require further research.

One of the more interesting applications of boron isotopes has been determining the paleo-pH of the oceans. Boron is readily incorporated into carbonates, with modern marine carbonates having B concentrations in the range of 15–60 ppm. In modern foraminifera, $\delta^{11}\text{B}$ is roughly 20‰ lighter than the seawater in which they grow. This fractionation seems to result from the kinetics of B coprecipitation in CaCO_3 , in which incorporation of B in carbonate is preceded by surface adsorption of $\text{B}(\text{OH})_4^-$ (Vengosh *et al.*, 1991; Heming and Hanson, 1992).

We noted earlier that boron is present in seawater both as $\text{B}(\text{OH})_3$, and $\text{B}(\text{OH})_4^-$. Since the reaction between the two may be written as:



the equilibrium constant for this reaction is:

$$-pK^{app} = \ln \frac{\text{B}(\text{OH})_4^-}{\text{B}(\text{OH})_3} - pH \quad (9.71)$$

The relative abundance of these two species is thus pH-dependent. Furthermore, we can easily show that the isotopic composition of these two species can vary even if the isotopic composition of seawater is constant. From mass balance we have:

$$\Delta^{11}\text{B}_{\text{SW}} = \delta^{11}\text{B}_3 f + \delta^{11}\text{B}_4 (1 - f) \quad (9.72)$$

where f is the fraction of $\text{B}(\text{OH})_3$ (and $1 - f$ is therefore the fraction of $\text{B}(\text{OH})_4^-$), $\delta^{11}\text{B}_3$ is the isotopic composition of $\text{B}(\text{OH})_3$, and $\delta^{11}\text{B}_4$ is the isotopic composition of $\text{B}(\text{OH})_4^-$. If the isotopic compositions of the two species are related by a constant fractionation factor, Δ_{3-4} , we can write eqn. 9.72 as:

$$\begin{aligned} {}^{11}\text{B}_{\text{SW}} &= \delta^{11}\text{B}_3 f + \delta^{11}\text{B}_4 - \delta^{11}\text{B}_4 f \\ &= \delta^{11}\text{B}_4 - \Delta_{3-4} f \end{aligned} \quad (9.73)$$

Solving for $\delta^{11}\text{B}_4$, we have:

$$\delta^{11}\text{B}_4 = {}^{11}\text{B}_{\text{SW}} + \Delta_{3-4}f \quad (9.74)$$

Thus assuming a constant fractionation factor and isotopic composition of seawater, the $\delta^{11}\text{B}$ of the two B species will depend only on f , which, as we can see in eqn. 9.71, will depend on pH.

If the mechanism for incorporation of B in carbonate presented earlier is correct, the fractionation of $^{11}\text{B}/^{10}\text{B}$ between calcite and seawater will be pH-dependent. There is still some debate as to the exact mechanism of boron incorporation in carbonate, in particular whether only borate ion or both boric acid and borate ion can be incorporated. Regardless of the exact mechanism, the isotopic composition of boron in carbonate precipitated from seawater has been shown to be a strong function of pH (Sanyal *et al.*, 1996), allowing in principle the reconstruction of paleoseawater pH from carbonates. There are some additional factors that must be considered: (1) different carbonate-secreting species may fractionate B isotopes slightly differently, perhaps because they alter the pH of their micro-environment, or perhaps because $\text{B}(\text{OH})_3$ is also utilized to varying degrees; (2) the fractionation factor is temperature-dependent; and (3) the B isotopic composition of seawater may vary with time. Nevertheless, if care is exercised to account for “vital” effects and variation in the isotopic composition and temperature of seawater, the B isotopic composition of marine biogenic carbonate preserved in sediment should reflect the pH of the water from which they were precipitated.

The pH of seawater, in turn, is largely controlled by the carbonate equilibrium, and depends therefore on the partial pressure of CO_2 in the atmosphere (see Example 6.2). Thus if the pH of ancient seawater can be determined, it should be possible to estimate p_{CO_2} of the ancient atmosphere. Given the concern about the relation of future climate to future p_{CO_2} , it is obviously interesting to know how these factors related in the past.

Pearson and Palmer (2000) measured $\delta^{11}\text{B}$ in foraminiferal carbonate extracted from Ocean Drilling Program (ODP) cores, and from this calculated pH based on eqns. 9.71 and 9.74. To minimize the effect of tempera-

ture on the fractionation factor, they restricted their study to cores from regions that were tropical at the time of deposition. To minimize vital effects, they used only one species of planktonic foraminifera for the Neogene period, *G. trilobus* (also known as *G. sacculifer*), which is thought to incorporate B with no vital effect. For the Paleogene, they used 6 species where the vital effect was arguably minimal. They argued that changes in the B isotopic composition of seawater should be slow to occur since the residence time of B in seawater is roughly 20 million years. Nevertheless, they account for a small variation, roughly 1.7‰, in seawater $\delta^{11}\text{B}$ over Tertiary time. The results suggest dramatically lower seawater pH and dramatically higher p_{CO_2} in the Paleogene. The apparent variation in p_{CO_2} is qualitatively consistent with what is known about Tertiary climate change – namely that a long-term cooling trend began in the early to middle Eocene. In contrast to the Paleogene, Figure 9.47 shows that the Neogene was characterized by atmospheric p_{CO_2} near or slightly below modern pre-industrial levels.

On a more limited time-scale, Hönisch and Hemming (2005) and Hönisch *et al.* (2009) investigated $\delta^{11}\text{B}$ during the Pleistocene. They controlled for temperature by analyzing the Mg/Ca ratio of the carbonate shells, which is known to be strongly temperature-dependent. For the last two glacial cycles, their calculated pH values ranged from 8.11 to 8.32, corresponding to a p_{CO_2} range of ~180 to ~325 ppm, in good agreement with CO_2 concentrations measured in bubbles in the Vostok ice core. They found that whereas over the last 400,000 years p_{CO_2} has varied from 180 and 300 ppmv in glacial and interglacial periods, respectively, the variation had been 210 and 280 ppmv in the early Pleistocene. The calculated average p_{CO_2} values for the early and late Pleistocene are 248 and 241 ppmv, respectively, and statistically indistinguishable.

