

## STABLE ISOTOPE APPLICATIONS I: HIGH TEMPERATURES

### INTRODUCTION

Stable isotopes have a number of uses in high temperature geochemistry (i.e., igneous and metamorphic geochemistry), which we will treat in the next several lectures. Perhaps the most important of these is geothermometry, i.e., deducing the temperatures at which mineral assemblages equilibrated. This application makes use of the temperature dependency of fractionation factors. Other important applications include reconstructing ancient hydrothermal systems, detecting crustal assimilation in mantle-derived magmas, and tracing recycled crust in the mantle. These applications primarily involve O isotopes. Before discussing these subjects, let's briefly review the factors governing isotopic fractionation.

### TEMPERATURE DEPENDENCE OF EQUILIBRIUM FRACTIONATIONS

In Lecture 25, we found that the translational and rotation contributions to the partition function do not vary with temperature. In our example calculation at low temperature, we found the vibrational contribution varies with the inverse of absolute temperature. At higher temperature, the

$\exp(-h\nu/kT)$  term in equation 25.35 becomes finite and this relationship breaks down. As a result, the temperature dependence of the equilibrium constant can generally be described as:

$$\ln K = A + \frac{B}{T^2} \quad 28.1$$

where A and B are constants. At infinite temperature, the fractionation is unity; i.e.,  $\ln K \approx 0$ . Because of the nature of this temperature dependency, fractionation of stable isotopes at mantle temperatures will usually be small. This is one reason why stable isotopes are useful tracers of crustal assimilation and recycling.

It must be emphasized that the simple calculations in Lecture 25 are applicable only to a gas whose vibrations can be approximated by a simple harmonic oscillator. Real gases show fractionations that are complex functions of temperature, with minima, maxima, inflections, and cross-overs.

### Compositional and Structural Dependence of Equilibrium Fractionations

The nature of the chemical bond is of primary importance in determining isotope fractionations. In general, bonds to ions with a high ionic potential and low atomic mass are associated with high vibrational

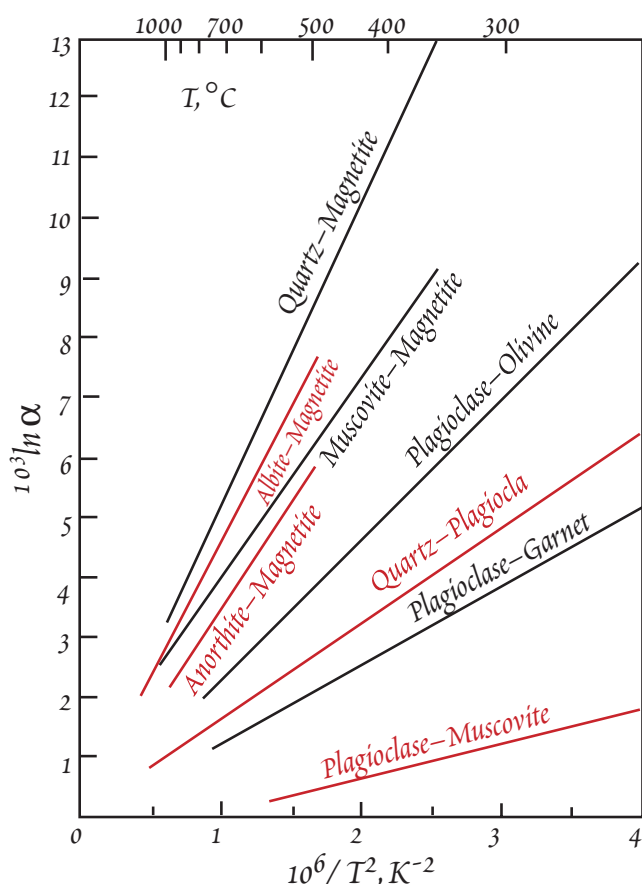


Figure 28.1. Calculated oxygen isotope fractionation for several mineral pairs as a function of temperature (from O'Neil, 1986).

frequencies and have a tendency to incorporate the heavy isotope preferentially. For example, quartz ( $\text{SiO}_2$ ) is typically the most  $^{18}\text{O}$ -rich mineral and magnetite the least (O is bonded to  $\text{Si}^{4+}$  in quartz and  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in magnetite). The covalent bonding of the basic mineral structure is most important in determining fractionations: the bonding between Si and O is largely covalent, the bonding between Fe and O is largely ionic. Substitution of cations in a primarily ionic site has little isotopic effect. Thus, for example, we would expect relatively little O isotopic fractionation between K-feldspar and Na-feldspar. This turns out to be the case: the fractionation is of the order of 0.1 permil at room temperature. The substitution of Al for Si in plagioclase is important (substitution of Ca for Na is much less important), leading to a 1.1 permil fractionation between anorthite and albite at room temperature. Table 28.1 lists the parameters for the temperature dependence of silicate and oxide fractionation factors at low temperatures.

Carbonates tend to be very  $^{18}\text{O}$  rich because O is bonded to a small, highly charged atom,  $\text{C}^{4+}$ . The fractionation relative to water,  $\Delta^{18}\text{O}$  (the  $\Delta$  is the difference rather than the fraction) is about 30 for calcite. The cation (i.e., Ca or Mg in carbonate) has a secondary role (because of the effects of its mass on vibrational frequency). The  $\Delta^{18}\text{O}$  decreases to about 25 for Ba (about 3 times the mass of Ca).

Crystal structure usually plays a secondary role. The  $\Delta^{18}\text{O}$  between aragonite and calcite is of the order of 0.5 permil. But there apparently is a large fractionation (10 permil) of C between graphite and diamond at room temperature.

Pressure effects turn out to be pretty small, 0.1 permil at 20 kbars and less. The reason should be fairly obvious: there is no volume change in isotope exchange reactions, and pressure effects depend on volume changes. The volume of an atom is entirely determined by its electronic structure, which does not depend on the mass of the nucleus. On the other hand, there will be some minor fractionation

TABLE 28.1. COEFFICIENTS OXYGEN ISOTOPE FRACTIONATION AT LOW TEMPERATURES:

$$\Delta_{\text{QZ}-\phi} = A + B \times 10^6 / T^2$$

$\phi$	A	B
Feldspar	0	$0.97 + 1.04b^*$
Pyroxene	0	2.75
Garnet	0	2.88
Olivine	0	3.91
Muscovite	-0.60	2.2
Amphibole	-0.30	3.15
Biotite	-0.60	3.69
Chlorite	-1.63	5.44
Ilmenite	0	5.29
Magnetite	0	5.27

\*  $b$  is the mole fraction of anorthite in the feldspar. This term therefore accounts for the compositional dependence discussed above. From Javoy (1976).

