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STABLE ISOTOPE APPLICATIONS: 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 19, 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 $e^{-hv/kT}$ term in equation 19.35 becomes finite and this relationship breaks down. It higher temperature, the equilibrium constant becomes generally proportional to the inverse square of temperature:



 $\ln K = A + \frac{B}{T^2}$ 21.1

Figure 21.1. a. Comparison of quartz-mineral fractionation factors estimated from the difference in oxygen site potential ($V_{qtz} - V_{mineral}$) and experimentally observed fractionation factors at 1000 K. b. Comparison of fractionation factors estimated through the increment method, which also considers cation mass, and experimentally observed fractionation factors at 1000 K. From Chacko, et al. (2001).

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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 19 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 crossovers.

COMPOSITIONAL AND STRUCTURAL DEPENDENCE OF EQUILIBRIUM FRACTIONATIONS

The nature of the chemical bond is of primary important in determining isotope fractionations. *In* general, bonds to ions with a high ionic potential and low atomic mass are associated with high vibrational frequencies and have a tendency to incorporate the heavy isotope preferentially. This point is illustrated by the site-potential method of estimating fractiona-

tion factors (Smyth, 1989). The site potential is simply the energy required (e.g., in electron volts) to remove an atom from its crystallographic site and is a measure of bond strength. Figure 21.1a shows that the there is a strong correlation between the difference in oxygen site potential in minerals and the fractionation factor between those two minerals. The solid line shows that silicates plot along a line with the equation Δ_{1000K} (qtz-mineral) = 0.751 (V_{qtz}-V_{mineral}). Oxides (and to a less extent, apatite and calcite) fall off this correlation. The deviation in the case of calcite and apatite probably reflects the more strongly covalent nature of oxygen bonds in those minerals. In the case of the oxides, it reflects the varying mass of the cation, as cation mass affects bond strength. In silicates, oxygens are primarily bound to Si and secondarily to other cations. However, in oxides such as rutile, perovskite, and magnetite, oxygen is bound primarily to Fe or Ti, which of course have very different masses than Si. The "increment method" of estimating fractionation factors (e.g., Zhang, 1999) takes account of the cation ion mass. As Figure 21.1b shows, this method produces and improved agreement of calculated and experimentally observed fractionation factors for the oxides.

Substitution of cations in a primarily ionic site in silicates has only a minor effect on fractionation factors. Thus, for example, we would expect relatively little O isotopic

TABLE	21.1.	COEFFICIENTS	Oxygen	ISOTOPE
Fracti	ONATIO	ON AT LOW TEM	PERATURES	:

$\Delta_{\rm QZ-\phi} = A + B \times 10^6 / T^2$					
φ	А	В			
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 21.2. COEFFICIENTS FOR OXYGEN ISOTOPE FRACTIONATIONS AT ELEVATED TEMPERATURES (600° – 1300°C)

<u>`</u>		,				
	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 $1000\alpha_{A\lambda-A\iota} = 1.81 \times 10^6/T^2$ (T in kelvins). From Chiba, et al. (1989).

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fractionation between K-feldspar and Na-feldspar. This turns out to be the case: the fractionation is of the order of 0.1 per mil at room temperature. The substitution of Al for Si in plagioclase is somewhat more 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 21.1 lists the parameters for the temperature dependence of silicate and oxide fractionation factors at low temperatures.

Carbonates tend to be very ¹⁸O rich because O is bonded to a small, highly charged atom, C⁴⁺. The fractionation relative to water, Δ^{18} O (the Δ 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 Δ^{18} O decreases to about 25 for Ba (about 3 times the mass of Ca).

Crystal structure usually plays a secondary role. The Δ^{18} 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 small, 0.1 permil at 20 kbars and less. The reason should be fairly obvious: there is no volume change is 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 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 silicon and ionically bonded to other cations (e.g., Mg, Fe, Ca, etc.), fractionation of



Figure 21.2. Calculated oxygen isotope fractionation for several mineral pairs as a function of temperature (from O'Neil, 1986).

oxygen isotopes between these phases and during melting are relatively small, although still significant. Table 21.2 lists fractionation factors for silicate and oxide minerals at high temperatures.

GEOTHERMOMETRY

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 21.1). In actuality, the constants A and B in equation 21.1 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

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matter they can be described as constants. We have also noted that at temperatures close to room temperature and below, the form of equation 21.1 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 often 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. Indeed, there are too many isotope geothermometers for all of them to be even mentioned here. We can begin by considering silicate systems. Figure 21.2 shows fractionation factors between various silicates and oxides as a function of temperature. Tables 21.1 and 21.2 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:

$$\Delta \simeq 1000 \ln \alpha_{Q_{z-\phi}} = A + \frac{B}{T^2} \times 10^6$$
 21.2

with temperature expressed in kelvins. Recall that fundamental rule of thermodynamics 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 21.1 may be used to obtain the fractionation between any of the two phases shown.

