TYING UP LOOSE ENDS: MASS INDEPENDENT FRACTIONATION ON EARTH; LI AND B ISOTOPES

MASS INDEPENDENT FRACTIONATION

Mass Independent Fractionation of Oxygen

Oxygen and sulfur have both have more than two isotopes, as do, of course, many other elements. How do we expect the fractionations between various isotope ratios to be related? For example, if a 4‰ fractionation of $\delta^{18}O$ is observed in a particular sample, what value of $\delta^{17}O$ do we predict? In Lecture 27 we noted that the fractionation should depend on mass and that theoretically, we would expect $\Delta^{18}O/\Delta^{17}O$ should be $\approx 0.53$. Empirically, we find that, the ratio of fractionation of $^{17}O/^{16}O$ to that of $^{18}O/^{16}O$ is almost always close to this value, about 0.52. Thus the fractionation between isotopes does seem to be proportional to the difference in mass – this is referred to as mass dependent fractionation.

There are, however, some exceptions where the ratio of fractionation of $^{17}O/^{16}O$ to that of $^{18}O/^{16}O$ is close to 1. Since the extent of fractionation in these cases seems independent of the mass difference, this is called mass independent fractionation. Mass independent fractionation is rare. It was first observed oxygen isotope ratios in meteorites (Lecture 17) and has subsequently been observed in oxygen isotope ratios of atmospheric gases, most dramatically in stratospheric ozone (Figure 27.1), and most recently in sulfur isotope ratios of Archean sediments and modern sulfur-bearing aerosols in ice. The causes of mass independent fractionation are poorly understood and it seems likely there may be more than one cause.

There is at least a partial theoretical explanation in the case of atmospheric ozone (Gao and Marcus, 2001). Their theory can be roughly explained as follows. Formation of ozone in the stratosphere typically involves the energetic collision of monatomic and molecular oxygen, i.e.:

$$O + O_2 \rightarrow O_3$$

The ozone molecule thus formed is in a vibrationally excited state and, consequently, subject to disso-
Mass Independent Sulfur Isotope Fractionation and the Rise of Atmospheric Oxygen

In the modern Earth, variations in sulfur isotope ratios are essentially always mass dependent and $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ are related to variations in $\delta^{34}\text{S}$ as

$$\delta^{33}\text{S} = 0.515 \times \delta^{34}\text{S}$$

and

$$\delta^{36}\text{S} = 1.90 \times \delta^{34}\text{S}$$

However, Farquhar et al. (2000) found that relationships do not hold for sulfur in many Archean sediments and ore deposits. Let’s define the quantities $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ as:

$$\Delta^{33}\text{S} = \delta^{33}\text{S} - 0.515 \times \delta^{34}\text{S}$$

and

$$\Delta^{36}\text{S} = \delta^{36}\text{S} - 1.90 \times \delta^{34}\text{S}$$

Farquhar et al. found that many sulfides (primarily pyrite) in sediments and metasediments formed prior to 2500 Ma have positive $\Delta^{33}\text{S}$ and negative $\Delta^{36}\text{S}$ while hydrothermal sulfide ores and sedimentary sulfates (mainly barite) have negative $\Delta^{33}\text{S}$ and positive $\Delta^{36}\text{S}$ (Figure 27.2). During the Archean, $\Delta^{35}\text{S}$, i.e., deviations from mass-dependent fractionation, of over 3‰ occurred. Farquhar et al. found smaller deviations, up to $\frac{1}{2}$‰ in rocks from the period 2500-2000 Ma. They found no significant deviations from mass dependent fractionation in rocks younger than 2000 Ma.