TABLE 28.2. COEFFICIENTS FOR OXYGEN ISOTOPE FRACTIONATIONS AT ELEVATED TEMPERATURES (600° – 1300°C)

	Cc	Ab	An	Di	Fo	Mt
Qz	0.38	0.94	1.99	2.75	3.67	6.29
Cc		0.56	1.61	2.37	3.29	5.91
Ab			1.05	1.81	2.73	5.35
An				0.76	1.68	4.30
Di					0.92	3.54
Fo						2.62

Coefficients are for mineral pair fractionations expressed as:  $1000\alpha = B \times 10^6 / T^2$  where  $B$  is given in the Table. Qz: quartz, Cc: calcite, Ab: albite, An: anorthite, Di: diopside, Fo: forsterite, Mt: magnetite. For example, the fractionation between albite and diopside is  $1000\alpha_{\text{Ab-Di}} = 1.81 \times 10^6 / T^2$  ( $T$  in kelvins). From Chiba, et al. (1989).

TABLE 28.3. COEFFICIENTS FOR SULFUR ISOTOPE FRACTIONATION:

$$\Delta_{\phi-\text{H}_2\text{S}} = A + B \times 10^6 / T^2 \text{ (T IN KELVINS)}$$

$\phi$	B	A	T°C Range
$\text{CaSO}_4$	$6.0 \pm 0.5$	5.26	200-350
$\text{SO}_2$	$-5 \pm 0.5$	4.7	350-1050
$\text{FeS}_2$		$0.4 \pm 0.08$	200-700
$\text{ZnS}$		$0.10 \pm 0.05$	50-705
$\text{CuS}$		$-0.4 \pm 0.1$	
$\text{Cu}_2\text{S}$		$-0.75 \pm 0.1$	
$\text{SnS}$		$-0.45 \pm 0.1$	
$\text{MoS}_2$		$0.45 \pm 0.1$	
$\text{Ag}_2\text{S}$		$-0.8 \pm 0.1$	
$\text{PbS}$		$-0.63 \pm 0.05$	50-700

From Ohmoto and Rye (1979)

that results from changes in vibrational frequency as crystals are compressed.

Because oxygen occupies a generally similar lattice site in virtually all mantle minerals: it is covalently bonded to oxygen and ionically bonded to other cations (e.g., Mg, Fe, Ca, etc.), fractionation of oxygen isotopes are relatively small, though still significant. Table 28.2 lists fractionation factors for silicate and oxide minerals at high temperatures.

### GEOOTHERMOMETRY

One of the principal uses of stable isotopes is as geothermometers. Like conventional chemical geothermometers, stable isotope geothermometers are based on the temperature dependence of the equilibrium constant (equation 28.1). In actuality, the constants A and B in equation 28.1 are slowly varying functions of temperature, such that K tends to zero at absolute 0, corresponding to complete separation, and to 1 at infinite temperature, corresponding to no isotope separation. We can obtain a qualitative understanding of why this as so by recalling that the entropy of a system increases with temperature. At infinite temperature, there is complete disorder, hence isotopes would be mixed randomly between phases (ignoring for the moment the slight problem that at infinite temperature there would be neither phases nor isotopes). At absolute 0, there is perfect order, hence no mixing of isotopes between phases. A and B are, however, sufficiently invariant over a range of geologically interesting temperatures that as a practical matter they can be described as constants. We have also noted that at temperatures close to room temperature and below, the form of equation 28.1 changes to  $K \propto 1/T$ .

Because of the dependence of the equilibrium constant on the inverse square of temperature, stable isotope geothermometry is employed primarily at low and moderate temperatures, that is, non-magmatic temperatures. At temperatures greater than 800°C or so (there is no exact cutoff), the fractionations are generally too small for accurate temperatures to be calculated from them.

In principal, a temperature may be calculated from the isotopic fractionation between any phases provided the phases achieved equilibrium and the temperature dependence of the fractionation factor is known. And indeed, there are too many isotope geothermometers for all of them to be even mentioned here. We can begin by considering silicate systems. Figure 28.1 shows fractionation factors between various silicates and oxides as a function of temperature. Tables 28.1 and 28.2 list coefficients A and B for temperature dependence of the fractionation factor between quartz and other common silicates and oxides when this temperature dependence is expressed as:

$$\Delta \approx 1000 \ln \alpha_{Qz-\phi} = A + B \times 10^6/T^2 \quad 28.2$$

with temperature expressed in kelvins. Recall that fundamental rule of physics states that if phases A and C and A and B are in equilibrium with each other, then C is also in equilibrium with B. Thus Table 28.1 may be used to obtain the fractionation between any of the two phases shown.

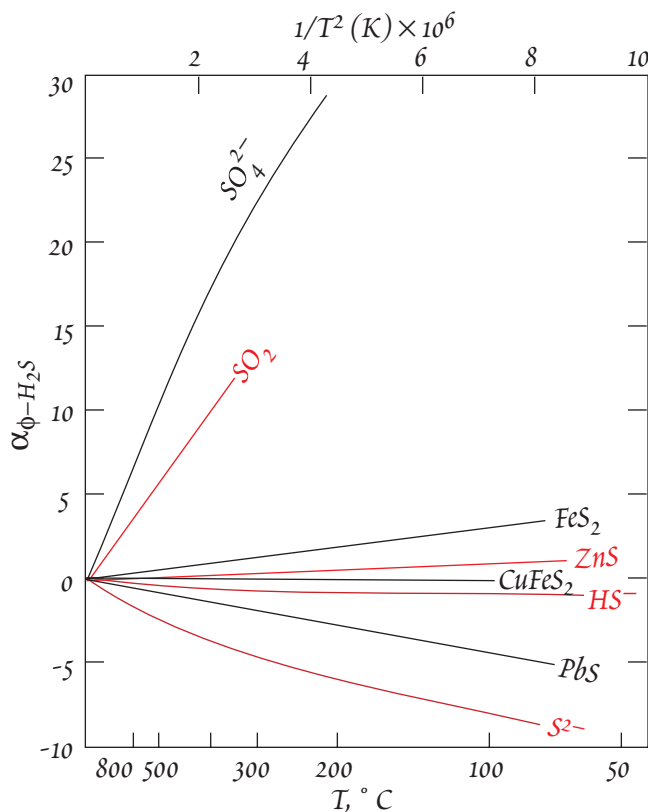


Figure 29.2. Relationship of S isotope fractionation between  $H_2S$  and other sulfur-bearing species and temperature. From Ohmoto and Rye (1979).

