

CHAPTER 11: GEOCHEMISTRY OF THE SOLID EARTH I: THE MANTLE AND CORE

INTRODUCTION

Though sizable pieces of mantle occasionally crop out on the Earth's surface as alpine massifs or ophiolites, and small pieces, xenoliths, are occasionally brought to the surface by volcanic eruptions, much of what we know about the mantle has been deduced indirectly. Indirect methods of study include determination of geophysical properties such as heat flow, density and seismic velocity. Another indirect method of study is examination of volcanic rocks produced by partial melting of the mantle. Finally, the composition of chondrites is an important constraint on the composition of the mantle.

The mantle was once viewed as being homogeneous, but we now realize that the chemistry of the mantle is heterogeneous on all scales. On a large scale, the mantle appears to consist of a number of reservoirs that have complex histories. The best evidence for this large-scale heterogeneity comes from trace element and isotope ratio studies of volcanic rocks, but there is also evidence that the major element composition of the mantle varies. While trace elements may vary by an order of magnitude or more, the major element variations are much more subtle, just as they are in volcanic rocks and in the crust. Isotope studies have proven tremendously valuable in understanding the mantle for several reasons. First, unlike trace element and major element concentrations, isotope ratios do not change during the magma generation process (except by mixing of the magma with other components such as assimilated crust). Second, radiogenic isotope ratios provide *time-integrated* information about the parent/daughter ratios, and therefore allow inferences about the history of the mantle.

COMPOSITION OF THE EARTH'S MANTLE

Table 11.1 lists the relative masses of the various shells of the Earth. From a geochemical perspective, these are the Earth's major chemical reservoirs. The mantle is by far the largest single reservoir, and constitutes over 99% of the mass of the silicate Earth, the mass of the crust being less than 1%. The crust has apparently been created from the mantle through partial melting over geologic time. For the major elements, this process of crust formation does not change the composition of the mantle on the whole because the volume of the crust is so small (but extraction of partial melts undoubtedly has affected the major element composition of the mantle *locally*). With the exception of highly incompatible elements, which can be highly concentrated in the crust, and siderophile and possibly chalcophile elements, which are concentrated in the core, major lithophile elements are present in the mantle in the same proportions as in the Earth as a whole. Since we assume that chondritic meteorites are a good representation of Solar System composition, we naturally want to compare the composition of the mantle to that of chondrites. Thus the composition of meteorites is an important constraint on the composition of the mantle and the Earth as a whole.

COSMOCHEMICAL CONSTRAINTS ON THE EARTH'S COMPOSITION

In Chapter 10 we considered the composition of that part of the Solar System accessible to sampling: meteorites, the solar surface (deduced from optical spectra and solar wind particles), and the Moon. The meteorite data provide first order constraints on the formation and composition of the Earth. Two important cosmochemical assumptions guide our thinking about the composition of the Earth: (1) *the entire solar system formed more or less simultaneously from one gaseous, dusty nebula*, (2) *the composition from which the solar system formed was similar to that of CI chondrites except for the most volatile elements (e.g., H, N, noble gases)*. The last statement should not be construed to mean that all bodies that formed from this nebula are of chondritic composition.

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Table 11.1. VOLUMES AND MASSES OF THE EARTH'S SHELLS

	Thickness (km)	Volume 10^{27} cm^3	Mean Density g/cc	Mass 10^{24} kg	Mass Percent
Atmosphere				0.000005	0.00009
Hydrosphere	3.80	0.00137	1.03	0.00141	0.024
Crust	17	0.008	2.8	0.024	0.4
Mantle	2883	0.899	4.5	4.016	67.2
Core	3471	0.175	11.0	1.936	32.4
Whole Earth	6371	1.083	5.52	5.976	100.00

Thus far there is essentially no evidence to contradict the first assumption (provided we interpret "simultaneous" in a geologic sense; i.e., this process may have taken up to 100 million years); the second assumption certainly holds to a first approximation, beyond that there is some uncertainty. In defense of it, however, we should emphasize the isotopic homogeneity of the solar system. The isotopic anomalies we have discussed previously are very much the expectation to the rule and serve to emphasize the general homogeneity of the solar system (except, of course, for oxygen). *The implication is that the presolar nebula was well mixed.* We can reasonably conclude that it was *initially* chemically homogeneous as a result.

In summary, we can draw the following conclusions relevant to the formation and composition of the Earth from cosmochemistry:

1. The material from which the solar system formed was of CI chondritic composition (plus gases).
2. Despite (1), the composition of bodies formed from this nebula is variable. This is apparent from the composition of chondrites as well as from density variations of the planets.
3. Formation of planetary bodies begin shortly (a few million years at most) after newly synthesized elements were added to the solar nebula (as evidenced by the oldest ages from the Moon and differentiated meteorites).
4. Iron meteorites clearly reflect segregations of metallic liquid from material of approximately chondritic composition. Certainly the existence of stony-irons, which are irons with silicate inclusions, demonstrates that segregated silicate and iron metal fractions existed in the parent bodies. Since the ages of these meteorites are nearly indistinguishable from those of chondrites, it suggests core formation in planets got under way very early. In the most likely case, cores had already segregated in the planetismals and planetary embryos from which the planets formed.
5. The Moon seems to have had a magma ocean. The Earth may well have had one as well.

Upper Mantle Composition

Most geochemists and geophysicists believe the mantle is ultramafic in composition, peridotitic to be more specific. *Peridotite* is a rock dominated by olivine (*peridot* is the gem name for olivine). The nomenclature of ultramafic rocks is summarized in Figure 11.1. If the olivine exceeds 90% of the rock, it is termed a *dunite*. If the rock consists al-

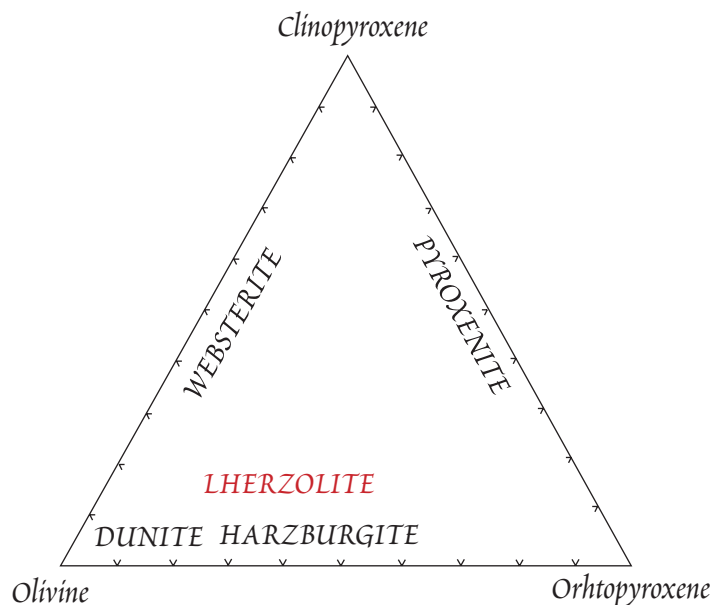


Figure 11.1. Ultramafic rock nomenclature.

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most exclusively of olivine and orthopyroxene, it is called a *harzburgite*. A *websterite* is a rock consisting almost exclusively of olivine and clinopyroxene. A rock consisting of over 90% pyroxene is a *pyroxenite* (clinopyroxenite or orthopyroxenite as the case may be; a pyroxenite is an ultramafic rock, but not a peridotite). Rocks with substantial amounts of both pyroxenes as well as olivine are *lherzolites*. This can be prefaced by the name of the Al-bearing phase, e.g., spinel lherzolite, whose nature depends on pressure. In the upper mantle, olivine is thought to be the dominant mineral, followed by orthopyroxene, clinopyroxene, and an Al-bearing phase, which can be plagioclase, spinel, or garnet, depending on the pressure. The upper mantle is thought to be dominantly *lherzolitic*. An alternative term is *pyrolite* (pyroxene-olivine rock), coined by A. E. Ringwood. Pyrolite, however, is associated with a specific composition (e.g., Table 11.2), though this composition has been revised numerous times.

Any estimate of upper mantle composition must satisfy a number of constraints. First, it should match the composition of direct mantle samples such as xenoliths (Figure 11.2). Second, it must yield basalt upon melting. Third, it must have seismic velocities (Figure 11.3) and densities (Figure 11.4) matching those observed. Finally, it should have an approximately chondritic composition (as we shall see, the upper mantle does not appear to be exactly chondritic). A lherzolitic or pyrolitic composition appears to fit these constraints. However, lherzolitic compositions are not unique in meeting these some of these constraints, and some have argued that the mantle, or at least the upper mantle, is dominantly eclogitic. *Eclogite* is a rock consisting almost exclusively of garnet and omphacitic pyroxene (i.e., Na-, Al-rich). This is the mineralogy of basalt at high pressure. It was once argued by some that the upper mantle composition was closer to eclogite than peridotite, because it seemed to fit seismic velocity distribution better. But the idea was not accepted, primarily because it failed to match the chondritic composition sufficiently well, and because

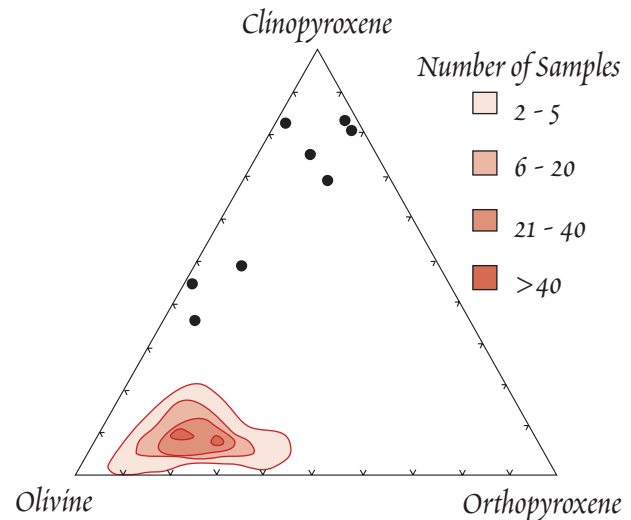


Figure 11.2. Abundances of modal mineralogy in xenoliths from Kilbourne Hole, NM.

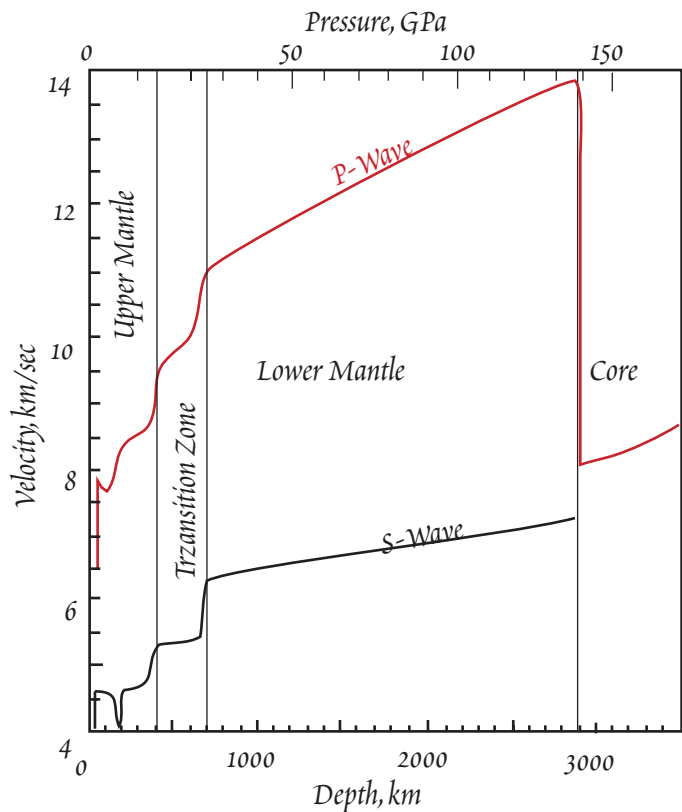


Figure 11.3. Mantle seismic velocities.