Although still somewhat controversial, paleoseawater pH reconstruction based on boron isotopes has become better grounded in the last few years. Some of the controversy centered around the lack of experimental determination of the fractionation factor between $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ (Pagani *et al.*, 2005; Zeebe, 2005). This has been partially resolved by Klochko *et al.* (2006) who experimentally determined the fractionation factor

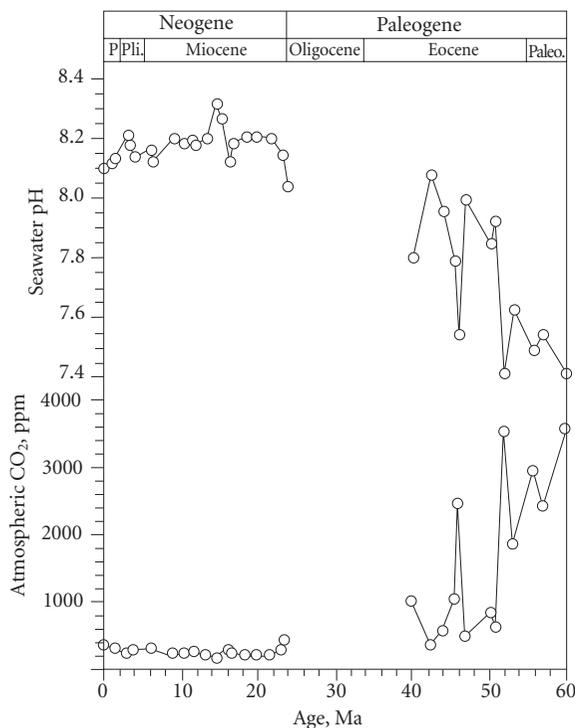


Figure 9.47 Top graph shows the variation in pH of surface seawater during Tertiary time as inferred from $\delta^{11}\text{B}$ in shells of planktonic foraminifera in ODP cores. Bottom graph shows the concentration of atmospheric CO_2 calculated from seawater pH. Reprinted by permission from McMillan Publishers Ltd: Pearson and Palmer (2000).

to be 1.0272 ± 0.0006 and independent of temperature. This value differs from the theoretically estimated value of 1.0194, which had previously been used for paleo-oceanographic calculations. However, the theoretical value is hampered by uncertainties in measured vibrational frequencies, and attempts to calculate it *ab initio* from molecular orbital theory result in uncertainties that are too large to be useful. In addition to this, there are additional uncertainties in the mechanism of incorporation of boron into carbonate and the associated fractionation factor, and uncertainties in how $\delta^{11}\text{B}$ in seawater has varied with time, and the requirement of high-precision measurement of B isotope ratios. Foster (2008) has shown that paleo- CO_2 determined from foraminifera in cores from the Caribbean agree well with CO_2 in the Vostok ice core using the experimentally determined fractionation factor.

9.9.2 Li isotopes

Terrestrial lithium isotopic variation is dominated by the strong fractionation that occurs between minerals, particularly silicates, and water. Indeed, this was first demonstrated experimentally by Urey in the 1930s. This fractionation in turn reflects the chemical behavior of Li. Li forms bonds with a high degree of covalent character. The ionic radius of Li^+ is small (78 pm) and Li readily substitutes for Mg^{2+} , Fe^{2+} , and Al^{3+} in crystal lattices, mainly in octahedral sites. In aqueous solution, it is tetrahedrally coordinated by 4 water molecules (the solvation shell) to which it is strongly bound, judging from the high solvation energy. These differences in atomic environment, differences in binding energies, the partly covalent nature of bonds, and the low mass of Li all lead to strong fractionation of Li isotopes.

Modern study of Li isotope ratios began with the work of Chan and Edmond (1988). They found that the isotopic composition of seawater was uniform within analytical error, with a $\delta^7\text{Li}$ value of +33‰. Subsequent work suggests that $\delta^7\text{Li}$ in seawater might vary by as much as 4‰, but the degree to which this variation reflects analytical error and inter-laboratory biases remains unclear, as the residence time of Li in the ocean (1.5–3 Ma) is much longer than the mixing time.

As is the case for boron, seawater represents one extreme of the spectrum of isotopic compositions in the Earth (see Figure 9.48). During mineral–water reactions, the heavier isotope, ^7Li , is preferentially partitioned into the solution. Thus weathering on the continents results in river water being isotopically heavy, +23.5‰ on average, compared with average continental crust, which has $\delta^7\text{Li}$ of ~ 0 , and the suspended load of rivers which has $\delta^7\text{Li} \approx +2$ (Teng *et al.*, 2004). Thus seawater is some 10 per mil heavier than average river water, so additional fractionation must occur in the marine environment. This likely includes adsorption onto particles (although Li is less prone to adsorption than most other metals), authigenic clay formation, and low-temperature alteration of oceanic crust. Chan *et al.* (1992) estimated the fractionation factor for clay-solution exchange at -19% . Reported $\delta^7\text{Li}$ values in marine non-carbonate sediments range from -1 to $+15\%$, but Chan and

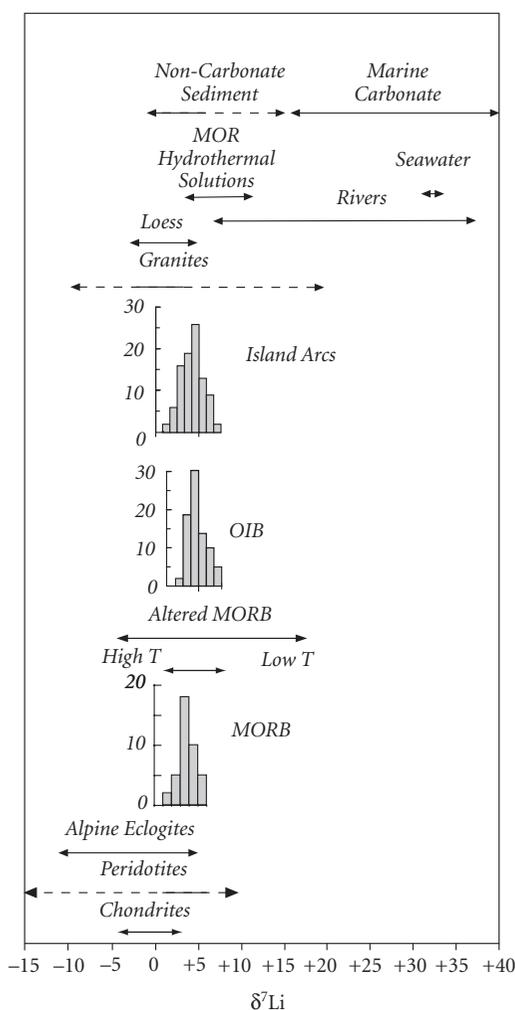


Figure 9.48 Li isotopic composition of terrestrial materials.