The other isotope that has been used extensively for geothermometry of igneous and metamorphic rocks is sulfur. Its principal application has been in determining the temperature of deposition of sulfide ores, most of which precipitate from hydrous fluids. Sulfur may be present in fluids as any one of several species. Since isotope fractionation depends on bond strength, the predicted order of  $^{34}\text{S}$  enrichment is:  $\text{SO}_4^{2-} > \text{SO}_3^{2-} > \text{SO}_2 > \text{SCO} > \text{S}_x \sim \text{H}_2\text{S} \sim \text{HS}^- > \text{S}^{2-}$  (Ohmoto and Rye, 1979). Figure 28.2 shows the temperature dependence of fractionation factors between  $\text{H}_2\text{S}$  and other phases, and Table 28.3 lists coefficients for the equation:

$$\Delta \approx 1000 \ln \alpha_{\phi-\text{H}_2\text{S}} = A + \frac{B}{T^2} \times 10^6 \quad 28.3$$

$\text{CO}_2$  and other carbon-bearing species are ubiquitous in meteoric and hydrothermal waters. Carbonates often precipitate from such solutions and the fractionation between carbon-species provides yet another opportunity for geothermometry. Figure 28.3 shows carbon isotope fractionation factors between  $\text{CO}_2$  and other carbon bearing species as a function of temperature. The figure includes fractionation factors both calculated from theory and observed vibrational frequencies (calcite, carbonate ion, carbon monoxide, methane) and empirical determined values (dolomite, bicarbonate ion, carbonic acid). Table 28.4 lists coefficients for a third degree polynomial expression of temperature dependence.

### The Importance of Equilibrium

All geothermometers are based on the apparently contradictory assumptions that complete equilibrium was achieved between phases during, or perhaps after, formation of the phases, but that the phases did not re-equilibrate at any subsequent time. The reason these assumptions can be made and geothermometry works at all is the exponential dependence of reaction rates on temperature. Isotope geothermometers have these same implicit assumptions about the achievement of equilibrium as other systems.

The importance of the equilibrium basis of the geothermometry must be emphasized. Because most are applied to relatively low temperature situations, violation of the assumption that complete equilibrium was achieved is not uncommon. We have seen that isotopic fractionations may arise from kinetic as well as equilibrium effects. If reactions do not run to completion, the isotopic differences may reflect kinetic effects as much as equilibrium effects. Other problems can result in incorrect temperature as well: the system may partially re-equilibrate at some lower temperatures during cooling; free energies of isotope exchange reactions are low, meaning there is little chemical energy available to drive the reaction to equilibrium. Indeed, isotopic equilibrium probably often depends on other reactions occurring which mobilize the element involved in the exchange. Solid-state exchange reactions will be particularly slow at temperatures well below the melting point. Equi-

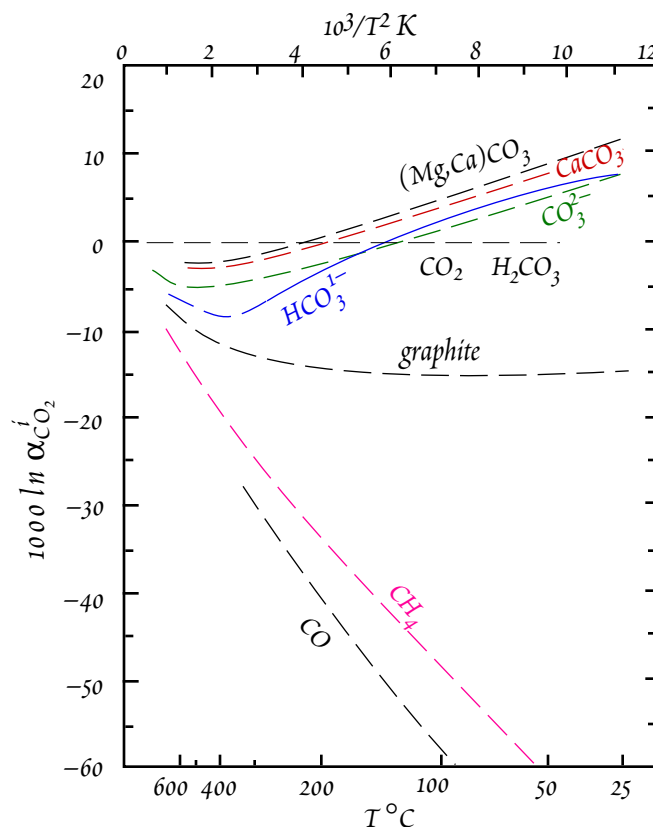


Figure 28.3. Fractionation factors for distribution of carbon isotopes between  $\text{CO}_2$  and other carbon-bearing species as a function of temperature. From Ohmoto and Rye (1979).

TABLE 28.4 ISOTOPE FRACTIONATION FACTORS OF CARBON COMPOUNDS WITH RESPECT TO CO<sub>2</sub>  
 $1000 \ln \alpha = A \times 10^8/T^3 + B \times 10^6/T^2 + C \times 10^3/T + D$

$\phi$	A	B	C	D	T°C Range
CaMg(CO <sub>3</sub> ) <sub>2</sub>	-8.914	8.737	-18.11	8.44	≤600
Ca(CO <sub>3</sub> )	-8.914	8.557	-18.11	8.24	≤600
HCO <sub>3</sub> <sup>-</sup>	0	-2.160	20.16	-35.7	≤290
CO <sub>3</sub> <sup>2-</sup>	-8.361	-8.196	-17.66	6.14	≤100
H <sub>2</sub> CO <sub>3</sub>	0	0	0	0	≤350
CH <sub>4</sub>	4.194	-5.210	-8.93	4.36	≤700
CO	0	-2.84	-17.56	9.1	≤330
C	-6.637	6.921	-22.89	9.32	≤700

From Ohmoto and Rye (1979).

Rye (1979) noted a number of factors that may contribute to the lack of fit, such as impure mineral separates used in the analysis; for example, 10% of the galena in sphalerite and visa versa would result in an estimated temperature of 215°C if the actual equilibration temperature was 145°C. Different minerals may crystallize at different times and different temperatures in a hydrothermal system and hence would never be in equilibrium. In general, those minerals in direct contact with each other give the most reliable temperatures. Real disequilibrium may also occur if crystallization is kinetically controlled. The generally good fit to the higher temperature sulfides and poor fit to the low temperature ones suggests kinetics may indeed be an important factor.