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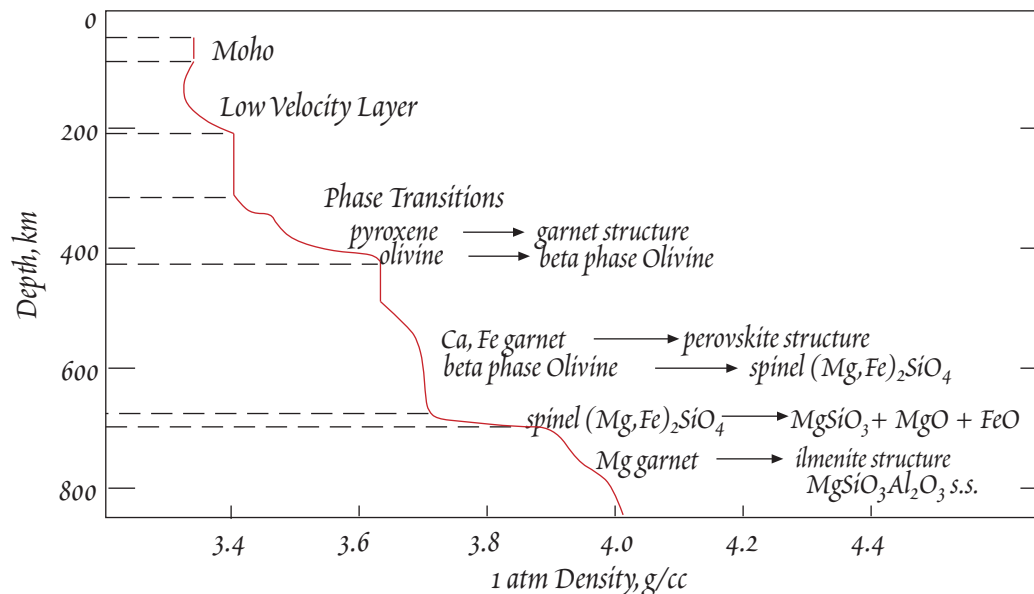


Figure 11.4. Phase assemblages and 1 atm density of the mantle.

eclogites are considerably rarer as xenoliths than peridotites. Also seismic anisotropy* observed in some parts of the upper mantle suggests the mantle is too rich in olivine to be eclogite. However, in the last decade Don Anderson (e.g., Anderson, 1989b) has argued for an upper mantle consisting of olivine bearing eclogite, for which he coined the term *piclogite*[†]. The eclogite, which he argues was produced by crystal accumulation in a primordial magma ocean, is the source of MORB in his model. This idea has not been particularly well received by geochemists, perhaps even less so by petrologists.

Most studies rely on the composition of mantle xenoliths to estimate mantle compositions (the composition of peridotite massifs, which also represent mantle samples, but these have inevitably been affected by secondary processes). However, while formation of the crust and other processes have not affected the major element composition of the bulk mantle, the compositions of individual xenoliths often have been affected by igneous processes. Despite this, xenoliths provide evidence that the upper mantle differs in composition from chondrites. Whether the estimated upper mantle composition is also the composition of the entire mantle depends on whether the mantle is chemically layered. This is an important and unresolved question, and one to which we shall return.

Table 11.2 compares several estimates for the major and minor element composition of the mantle made over the last decade with the composition of CI chondrites after subtracting the most volatile elements in the latter (column 1). Clearly chondrites are much richer in siderophiles (e.g., Fe, Ni) than all these estimated mantle compositions. The chondritic composition matches the mantle composition much better after a sufficient amount of the siderophile elements has been removed to form

* Seismic anisotropy refers to the case where seismic waves travel faster in one direction than an other. This can ultimately be related to crystallographic properties. In olivine, seismic velocities are faster along one crystallographic axis than the others. Since garnet has a cubic (isotropic) structure, seismic velocity is equal in all crystallographic directions, as is the velocity of light. Seismic anisotropy can only occur only when there is some tendency for crystallographic axes of individual mineral grains to be aligned parallel. This is thought to arise in the mantle from flow associated with convection.

[†] Piclogite comes from combining *picrite*, which is an olivine-rich basalt, and eclogite. Piclogite would be the high pressure equivalent of picrite.

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the Earth's core. However, even after removing the siderophile and highly volatile elements, there are significant differences between the apparent composition of the mantle and chondrites.

First, the mantle is depleted in the alkali elements (e.g., K and Na in Table 11.2). There are several lines of evidence for this depletion of alkali elements. The depletion in moderately volatile elements is also apparent by comparing Sr isotope ratios of the mantle and chondrites, as Gast demonstrated in 1960. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the mantle imply Rb/Sr ratios more than an order of magnitude lower than chondritic. Some of the Rb depletion of the mantle may be explained by extraction of the Rb into the crust. Indeed more than half the Earth's Rb may be in the crust. However, the terrestrial Rb/Sr ratio appears to be nearly an order of magnitude lower than chondritic (0.03 vs. 0.25) even when crustal Rb is considered. Independent of Sr isotope considerations, a number of other studies have demonstrated depletion of K, Rb, and Cs in the Earth.

Table 11.2. Comparison of Estimated Silicate Earth Compositions

	CI Chondrites	CI Chondritic Mantle & Core ¹	Hart & Zindler LOSIMAG ²	Ringwood ³ Pyrolite	McDonough & Sun ⁴ Pyrolite	Allegre et al. ⁵ PRIMA
SiO ₂	22.77	49.52	45.96	44.76	45.0	46.12
Al ₂ O ₃	1.64	3.56	4.06	4.46	4.45	4.09
FeO	24.49	7.14	7.54	8.43	8.05	7.49
MgO	16.41	35.68	37.78	37.23	37.8	37.77
CaO	1.30	2.82	3.21	3.60	3.55	3.23
Na ₂ O	0.67	0.292	0.332	0.61	0.36	0.36
K ₂ O	0.067	0.028	0.032	0.029	0.029	0.034
Cr ₂ O ₃	0.39	0.412	0.468	0.43	0.384	0.38
MnO	0.256	0.115	0.130	0.14	0.135	0.149
TiO ₂	0.073	0.159	0.181	0.21	0.20	0.18
NiO	1.39	0.244	0.277	0.241	0.25	0.25
CoO	0.064	0.012	0.013	0.013	0.013	0.07
P ₂ O ₅	0.274	0.018	0.019	0.015	0.021	
Sum	69.79	100.0	100.0			
HVE ⁶	30.21	30.21	30.21			
MVE ⁷		1.258	1.258			
SVE ⁸			5.33			
Fe	74.44	85.62				79.39
Ni	4.53	5.16				4.87
Co	0.2081	0.237				0.253
S						2.3
O		20.81	8.99			4.10
Core Sum		100.0	100.0			
Total	99.9	99.7	99.4			

¹removing HVE, MVE and siderophiles and some oxygen from mantle to form core; renormalizing silicate mantle and core separately. Hart and Zindler (1986)

²Low-Si-Mg Earth with siderophiles and some oxygen removed from mantle to form core; renormalizing silicate mantle and core separately. Hart and Zindler (1986)

³Estimated Primitive Upper Mantle Composition of Ringwood (1991)

⁴Estimated Primitive Mantle Composition from McDonough and Sun (1995)

⁵Primitive Mantle ("PRIMA") of Allegre et al. (1995)

⁶HVE = Highly Volatile Elements, includes H₂O, S, C, organics, etc.

⁷MVE = Moderately Volatile Elements, includes Na, K, P, Cr, Mn

⁸SVE = Slightly Volatile Elements, Si and Mg

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This depletion is thought to encompass all the moderately volatile elements (see Figure 9.29) as all appear to be depleted in the mantle. Many of the moderately volatile elements are siderophile or chalcophile, so their depletion in the mantle may also reflect extraction into the core.

The Earth's depletion in moderately volatile elements is not entirely surprising, given that it, along with the other terrestrial planets, is obviously depleted in the atmosphere elements. Since the depletion in the highly volatile elements is a feature shared by all the terrestrial planets, it is probably due to high temperatures in the inner solar nebula during the initial stages of accretion. Thus these elements probably did not condense and were not accreted to the planetismals that ultimately formed the terrestrial planets. An enhanced solar wind during the T-Tauri phase of the Sun might also have caused loss of volatiles that were accreted. Finally, high temperatures achieved during formation of the Earth (due to release of gravitational energy), particularly as a result of the giant impact, probably contributed to volatile loss.

The depletion of the Earth in volatile elements is well established, and more recent work has focused on comparing the relative concentrations of remaining major elements, particularly Mg, Si, Ca, and Al in the mantle with those of CI chondrites.

Table 11.2 reflects a general agreement that the upper mantle is depleted in silicon relative to a 'chondritic' upper mantle. This depletion can be demonstrated in several ways, but we will consider only the approach of Hart and Zindler (1986). Figure 11.5a shows the Mg/Si ratio plotted against the Nd/Si ratio for mantle xenoliths and various classes of chondritic meteorites. The xenoliths and chondrites form 2 distinct arrays. Hart and Zindler argued that the "meteorite array" reflects fractionation during processes occurring in the solar nebula or during planet formation (e.g., volatilization), whereas the "terrestrial array" reflects processes occurring in the Earth's mantle such as partial melting. For example, the dashed line shows that extraction of a partial melt would drive composition off the meteorite array in the general trajectory of the terrestrial array. Since the bulk mantle composition should not have been affected by crust formation, Hart and Zindler, following earlier work by Jagoutz et al. (1979), reasoned that it should lie at the intersection of the meteorite and terrestrial arrays. A similar sort of analysis can be done with Al/Si (Figure 11.5b) and Ca/Si

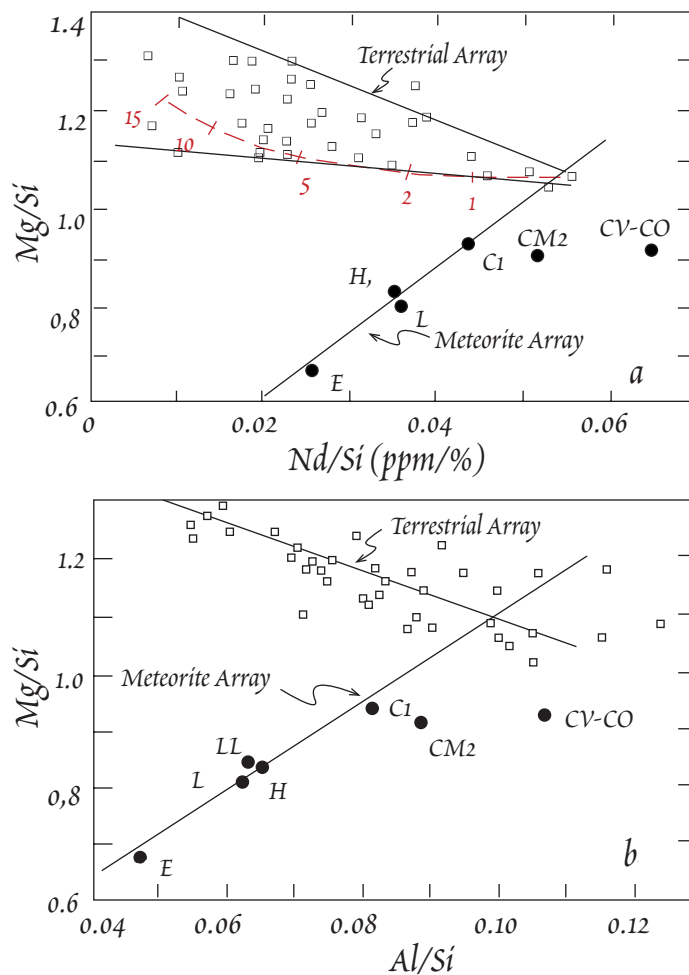


Figure 11.5. a.) Variation of Mg/Si as a function of Nd/Si in terrestrial mantle xenoliths and meteorites. b.) Variation of Mg/Si as a function of Al/Si in terrestrial mantle xenoliths and meteorites. The data suggest the Earth is depleted in Mg and Si relative to chondrites. Dashed line is the trajectory of residual mantle compositions following melt extraction with the % melt extracted shown by the tic marks. After Hart and Zindler (1986).

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ratios. Using this approach, Hart and Zindler concluded that the upper mantle, is depleted in Si. If the mantle is not chemically layered, then the entire Earth must be depleted in Si and Mg relative to chondrites. Ringwood (1989) argued that the depletion in Si is a general feature of the inner solar system, and reflects the more volatile nature of SiO compared to the gaseous phases of Al, Mg, Ca, and Fe.