Frey (2003) suggested, based on new data and reanalysis of older samples, that the range is only +1 to +6‰. Marine carbonate sediments, which tend to be Li-poor, typically have higher $\delta^7\text{Li}$ than non-carbonate sediments.

Fresh MORB has $\delta^7\text{Li}$ of $+3.8 \pm 1.3\text{‰}$ (White and Klein, 2013), a range not much larger than that expected from analytical error alone. Oceanic island basalts (OIB) have on average higher $\delta^7\text{Li}$ $+4.9 \pm 1.2\text{‰}$. The highest $\delta^7\text{Li}$ occurs on islands characterized by particularly radiogenic Pb (the so-called HIMU OIB group), such as on some islands of the Cook-Austral chain. Here, $\delta^7\text{Li}$ may be as high as +8‰. This may reflect a recycled crustal component in their sources (e.g., Vlas-telic *et al.*, 2009).

There appears to be little relationship between $\delta^7\text{Li}$ and other geochemical parameters in igneous rocks, such as MgO concentration, suggesting Li experiences little isotopic fractionation during fractional crystallization, and perhaps also partial melting (Tomascak *et al.*, 1999). Mantle peridotites show a considerable range, from -15‰ to +10‰, but unmetasomatized peridotites have a range of only 0‰ to +7‰, just slightly larger than that of MORB. Alpine eclogites can have distinctly light isotopic compositions. These rocks are thought to be fragments of basaltic oceanic crust deeply subducted and metamorphosed, then subsequently rapidly exhumed during the Alpine orogeny. Their light isotopic compositions presumably reflect preferential partitioning of ^7Li into the fluid produced as the rocks were dehydrated during metamorphism.

Diffusion represents another mechanism by which Li isotopes may fractionate. As we noted earlier in the chapter, lighter isotopes of an element will diffuse faster than heavier isotopes. The relatively large mass difference between ^7Li and ^6Li (17%) results in substantially faster diffusion of ^6Li . Richter *et al.* (1999) found that the ratio of diffusion coefficients for isotopes of an ion diffusing in molten silicates obeyed the relation:

$$\frac{D_1}{D_2} = \left(\frac{m_2}{m_1} \right)^\beta \quad (9.75)$$

where β is an empirical parameter determined experimentally. Richter *et al.* (2003) found that the value of β was 0.215 for Li, implying 3% faster diffusion of ^6Li . In molten basalt-rhyolite diffusion experiments, this more rapid diffusion of ^6Li produced isotopic variations as great as 40‰ over 10 mm distances in 15 hours. Comparable isotopic variations have been observed in nature. Teng *et al.* (2006) observed that the isotopic composition of Li diffusing out of a pegmatite into surrounding amphibolite decreased from +7.6‰ to -19.9‰ over a distance of 10 m. Because of its small ionic size and charge, Li diffuses more readily than most other elements. Indeed, Richter *et al.* found it diffused 2 orders of magnitude faster than Ca. This rapid diffusion also contributes to the large potential for diffusional isotopic fractionation.

$\delta^7\text{Li}$ in oceanic crust altered by seawater at low temperatures takes up Li from solution and has high $\delta^7\text{Li}$ compared with fresh basalt. In hydrothermal reactions, however, Li is extracted from basalt into solution and hydrothermal fluids can have Li concentrations up to 50 times greater than seawater. ^7Li is extracted more efficiently than ^6Li during this process, so hydrothermally altered basalt can have $\delta^7\text{Li}$ as low as -2% . Serpentinites (hydrothermally altered peridotite) can have even lower $\delta^7\text{Li}$. Because they extract Li from oceanic crust so completely, hydrothermal solutions have Li isotopic compositions intermediate between MORB and seawater despite this fractionation.

The average $\delta^7\text{Li}$ of island arc volcanics, $+4.05 \pm 1.5\%$, is only slightly higher than that of MORB. This is somewhat surprising since other isotopic evidence clearly demonstrates that island arc magmas contain com-

ponents derived from subducted oceanic crust and sediment. Furthermore, while $\delta^7\text{Li}$ has been shown in some cases to correlate with chemical and isotopic indicators of a subduction component, this is not always the case.

It seems nevertheless likely that the subduction process has profoundly influenced the isotopic composition of the mantle over time. As a consequence of fractionation occurring during weathering, seawater is strongly enriched in ^7Li . This enrichment is imprinted upon the oceanic crust as it reacts with seawater. When the oceanic crust is returned to the mantle during subduction, the mantle becomes progressively enriched in ^7Li . The continental crust, on the other hand, becomes progressively depleted in ^7Li over time. Elliott *et al.* (2004) calculated that this process has increased $\delta^7\text{Li}$ in the mantle by 0.5 to 1‰ and decreased $\delta^7\text{Li}$ of the continental crust by 3‰ over geologic time.