Javoy (1976) suggested a graphical method to test for oxygen-isotope equilibrium based on a rearrangement of 28.2. Choosing a ubiquitous index mineral, for example quartz, we may rewrite 28.2 for each quartz-mineral pair as:

$$\Delta_{QZ-\phi} - A_{QZ-\phi} = B_{QZ-\phi} \times 10^6/T^2$$

The left hand side of the equation is then plotted against the right hand side. If equilibrium has been achieved, all points should lie on a line, a "geotherm". Figure 28.5 shows an example of a monzonite. All quartz mineral pairs lie reasonably close to the line, suggesting general equilibrium. Biotite lies slightly off, indicating it was not in equilibrium with quartz.

Isotope geothermometers do have several advantages over conventional chemical ones. First, as we have noted, there is no volume change associated with isotopic exchange reactions and hence little pressure dependence of the equilibrium constant (however, Rumble has suggested an indirect pressure de-

librium between solid phases will thus generally depend on reaction of these phases with a fluid. Of course, this is true of 'conventional' chemical reactions as well, and metamorphism generally occurs in the presence of a fluid.

Figure 28.4 compares sphalerite–galena sulfur isotope temperatures with fluid-inclusion homogenization temperatures. Excluding the Pine Point data, the best fit to the data is fairly close to that expected from the fractionation factors listed in Table 28.3:  $\Delta_{sp-gn} = 0.73 \times 10^6/T^2$ . Many of the points fall off the expected curve, indicating disequilibrium. Ohmoto and

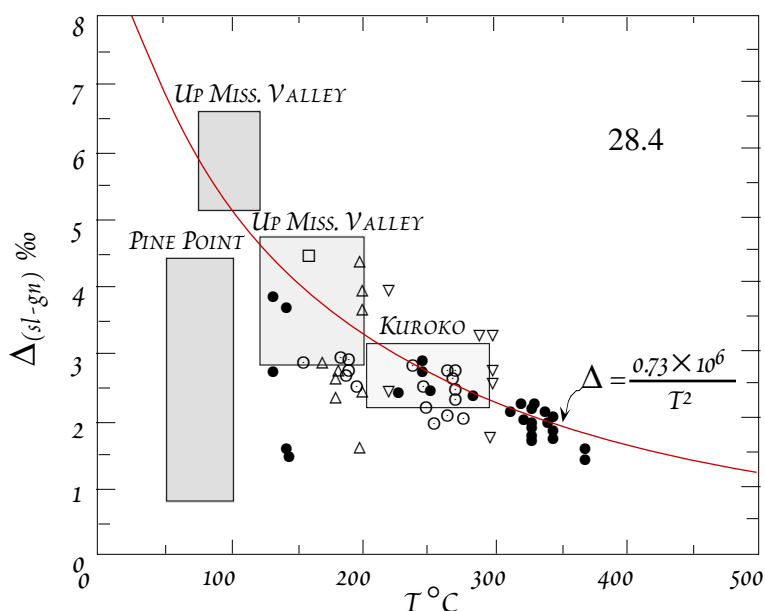


Figure 28.4. Comparison of temperatures determined from sphalerite–galena sulfur isotope fractionation with fluid-inclusion homogenization temperatures. ●: Creede, CO, ▽: Sunnyside, ○: Finlandia vein, △: Pasto Bueno, □: Kuroko. From Ohmoto and Rye (1979).

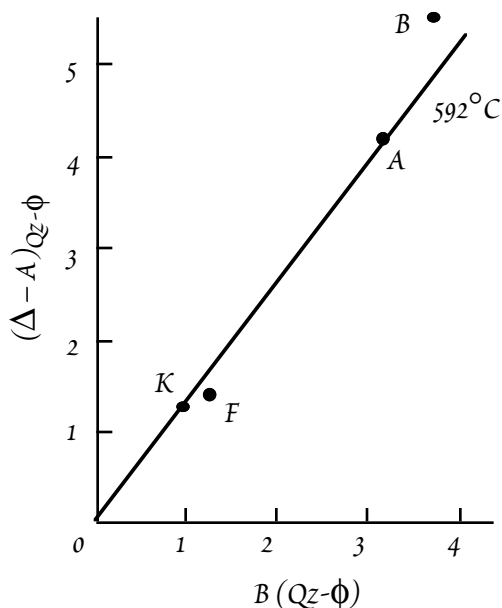


Figure 28.5.  $\Delta_{QZ-\phi} - A_{QZ-\phi}$  vs.  $B_{QZ-\phi} \times 10^6/T^2$  for a monazite with the phases A: amphibole, B: biotite, K: K-feldspar, and F: plagioclase. Slope of the line through the 3 points corresponds to a temperature of 592°C.

pendence, wherein the fractionation factor depends on fluid composition which in turn depends on pressure). Second, whereas conventional chemical geothermometers are generally based on solid solution, isotope geothermometers can make use of pure phases such as  $\text{SiO}_2$ , etc. Generally, any dependence on the composition of phases in isotope geothermometers involved is of relatively second order importance. For example, isotopic exchange between calcite and water is independent of the concentration of  $\text{CO}_2$  in the water. Compositional effects can be expected only where composition affects bonds formed by the element involved in the exchange. For example, we noted substitution of Al for Si in plagioclase affects O isotope fractionation factors because the nature of the bond with oxygen. The composition of a  $\text{CO}_2$  bearing solution, however, should not affect isotopic fractionation between calcite and dissolved carbonate because the oxygen is bonded with C regardless of the presence of other ions (if we define the fractionation as between water and calcite, some effect is possible if the O in the carbonate radical exchanges with other radicals present in the solution).