This raises the obvious question of what process or processes operated during the Archean that could produce mass independent fractionation? Why does this process no longer operate? As mentioned earlier, mass independent isotope fractionation has been observed during laboratory photolysis of SO$_2$ and SO using ultraviolet light. This, together with the observation that ozone and molecular oxygen absorb ultraviolet radiation, provides a possible explanation. Modern volcanic eruptions loft vast quantities of SO$_2$ into the atmosphere and Archean eruptions likely did as well. If the Archean atmosphere lacked O$_2$ and O$_3$, ultraviolet radiation could penetrate deeply into it and photodissociate SO$_2$. According to experiments, these reactions produce sulfate with negative $\Delta^{35}\text{S}$ and elemental sulfur with positive $\Delta^{33}\text{S}$. The sulfate would dissolve in rain and ultimately find its way into the oceans. Some of this would precipitate as barite, BaSO$_4$. Some sulfate would be reduced in hydrothermal systems and precipitate as metal sulfides. Both these processes occur in modern oceans. The S would form particulate S$_8$ and also be swept out of the atmosphere by rain and ultimately incorporated into sediments, where it would react to form sedimentary sulfides. The latter also requires an absence of O$_2$ in the atmosphere – elemental S in the modern atmosphere would be quickly oxidized.
Mass independent fractionation in Archean sulfur thus provides evidence that the early atmosphere lacked free oxygen. This is entirely consistent with other evidence, such as the oxidation state of paleosols and detrital minerals, that the atmosphere did not contain significant amounts of O\(_2\) until the early Proterozoic, about 2.3 billion years ago. Farquhar and Wing (2003) and Kasting and Catling (2003) provide excellent reviews on this topic.

**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 about 20 years ago. This is perhaps because both elements have low abundances in the Earth compared to 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 1980’s, 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 abun-
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Spring 2009

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., B(OH)$_4$) coordination (the only exception is boron bound to fluorine, e.g., 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 B(OH)$_3$ and B(OH)$_4$ with $^{11}$B preferentially found in the B(OH)$_3$ form. In solution, the reaction between trigonal and tetrahedral boron is quite fast, implying equilibrium can be expected and that the isotopic fractionation should reflect this equilibrium.

In natural aqueous solutions boron occurs as both boric acid, B(OH)$_3$, and the borate ion, B(OH)$_4^-$, the dominant species being determined by pH. At pH of around 9 and above, B(OH)$_4^-$ dominates, at lower pH B(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 B(OH)$_3$ form. Most fresh waters are a little more acidic so B(OH)$_3$ will be more dominant; only in highly alkaline solutions, such as saline lakes, will B(OH)$_4^-$ be dominant. The most common boron mineral in the crust is tourmaline (Na(Mg,Fe,Li,Al)$_4$Si$_3$O$_8$BO$_3$(OH,F)$_4$), in which boron is present in BO$_3$ groups. In clays, boron appears to occur primarily as B(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. Boron is an incompatible element in igneous rocks and is very fluid-mobile. It is also readily adsorbed onto 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 27.3 illustrates the variation in B isotopic composition in a variety of geologic materials. Spivack and Edmond (1987) found the δ$^{11}$B of seawater to be +39.5‰, and was uniform within analytical error (±0.25‰). Fresh mid-ocean ridge basalts typically have δ$^{11}$B of about -4‰. Oceanic island basalts (OIB) have slightly lighter δ$^{11}$B (e.g., Chaussidon and Jambon, 1994). The average B isotopic composition of the continental crust probably lies between -13‰ and -8‰ (Chaussidon and Abarède, 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 above, 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 δ$^{11}$B of seawater (Spivack and

* NIST stands for the U.S. National Institute of Standards and Technology and was formerly known as the National Bureau of Standards (NBS). SRM stands for standard reference material.
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 $^{10}$B-rich composition. Ishikawa and Nakamura (1993) noted that ancient limestones and cherts have more negative $\delta^{11}$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 $\delta^{11}$B, with altered oceanic crust having $\delta^{11}$B in the range of 0 to +25‰. Smith et al. (1995) estimated that average altered oceanic crust contains 5 ppm B and $\delta^{11}$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 $\delta^{11}$B 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 hydrothermal altered basalts recovered by the Ocean Drilling Project generally confirm these inferences, as they are boron-poor and have $\delta^{11}$B close to 0 (Ishikawa and Nakamura, 1992).