REFERENCES AND SUGGESTIONS FOR FURTHER READING

- Benton, L.D., Ryan, J.G. and Tera, F. 2001. Boron isotope systematics of slab fluids as inferred from a serpentine seamount, Mariana Forearc. *Earth and Planetary Science Letters*, 187: 273–82.
- Bigeleisen, J. and Mayer, M.G. 1947. Calculation of equilibrium constants for isotopic exchange reactions. *J. Chem. Phys.*, 15: 261–7.
- Bottinga, Y. and Javoy, M. 1973. Comments on oxygen isotope geothermometry. *Earth and Planetary Science Letters*, 20: 250–65.
- Bowen, R. 1988. *Isotopes in the Earth Sciences*. Barking, Essex, Elsevier Applied Science Publishers.
- Boyd, S.R. and Pillinger, C.T. 1994. A preliminary study of $^{15}\text{N}/^{14}\text{N}$ in octahedral growth form diamonds. *Chemical Geology*, 116: 43–59.
- Broecker, W. and Oversby, V. 1971. *Chemical Equilibria in the Earth*. New York, McGraw-Hill.
- Cerling, T.E., Wang, Y. and Quade, J. 1993. Expansion of C_4 ecosystems as an indicator of global ecological change in the late Miocene. *Nature*, 361: 344–5.
- Chan, L.-H. and Edmond, J.M. 1988. Variation of lithium isotope composition in the marine environment: a preliminary report. *Geochimica et Cosmochimica Acta*, 52: 1711–17.
- Chan, L.H., Edmond, J.M., Thompson, G. and Gillis, K. 1992. Lithium isotopic composition of submarine basalts: implications for the lithium cycle of the oceans. *Earth and Planetary Science Letters*, 108: 151–60.
- Chan, L.-H. and Frey, F.A. 2003. Lithium isotope geochemistry of the Hawaiian plume: results from the Hawaii Scientific Drilling Project and Koolau Volcano. *Geochem. Geophys. Geosyst.*, 4: doi: 10.1029/2002GC000365.
- Chaussidon, M. and Albarède, F. 1992. Secular boron isotope variations in the continental crust: an ion microprobe study. *Earth and Planetary Science Letters*, 108: 229–41.
- Chaussidon, M., Albarède, F. and Sheppard, S.M.F. 1987. Sulphur isotope heterogeneity in the mantle from ion microprobe measurements of sulphide inclusions in diamonds. *Nature*, 330: 242–4.
- Chaussidon, M., Albarède, F. and Sheppard, S.M.F. 1989. Sulphur isotope variations in the mantle from ion microprobe analyses of micro-sulphide inclusions. *Earth and Planetary Science Letters*, 92: 144–56.
- Chaussidon, M. and Jambon, A. 1994. Boron content and isotopic composition of oceanic basalts: geochemical and cosmochemical implications. *Earth and Planetary Science Letters*, 121: 277–91.
- Chaussidon, M. and Marty, B. 1995. Primitive boron isotope composition of the mantle. *Science*, 269: 383–6.
- Chaussidon, M., Sheppard, S.M.F. and Michard, A. 1991. Hydrogen, sulfur and neodymium isotope variations in the mantle beneath the EPR at $12^\circ 50' \text{N}$, in *Stable Isotope Geochemistry: A Tribute to Samuel Epstein* (eds H.P. Taylor, J.R. O'Neil and I.R. Kaplan), pp. 325–38. San Antonio, Geochemical Society.

- Chiba, H., Chacko, T., Clayton, R.N. and Goldsmith, J.R. 1989. Oxygen isotope fractionations involving diopside, forsterite, magnetite, and calcite: application to geothermometry. *Geochimica et Cosmochimica Acta*, 53: 2985–95.
- Craig, H. 1963. The isotopic composition of water and carbon in geothermal areas, in *Nuclear Geology on Geothermal Areas* (ed. E. Tongiorgi), pp. 17–53. Pisa, CNR Lab. Geol. Nucl.
- Criss, R.E. and Taylor, H.P. 1986. Meteoric-hydrothermal systems, in *Stable Isotopes in High Temperature Geological Processes, Reviews in Mineralogy 16* (eds J.W. Valley, H.P. Taylor and J.R. O’Neil), pp. 373–424. Washington, Mineralogical Society of America.
- Dansgaard, W. 1964. Stable isotopes in precipitation. *Tellus*, 16: 436–63.
- Deloule, E., Albaredo, F. and Sheppard, S.M.F. 1991. Hydrogen isotope heterogeneity in the mantle from ion probe analysis of amphiboles from ultramafic rocks. *Earth and Planetary Science Letters*, 105: 543–53.
- DeNiro, M.J. 1987. Stable isotopy and archaeology. *American Scientist*, 75: 182–91.
- DeNiro, M.J. and Epstein, S. 1978. Influence of diet on the distribution of carbon isotopes in animals. *Geochimica et Cosmochimica Acta*, 42: 495–506.
- DeNiro, M.J. and Epstein, S. 1981. Influence of diet on the distribution of nitrogen isotopes in animals. *Geochimica et Cosmochimica Acta*, 45: 341–51.
- DeNiro, M.J. and Hasdorf, C.A. 1985. Alteration of $^{15}\text{N}/^{14}\text{N}$ and $^{13}\text{C}/^{12}\text{C}$ ratios of plant matter during the initial stages of diagenesis: studies utilizing archeological specimens from Peru. *Geochimica et Cosmochimica Acta*, 49: 97–115.
- Eiler, J.M. 2007. “Clumped-isotope” geochemistry – the study of naturally-occurring, multiply-substituted isotopologues. *Earth and Planetary Science Letters*, 262: 309–27.
- Eldridge, C.S., Compston, W., Williams, I.S., Harris, J.W. and Bristow, J.W. 1991. Isotope evidence for the involvement of recycled sediment in diamond formation. *Nature*, 353: 649–53.
- Elliott, T., Jeffcoate, A. and Bouman, C. 2004. The terrestrial Li isotope cycle: light-weight constraints on mantle convection. *Earth and Planetary Science Letters*, 220: 231–45.
- Emiliani, C. 1955. Pleistocene temperatures. *Journal of Geology*, 63: 538–78.
- Farquhar, J., Bao, H. and Thiemens, M. 2000. Atmospheric influence of Earth’s earliest sulfur cycle. *Science*, 289: 756–8.
- Farquhar, J. and Wing, B.A. 2003. Multiple sulfur isotopes and the evolution of atmospheric oxygen. *Earth and Planetary Science Letters*, 213: 1–13.
- Farquhar, J., Wing, B.A., McKeegan, K.D., *et al.* 2002. Mass-independent fractionation sulfur of inclusions in diamond and sulfur recycling on early Earth. *Science*, 298: 2369–72.
- Faure, G. 1986. *Principles of Isotope Geology*, 2nd edn. New York, John Wiley & Sons, Ltd.
- Ferronsky, V.I., and Polyakov, V.A. 1982. *Environmental Isotopes in the Hydrosphere*. Chichester, John Wiley and Sons Ltd.
- Fogel, M.L., and Cifuentes, M.L. 1993. Isotope fractionation during primary production, in *Organic Geochemistry: Principles and Applications* (eds M.H. Engel and S.A. Macko), pp. 73–98. New York, Plenum Press.
- Foster, G.L. 2008. Seawater pH, pCO₂ and [CO₂³⁻] variations in the Caribbean Sea over the last 130 kyr: A boron isotope and B/Ca study of planktic foraminifera. *Earth and Planetary Science Letters*, 271: 254–66.
- Gao, Y.Q. and Marcus, R.A. 2001. Strange and unconventional isotope effects in ozone formation. *Science*, 293: 259–63.
- Goldhaber, M., Church, S.E., Doe, B.R., *et al.* 1995. Sources and transport paths for MVT ore deposit lead and sulfur in the midcontinent of the USA, in *International Field Conference on Carbonate-Hosted Lead-Zinc Deposits – Extended Abstracts* (eds D.L. Leach and M.B. Goldhaber), pp. 111–14. Littleton, CO, Society of Economic Geologists.
- Harmon, R.S. and Hoefs, J. 1995. Oxygen isotope heterogeneity of the mantle deduced from global ^{18}O systematics of basalts from different tectonic settings. *Contributions to Mineralogy and Petrology*, 120: 95–114. doi: 10.1007/bf00311010.
- Hayes, J.D., Imbrie, J. and Shackleton, N.J. 1976. Variations in the Earth’s orbit: pacemaker of the ice ages. *Science*, 194: 1121–32.
- Heming, N.G. and Hanson, G.N. 1992. Boron isotopic composition and concentration in modern marine carbonates. *Geochimica et Cosmochimica Acta*, 56: 537–43.
- Hoefs, J. 1987. *Stable Isotope Geochemistry*, 3rd edn. Berlin, Springer-Verlag.
- Hofmann, A.W. and White, W.M. 1982. Mantle plumes from ancient oceanic crust. *Earth and Planetary Science Letters*, 57: 421–36.
- Hönisch, B. and Hemming, N.G. 2005. Surface ocean pH response to variations in pCO₂ through two full glacial cycles. *Earth and Planetary Science Letters*, 236: 305–14. doi: 10.1016/j.epsl.2005.04.027.
- Hönisch, B., Hemming, N.G., Archer, D., Siddall, M. and McManus, J.F. 2009. Atmospheric carbon dioxide concentration across the Mid-Pleistocene transition. *Science*, 324: 1551–4. doi: 10.1126/science.1171477.