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 ³⁴S enrichment is: SO_4^{2-} > SO_3^{2-} > SO_2 > SCO > $S_x ~ H_2S ~HS^{1-} > S^{2-}$ (Ohmoto and Rye, 1979). Figure 21.3 shows the temperature dependence of fractionation factors between H₂S and other phases, and Table 21.3 lists coefficients for the equation:

$$\Delta \approx 1000 \ln \alpha_{\phi - H_2 S} = A + \frac{B}{T^2} \times 10^6 \quad 21.3$$

 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 21.4 shows carbon isotope fractionation factors between 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, and carbonic acid). Table 21.4 lists



Figure 21.3. Relationship of S isotope fractionation between H_2S and other sulfur-bearing species and temperature. From Ohmoto and Rye (1979).

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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 common. 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-equilibration 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 are particularly slow at temperatures well below the melting point. Equilibrium 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 21.5 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 21.3: $\Delta_{sp-gn} = 0.73 \times$

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TABLE 21.3. COEFFICIENTS FOR SULFUR ISOTOPE FRACTIONATION:

$\Delta_{\varphi-H_2S} = A + B \times 10^6 / T^2$ (T in Kelvins)				
φ	В	А	T°C	
			Range	
$CaSO_4$	$6.0{\pm}0.5$	5.26	200-350	
SO_2	-0.5 ± 0.5	4.7	350-1050	
FeS ₂	$0.4{\pm}0.08$		200-700	
ZnS	$0.10{\pm}0.05$		50-705	
CuS	-0.4 ± 0.1			
Cu ₂ S	-0.75 ± 0.1			
SnS	-0.45 ± 0.1			
MoS_2	0.45 ± 0.1			
Ag_2S	-0.8 ± 0.1			
PbS	-0.63±0.05		50-700	

From Ohmoto and Rye (1979)



Figure 21.4. Fractionation factors for distribution of carbon isotopes between CO_2 and other carbon-bearing species as a function of temperature. From Ohmoto and Rye (1979).

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 $10^6/T^2$. Many of the points fall off the expected curve, indicating disequilibrium. Ohmoto and 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.

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 dependence, 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 SiO_{2} , etc. Generally, any dependence on the composition of phases in isotope geothermometers involved is of relatively second order importance. For example,

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TABLE 21.4 ISOTOPE FRACTIONATION FACTORS OF CARBON COMPOUNDS WITH RESPECT TO CO_2

$1000 \text{Ln} \alpha = A \times 10^8 / \text{T}^3 + B \times 10^6 / \text{T}^2 + C \times 10^3 / \text{T} + D$						
φ	А	В	С	D	T°C	
					Range	
$CaMg(CO_3)_2$	-8.914	8.737	-18.11	8.44	≤600	
Ca(CQ ₃)	-8.914	8.557	-18.11	8.24	≤600	
HCQ_3^{1-}	0	-2.160	20.16	-35.7	≤290	
CO_3^{2-2}	-8.361	-8.196	-17.66	6.14	≤100	
$H_2 CO_3$	0	0	0	0	≤350	
CH_4	4.194	-5.210	-8.93	4.36	≤700	
CO	0	-2.84	-17.56	9.1	≤330	
С	-6.637	6.921	-22.89	9.32	≤700	

From Ohmoto and Rye (1979).



Figure 21.5. Comparison of temperatures determined from sphalerite–galena sulfur isotope fractionation with fluid-inclusion homogenization temperatures. •: Creede, CO, \forall : Sunnyside, O: Finlandia vein, Δ : Pasto Bueno, \Box : Kuroko. From Ohmoto and Rye (1979).

isotopic exchange between calcite and water is independent of the concentration of 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 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 fractiona-

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tion 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. 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

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Figure 21.7 of MORB (+5.7). After Harmon and Hoefs (1994).

ratios, which can be changed by chemical processes. The effects of the melting process on most stable isotope ratios of interest are small, but 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, although 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 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 21.6 shows the oxygen isotope composition of olivines and clinopyroxenes in 76 peridotite xenoliths analyzed by Mattey 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. Mattey et al. (1994) estimated the bulk composition of these samples to be about +5.5 per mil.