Though it is less obvious, all the estimated mantle compositions in Table 11.2 also have high abundances of the most refractory elements, Ca, Al, and Ti, relative to Mg. For example, the chondritic Al/Mg ratio is 0.123 whereas estimates of upper mantle Al/Mg ratio ranges from 0.133 (Allegre et al., 1985) to 0.147 (Ringwood, 1991). Estimates of the upper mantle Ca/Mg ratio range from 0.101 (Hart and Zindler, 1986; Allegre et al., 1995) to 0.115 (Ringwood, 1991), and are all higher than the chondritic value of 0.094. Assuming these estimates are correct, the upper mantle appears to be enriched in the highly refractory elements by 7 to 50%. If the mantle is not chemically zoned, then the Earth as a whole is enriched in the highly refractory elements.

Palme and Nickel (1985) argued that the Ca/Al ratio of the mantle is also non-chondritic (0.887 for the upper mantle vs. 0.766 for chondrites). Since Ca and Al are both among the most refractory elements whose relative abundances is uniform in all classes of chondrites (despite variations in abundances of more volatile elements), it would be surprising indeed if the Ca/Al ratio of the Earth as a whole were not chondritic. Palme and Nickel argued that the difference between their estimated upper mantle Ca/Al ratio and the chondritic one reflects early mantle differentiation, perhaps during crystallization of a magma ocean, that resulted in a high Ca/Al ratio in the upper mantle and a low Ca/Al ratio in the lower mantle. Hart and Zindler (1986) disputed the high Ca/Al estimated by Palme and Nickel, arguing it reflects an overabundance of clinopyroxene in the xenoliths analyzed by Palme and Nickel. The dispute points out the difficulties in using xenoliths, all of which have been affected by various processes, to estimate upper mantle compositions. Most recent estimates of the silicate Earth composition have Ca/Al values close to the chondritic one (0.76 to 0.78).

PHASE TRANSITIONS IN THE MANTLE

The mineral assemblage of the mantle changes as pressure increases. Understanding the phase relationships in the mantle is important for two reasons. First, seismic velocities and densities are the most important constraint on the bulk composition of the mantle, and these depend on the mineral assemblage. Second, the pressure at which phase transitions occur is composition dependent, so that the depths at which phase transitions occur, as reflected by changes in seismic velocity, constrain the composition of the mantle.

In the upper 200 km or so, the only important phase changes are the nature of the aluminous phase. This changes from plagioclase to spinel ($MgAl_2O_4$) at about

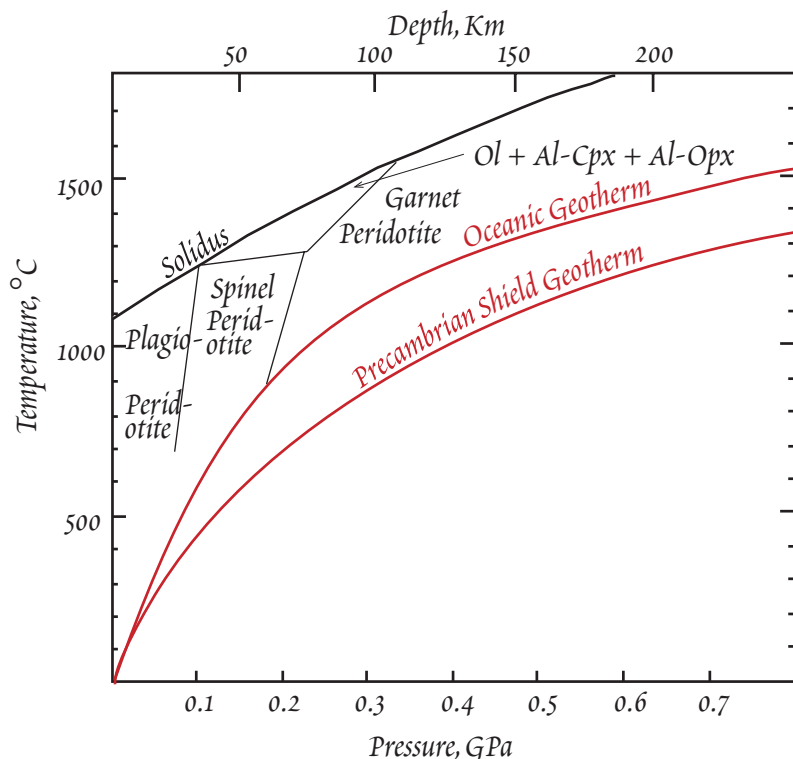


Figure 11.6. Upper mantle phase diagram.

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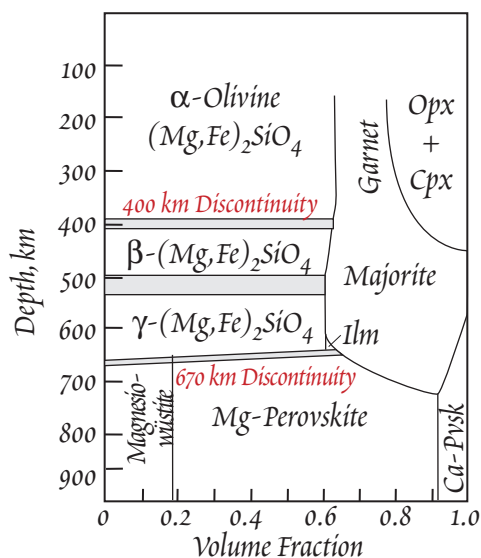


Figure 11.7. Mineral assemblages in the upper 1000 km of the mantle. From Ringwood (1991).

this depth interval is often called the transition region. At about 400 km, or 14 GPa, olivine undergoes a structural change from the low pressure, or α form, to the β form. In contrast to the pyroxene-to-majorite phase change, this phase boundary is relatively sharp, with a transition interval of 9-17 km. The α to β transition results in an 8% increase in density.

At about 500 km depth or so, olivine undergoes a further structural change to the γ -form. The structure is similar to that of $MgAl_2O_4$ spinel, and this phase is sometimes, somewhat confusingly, referred to simply as spinel, though the name *ringwoodite*, has been applied to γ -olivine found in shocked meteorites. The change from β to γ -olivine is thought to be more gradual than the α - β transition, occurring over a depth interval of 30 km, and involves only a 2% increase in density. In both the β and γ phases silicon remains in tetrahedral coordination.

Within the transition zone, some of the Mg and Ca in majorite begin to exsolve to form $CaSiO_3$ in the perovskite structure and $MgSiO_3$ in the ilmenite structure. The proportion of $CaSiO_3$ perovskite increases with depth until majorite disappears at about 720 km. $MgSiO_3$ ilmenite persists only to 660 km.

A very sharp and large increase in seismic velocity occurs at around 660[‡] km depth, and is called the 660 seismic discontinuity[§]. This depth marks the beginning of the lower mantle. Over the years there has been considerable debate as to whether this discontinuity is a chemical boundary or a phase change. There is now complete agreement that it is primarily due to a phase change, though debate continues whether it might also be a chemical boundary (a question discussed below). At this depth γ -olivine disproportionates to form $(Mg,Fe)SiO_3$ in the perovskite structure and $(Mg,Fe)O$ magnesiowüstite, with the Fe going preferentially in the magnesiowüstite. This phase change results in a density increase of about 11%. The $(Mg,Fe)SiO_3$ perovskite has the chemical stoichiometry of pyroxene, but the silicons are in octahedral coordination. The structure, illustrated in Figure 11.8, is similar to that of the "high-temperature" cuprate superconductors discovered in the 1980's.

[‡] The exact depth of the transition has been debated and maybe anywhere between 650 and 690 km. In fact, the depth at which the transition occurs could vary due to lateral variations in temperature within the mantle, or because of mantle convection.

[§] This is also variously known as the 650 discontinuity and the 670 discontinuity.

30 km depth, and from spinel to garnet at 60 to 90 km depth, depending on composition and temperature.

The garnet peridotite assemblage remains stable to depths of about 300 km. At this depth, appreciable amounts of pyroxenes begin to dissolve in garnet, forming a solid solution with the general composition $M_2(MSi,Al_2)Si_3O_{12}$ where M is Mg, Fe, or Ca. This garnet, called *majorite*, differs from those found at lower pressure in that up to a quarter of the silicon atoms are in octahedral coordination (i.e., surrounded by 6 oxygens rather than 4). The octahedral coordination is favored because the anions such as oxygen are more compressible than are cations such as silicon. When compressed, more oxygens can be packed around each silicon atom. This phase change is a gradual one, with complete conversion of pyroxenes to majorite at about 460 km depth (Figure 11.7). The phase change results in a roughly 10% increase in density of the "pyroxene" component.

THE TRANSITION ZONE

Between 400 and 670 km depth seismic velocities increase more rapidly than elsewhere (Figure 11.3) and

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High pressure experiments carried out with the diamond anvil show that the transition is quite sharp, occurring within a pressure interval of 0.15 GPa at 1600° C. The transition has a negative Clapeyron slope ($P \text{ (GPa)} = 27.6 - 0.0025 T \text{ (°C)}$; e.g., Chopelas, et al., 1994), so that it will occur at somewhat shallower depth in hot regions, such as areas of mantle upwelling, and at greater depth in cooler regions, such as subducted lithosphere, though since the Clapeyron slope is shallow, the effect is small. The affect of these differences is to oppose motion across the boundary, and therefore to stabilize any chemical differences that might exist between the upper and lower mantle. To understand this, consider a sinking subducted lithospheric slab. Such slabs sink through the upper mantle because they are denser than surrounding mantle. Let's arbitrarily suppose that it is 200° cooler than surrounding mantle. As a result it will undergo the γ -olivine-perovskite phase change at about 0.5 GPa greater pressure (15 km or so deeper) than surrounding mantle. As the slab penetrates to below 660 km, its density contrast between the slab and surrounding mantle will be reduced, because γ -olivine is the principal phase in the slab whereas Mg-perovskite is the major phase in the surrounding mantle. The reduced density contrast results in less gravitation energy to cause further sinking of the slab. For similar reasons, the phase transition will also tend to oppose the motion of rising hot mantle, mantle plumes for example. Indeed, there is seismological evidence that the discontinuity is deflected downward under subduction zones. Though the negative Clapeyron slope opposes motion across the boundary, it is probably not sufficient to prevent it entirely unless the 660 discontinuity is also a chemical boundary.

As we noted above, there is no question that phase transitions are primarily responsible for the increase in seismic velocity observed in the transition zone (Figure 11.3). Anderson (1989) argues, however, that change in seismic velocity at 400 km is smaller than what should occur in an olivine-rich (i.e., lherzolitic) mantle, and therefore that the upper mantle must be piclogitic rather than lherzolitic. Ringwood (1991) argued that, because of the negative Clapeyron slope, many slabs are not dense enough to sink through the 660 discontinuity and therefore pile up above it. In his view, there is a layer of 50 km thickness or so of accumulated oceanic crust above the 670 discontinuity. Resolution of these questions requires better data on the elastic properties of phases within the transition zone.

COMPOSITION OF THE LOWER MANTLE

The lower mantle, the region between the 660 km seismic discontinuity and the core-mantle boundary at 2900 km, is substantially less accessible to study than is the upper mantle. Its composition must be inferred indirectly. The only direct constraint on its composition is its seismic properties. The assumption that the Earth is approximately chondritic forms another constraint. It is generally agreed that the lower mantle is grossly similar in composition to the upper mantle, i.e., composed dominantly of SiO_2 , MgO , and FeO with lesser amounts of CaO , Al_2O_3 , TiO_2 , etc. However, there is substantial disagreement as to its precise composition, in particular whether it is richer in FeO and SiO_2 than the upper mantle.