- Imbrie, J. 1985. A theoretical framework for the Pleistocene ice ages. *Journal of the Geological Society London*, 142: 417–32.
- Imbrie, J., Hayes, J.D., Martinson, D.G., *et al.* 1985. The orbital theory of Pleistocene climate: support from a revised chronology of the marine $\delta^{18}\text{O}$ record, in *Milankovitch and Climate, Part 1* (eds A.L. Berger, J. Imbrie, J. Hayes, G. Kukla and B. Saltzman), pp. 269–305. Dordrecht, D. Reidel.
- Ishikawa, T. and Nakamura, E. 1992. Boron isotope geochemistry of the oceanic crust from DSDP/ODP Hole 504B. *Geochimica et Cosmochimica Acta*, 56: 1633–9.
- Ishikawa, T. and Nakamura, E. 1993. Boron isotope systematics of marine sediments. *Earth and Planetary Science Letters*, 117: 567–80.
- Ishikawa, T., Tera, F. and Nakazawa, T. 2001. Boron isotope and trace element systematics of the three volcanic zones in the Kamchatka arc. *Geochimica et Cosmochimica Acta*, 65: 4523–37.
- Javoy, M. 1977. Stable isotopes and geothermometry. *Journal of the Geological Society London*, 133: 609–39.
- Javoy, M. and Pineau, F. 1991. The volatile record of a “popping” rock from the Mid-Atlantic Ridge at 14°N: chemical and isotopic composition of the gas trapped in the vesicles. *Earth and Planetary Science Letters*, 107: 598–611.
- Johnson, C.M., Beard, B.L. and Albarede, F. 2004. *Geochemistry of Non-Traditional Stable Isotopes: Reviews in Mineralogy Volume 454*. Washington, Mineralogical Society of America.
- Johnson, D.G., Jucks, K.W., Traub, W.A. and Chance, K.V. 2001. Isotopic composition of stratospheric ozone. *Journal of Geophysical Research*, 105: 9025–31.
- Jouzel, C., Lorius, C., Perfit, J.R., *et al.* 1987. Vostok ice core: a continuous isotope temperature record over the last climatic cycle (160,000 years). *Nature*, 329: 403.
- Jouzel, J., Barkov, N.I., Barnola, J.M., *et al.* 1993. Extending the Vostok ice-core record of paleoclimate to the penultimate glacial period. *Nature*, 364: 407–12.
- Jouzel, J., Masson-Delmotte, V., Cattani, O., *et al.* 2007. Orbital and millennial Antarctic climate variability over the last 800,000 years. *Science*, 317: 793–6.
- Jouzel, J., Waelbroeck, C., Malaizé, B., *et al.* 1996. Climatic interpretation of the recently extended Vostok ice records. *Climate Dynamics*, 12: 513–21.
- Kasting, J.F. and Catling, D. 2003. Evolution of a habitable planet. *Ann. Rev. Astron. Astrophys.*, 41: 429–63.
- Kawabe, I. 1979. Calculation of oxygen isotopic fractionation in quartz-water system with special reference to the low temperature fractionation. *Geochimica et Cosmochimica Acta*, 42: 613–21.
- Klochko, K., Kaufman, A.J., Yao, W., Byrne, R.H. and Tossell, J.A. 2006. Experimental measurement of boron isotope fractionation in seawater. *Earth and Planetary Science Letters*, 248: 276–85. doi: 10.1016/j.epsl.2006.05.034, 2006.
- Kroopnick, P., Weiss, R.F. and Craig, H. 1972. Total CO_2 , ^{13}C and dissolved oxygen- ^{18}O at GEOSECS II in the North Atlantic. *Earth and Planetary Science Letters*, 16: 103–10.
- Kyser, K.T. 1986. Stable isotope variations in the mantle, in *Stable Isotopes in High Temperature Geologic Processes* (eds J.W. Valley, H.P. Taylor and J.R. O’Neil), pp. 141–64. Washington, Mineralogical Society of America.
- Lawrence, J.R. and Meaux, J.R. 1993. The stable isotopic composition of ancient kaolinites of North America, in *Climate Change in Continental Isotopic Records, Geophysical Monograph 78* (eds P.K. Swart, K.C. Lohmann, J. McKenzie and S. Savin), pp. 249–61. Washington, American Geophysical Union.
- Lawrence, J.R. and Taylor, H.P. 1972. Hydrogen and oxygen isotope systematics in weathering profiles. *Geochimica et Cosmochimica Acta*, 36: 1377–93.
- Marty, B. and Dauphas, N. 2003. The nitrogen record of crust-mantle interaction and mantle convection from Archean to present. *Earth and Planetary Science Letters*, 206: 397–410.
- Mattey, D.P. 1987. Carbon isotopes in the mantle. *Terra Cognita* 7: 31–8.
- Mattey, D., Lowry, D. and Macpherson, C. 1994. Oxygen isotope composition of mantle peridotite. *Earth and Planetary Science Letters*, 128: 231–41.
- Mauersberger, K. 1987. Ozone isotope measurements in the stratosphere. *Geophysical Research Letters*, 14: 80–83.
- Milankovitch, M. 1938. Astronomische mittel zur erforschung der erdgeschichtlichen klimate. *Handbuch der Geophysik*, 9: 593–698.
- Mojzsis, S.J., Arrhenius, G., McKeegan, K.D., *et al.* 1996. Evidence for life on Earth before 3800 million years ago. *Nature*, 384: 55–9.
- Muehlenbachs, K. and Byerly, G. 1982. ^{18}O enrichment of silicic magmas caused by crystal fractionation at the Galapagos Spreading Center. *Contributions to Mineralogy and Petrology*, 79: 76–9.
- Ohmoto, H. and Rye, R.O. 1979. Isotopes of sulfur and carbon, in *Geochemistry of Hydrothermal Ore Deposits* (ed. H. Barnes). New York, John Wiley and Sons, Ltd.
- Ohmoto, H. 1986. Stable isotope geochemistry of ore deposits, in *Stable Isotopes in High Temperature Geological Processes, Reviews in Mineralogy 16* (eds J.W. Valley, H.P. Taylor and J.R. O’Neil), pp. 491–560. Washington, Mineralogical Society of America.