### STABLE ISOTOPE COMPOSITION OF THE MANTLE

Before we can use stable isotope ratios as indicators of crustal assimilation and tracers of crustal recycling, we need to define the stable isotopic composition of "uncontaminated" mantle. It is, however, important to recognize from the outset that, in a strict sense, there may be no such thing. We found in our consideration of radiogenic isotope ratios that no samples of "primitive" mantle have been recovered: the mantle, or at least that portion sampled by volcanism, has been pervasively processed. Much of this processing may have involved only extraction of partial melts. This process would have had a very minimal effect on O isotope ratios, and probably only a small effect on other stable isotope ratios. However, the process of oceanic crust creation and destruction has undoubtedly been going on for much, if not all, of geologic time. A very considerable amount of oceanic crust has been subducted during this time, perhaps accompanied by sediment. As we shall see, the stable isotopic composition of the oceanic crust is extensively modified by hydrothermal processes and low temperature weathering. Subduction of this material has the potential for modifying the stable isotopic composition of the mantle. Thus while we will attempt to use stable isotope ratios to identify "contamination" of mantle by subduction, we must recognize all of it may have been "contaminated" to some degree.

Other problems arise in defining the stable isotope composition of the mantle. We relied heavily on basalts as mantle samples in defining the radiogenic isotope composition of the mantle. We could do so because radiogenic isotope ratios are not changed in the magma generation process. This will not be strictly true of stable isotope ratios, which can be changed by chemical processes. The effects of the melting process on most stable isotope ratios of interest are probably fairly small, though perhaps not completely negligible. Degassing does significantly affect stable isotope ratios, particularly those of carbon and hydrogen, which compromises the value of magmas as a mantle sample. Once oxides begin to crystallize, fractional crystallization will affect oxygen isotope ratios, though the resulting changes are at most a few per mil. Finally, weathering and hydrothermal processes can affect stable isotope ratios of basalts and other igneous rocks. Because hydrogen, carbon, nitrogen, and sulfur are all trace elements in basalts but are quite abundant at the Earth's surface, these elements are particularly susceptible to weathering effects. Even oxygen, which constitutes nearly 50% by



weight of silicate rocks, is readily affected by weathering. Thus we will have to proceed with some caution in using basalts as samples of the mantle for stable isotope ratios.

### Oxygen

Assessing the oxygen isotopic composition of the mantle, and particularly the degree to which its oxygen isotope composition might vary, has proved to be more difficult than expected. One approach has been to use basalts as samples of mantle, as is done for radiogenic isotopes. Relatively little isotope fractionation occurs during partial melting, so the oxygen isotopic composition of basalt should be the same as that in the mantle source within a few tenths per mil. However, assimilation of crustal rocks by magmas and oxygen isotope exchange during weathering complicate the situation. An alternative is to use direct mantle samples such as xenoliths occasionally found in basalts, although these are considerably rarer than are basalts.

Figure 28.6 shows the oxygen isotope composition of olivines and clinopyroxenes in 76 peridotite xenoliths analyzed by Matthey et al. (1994) using the laser fluorination technique. The total range of values observed is only about twice that expected from analytical error alone, suggesting the mantle is fairly homogeneous in its isotopic composition. The difference between co-existing olivines and clinopyroxenes averages about 0.5 per mil, which is consistent with the expected fractionation between these minerals at mantle temperatures. Matthey et al. (1994) estimated the bulk composition of these samples to be about +5.5 per mil.

Figure 28.7 shows the distribution of  $\delta^{18}\text{O}$  in selected basalts from 4 different groupings. To avoid the weathering problems we discussed above, Harmon and Hoefs (1995) included only submarine basaltic glasses and basalts that had less than 0.75% water or had erupted historically in their compilation. There are several points worth noting in these data.

MORB are significantly more homogeneous than are other basalts. MORB have a mean  $\delta^{18}\text{O}_{\text{SMOW}}$  of +5.7‰ and a standard deviation of  $\pm 0.2$ ‰. Thus the depleted upper mantle appears to be a comparatively homogeneous and well-mixed reservoir for oxygen, just as it is for other elements. Oceanic island basalts, which presumably sample mantle plumes, are slightly less enriched in  $^{18}\text{O}$  (mean  $\delta^{18}\text{O}_{\text{SMOW}} = +5.5$ ‰), and are also more variable ( $1\sigma = 0.5$ ‰). The histogram shown excludes Iceland, be-

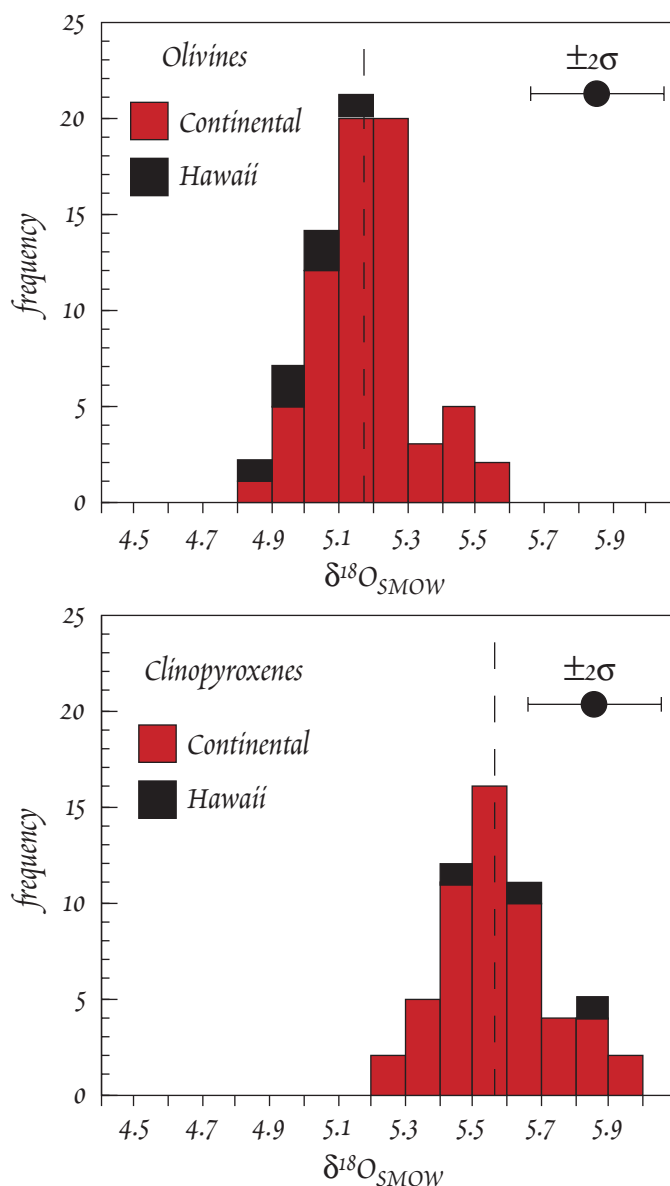


Figure 28.6. Oxygen isotope ratios in olivines and clinopyroxenes from mantle peridotite xenoliths. Data from Matthey et al. (1994).