Perovskite and magnesiowüstite appear to remain the principal phases throughout the lower mantle. Perovskite constitutes about 80% of the lower mantle, and thus is the most abundant mineral in the Earth. The magnesiowüstite/perovskite partition coefficient for Fe decreases with increasing pressure, so that the proportion of Fe in perovskite should increase somewhat with depth up to about

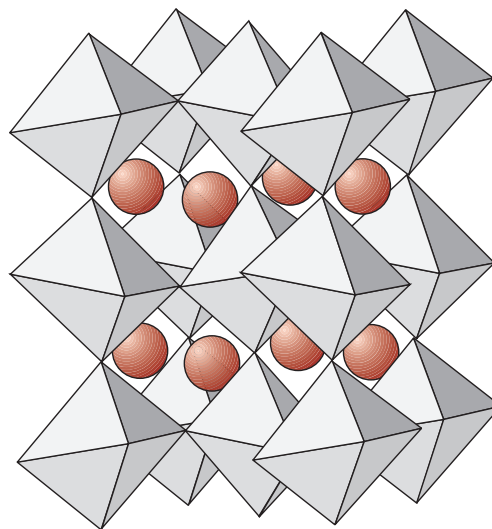


Figure 11.8. The structure of MgSiO_3 perovskite. The structure consists of corner-sharing SiO_6 octahedra with Mg^{2+} in dodecahedral sites.

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30 GPa (~900 km), and this is constant at greater pressure. At this depth, the mole fractions of Mg ($\text{Mg}/(\text{Mg}+\text{Fe})$) in MgSiO_3 -perovskite and magnesiowüstite ($(\text{Mg},\text{Fe})\text{O}$) for a pyrolite composition are about 0.93 and 0.80 respectively.

There has been some debate about how Al_2O_3 is accommodated in lower mantle minerals. Some have argued that a separate aluminous phase forms. The most recent experiments however, suggest that while a separate aluminous phase forms at relatively low pressure (20-30 GPa, corresponding to the region of 600-800 km), at pressures above about 35 GPa, Mg-perovskite apparently accepts all available Al_2O_3 in its structure, so that there is no separate aluminous phase in the lower mantle (e.g., Kesson et al., 1994) below about 800 km. However, the solid solution between Mg-perovskite and Ca-perovskite appears to be quite limited, so that Ca perovskite is probably present as a separate phase, and probably accepts all the Na_2O .

There is considerable uncertainty about the composition of the lower mantle, and there are two principal viewpoints on the question. In the first, the lower mantle is compositionally similar to the upper mantle, i.e., an approximately pyrolitic composition, with no major chemical boundaries. In this case, the lower mantle would consist of 80% perovskite, with about 10% magnesiowüstite (Figure 11.7). Proponents of the second view claim that an essentially pure perovskite lower mantle better fits seismic observations. A second argument favoring a pure perovskite lower mantle is that it is richer in SiO_2 and therefore closer to chondritic than upper mantle compositions. At present, the density and elastic properties of lower mantle minerals are not sufficiently well known to distinguish between these alternatives, as the predicted densities of the pyrolite and chondritic models of the lower mantle differ by less than 0.06 g/cc. Uncertainties about the temperature of the lower mantle, and the coefficient of thermal expansion of lower mantle materials, compound the problem. Though a 'chondritic' lower mantle does seem to match the seismic observations slightly better, a pyrolite composition appears to match the seismic observations within about 1%, which is less than the combined uncertainty of the seismic observations and the values for seismic properties of lower mantle materials. D. Anderson and R. Jeanloz, among others, also argue that the lower mantle is richer in iron than the upper mantle. Jeanloz has suggested a molar $\text{Mg}/(\text{Mg}+\text{Fe})$ ratio of about 0.8 for the lower mantle, compared to 0.9 for the upper mantle.

The importance of this problem to both the present working of the Earth and its past evolution should be emphasized. If the mantle is chemically stratified or layered, that is if the composition below the 660 discontinuity differs from that above, it implies that convection within the mantle is layered; moreover, it implies there is little chemical exchange between the upper and lower mantles. In this case, it seems unlikely that subducted lithospheric slabs penetrate to depths greater than 660 km. Similarly, if the mantle is layered, mantle plumes, which are responsible for most interplate volcanism, probably arise from the 660 km discontinuity rather than the core-mantle boundary. A layered mantle also implies that the continental crust was derived only from the upper mantle, which has important implications for mass balance models of the Earth, which we consider below. On the other hand, a homogenous mantle allows, but does not require, whole mantle convection. Finally, it is possible, and perhaps likely, that if the mantle is layered, this layering originated during crystallization of an early magma ocean, a question to which we will return.

D'' AND THE CORE-MANTLE BOUNDARY

For the most part, seismic velocities increase smoothly throughout the lower mantle and appear to be consistent with self-compression of chemically homogeneous material. However, the lower two hundred kilometers or so of the mantle appear to be seismically peculiar. Within this layer, known as D'' (d-double-prime), both P- and S-wave velocity gradients are smaller than elsewhere. Furthermore, the thickness of D'' varies significantly. Though the anomalous gradients in this region have been recognized for 50 years, the extremely heterogeneous nature of D'' has only recently been discovered. The shallow seismic gradients can be fairly easily explained if this region is a thermal boundary layer between the core and the mantle, as it would be hotter. The heterogeneity cannot be so easily explained, and is the subject of debate. Again, there are two views. In the first view, the

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region is a chemical boundary layer and is produced by reaction between silicates of the mantle and the FeNi core. In the other view, the heterogeneity arises from the presence of subducted oceanic lithosphere that has sunk to the base of the mantle. In this latter view, the D'' layer is the source of mantle plumes, which we discuss in a subsequent section.

THE "PRIMITIVE MANTLE"

An important concept in mantle geochemistry is that of the "primitive mantle" composition. Primitive mantle is defined as the composition of the mantle after separation of the core, but before separation of the crust. It is thus equivalent to the "Bulk Silicate Earth" composition. As we will see, it seems likely that the core formed very early, perhaps before accretion was complete, whereas the crust seems to have formed much more slowly, so equating primitive mantle with bulk silicate earth seems reasonable.

TABLE 11.3. PRIMITIVE MANTLE CONCENTRATIONS

Li	1.6	Ge	1.1	Nd	1.225
Be	0.066	As	0.13	Sm	0.381
B	0.5	Se	0.05	Eu	0.145
C	250	Br	0.075	Gd	0.526
F	26	Rb	0.60	Tb	0.093
Na	2545	Sr	19.9	Dy	0.651
Mg	219407	Y	4.05	Ho	0.146
Al	22985	Zr	10.5	Er	0.428
Si	214766	Nb	0.651	Tm	0.058
P	95	Mo	0.065	Yb	0.439
S	350	Ru	0.0042	Lu	0.065
Cl	330	Rh	0.001	Hf	0.283
K	240	Pd	0.005	Ta	0.037
Ca	23858	Ag	0.008	W	0.021
Sc	15.5	Cd	0.04	Re	0.00028
Ti	1153	In	0.013	Os	0.0034
V	82	Sn	0.175	Ir	0.0033
Cr	2935	Sb	0.005	Pt	0.0068
Mn	1080	Te	0.013	Au	0.00075
Fe	65500	I	0.011	Hg	0.01
Co	105	Cs	0.021	Tl	0.007
Ni	1890	Ba	6.189	Pb	0.18
Cu	30	La	0.624	Bi	0.0025
Zn	56	Ce	1.637	Th	0.0813
Ga	3.9	Pr	0.238	U	0.0203

All concentrations in ppm.

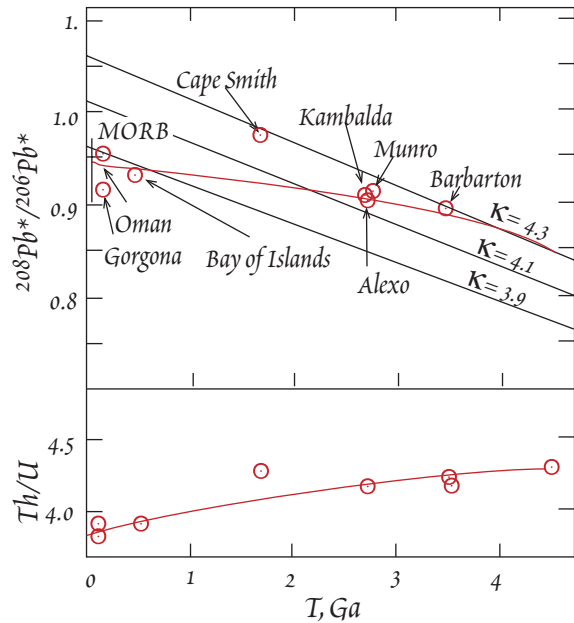


Figure 11.9. Apparent Th/U ratio of magma sources as a function of time. $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ is the ratio of radiogenic ^{208}Pb to radiogenic ^{206}Pb . The plot shows data for komatiites (komatiites are ultramafic lavas produced by relatively high degrees of melting) and ophiolites (Bay of Islands and Oman), which are oceanic crustal sections. After Allègre et al. (1986).

In estimating primitive mantle composition, we start with the assumption of an approximately chondritic Earth. The primitive mantle composition will differ from chondritic, however, as a result of two processes: loss of volatiles from the inner Solar System or during formation of the Earth, and loss of siderophile elements to the Earth's core.

Though the compositions of the various classes of chondrites differ, they do have constant relative abundances of the highly refractory lithophile elements, i.e., those elements concentrated in CAI's (see Chapter 10): Al, Ca, Sc, Ti, Sr, Y, Zr, Nb, Ba, REE, Hf, Ta, Th, and U. Thus for example, the Sm/Nd ratio is nearly constant in different meteorites despite variations in the absolute abundances of Sm and Nd. This being the case, it is reasonable to assume that these elements are present in the same relative abundances in the silicate Earth as in chondrites. This group includes the parents and daughters of the Sm-Nd and Lu-Hf radioactive decay schemes. It is this assumption that the Sm/Nd ratio of the Earth is

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chondritic that makes this decay scheme so useful (among other things). Note also that some important elements in isotope geochemistry are absent from this group: Re, Os, Rb and Pb.

Though both Th and U are refractory elements, there is evidence that the Th/U ratio of the Earth might be somewhat higher than the chondritic ratio. The Anders and Grevesse tabulation (Table 10.2) yields a chondritic Th/U ratio of about 3.8. But Pb isotope systematics of meteorites suggest a higher ratio, closer to 4.0. Allègre et al. (1986) have argued the ratio is as high as 4.2. Figure 11.9 illustrates one piece of evidence they use to support this hypothesis. As we demonstrate in a subsequent section, a time-integrated Th/U ratio may be calculated from $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ ratios (the asterisk is used to designate radiogenic ^{208}Pb and radiogenic ^{206}Pb). When Allègre et al. (1986) did this for a series of mafic and ultramafic rocks of various ages, they found evidence for a decrease of the Th/U ratio of the mantle with time. The curve through the data suggests the mantle had a Th/U ratio of about 4.2 at 4.55 Ga. The importance of this derives from recent work on Th isotope ratios, which indicates that present upper mantle Th/U ratios are about 2.3, which is much lower than time-averaged ratio derived from $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ ratios, which is about 3.6-3.8. If the primitive mantle Th/U is as low as 3.8 and the present mantle ratio is 2.3, a time integrated ratio approaching 3.8 suggests the low present Th/U is a relatively young feature. However, if the primitive mantle Th/U is 4.2, as Allègre et al. argue, the a more gradual depletion of Th/U is possible.