- O'Leary, M.H. 1981. Carbon isotope fractionation in plants, *Phytochemistry*, 20, 553-567.
- O'Neil, J.R. 1986. Theoretical and experimental aspects of isotopic fractionation, in *Stable Isotopes in High Temperature Geological Processes, Reviews in Mineralogy 16* (eds J.W. Valley, H.P. Taylor and J.R. O'Neil), pp. 1-40. Washington, Mineralogical Society of America.
- Pagani, M., Lemarchand, D., Spivack, A.J. and Gaillardet, J. 2005. A critical evaluation of the boron isotope-pH proxy: The accuracy of ancient ocean pH estimates. *Geochimica et Cosmochimica Acta*, 69: 953-61.
- Palmer, M.R. 1991. Boron-isotope systematics of Halmahera arc (Indonesia) lavas: evidence for involvement of the subducted slab. *Geology*, 19: 215-17.
- Palmer, M., Spivack, M. and Edmond, J.M. 1987. Temperature and pH controls over isotopic fractionation during adsorption of boron on marine clay. *Geochimica et Cosmochimica Acta*, 51: 2319-23.
- Park, R. and Epstein, S. 1960. Carbon isotope fractionation during photosynthesis. *Geochimica et Cosmochimica Acta*, 21: 110-26.
- Pearson, P.N. and Palmer, M.R. 2000. Atmospheric carbon dioxide concentrations over the past 60 million years. *Nature*, 406: 695-9.
- Poreda, R., Schilling, J.G. and Craig, H. 1986. Helium and hydrogen isotopes in ocean-ridge basalts north and south of Iceland. *Earth and Planetary Science Letters*, 78: 1-17.
- Quade, J., Cerling, T.E. and Bowman, J.R. 1989. Development of Asian monsoon revealed by marked ecological shift during the latest Miocene in northern Pakistan. *Nature*, 342: 163-6.
- Richet, P., Bottinga, Y. and Javoy, M. 1977. A review of hydrogen, carbon, nitrogen, oxygen, sulphur, and chlorine stable isotope fractionation among gaseous molecules. *Annual Review Earth and Planetary Science Letters*, 5: 65-110.
- Richter, F.M., Davis, A.M., DePaolo, D.J. and Watson, E.B. 2003. Isotope fractionation by chemical diffusion between molten basalt and rhyolite. *Geochimica et Cosmochimica Acta*, 67: 3905-23. doi: 10.1016/s0016-7037(03)00174-1.
- Richter, F.M., Liang, Y. and Davis, A.M. 1999. Isotope fractionation by diffusion in molten oxides. *Geochimica et Cosmochimica Acta*, 63: 2853-61. doi: 10.1016/s0016-7037(99)00164-7.
- Rosing, M. 1999. ¹³C-depleted carbon microparticles in >3700 Ma sea-floor sedimentary rocks from West Greenland. *Science*, 283: 674-6.
- Sakai, H., Des Marais, D.J., Ueda, A. and Moore, J.G. 1984. Concentrations and isotope ratios of carbon, nitrogen, and sulfur in ocean-floor basalts. *Geochimica et Cosmochimica Acta*, 48: 2433-42.
- Sanyal, A., Hemming, N.G., Hanson, G.N. and Broecker, W.S. 1995. Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera. *Nature*, 373: 234-6.
- Sanyal, A., Hemming, N.G., Broecker, W.S.L., et al. 1996. Oceanic pH control on the boron isotopic composition of foraminifera: evidence from culture experiments. *Paleoceanography*, 11: 513-17.
- Savin, S.M. and Epstein, S. 1970. The oxygen and hydrogen isotope geochemistry of clay minerals. *Geochimica et Cosmochimica Acta*, 34: 25-42.
- Schidlowski, M. 1988. A 3800-million year isotopic record of life from carbon in sedimentary rocks. *Nature*, 333: 313-18.
- Schoeninger, M.J. and DeNiro, M.J. 1984. Nitrogen and carbon isotopic composition of bone collagen from marine and terrestrial animals. *Geochimica et Cosmochimica Acta*, 48: 625-39.
- Schwarcz, H.P., Agyei, E.K. and McMullen, C.C. 1969. Boron isotopic fractionation during clay adsorption from sea-water. *Earth and Planetary Science Letters*, 6: 1-5.
- Shackleton, N.J. and Opdyke, N.D. 1973. Oxygen isotope and paleomagnetic stratigraphy of an equatorial Pacific core V28-238: oxygen isotope temperatures and ice volumes on a 10⁵ and 10⁶ year time scale. *Quaternary Research*, 3: 39-55.
- Sheppard, S.M.F. and Epstein, S. 1970. D/H and ¹⁸O/¹⁶O ratios of minerals of possible mantle or lower crustal origin. *Earth and Planetary Science Letters*, 9: 232-9.
- Sheppard, S.M.F. and Harris, C. 1985. Hydrogen and oxygen isotope geochemistry of Ascension Island lavas and granites: variation with fractional crystallization and interaction with seawater. *Contributions to Mineralogy and Petrology*, 91: 74-81.
- Sheppard, S.M.F., Nielsen, R.L. and Taylor, H.P. 1969. Oxygen and hydrogen isotope ratios of clay minerals from porphyry copper deposits. *Economic Geology*, 64: 755-77.
- Smith, H.J., Spivack, A.J., Staudigel, H. and Hart, S.R. 1995. The boron isotopic composition of altered oceanic crust. *Chem. Geol.*, 126: 119-35.
- Spivack, A. and Edmond J.M. 1987. Boron isotope exchange between seawater and the oceanic crust. *Geochimica et Cosmochimica Acta*, 51: 1033-44.
- Spivack, A.J., You, C.-F. and Smith H.J. 1993. Foraminiferal boron isotope ratios as a proxy for surface ocean pH over the past 21 Myr. *Nature*, 363: 149-51.
- Taylor, H.P. 1974. The application of oxygen and hydrogen studies to problems of hydrothermal alteration and ore deposition. *Economic Geology*, 69: 843-83.