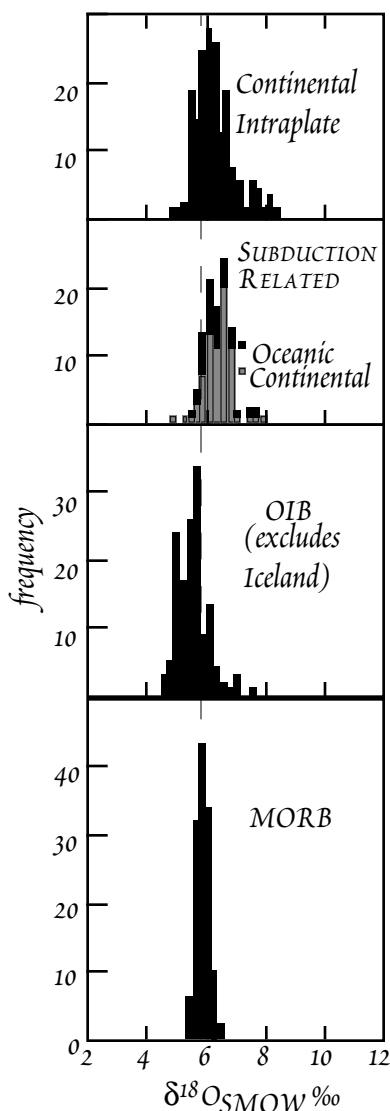


Figure 28.7 of MORB (+5.7).  
After Harmon and Hoefs (1994).

Rayleigh distillation occurs, that is if bubbles do not remain in equilibrium with the liquid, then the basalt that eventually erupts may have carbon that is substantially lighter than the carbon originally dissolved in the melt. Furthermore, MORB are pervasively contaminated with a very  $^{13}\text{C}$ -depleted carbon. This carbon is probably organic in origin, and recent observations of an eruption on the East Pacific Rise suggest a source. Following the 1991 eruption at 9°30' N, there was an enormous 'bloom' of bacteria stimulated by the release of  $\text{H}_2\text{S}$ . Bacterial mats covered everything. The remains of these bacteria may be the source of this organic carbon. Fortunately, it appears possible to avoid most of this contamination by the step-wise heating procedure now used by most laboratories. Most of the contaminant carbon is released at temperatures below 600°C, whereas most of the basaltic carbon is released above 900°C.

Figure 28.8 shows  $\delta^{13}\text{C}$  in various mantle and mantle-derived materials. MORB have a mean  $\delta^{13}\text{C}$  of -6.5 and a standard deviation of 1.7. Hawaiian basalts appear to have slightly heavier carbon. Xenoliths in oceanic island basalts are also slightly heavier than MORB. Whether this reflects a real difference in isotopic composition or merely the effect of fractionation is unclear. The most  $\text{CO}_2$ -

cause Icelandic basalts are quite anomalous in their low  $\delta^{18}\text{O}$  (mean  $\sim 4.5\text{‰}$ ). This has been shown to be due primarily to assimilation of older basaltic crust that has equilibrated with meteoric water, which is quite  $^{18}\text{O}$  depleted at the latitude of Iceland. There is, however, some evidence to suggest even primary Icelandic basalts are depleted in  $^{18}\text{O}$  relative to MORB. Subduction-related basalts (i.e., island arc basalts and their continental equivalents) are shifted to more positive  $\delta^{18}\text{O}$  values. This may well reflect contributions from the subducting slab, and we shall explore this further in a later lecture. Continental subduction-related basalts are more  $^{18}\text{O}$  rich than their oceanic equivalents, most likely due to assimilation of continental crust. Finally, continental intraplate volcanics are more enriched in  $^{18}\text{O}$  than are OIB, again suggestive of crustal assimilation.

### Carbon

The stable isotopes of H, C, N, and S are much more difficult to analyze in igneous rocks. These elements are generally trace elements and are volatile. With rare exceptions, they have a strong tendency to exsolve from the melt and escape as gases as magmas approach the surface of the earth. Not only are these elements lost during degassing, but they can be isotopically fractionated by degassing. Thus there is far less data on the isotopes of these elements in basalts, and the meaning of this data is somewhat open to interpretation.

Most carbon in basalts is in the form of  $\text{CO}_2$ , which has limited solubility in basaltic liquids. As a result, basalts begin to exsolve  $\text{CO}_2$  before they erupt. Thus virtually every basalt sample has lost some carbon, and subareal 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. As a result, the data set is restricted to MORB, samples recovered from Loihi and the submarine part of Kilauea's East Rift Zone, and a few other seamounts.

The question of the isotopic composition of mantle carbon is further complicated by fractionation and contamination. There is a roughly 4‰ fractionation between  $\text{CO}_2$  dissolved in basaltic melts and the gas phase, with  $^{13}\text{C}$  enriched in the gas phase. If



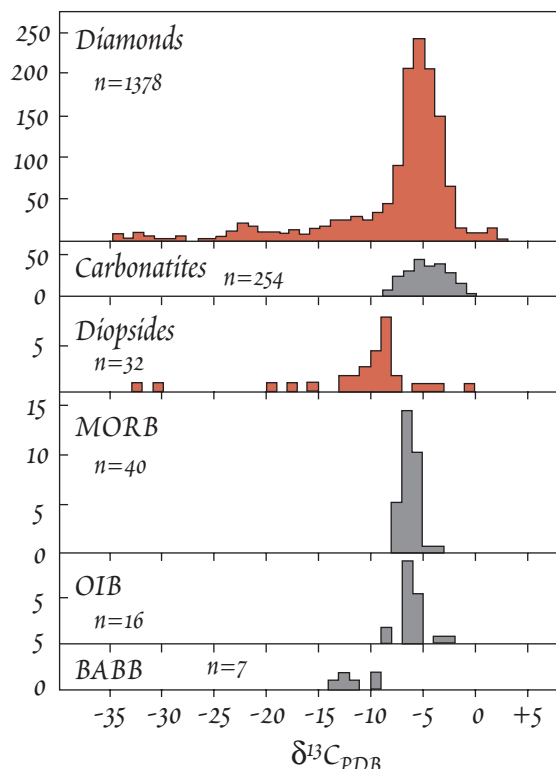


Figure 28.8. Carbon isotope ratios in mantle (red) and mantle-derived materials (gray). After Matthey (1987).

rich MORB samples have  $\delta^{13}\text{C}$  of about -4. Since they are the least degassed, they presumably best represent the isotopic composition of the depleted mantle (Javoy and Pineau, 1991). If this is so, there may be little difference in carbon isotopic composition between MORB and oceanic islands sampled thus far (which include only Hawaii, Reunion, and Kerguelen). Gases released in subduction zone volcanos have  $\delta^{13}\text{C}$  that ranges from 0 to -10‰, with most values being in the range of -2 to -4‰, comparable to the most gas-rich MORB (Javoy, et al., 1986). Continental xenoliths are more heterogeneous in carbon isotopic composition than other groups, and the meaning of this is unclear. Carbonatites have somewhat lighter carbon than most MORB.