The abundance of other elements in the silicate Earth can also be estimated through various indirect approaches. For example, the abundance of Rb has been estimated by comparing Rb-Sr and Sm-Nd isotope systematics, and also from the Rb/Ba ratio of mantle-derived basalts, which is constant (Hofmann and White, 1983). The Pb concentration in the Earth can be estimated by noting that most major reservoirs in the Earth have Pb isotope ratios consistent with a μ ($^{238}\text{U}/^{204}\text{Pb}$) of about 8. K concentration can be estimated by noting that the K/U ratio of most materials is about 10000. Table 11.3 lists estimated concentrations of the elements in the Primitive Mantle (= bulk silicate Earth). The values were calculated as follows. First a 'chondritic mantle' was calculated, following Hart and Zindler (1986), by subtracting an appropriate amount of the volatile and moderately volatile elements and enough of the major siderophiles to form the core. The Si was then adjusted downward to

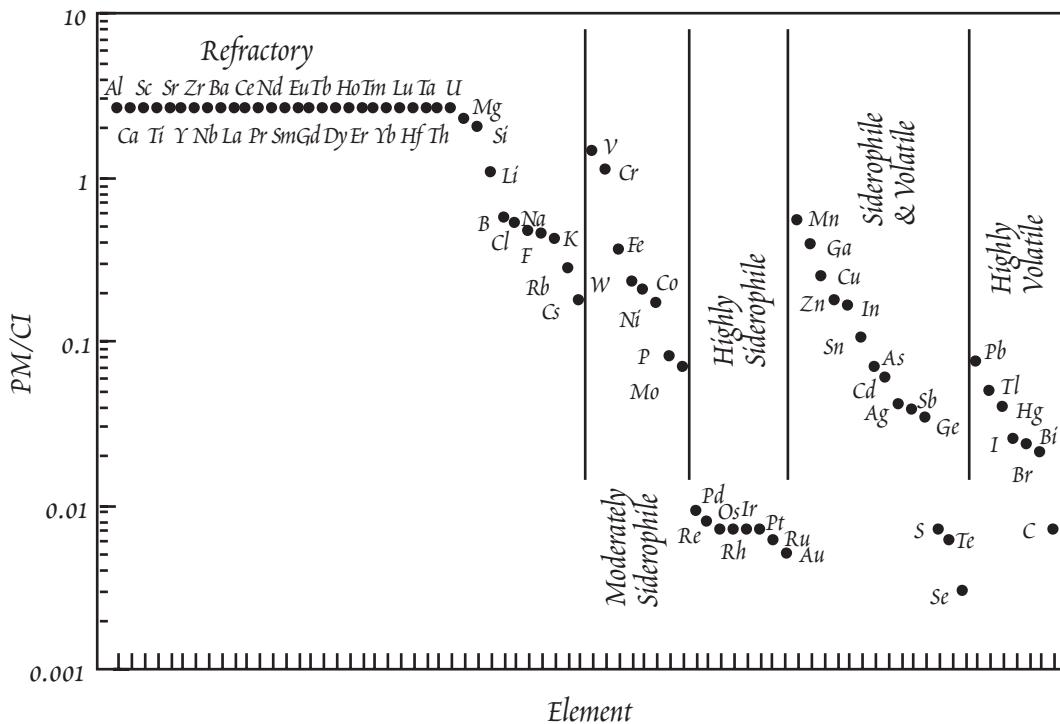


Figure 11.10. Abundances of the elements in the Primitive Mantle compared to CI chondrites.

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accord with observations on mantle xenoliths (Hart and Zindler, 1986). The observed concentrations of the major refractory elements, Al, Ca, and Ti, in this upper mantle (Hart and Zindler, 1986) appear to be about 15% enriched relative to this calculated 'chondritic mantle'. On this basis, it was assumed that refractory lithophile trace elements (e.g., REE) were also 15% overabundant. The remaining element concentrations were taken from McDonough (1987) or Hofmann (1988) with some minor adjustments. Figure 11.10 compares these estimated primitive mantle concentrations with CI chondrites. These primitive mantle concentrations should not, of course, be taken as gospel and will undoubtedly be revised in the future.

MAGMA OCEAN AND MANTLE DIFFERENTIATION

Several observations suggest the Earth underwent extensive melting when it formed. First, the energetics of the formation of the Earth and its core suggest extensive melting occurred. The gravitational energy released by accretion of the Earth from nebular dust is sufficient to melt the entire planet. Whether this occurs or not, however, depends on how efficiently heat is lost during accretion, and how quickly accretion occurs. If the Moon formed as a result of a giant impact, the impact would release enough energy to cause very extensive melting. Formation of the core would also release a large amount of energy. In addition, there is evidence for a magma ocean on the Moon. Given that the gravitational energy released by accreting the Earth is even greater, it is difficult to see how formation of a terrestrial magma ocean could not have formed. Second, the solidus and liquidus of peridotite converge at high pressure (Figure 11.11). Some petrologists have argued that this is unlikely to be coincidental and they conclude that the lherzolitic upper mantle is a minimum melt or eutectic composition of a "chondritic mantle" composition (i.e., Table 11.2 column 2).

According to some, crystallization of a magma ocean would produce a chemically stratified mantle. The magma ocean would have crystallized both from the top down, because heat can only be lost from the surface of the Earth. It would have simultaneously crystallized from the bottom up (Figure 11.12), because the P-T slope of the solidus is greater than that of an adiabatic gradient (vigorous convection within the magma ocean would have kept temperatures nearly adiabatic). Presumably, a protocrust would have quickly formed as the surface of the magma ocean crystallized. This protocrust, like that of the Moon, might have been rich in plagioclase because plagioclase is less dense than a melt of lherzolitic composition (provided it is relatively dry) and hence floats to the surface. Plagioclase, however, would have crystallized only within the upper 30 km of so, since it is not stable at greater pressure. If melting was extensive enough to extend into the Mg-perovskite stability field (shallower than at present because of higher temperature), Mg-perovskite crystallizing in the lower part of the magma ocean would have sunk out of the magma due to its higher density. Mg-

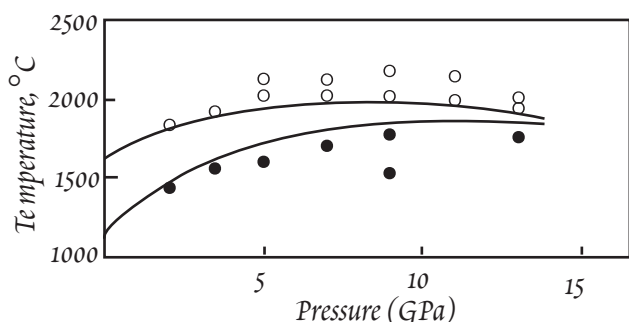


Figure 11.11. Solidus and Liquidus of peridotite at high pressure. Closed symbols are experiments in which there was no evidence of melting, red half-filled circles are experiments that partially melted, and open circles are experiments that totally melted. From Scarfe and Takahashi (1986).

perovskite has a slightly higher Si/Mg ratio than chondrites or lherzolite, so the residual liquid would have been depleted in Si by Mg-perovskite crystallization. This liquid would also have been strongly enriched in Na and Ca and modestly enriched in Al, which are excluded from perovskite, and depleted in Ti, which is enriched in Mg-perovskite. Except in the uppermost part, olivine crystallizing above the depth of the present transition zone would be less dense than the melt and would have floated upward, enriching the upper mantle in olivine. Majorite garnet, which crystallizes later than perovskite and olivine, would have also been denser than the liquid and would have settled, depleting the upper mantle in Al and other elements,

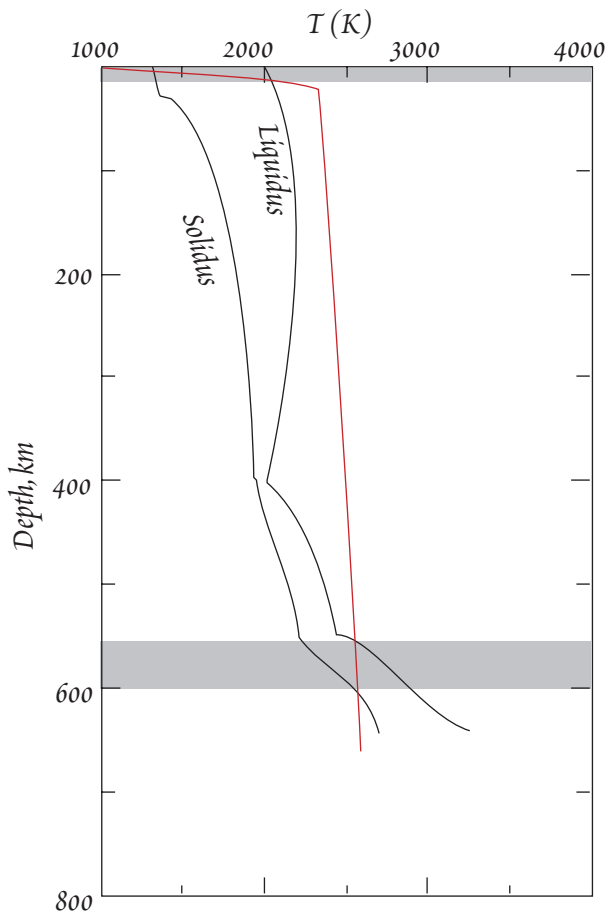


Figure 11.12. Solidus, liquidus and thermal gradient in a terrestrial magma ocean. Crystallization occurs in the gray regions where temperature is between the solidus and liquidus. This occurs at the very top where temperatures are not adiabatic and at the bottom, where the solidus temperature exceeds the adiabatic temperature.

Thus the magma ocean would crystallize without producing a stratified mantle.

Even if crystallization of a magma ocean had produced a stratified mantle, this stratification may not persist, since subsequent convection could have destroyed it. Little, if any of the presently observed mantle heterogeneity can be related to a primordial magma ocean. However, there is some evidence that a stratified mantle did form and persisted for a billion years or so.

THE CORE AND CORE FORMATION

We know little about the composition of the core or how it formed. Various lines of evidence, primarily geophysical, indicate the core consists of Fe-Ni

such as the heavy rare earths, that partition into garnet. Thus in the view of some, crystallization of a magma ocean could produce a chemically stratified mantle in which the upper mantle has a lower than chondritic Si/Mg ratio and a higher than chondritic Ca/Al ratio.

There are, however, several questions about this scenario. Kato et al. (1988) determined Mg-perovskite-liquid partition coefficients for a number of elements. Hf and Sc appear to strongly partition into perovskite, whereas rare earths, such as Sm, are not. Fractional crystallization of perovskite would change the Hf/Sm and Sm/Sc ratios more rapidly than the Si/Mg ratio (Figure 11.13). However, both the Hf/Sm and Sm/Sc ratios appear to be approximately chondritic in the upper mantle. Fractional crystallization of perovskite would also increase the Lu/Hf ratio, whereas Hf isotope data suggest the early mantle had an approximately chondritic Lu/Hf ratio. In addition, Tonks and Melosh (1990) argued that convection in the magma ocean would be so vigorous that nucleating crystals would be swept out of the crystallization zones before they had time to grow to sufficient size to settle out.

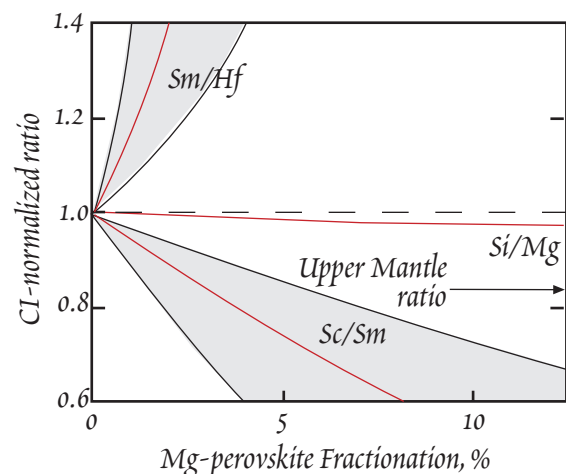


Figure 11.13. Effect of fractional crystallization of Mg-perovskite on Sm/Hf, Sc/Sm, and Si/Mg ratios in a magma ocean that is initially chondritic. 10% Mg-perovskite fractionation drastically changes the Sm/Hf and Sc/Sm ratios, but only slightly changes the Si/Mg ratio. From Ringwood (1991).

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alloy. Iron meteorites contain 5-10% Ni, so the concentration of the core probably falls in this range. About 5.7% Ni in the core is required to explain the observed depletion of the mantle in Ni. Density considerations, however, require about 10% of some lighter element as well. What the light element is has been the subject of endless debate, and a resolution of the question in the near future does not seem likely. The principle candidates are S and O.

Sulfur is an obvious candidate for several reasons. First, it is severely depleted in the silicate Earth (Figure 11.10). Sulfur is volatile, and much of its depletion may be due to this. However, it is more depleted than similarly volatile elements, e.g., Zn, which strongly suggests its presence in the core. Second, iron meteorites often contain considerable amounts of FeS (troilite), indicating S was extracted into the cores of meteorite parent bodies. Finally, FeS and Fe liquids are completely miscible at low temperature, so that S would have readily dissolved into droplets of Fe liquid in the accreting Earth. Ahrens and Jeanloz (1987) found that a core with about 11% S would match the observed seismic properties of the core reasonably well. Allègre et al. (1995) estimate the core has about 2% S, based on the correlation between K/Ca and S/Ca in meteorites and an estimate of the terrestrial K/Ca value.