Figure 21.7 shows the distribution of δ^{18} O in selected basalts from 4 different groupings. To avoid the weathering problems we discussed above, Harmon and Hoefs (1994) 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 $\delta^{18}O_{SMOW}$ of +5.7‰ and a standard deviation of ±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 ¹⁸O (mean $\delta^{18}O_{SMOW}$ = +5.5‰), and are also more variable (1 σ = 0.5‰). The histogram shown excludes Iceland, because Ice-

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landic basalts are quite anomalous in their low $\delta^{18}O$ (mean ~ 4.5‰). This has been shown to be due primarily to assimilation of older basaltic crust that has equilibrated with meteoric water, which is quite ¹⁸O depleted at the latitude of Iceland. There is, however, some evidence to suggest even primary Icelandic basalts are depleted in ¹⁸O relative to MORB. Subduction-related basalts (i.e., island arc basalts and their continental equivalents) are shifted to more positive $\delta^{18}O$ 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 ¹⁸O rich than their oceanic equivalents, most likely due to assimilation of continental crust. Finally, continental intraplate volcanics are more enriched in ¹⁸O 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 CO_2 , which has limited solubility in basaltic liquids at low pressure. As a result, basalts begin to exsolve 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 vola-

tiles). 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 CO₂ dissolved in basaltic melts and the gas phase, with ¹³C enriched in the gas phase. If 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 Furthermore, MORB are pervasively conmelt. taminated with a very ¹³C-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 H₂S. 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 21.8. Carbon isotope ratios in mantle (red) and mantle-derived materials (gray). After Mattey (1987).

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Figure 21.8 shows δ^{13} C in various mantle and mantle-derived materials. MORB have a mean δ^{13} 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 CO₂-rich MORB samples have δ^{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). 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 δ^{13} 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 21.8). Most diamonds have δ^{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, diamonds can be divided between peridotitic and eclogitic. Most peridotitic diamonds have δ^{13} C close to -5‰, while eclogitic diamonds are much more isotopically variable. Most, though not all, of the diamonds with very negative δ^{13} 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 δ^{13} 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 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 CO_2 . Basalts erupted beneath a kilometer of



Figure 21.9. Effect of degassing and posteruptive processes on the water content and δD of basalts. From Kyser and O'Neil (1984).

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more of water probably retain most of their dissolved water. However, basalts, particularly submarine basalts, are far more readily contaminated with hydrogen (i.e., with water) than with carbon. Furthermore, the effect on hydrogen isotopic composition depends on the mode of contamination, as Figure 21.9 indicates. Direct addition of water or hydrothermal reactions will raise δD (because there is little fractionation during these processes), while low temperature weathering and hydration will lower δD , because hydrogen, rather than deuterium, is preferentially incorporated into alteration phases. Loss of H₂ and CH₄, which may partition into a CO₂ 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 21.10 indicates, MORB have mean δD_{SMOW} of about -67.5% and a standard deviation of $\pm 14\%$. How much of this variability reflects the processes shown in Figure 21.9 and how much re-



Figure 21.10. 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.

flects true heterogeneity in the mantle is unclear. Kyser (1986) has argued that mantle hydrogen is homogeneous with δD_{SMOW} of -80%. The generally heavier isotopic composition of MORB, he argues, reflects H₂O loss and other processes. However, Poreda, et al., (1986) found that δD 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 δD 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 δD very similar to MORB.

Hydrous minerals in xenoliths also provide a sample of mantle hydrogen. As Figure 21.10 shows, phlogopites have δD that is generally similar to that of MORB, though some lighter 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 deference between the mean δD 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 21.11 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

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Figure 21.11. Isotopic composition of nitrogen in rocks and minerals of the crust and mantle. Modified from Boyd and Pillinger (1994).

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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 (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 21.11, high δ^{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 δ^{13} C diamonds have generally positive δ^{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 δ^{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 $\delta^{15}N$, 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 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 SO₄²⁻ is lost, the remaining sulfur would become lighter. Total sulfur in MORB has $\delta^{34}S_{CDT}$ 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 δ^{34} 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 $\delta^{34}S$ (–5 to +8‰). Low Ni sulfides in oceanic island basalts, kimberlites, and pyroxenites had more variable $\delta^{34}S$ that sulfides in peridotites and peridotite minerals. They argued there is a fractionation of +3‰ between sulfide liquid and sulfide dissolved in silicate

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melt. Carbonatites have δ^{34} S between +1 and -3% (Hoefs, 1986; Kyser, 1986). Overall, it appears the mantle has a mean δ^{34} 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 (δ^{13} C ~ -4‰) had δ^{34} S of about +1‰ while eclogitic diamonds had higher, and much more variable δ^{34} S (+2 to +10‰). Eldridge et al. (1991) found that δ^{34} 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 δ^{34} S between +4‰ and -4‰. Low Ni sulfides, which are presumably of eclogitic paragenesis, had much more variable δ^{34} S (+14‰ to -10). These results are consistent with the idea that eclogitic diamonds are derived from subducted crustal material.

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