Diamonds show a large range of carbon isotopic compositions (Figure 28.8). Most diamonds have  $\delta^{13}\text{C}$  within the range of -2 to -8‰, hence similar to MORB. However, some diamonds have much lighter carbon. Based on the inclusions they contain, diamonds 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, 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 are anomalous relative to nitrogen in other mantle materials yet similar to nitrogen in sedimentary rocks.

### Hydrogen

Like carbon, hydrogen can be lost from basalts during degassing. On the one hand, the problem is somewhat less severe than for carbon because the solubility of water in basalt is much greater than that of  $\text{CO}_2$ . Basalts erupted beneath a kilometer of more of water probably retain most of their dissolved water. However, basalts, particularly submarine basalts, are far more readily contaminated

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with hydrogen (i.e., with water) than with carbon. Furthermore, the effect on hydrogen isotopic composition depends on the mode of contamination, as Figure 28.9 indicates. Direct addition of water or hydrothermal reactions will raise  $\delta D$  (because there is little fractionation during these processes), while low temperature weathering and hydration will lower  $\delta D$ , because hydrogen, rather than deuterium, is preferentially incorporated into alteration phases. Loss of  $H_2$  and  $CH_4$ , which may partition into a  $CO_2$  gas phase when it forms, could also affect the hydrogen isotopic composition of basalts. However, the available evidence suggests that these species constitute only a small fraction of the hydrogen in basalts, so this effect is likely to be minor.

As Figure 28.10 indicates, MORB have mean a  $\delta D_{SMOW}$  of about  $-67.5\text{‰}$  and a standard deviation of  $\pm 14\text{‰}$ . How much of this variability reflects the processes shown in Figure 28.9 and how much reflects true heterogeneity in the mantle is unclear. Kyser (1986) has argued that mantle hydrogen is homogeneous with  $\delta D_{SMOW}$  of  $-80\text{‰}$ . The generally heavier isotopic composition of MORB, he argues, reflects  $H_2O$  loss and other processes. However, Poreda, et al., (1986) found that  $\delta D$  in basalts from the Reykjanes Ridge south of Iceland correlated significantly with La/Sm and other trace element ratios, suggesting at least some of the isotopic variation of hydrogen in basalts reflects real variations in the mantle. Submarine basalts from Kilauea's East Rift Zone have higher  $\delta D$  than MORB. Kyser and O'Neil (1984) argued that these higher values result from the addition of water to the magma in the rift zone. Hawaiian submarine basalts analyzed by Garcia et al. (1989) have  $\delta D$  very similar to MORB.

Hydrous minerals in xenoliths also provide a sample of mantle hydrogen. As Figure 28.10 shows, phlogopites have  $\delta D$  that is generally similar to that of MORB, though some lighter values also occur. Amphiboles have much more variable  $\delta D$  and have heavier hydrogen on average. Part of this difference probably reflects equilibrium fractionation. The fractionation between water and phlogopite is close to  $0\text{‰}$  in the temperature range  $800^\circ\text{--}1000^\circ\text{C}$ , whereas the fractionation between water and amphibole is about  $-15\text{‰}$ . However, equilibrium fractionation alone cannot explain either the variability of amphiboles or the difference between the mean  $\delta D$  of phlogopites and amphiboles. Complex processes involving in amphibole formation that might include Rayleigh distillation may be involved in the formation of mantle

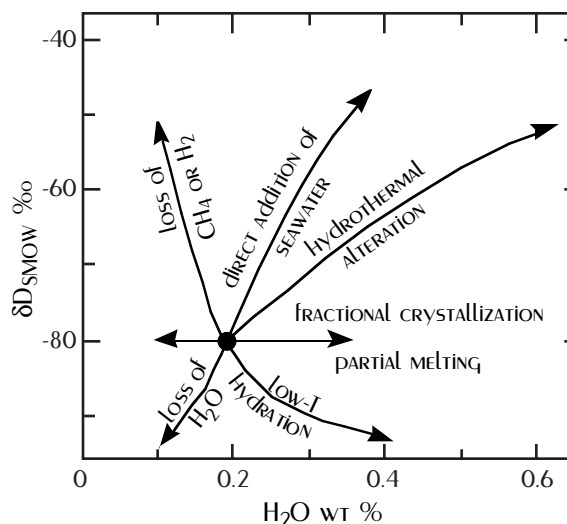


Figure 28.9. Effect of degassing and post-eruptive processes on the water content and  $\delta D$  of basalts. From Kyser and O'Neil (1984).

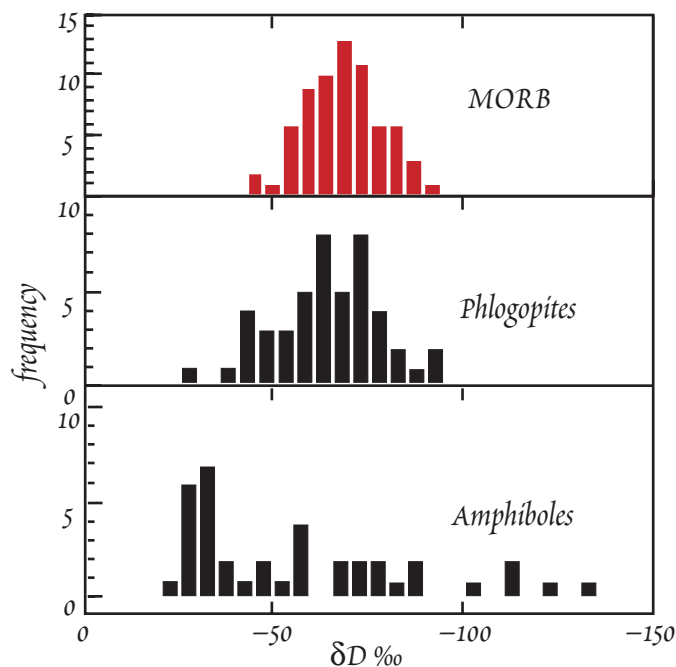


Figure 28.10.  $\delta D$  in MORB and in mantle phlogopites and amphiboles. The MORB and phlogopite data suggest the mantle has  $\delta D_{SMOW}$  of about  $-60$  to  $-90$ .

amphiboles. This would be consistent with the more variable water content of amphiboles compared to phlogopites.