- Taylor, H.P. 1980. The effects of assimilation of country rocks by magmas on $^{18}\text{O}/^{16}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ systematics in igneous rocks. *Earth and Planetary Science Letters*, 47: 243–54.
- Taylor, H.P. and Sheppard, S.M.F. 1986. Igneous rocks: I. Processes of isotopic fractionation and isotope systematics, in *Stable Isotopes in High Temperature Geological Processes* (eds J.W. Valley, H.P. Taylor and J.R. O'Neil), pp. 227–71. Washington, Mineralogical Society of America.
- Teng, F.-Z., McDonough, W.F., Rudnick, R.L., *et al.* 2004. Lithium isotopic composition and concentration of the upper continental crust. *Geochimica et Cosmochimica Acta*, 68: 4167–78.
- Teng, F.-Z., McDonough, W.F., Rudnick, R.L. and Walker, R.J. 2006. Diffusion-driven extreme lithium isotopic fractionation in country rocks of the Tin Mountain pegmatite. *Earth and Planetary Science Letters*, 243: 701–10. doi: 10.1016/j.epsl.2006.01.036.
- Tomascak, P.B. 2004. Developments in the understanding and application of lithium isotopes in the Earth and planetary sciences, in *Geochemistry of Non-Traditional Stable Isotopes, Reviews in Mineralogy Volume 55* (ed. C.M. Johnson), pp. 153–195. Washington, Mineralogical Society of America.
- Tomascak, P.B., Tera, F., Helz, R.T. and Walker, R.J. 1999. The absence of lithium isotope fractionation during basalt differentiation: new measurements by multicollector sector ICP-MS. *Geochimica et Cosmochimica Acta*, 63: 907–10.
- Tonarini, S., Leeman, W.P. and Leat, P.T. 2011. Subduction erosion of forearc mantle wedge implicated in the genesis of the South Sandwich Island (SSI) arc: Evidence from boron isotope systematics. *Earth and Planetary Science Letters*, 301: 275–84. doi: 10.1016/j.epsl.2010.11.008.
- Urey, H. 1947. The thermodynamic properties of isotopic substances. *Journal of the Chemical Society (London)*, 1947: 562–81.
- Valley, J.W., Taylor, H.P. and O'Neil, J.R. (eds) 1986. *Stable Isotopes in High Temperature Applications, Reviews in Mineralogy Volume 16*. Washington, Mineralogical Society of America.
- Vengosh, A., Kolodny, Y., Starinsky, A., Chivas, A. and McCulloch, M. 1991. Coprecipitation and isotopic fractionation of boron in modern biogenic carbonates. *Geochimica et Cosmochimica Acta*, 55: 2901–10.
- Vlastelic, I., Koga, K., Chauvel, C., Jacques, G. and Telouk, P. 2009. Survival of lithium isotopic heterogeneities in the mantle supported by HIMU-lavas from Rurutu Island, Austral Chain. *Earth and Planetary Science Letters*, 286: 456–66. doi: 10.1016/j.epsl.2009.07.013.
- Wang, Y., Cerling, C.E. and McFadden, B.J. 1994. Fossil horse teeth and carbon isotopes: new evidence for Cenozoic dietary, habitat, and ecosystem changes in North America. *Paleogeogr., Paleoclim., Paleoecol.* 107: 269–79.
- White, W.M. and Klein, E. 2013. The composition of the oceanic crust, in *Treatise on Geochemistry, vol. 3: The Crust* (ed. R. Rudnick). Amsterdam, Elsevier.
- You, C.-F. 1994. Comment on “Boron content and isotopic composition of oceanic basalts: geochemical and cosmochemical implications” by M. Chaussidon and A. Jambon. *Earth and Planetary Science Letters*, 128: 727–30.
- Zeebe, R. 2005. Stable boron isotope fractionation between dissolved $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$. *Geochimica et Cosmochimica Acta*, 69: 2753–66.