The more positive $\delta^{11}$B values of island arc volcanics (IAV) relative to MORB may in part reflect the incorporation of subducted marine sediment and altered oceanic crust into the sources of island arc magmas (e.g., Palmer, 1991). There is, however, some debate as to the extent the more positive $\delta^{11}$B values in IAV might also reflect assimilation of sediment or altered oceanic crust during magma ascent (e.g., Chaussidon and Jambon, 1994).

The differences in $\delta^{11}$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 $\delta^{11}$B of MORB reflects contamination of MORB magmas by alteration of the oceanic crust.
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B species will depend only on \( \delta \), which, as we can see in equation 27.4, will depend on pH. Thus, assuming a constant fractionation factor and isotope geochemistry of seawater in which they grow, this fractionation can be written as:

\[
\delta \text{B(SW)} = \delta \text{B(H)} + \delta \text{B(OH)} \]

The equilibrium constant for this reaction is:

\[
-pK_{\text{eq}} = \ln \frac{\text{B(OH)}_3}{\text{B(OH)}_4} - pH \]

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

\[
\delta^{11}\text{B}_{\text{SW}} = \delta^{11}\text{B}_3 f + \delta^{11}\text{B}_4 (1-f) \]

where \( f \) is the fraction of \( \text{B(OH)}_3 \) (and 1 - \( f \) is therefore the fraction of \( \text{B(OH)}_4 \)), \( \delta^{11}\text{B}_3 \) is the isotopic composition of \( \text{B(OH)}_3 \) and \( \delta^{11}\text{B}_4 \) is the isotopic composition of \( \text{B(OH)}_4 \). If the isotopic composition of the two species are related by a constant fractionation factor, \( \Delta_{3,4} \), we can write 27.5 as:

\[
\delta^{11}\text{B}_{\text{SW}} = \delta^{11}\text{B}_3 f + \delta^{11}\text{B}_4 - \Delta_{3,4} f \]

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

\[
\delta^{11}\text{B}_4 = \frac{\delta^{11}\text{B}_{\text{SW}}}{\Delta_{3,4}} \]

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 equation 27.4, will depend on pH.
If the mechanism for incorporation of B in carbonate suggested by Vengosh et al. (1991) 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 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., 2000), allowing in principle the reconstruction of paleo-seawater 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 $\text{B(OH)}_3$ is also utilized to varying degrees, (2) the fractionation factor is temperature dependent, and (3) the B isotopic composition of seawater may vary.

<table>
<thead>
<tr>
<th>Neogene</th>
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![Graph](image)

Figure 27.4. Top graph shows the variation 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. Adapted from Pearson and Palmer (2000).
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. 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 $\delta^{11}$B in foraminiferal carbonate extracted from Ocean Drilling Program (ODP) cores and from this calculated pH based on equations 27.4 and 27.7. To minimize the effect of temperature 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 1 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 argue 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 $\delta^{11}$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 27.4 shows that the Neogene is characterized by atmospheric $p_{CO_2}$ near or slightly below modern pre-industrial levels. This aspect of the result is somewhat surprising, given the evidence for cooling through the Neogene, particularly over the last 10-15 Ma (e.g., Figure 26.10). If, as Figure 27.4 suggests, atmospheric $p_{CO_2}$ has been nearly constant through the Neogene, some factor other than the greenhouse effect must account for the cooling over this time.

On a more limited time scale, Hönisch and Hemming (2005) investigated $\delta^{11}$B over the last two glacial cycles (0-140 and 300-420 ka). In this study, they controlled for temperature by analyzing the Mg/Ca ratio of the carbonate shells, which is know to be strongly temperature dependent. Their calculated pH values ranged from 8.11 to 8.32, which in turn correspond to a $p_{CO_2}$ range of ~180 to ~325 ppm. These calculated $p_{CO_2}$ values are in good agreement with CO$_2$ concentrations measured in bubbles in the Vostok ice core.

Nevertheless, paleo-seawater pH reconstruction based on boron isotopes remains somewhat controversial. Pagani et al. (2005) and Zeebe (2005) point out that the fractionation factor between B(OH)$_3$ and B(OH)$_4^-$ has not been experimentally determined and remains somewhat uncertain. Attempts to calculate it theoretically are hampered by uncertainties in experimental determination of 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 $\delta^{11}$B in seawater has varied with time.