The idea that O might be the light element in the core is based on the observation that at high pressure FeO is miscible with Fe liquid, though it is not at low pressure. The eutectic composition in the Fe-FeO system at 16 GPa, still well below core pressures, contains about 10% FeO (e.g., Ringwood and Hibbertson, 1990). Furthermore, the Earth's mantle is depleted in oxygen compared with CI chondrites. The relevance of this last observation, however, is questionable, since the oxidation state of chondrites, and therefore presumably the solar nebula, clearly varied widely. Significant in this respect is the observation that based on O isotope ratios, the Earth appears to be more closely related to enstatite chondrites (Figure 9.23), which are highly reduced, than to other chondrites, and in particular to CI. Allègre et al. (1995) have estimated that the core contains about 4% O.

C, Si, P, Mg, and H have also been mentioned as the possible light element in the core. Allegre et al. (1995) estimated the core contains about 7% Si, which is based on the observed mantle deficit of Si and the assumption the Earth has the same Mg/Si ratio as carbonaceous chondrites. There are, however, some inconsistencies and questionable assumption in their approach. At present, the available observations simply do not allow us to specify the core composition very accurately.

The core undoubtedly contains the bulk of the Earth's inventory of other siderophile elements as well. Refractory siderophiles such as Re, Os, Ir, and Pt, among others, are probably present in chondritic relative abundance in the core, based on the same arguments made for chondritic relative abundances of lithophile elements. If the light element in the core is S, the core may also be rich in chalcophiles such as Pb.

It is generally assumed that core formation occurred very early in Earth's history, probably simultaneously with accretion. One line of evidence for this is the observation that the gravitational energy released by formation of the core from an initially homogeneous Earth is sufficient to raise the temperature of the Earth by 2000° C. Thus if core formation were catastrophic, i.e., happened rapidly,

it must have occurred before formation of any presently existing crust; i.e., before 4.2-4.3 Ga ago (the age of zircons recovered from the Jack Hills of Australia). Modeling of the physical aspects of accretion also suggests core formation would have occurred simultaneously with accretion. In addition, core formation appears to have occurred very early in meteorite parent bodies. *Prima facie* evidence of this is the existence of anomalies in the isotopic composition of Ag resulting from decay of short-lived ¹⁰⁷Pd. Certainly all those who have

Table 11.4. Liquid Silicate–Liquid Metal Partition Coefficients

Element	D ^{S/M}	Element	D ^{S/M}
W	1	Au	1 × 10 ⁻⁴
Re	5 × 10 ⁻⁴	P	0.24
Ir	5 × 10 ⁻⁵	Ga	0.8
Mo	8 × 10 ⁻⁴	Ag	0.01
Ni	2 × 10 ⁻⁴	Pb	0.15
Co	7 × 10 ⁻³		

from Jones and Drake (1986).

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considered the problem agree that core formation *started* very early. There has been some question as to when it was complete, with some arguing that it continued through most of geologic time.

As we found in Chapter 7, trace elements are useful in geochemistry because geochemical processes often lead to much greater variations in their abundances than in the major elements. Equilibration between metallic (Fe-Ni) liquid and silicate liquid is an example of a process that should lead to a large fractionation of trace elements.

Table 11.4 lists experimentally determined liquid silicate-liquid metal partition coefficients for a number of siderophile elements. These experiments were performed at low pressure with about 20% sulfur in the metal phase. Their relevance to the problem of core formation thus depends on 1) whether the core contains sulfur, 2) whether equilibration occurred at high or low pressure, and 3) the form (liquid or solid) of the silicate and metal phases at the time and point of equilibration. More fundamentally, it depends on whether core formation was an equilibrium or disequilibrium process.

There is as yet little consensus on any of these points. Most students of core formation prefer low-pressure equilibration. New material is added to the surface of the earth and hence the initial interaction between metal and silicate would occur near the surface at low pressures. Presumably, blobs (for lack of a better word) of metal grow and coalesce as they sink. The greater their size, the less the opportunity for equilibration with surrounding silicate. So on these grounds, low pressure partition coefficients may be more relevant than high pressure ones. Solid silicate-liquid silicate and solid metal-liquid metal partition coefficients for these elements are also available. From these data, any combination of metal-liquid equilibrium distribution coefficients can be calculated.

Accepting for the moment the relevance of the distribution coefficients in Table 11.4 to core formation, we can see that these values predict that the mantle should be highly depleted in elements such as Mo, Re, Au, and Ir. The partition coefficients can be compared with depletion factors (abundances relative to CI chondrites) in the mantle shown in Table 11.5. Although there is very rough qualitative agreement, there are significant discrepancies in detail. For example, Ir should be an order of magnitude more depleted than Re, and Ni should be a factor of 30 more depleted than Co. But the actual depletions of Ni and Co are similar, as are the depletion factors for all the platinumoid metals, all of which are highly siderophile (Figure 11.10). The mismatch tells us something is wrong with the partition coefficients or a simple model of equilibrium core formation. Assuming equilibration took place between solid, rather than liquid, silicate and metal generally only makes things worse.

Possible explanations for the discrepancy between predicted and observed depletion of siderophiles in the mantle include inefficient metal extraction or disequilibrium, discrepancy between the composition of the metal phase in experiments and the core (i.e., non-S bearing, O-bearing metal). All of these possibilities must be considered, but perhaps the best hypothesis is that core formation ended before the Earth had completely accreted. To illustrate the effect of this, imagine that core formation effectively extracts all Re and Ir from the mantle, as would be the case for complete equilibrium with distribution coefficients given in Table 11.4. Then imagine new material equivalent to 1% of the mass of the mantle and with chondritic abundances of Re and Ir is added to the mantle. The mantle would be highly depleted in these elements, concentrations of these elements would be close to 0.01 times the chondritic abundances, but the Re/Ir ratio would be close to chondritic, despite the order of magnitude difference in their distribution coefficients. Yet another possible explanation relates to how metal and silicate are distributed during the hypothesized giant impact (e.g., Newsom and Taylor, 1989).

Table 11.5. Siderophile and Chalcophile Element Abundances in the Upper Mantle

Element	Concentration/CI	Element	Concentration/CI
W	0.22	Au	0.05
Re	0.007	P	0.08
Ir	0.007	Ga	0.38
Mo	0.064	Ag	0.04
Ni	0.17	Pb	0.07
Co	0.21		

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Some authors (e.g., Allègre et al., 1983) have ascribed the excess radiogenic nature of mantle Pb isotope ratios (i.e., that they lie to the right of the geochron) to continued growth of the core and extraction of Pb (and other things) from the mantle long after formation of the Earth. This would, of course produce higher U/Pb ratios, and ultimately higher $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ than in a closed system. Newsom et al. (1986) showed that this is unlikely by examination of the relationship between Pb isotopes and siderophile element concentrations in mantle-derived volcanic rocks. They found that the ratio of Mo, a siderophile, to Pr, a lithophile light rare earth, was uniform in the mantle and did not correlate with Pb isotope ratios. A correlation is expected if post-accretion core growth extracted Pb from the mantle because Mo would be more drastically extracted than Pb (Table 11.4), decreasing the Mo/Pr ratio and increasing the U/Pb ratio. That the Mo/Pr ratio is uniform implies that in the modern mantle, Mo behaves as do moderately incompatible lithophile elements, such as Pr. Apparently, no part of the mantle sampled by volcanism has experienced more siderophile depletion than any other part. In a subsequent study, Sims et al. (1990) found that the Mo/Ce ratio in mantle-derived rocks has been constant through time. Thus the core has not extracted siderophile elements from any part of the mantle sampled by volcanism.

MANTLE GEOCHEMICAL RESERVOIRS

EVIDENCE FROM OCEANIC BASALTS

Isotopic variations in oceanic basalts provide clear evidence that the mantle is presently heterogeneous. Oceanic basalts provide better evidence of this than continental basalts because the possibility of the former being contaminated by the crust through which they pass is much reduced. This is true for 3 reasons: oceanic crust is much thinner, it has a higher solidus, and it is compositionally similar to melts of the mantle (so that when assimilation does occur, it chemical affects are minimized). Of course, not all continental basalts appear to have been contaminated. Those that have apparently not been contaminated also show evidence of mantle heterogeneity. Xenoliths in basalts also provide evidence of mantle heterogeneity.

The fundamental isotopic variation in oceanic basalts is between mid-ocean ridge basalts (MORB) and oceanic island basalts (OIB). Figures 11.14 through 11.16 illustrates the differences in isotopic composition between these two groups as well as island arc volcanics, which we shall discuss in Chapter 12. In general, MORB have lower Sr and Os and higher Nd and Hf isotope ratios than OIB.

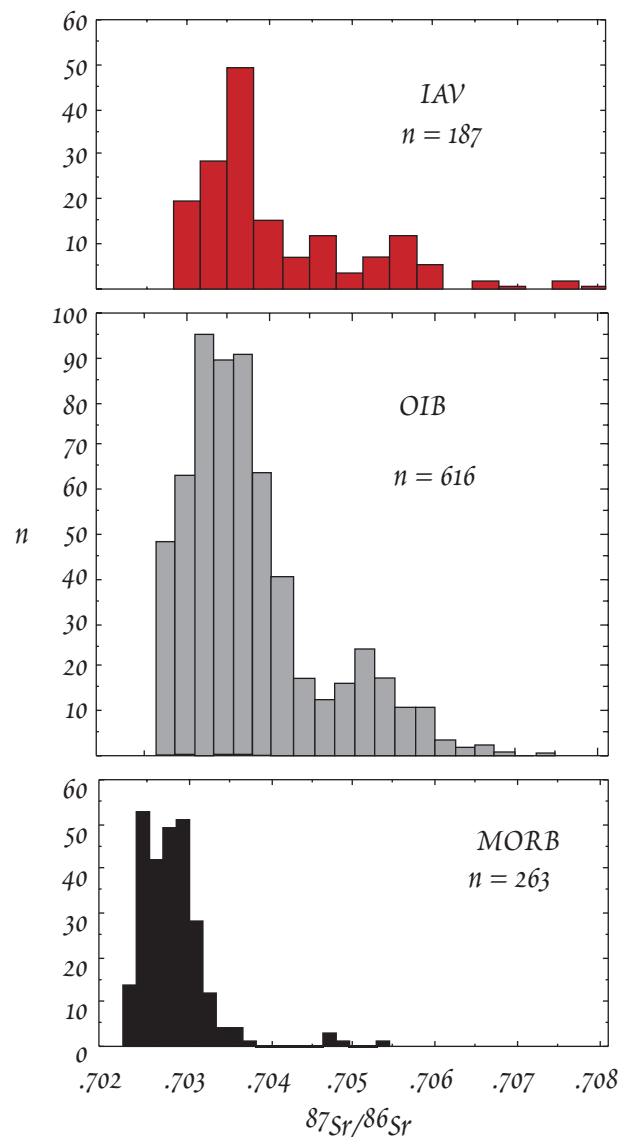


Figure 11.14 Comparison of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in mid-ocean ridge basalts (MORB), oceanic island basalts (OIB) and island arc volcanics (IAV).