Hydrous minerals in xenoliths also provide a sample of mantle hydrogen. As Figure 28.10 shows, phlogopites have  $\delta D$  that is generally similar to that of MORB, though some lighter values also occur. Amphiboles have much more variable  $\delta D$  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  $\delta D$  of phlogopites and amphiboles. Complex processes involving in amphibole formation 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 to phlogopites.

### Nitrogen

Figure 28.11 summarizes the existing data on the nitrogen ratios in the crust and mantle. There is far less data than for other stable isotope ratios because of the low concentrations and pervasive contamination problems. The solubility of  $N_2$  in basalts is very limited, though much of the nitrogen may be present as  $NH_4^+$ , which is somewhat more soluble. 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 in basalts, which, combined with its low abundance (generally less than a ppm), mean that accurate measurements are difficult to make. Measurements of  $\delta^{15}N_{ATM}$  in MORB range from about -2 to +12‰. The few available analyses of Hawaiian basalts range up to +20. At present, it is very difficult to decide to what degree this variation reflects contamination

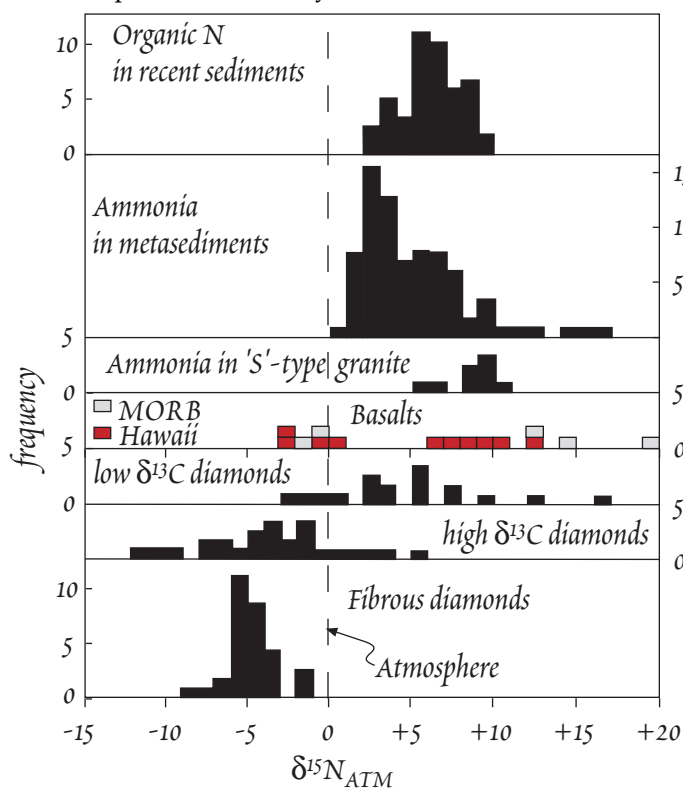


Figure 28.11. Isotopic composition of nitrogen in rocks and minerals of the crust and mantle. Modified from Boyd and Pillinger (1994).

(particularly by organic matter), fractionation during degassing, or real mantle heterogeneity. Perhaps all that can be said is that nitrogen in basalts appears to have positive  $\delta^{15}N$  on average.

Diamonds can contain up to 2000 ppm of N and hence provide an excellent sample of mantle N. As can be seen in Figure 28.11, high  $\delta^{13}C$  diamonds (most common, and usually of peridotitic paragenesis) have  $\delta^{15}N$  that range from -12 to +5 and average about -3‰, which contrasts with the generally positive values observed in basalts. Low  $\delta^{13}C$  diamonds have generally positive  $\delta^{15}N$ . Since organic matter and ammonia in crustal rocks generally have positive  $\delta^{15}N$ , this characteristic is consistent with the hypothesis that this group of diamonds are derived from subducted crustal material. However, since basalts appear to have generally positive  $\delta^{15}N$ , other interpretations are also possible. Fibrous diamonds, whose growth may be directly related to the kimberlite eruptions that carry them to the surface (Boyd et al., 1994), have more uniform  $\delta^{15}N$ ,

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with a mean of about -5‰. Since there can be significant isotopic fractionations involved in the incorporation of nitrogen into diamond, the meaning of the diamond data is also uncertain, and the question of the nitrogen isotopic composition of the mantle remains an open one.

### 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 sealevel. In the mantle, sulfur is probably predominantly or exclusively in the form of sulfide, but in basalts, which tend to be somewhat more oxidized, some of it may be present as SO<sub>2</sub> or sulfate. Equilibrium fractionation should lead to SO<sub>2</sub> being a few per mil lighter than sulfate. If H<sub>2</sub>S is lost during degassing the remaining sulfur would become heavier; if SO<sub>2</sub> or SO<sub>4</sub> is lost, the remaining sulfur would become lighter. Total sulfur in MORB has  $\delta^{34}\text{S}_{\text{CDT}}$  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  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  (-5 to +8‰). Low Ni sulfides in oceanic island basalts, kimberlites, and pyroxenites had more variable  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  between +1 and -3‰ (Hoefs, 1986; Kyser, 1986). Overall, it appears the mantle has a mean  $\delta^{34}\text{S}$  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 ( $\delta^{13}\text{C} \sim -4\text{‰}$ ) had  $\delta^{34}\text{S}$  of about +1‰ while eclogitic diamonds had higher, and much more variable  $\delta^{34}\text{S}$  (+2 to +10‰). Eldridge et al. (1991) found that  $\delta^{34}\text{S}$  in diamond inclusions was related to the Ni content of the sulfide. High Ni sulfide inclusions, which they argued were of peridotitic paragenesis, had  $\delta^{34}\text{S}$  between +4‰ and -4‰. Low Ni sulfides, which are presumably of eclogitic paragenesis, had much more variable  $\delta^{34}\text{S}$  (+14‰ to -10). These results are consistent with the idea that eclogitic diamonds are derived from subducted crustal material.

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