**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 1930’s. 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 δ7Li value of +33‰. Subsequent work suggests that δ7Li in seawater might vary by as much as 4‰, but the degree to which this variation reflects analytical error and interlaboratory 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. During mineral-water reactions, the heavier isotope, 7Li, is preferential partitioned into the solution. Thus weathering on the continents results in river water being isotopically heavy, +23.5‰ on average, compared to a average continental crust, which has δ7Li of ~0, and the suspended load of rivers which have δ7Li ≈ +2 (Teng et al., 2004). Thus seawater is some 10 per mil heavier than average river water, so additional fractionation must occur marine environment. This likely includes adsorption on particles (although Li is less prone to absorption 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 and the fractionation factor for low-temperature alteration of basalt at -19‰. Reported δ7Li values in marine non-carbonate sediments range from -1 to +15‰, but Chan and 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 δ7Li than non-carbonate sediment.

Fresh MORB has a very limited range of δ7Li of +1 to +6‰, with most values falling between +3 and +5, a range not much larger than that expected from analytical error alone. Oceanic island basalts (OIB) range to only slightly higher values, +7‰, than MORB, but only Hawaii has been studied in any detail. There appears to be little the relationship between δ7Li and petrological parameters, such as MgO concentration, suggesting Li experiences little isotopic fractionation during fractional crystallization, and perhaps also partial melting. 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.

δ7Li in oceanic crust altered by seawater at low temperatures takes up Li from solution and has high δ7Li compared to fresh basalt. In hydrothermal reactions, however, Li is extracted from basalt into the solution and hydrothermal fluids can 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 δ7Li as low as -2‰. On average, altered MORB have δ7Li of +11. Serpentinites (hydrothermally altered peridotite) can have low δ7Li. Because they extract Li from oceanic crust so completely, hydrothermal solutions have Li isotopic compositions intermediate between MORB despite this fractionation.
Alpine eclogites can have distinctly light isotopic compositions with a mean δ\(^7\)Li of -3‰. 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 \(^7\)Li into the fluid produced as the rocks were dehydrated during metamorphism. Thus although weathering initially increases δ\(^7\)Li of the oceanic crust, subsequent dehydration of it under metamorphic conditions appears to lower δ\(^7\)Li as it is subducted into the mantle.

Island arc lavas have a range of δ\(^7\)Li of +1 to +11, but all but a few values in the range +2 to +6, which is not very different from the range in MORB. This is somewhat surprising since other isotopic evidence clearly demonstrates island arc magmas contain components derived from subducted oceanic crust and sediment. Furthermore, while δ\(^7\)Li have been shown in some cases to correlate with chemical and isotopic indicators of a subduction component, this is not always the case.

In summary, there is little fractionation of Li isotopes during magmatic processes, but substantial fractionation does occur during weathering and metamorphism. Subduction of this weathered and/or metamorphosed material into the Earth’s interior can expect to lead to variability in mantle Li isotopic composition. Elliott et al. (2006) showed that δ\(^7\)Li correlated with Nd and Sr isotope ratios (Figure 27.6). Since Sr and Nd isotope ratios are not affected by melting or magma generation, this correlation demonstrates real variability in the Li isotope composition of the mantle, which could have only be created by subduction of weathered and/or metamorphosed material into the deep mantle. Interestingly, the correlation is opposite of that expected. We would expect oceanic crust and sediments to be incompatible element-rich, and therefore have high Sr and low Nd isotope ratios compared to normal mantle material. If alpine eclogites are representative of subducted oceanic crust, then this material should also have low δ\(^7\)Li, just the opposite of the correlation observed. Elliott et al. (2006) suggested mantle heterogeneity is produced not be recycling of oceanic crust, but by convectively mixing the fluid-modified mantle wedge above the subduction zone into the upper mantle. Whether this idea can be reconciled with other observations remains to be seen.

REFERENCES AND SUGGESTIONS FOR FURTHER READING