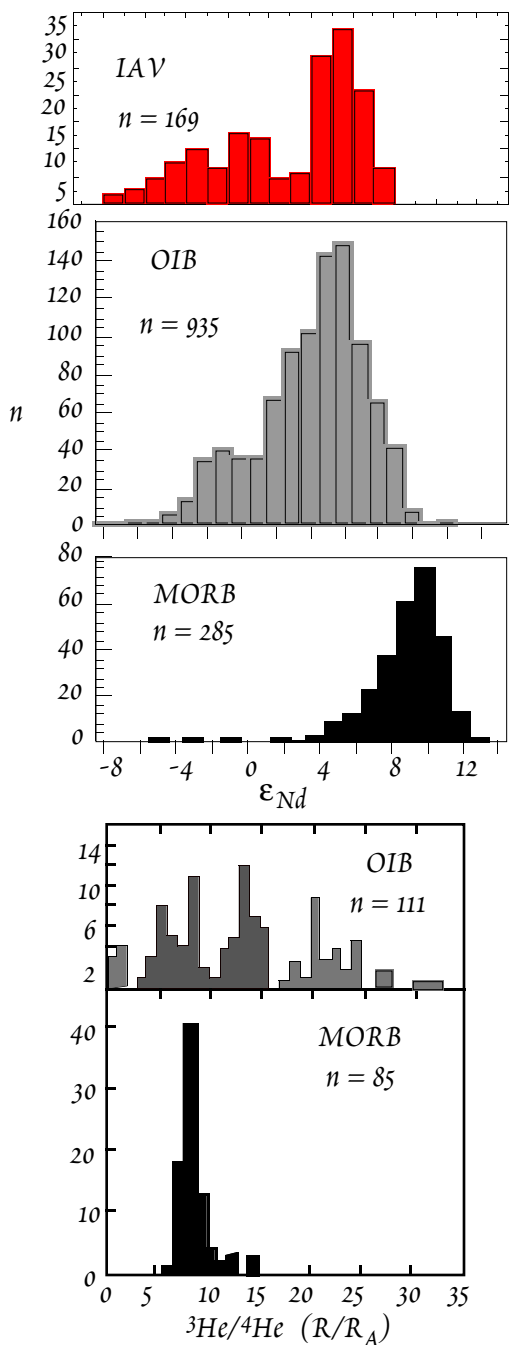


Figure 11.15. Comparison of ϵ_{Nd} and $^3\text{He}/^4\text{He}$ in mid-ocean ridge basalts (MORB), oceanic island basalts (OIB) and island arc volcanics (IAV).

These differences are consistent with MORB being derived from a mantle reservoir with consistently lower relative abundances of incompatible elements than OIB. For example, low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios imply low time-integrated Rb/Sr ratios of the MORB source, and Rb is known to be more incompatible than Sr.

The situation with Pb isotope ratios is not quite so clear. As may be seen in Figure 11.17, there is considerable overlap between MORB and OIB in $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, though OIB are on average higher. We found in Chapter 8 that Pb isotope ratios plotting to the right of the geochron imply time-integrated U/Pb ratios in the mantle that are higher than in the bulk silicate Earth, and this is the opposite of what would be expected from the relative compatibilities of U and Pb.

He isotope ratios also show greater complexity than Sr, Nd, and Hf isotope ratios (for historical reasons, He isotope ratios are generally expressed with ^4He , the radiogenic isotope, in the denominator). He isotope ratios in MORB are relatively uniform with a mean of about $8 R/R_A^*$, whereas OIB have ratios both higher and lower than this. He isotope ratios in the mantle are affected by 2 factors: growth of radiogenic ^4He from U and Th (Sm and other long-lived alpha emitters do not contribute significant ^4He) and degassing of primordial He. The conventional interpretation of higher $^3\text{He}/^4\text{He}$ ratios in many OIB is that these basalts come from reservoirs are less degassed than the MORB-source reservoir.

Figure 11.17 illustrates the difference between MORB and OIB in rare earth elements. Relative to chondrites, the light rare earths in MORB are underabundant compared to the heavier rare earths. The easiest way to produce such depletion in the mantle is to extract a melt from it. The incompatible elements, including the light rare earth elements (LREE), partition preferentially into the melt leaving a residue depleted in light rare earths. When the mantle melts again, the basalt produced will inherit this light rare earth depletion (though the basalt will not be as LREE depleted as its mantle source). Thus the mantle source of mid-ocean ridge basalts is thought to have suffered melt extraction in the past. The obvious place to store the incompatible elements extracted from the MORB source is the continental crust, a reservoir of very considerable size known to be enriched in these elements. At least in this gross sense, the evolution of the source of MORB is thought to be understood.

* Recall from Chapter 8 that He isotope ratios are typically reported relative to the atmospheric ratio, $R_A = 1.39 \times 10^{-6}$, hence a ratio of $8 R/R_A$ is equal to $8 \times 1.39 \times 10^{-6} = 1.11 \times 10^{-5}$.

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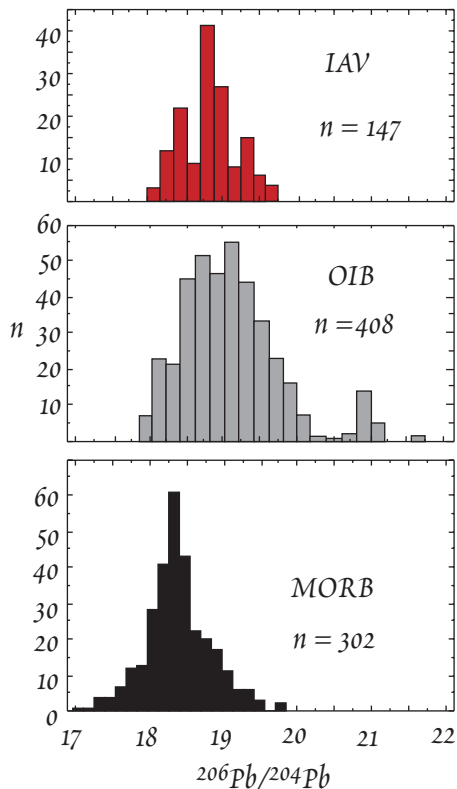


Figure 11.16. Comparison of Pb isotope ratios in MORB, OIB, and IAV.

OIB are generally light rare earth-enriched to varying degrees. Part of the difference in rare earth patterns of MORB and OIB may be due to the smaller degrees of melting involved in the generation of OIB magma. Many, though by no means all, OIB are alkalic, whereas almost all MORB are tholeiitic. Alkali basalts are generally thought to be produced by smaller degrees of melting than tholeiites. Not all the differences in rare earth patterns between OIB and MORB can be attributed to degree of melting — there must also be differences in the rare earth abundances in the mantle sources of these magmas.

There do seem to be some inter-oceanic differences in the composition of MORB. The Pacific has the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, the Atlantic the highest $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and the Indian the lowest $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. Thus the variation is not systematic in the sense of MORB from one ocean being more depleted than those from another. Another difference is that isotopic compositions in Pacific MORB are more uniform than those from other oceans. Some MORB, particularly those from ridge segments near oceanic islands (e.g., the Mid-Atlantic Ridge near the Azores and Iceland; the Galapagos Spreading Center near the Galapagos, etc.), have geochemical characteristics similar to OIB. These MORB are referred to as E-MORB (incompatible-element enriched) or P-MORB (mantle plume). The

remainder are referred to as normal or N-MORB.

Figure 11.18 compares the incompatible element abundances in MORB and typical OIB alkali basalt in a *spider diagram*, in which elements are ordered according to their incompatibility and normalized to primitive mantle values. Thus this kind of plot is also sometimes referred to as an *extended rare earth plot*. The incompatible element depletion of MORB is apparent. OIB are generally incompatible-element enriched, but the most incompatible elements (Cs, Rb, and Ba) are not as enriched as are the slightly less incompatible elements. Though part of this may be attributed to uncertainty in the choice of normalizing values for these elements (i.e., the primitive mantle abundances), this depletion in the most incompatible elements in OIB sources suggests even they have experienced prior depletion in incompatible elements due to melt extraction. This is consistent with Nd isotope ratios, which in most OIB are higher than chondritic, implying time-averaged higher than chondritic Sm/Nd ratios, and depletion in Nd relative to Sm.

In the view of most mantle geochemists and geophysicists, MORB are derived from the asthenosphere, which is that part of the upper mantle that directly underlies the lithosphere and is characterized by relatively low seismic velocities (Figure 11.3). Oceanic island basalts are thought to be derived from mantle plumes that rise from a thermal boundary layer at either the 660 discontinuity or the core-mantle boundary. There are some fairly straight-forward reasons for this. MORB are by far the most abundant volcanic rocks on the Earth and they are also compositionally the most uniform. This kind of basalt is erupted, with a few exceptions, wherever plates are moving apart. This is most easily explained if the MORB source is relatively close to the surface. Furthermore, the pull of subducting lithospheric slabs has been shown to be the primary force acting on lithospheric plates. Upwelling of mantle beneath mid-ocean ridges appears to be largely a passive response to the plate

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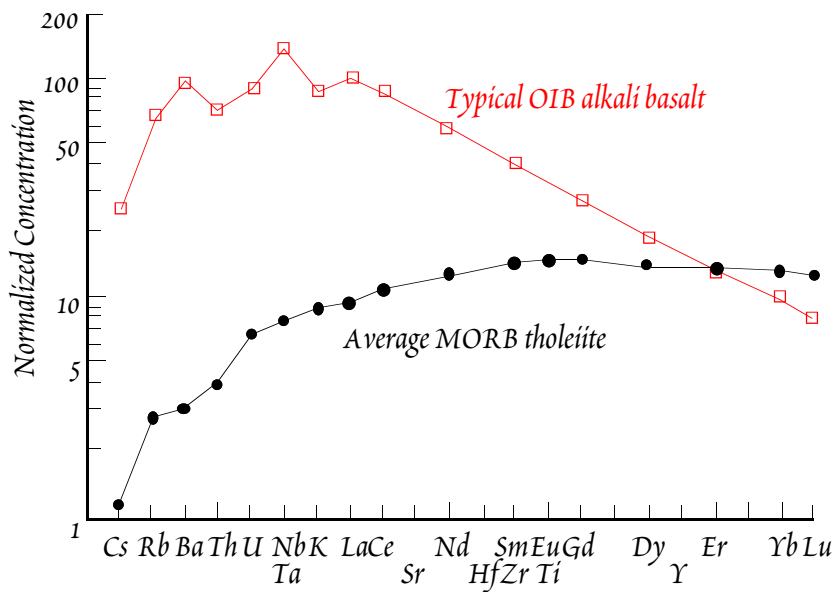


Figure 11.18. MORB tholeiite and OIB alkali basalt are compared in an extended rare earth plot or 'spider diagram' in which the elements are ordered with compatibility increasing to the right. Data are normalized to "primitive mantle" values. After Sun (1980).

MORB source through a OIB-source upper mantle which only rarely melts.

Alternative models have been proposed, however. For example, D. Anderson argues that the source of OIB basalts is the uppermost mantle 200 or 300 km of mantle, which in his model is lherzolitic. According to him, this region is underlain by piclogite, which extends down to the 660 discontinuity, and which is the source of MORB. Though strong arguments can be mounted against such models, they are difficult to disprove. They also appear to violate the 'elegance axiom' in that they are more complex. Here we adopt the majority viewpoint that the upper mantle is the source of MORB and that oceanic island basalts are derived from mantle plumes, which rise from the deep mantle. Let's now consider the evolution of these mantle reservoirs.

EVOLUTION OF THE DEPLETED UPPER MANTLE

Ancient mantle-derived rocks preserved in the continents provide evidence of how the mantle has evolved through time. Figure 11.19 shows initial ϵ_{Nd} values of mantle-derived igneous rocks. These data reveal the mantle had a positive ϵ_{Nd} by 3.8 Ga. The positive ϵ_{Nd} in turn implies the mantle was already LREE depleted. Indeed, since time is required before an increase in Sm/Nd ratios will be reflected in $^{143}Nd/^{144}Nd$, the depletion in light rare earths, and presumably other incompatible ele-

motion induced by this "slab-pull". Again, this suggests that the mantle that gives rise to MORB is fairly shallow. In contrast, there is clear evidence, such as topographic swells, of dynamic mantle upwelling associated with oceanic islands. That the locus of active volcanism remains approximately stationary for periods as long as 100 million years, indicating that this upwelling rises from depths beneath the convection associated with plate motions. The thrust of the reasoning is that it is easier to poke a few plumes through a MORB-source asthenosphere than to get a lot of

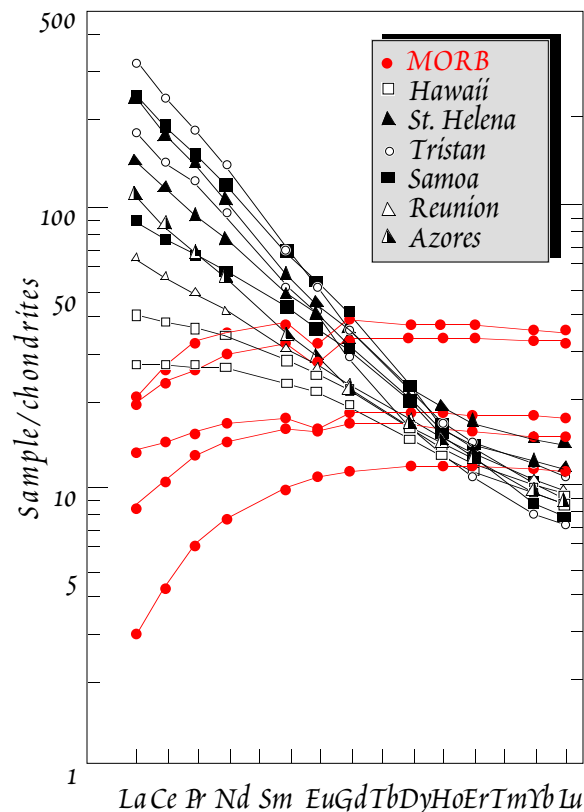


Figure 11.17. Rare earth patterns of mid-ocean ridge basalts and oceanic island basalts.