PROBLEMS

- Using the procedure and data in Example 9.1, calculate the fractionation factor $\Delta_{\text{CO-O}_2}$ for the $^{17}\text{O}/^{16}\text{O}$ ratio at 300K. What is the expected ratio of fractionation of $^{17}\text{O}/^{16}\text{O}$ to that of $^{18}\text{O}/^{16}\text{O}$ at this temperature?
- What would you predict would be the ratio of the diffusion coefficients of H_2O and D_2O in air?
- A granite contains coexisting feldspar (3% An content) and biotite with $\delta^{18}\text{O}_{\text{SMOW}}$ of 9.2‰ and 6.5‰ respectively. Using the information in Table 9.2, find the temperature of equilibration.
- Sphalerite and galena from a certain Mississippi Valley deposit were found to have $\delta^{34}\text{S}_{\text{CDT}}$ of +13.2‰ and +9.8‰ respectively.
 - Using the information in Table 9.4, find the temperature at which these minerals equilibrated.
 - Assuming they precipitated from an H_2S -bearing solution, what was the sulfur isotopic composition of the H_2S ?

5. Glaciers presently constitute about 2.1% of the water at the surface of the Earth and have a $\delta^{18}\text{O}_{\text{SMOW}}$ of ≈ -30 . The oceans contain essentially all remaining water. If the mass of glaciers were to increase by 50%, how would the isotopic composition of the ocean change (assuming the isotopic composition of ice remains constant)?
6. Consider the condensation of water vapor in the atmosphere. Assume that the fraction of vapor remaining can be expressed as a function of temperature (in kelvins):

$$f = \frac{T - 223}{50}$$

Also assume that the fractionation factor can be written as:

$$\ln \alpha = 0.0018 + \frac{12.8}{RT}$$

Assume that the water vapor has an initial $\delta^{18}\text{O}_{\text{SMOW}}$ of -9‰ . Make a plot showing how the $\delta^{18}\text{O}$ of the remaining vapor would change as a function of f , fraction remaining.

7. Calculate the $\delta^{18}\text{O}$ of raindrops forming in a cloud after 80% of the original vapor has already condensed, assuming (1) the water initially evaporated from the ocean with $\delta^{18}\text{O} = 0$, (2) the liquid–vapor fractionation factor $\alpha = 1.0092$.
8. A saline lake that has no outlet receives 95% of its water from river inflow and the remaining 5% from rainfall. The river water has $\delta^{18}\text{O}$ of -10‰ and the rain has $\delta^{18}\text{O}$ of -5‰ . The volume of the lake is steady-state (i.e., inputs equal outputs) and has a $\delta^{18}\text{O}$ of -3‰ . What is the fractionation factor, α , for evaporation?
9. Consider a sediment composed of 70 mol % detrital quartz ($\delta^{18}\text{O} = +10\text{‰}$) and 30 mol % calcite ($\delta^{18}\text{O} = +30\text{‰}$). If the calcite/quartz fractionation factor, α , is 1.005 at 300°C , determine the O isotopic composition of each mineral after metamorphic equilibrium at 300°C . Assume that the rock is a closed system during metamorphism, i.e., $\delta^{18}\text{O}$ of the whole rock does not change during the process.
10. Assume that α is a function of the fraction of liquid crystallized such that $\alpha = 1 + 0.008(1 - f)$. Make a plot showing how the $\delta^{18}\text{O}$ of the remaining liquid would change as a function of $1 - f$, fraction crystallized, assuming a value for Δ of 0.5‰ .
11. A basaltic magma with a $\delta^{18}\text{O}$ of $+6.0$ assimilates country rock with $\delta^{18}\text{O}$ of $+20$ as it undergoes fractional crystallization. Assuming a value of α of 0.998, make a plot of $\delta^{18}\text{O}$ vs. f for $R = 5$ and $R = 10$, going from $f = 1$ to $f = 0.05$.

Chapter 10

The big picture: cosmochemistry

10.1 INTRODUCTION

In the previous nine chapters we acquired a full set of geochemical tools. In this and subsequent chapters, we will apply these tools to understanding the Earth. Certainly any full understanding of the Earth includes an understanding of its origin and its relationship to its neighboring celestial bodies. That is our focus in this chapter.

The question of the origin of the Earth is closely tied to that of the composition of the Earth, and certainly the latter is central to geochemistry. Indeed, one of the primary objectives of early geochemists was to determine the abundance of the elements in the Earth. It is natural to wonder what accounts for these abundances and to ask whether the elemental abundances in the Earth are the same as the abundances elsewhere in the solar system and in the universe. We might also ask why the Earth consists mainly of oxygen, iron, magnesium, and silicon? Why not titanium, fluorine, and gold? Upon posing these questions, the realm of geochemistry melds smoothly into the realms of cosmochemistry and cosmology. Cosmochemistry has as its objective an understanding of the distribution and abundance of elements in the solar system, and, to a lesser degree, the cosmos (the latter is relegated to secondary stature because the data on objects outside the solar system are much less complete).

The composition of the Earth is unique: there is undoubtedly no other celestial body that has exactly the same composition as the Earth. Nevertheless, the composition of the Earth is similar to that of the other terrestrial planets: Mercury, Venus, Mars, and the Moon. The Earth also shares a common geochemical heritage with the remainder of the solar system, and all bodies in the solar system probably have similar abundances of some elements, and the same isotopic compositions of most elements. What we know of the composition of the remainder of the universe suggests that it has a composition that is grossly similar to our solar system: it is dominated by hydrogen and helium, with lesser amounts of carbon, oxygen, magnesium, silicon and iron, but there are local differences, particularly in the abundances of elements heavier than hydrogen and helium.

The unique composition of the Earth is the product of three sets of processes. These include those processes responsible for the creation of elements, that is, nucleosynthetic processes, the creation of the solar system, and finally the formation of the Earth itself. We will begin by considering nucleosynthesis. Meteorites are the principal record of formation of the solar system and of the planetary bodies within it, so we devote considerable space to understanding these objects. Perhaps ever since we acquired the capacity to contemplate the abstract, mankind has wondered