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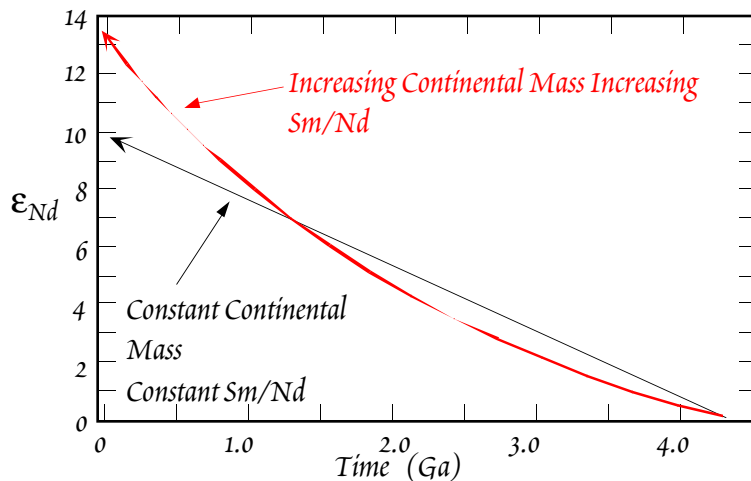


Figure 11.20. Comparison of the effects of fixed continental volume and increasing continental volume on the Sm/Nd ratio and ϵ_{Nd} evolution in the depleted mantle. A constant continental mass results in a constant Sm/Nd ratio of the depleted mantle and linear evolution of ϵ_{Nd} in the mantle. Growth of the continents through time leads to an increasing Sm/Nd of the mantle and a concave path for upward evolution of ϵ_{Nd} in the mantle.

not immediately mixed back into the upper mantle.

The idea certainly has some attractive features. First, a large amount of oceanic crust could have been created during early Archean times, and this process would certainly deplete the mantle in incompatible elements. Since heat flow was presumably higher in the early Archean than today, it is quite possible that plate velocities were higher then, implying more rapid creation and destruction of oceanic crust. Chase and Patchett (1988) calculate that if the rate of oceanic crust creation through time has decreased in proportion to radioactive heat production in the Earth, some 2×10^{23} g of oceanic crust would have been created by 3.5 Ga. If the percentage melting involved in the creation of oceanic crust is 10% (which is roughly the case for present oceanic crust), melt would have been extracted from some 2×10^{24} g of mantle, or about half the mass of the mantle, by 3.5 Ga. The resulting depletion in Nd relative to Sm would be sufficient to produce the ϵ_{Nd} values observed in the early Archean rocks preserved in continents.

Yet another possibility is that an early continental crust did form, but it was subsequently destroyed and recycled into the mantle. This possibility was first suggested by R. L. Armstrong in 1968, long before the isotopic data in Figure 11.19 were

ments, must have occurred hundreds of millions of years before the formation of the 3.8 Ga rocks. Thus we can trace the depletion of the upper mantle back to the earliest 500 Ma of Earth history.

Incompatible elements lost from the upper mantle must be stored elsewhere. It is generally assumed that this complimentary incompatible-element enriched reservoir is the continental crust. If this was true in early Archean times, the data in Figure 11.20 implies an extensive continental crust had formed prior to 4.0 Ga. However, very little continental crust of this age has been found. It is possible that such crust simply has not been identified, but that seems unlikely. Chase and Patchett (1988) argued that the complimentary reservoir to the depleted mantle was mafic or ultramafic oceanic crust, which was

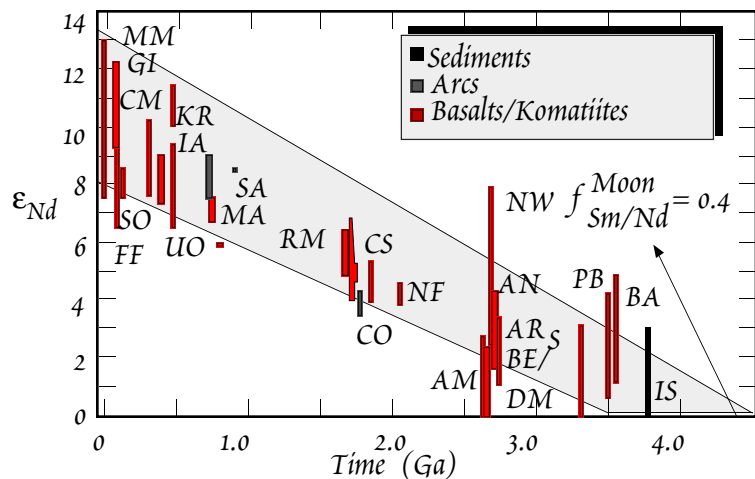


Figure 11.19. ϵ_{Nd} in rock suites for which there is little evidence of involvement of much older crust in their genesis (after Smith and Ludden, 1989).

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available. Armstrong argued that the continental crust reached its present mass by about 4.0 Ga and crustal mass has subsequently remained constant. Armstrong was the first to recognize the possibility that plate tectonics, which then was a new and revolutionary theory, provided a means of transporting material from the crust to the mantle. In Armstrong's model, new continental crust is continually created, but this creation is balanced by destruction of crust through erosion, deposition of the sediments on the oceanic crust, and subduction of this sediment into the mantle.

There are a number of reasons to believe that continental crust has been recycled into the mantle. As we shall see in the next chapter, there have clearly been additions to the continental crust through geologic time. If there has been no accompanying destruction of crust, the volume and mass of crust should have increased through geologic time. Armstrong pointed out that this should have led to flooding of the continents, as the oceans are confined to a smaller and smaller area. But this has not occurred. Armstrong also noted that virtually no deep ocean pelagic sediment is preserved on continents, implying that it is carried into the mantle during subduction. Though it was at one time widely believed that the sedimentary veneer on the oceanic crust is scraped off or "obducted" in subduction zones, careful study of several trenches shows little or no accumulation of sediment despite tens of millions of years of continuous subduction.

From a geochemical perspective, growth of the continental crust through time should lead to increasing incompatible element depletion of the upper mantle. This leads, for example, to an increase in the Sm/Nd ratio through time, which should result in the ϵ_{Nd} of the mantle following a concave upward path (Figure 11.20). In actuality, ϵ_{Nd} in the depleted mantle appears to follow a linear evolution, implying that the mass of the continents has not grown through time. However, there is an alternative explanation, proposed by Patchett and Chauvel (1984). They pointed out that if a growing continental mass could still result in constant Sm/Nd of the mantle if the volume of the depleted mantle grew.

Let's consider now consider the question of the volume of mantle that would have to be depleted in incompatible elements to create the continental crust. We start by assuming that the Earth consists of three reservoir: the continental crust, the volume of mantle depleted in incompatible elements as a result of formation of this crust, and an undepleted, or primitive mantle (Figure 11.21). For any radioactive decay system we can write a series of mass balance equations. For the Nd isotope system, we assume that the bulk Earth has ϵ_{Nd} of so, so we may write:

$$\sum_j M^j C^j \epsilon_{Nd}^j = 0 \tag{11.1}$$

where M^j is the mass of the j^{th} reservoir, C^j is the concentration of Nd in that reservoir, and ϵ_{Nd}^j is the value of ϵ_{Nd} in that reservoir. We also assume the Sm/Nd is chondritic. We'll use $f_{Sm/Nd}$ to denote the relative deviation of the Sm/Nd ratio from the chondritic value, i.e.:

$$f_{Sm/Nd} = \frac{{}^{147}Sm/{}^{144}Nd - {}^{147}Sm/{}^{144}Nd_{CHUR}}{{}^{147}Sm/{}^{144}Nd_{CHUR}} \tag{11.2}$$

Then we may write a similar mass balance for the Sm/Nd ratio for the Earth:

$$\sum_j M^j C^j f_{Sm/Nd}^j = 0 \tag{11.3}$$

The mass balance for the Nd concentration is:

$$\sum_j M^j C_{Nd}^j = M^0 C_{Nd}^0 \tag{11.4}$$

where M^0 is the mass of the silicate Earth and C_{Nd}^0 in the concentration of Nd in the silicate Earth. Finally, the masses of our three reservoirs must sum to the mass of the silicate Earth:

$$\sum_j M^j = M^0 \tag{11.5}$$

Since the half-life of ${}^{147}Sm$ is long compared to the age of the Earth, we may use the approximation:

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$$e^{\lambda t} = \lambda t + 1$$

and hence:

$$^{143}\text{Nd}/^{144}\text{Nd} = ^{143}\text{Nd}/^{144}\text{Nd}_i + ^{147}\text{Sm}/^{144}\text{Nd} \lambda t \quad 11.6$$

The equation may be transformed into epsilon notation, in which case it becomes:

$$\epsilon_{\text{Nd}} \cong \epsilon_{\text{Nd}}^i + f_{\text{Sm}/\text{Nd}} Q t \quad 11.7$$

where ϵ_{Nd}^i is the initial value of ϵ_{Nd} (i.e., at $t = 0$), and Q and $f_{\text{Sm}/\text{Nd}}$ are defined as:

$$Q_{\text{Nd}} = \frac{10^4 \lambda ^{147}\text{Sm}/^{144}\text{Nd}_{\text{CHUR}}}{^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}} \quad 11.8$$

Q_{Nd} is a constant with a value of 25.13 Ga^{-1} .

Assuming that the crust has grown from primitive mantle, then

$$\epsilon_{\text{Nd}}^c = f_{\text{Sm}/\text{Nd}}^c Q T^c \quad 11.9$$

where T^c is the average age of the crust. If the Earth consists of only three reservoirs for Nd, namely the continental crust, depleted mantle, and primitive mantle, and if the depleted mantle and crust evolved from a reservoir initially identical to primitive mantle the mass balance equation 11.1, 11.3, and 11.4 must hold for crust and depleted mantle alone. In this case, these equations can be combined with 11.9 to derive a relationship between the mass of the crust and the mass of the depleted mantle:

$$M^{\text{dm}}/M^c = \left(\frac{C_{\text{Nd}}^c}{C_{\text{Nd}}^0} - 1 \right) - \left(\frac{C_{\text{Nd}}^c}{C_{\text{Nd}}^0} \right) \frac{Q f_{\text{Sm}/\text{Nd}}^c T^c}{\epsilon_{\text{Nd}}^{\text{dm}}} \quad 11.10$$

Thus the mass ratio of depleted mantle to crust can be calculated if we know the Sm/Nd ratio of the crust, the ϵ_{Nd} of the depleted mantle, and the concentration of Nd in the crust and in primitive mantle. Figure 11.22 is a plot showing the solutions of 11.10 as a function of T^c for various values of $\epsilon_{\text{Nd}}^{\text{dm}}$ obtained by DePaolo (1980). Most estimates of the average age of the crust are between 2 and 2.5 Ga, and $\epsilon_{\text{Nd}}^{\text{dm}}$ is about +10. Possible solutions for the ratio of depleted mantle to whole mantle are in the range of 0.3 to 0.5, i.e., somewhere between a third and a half of the mantle must be depleted to the point of having ϵ_{Nd} of +10 to create the continental crust. A number of similar mass balance calculations that included other isotopic systems as well were published between 1979 and 1980, all of which obtained rather similar results. We may conclude from this that the volume of depleted mantle must be substantial, occupying at the least much of the upper mantle.

Interestingly, the fraction of the mantle above the 660 km seismic discontinuity is roughly 0.33. Thus these mass balance calculations are consistent with the 660 discontinuity being a chemical boundary between upper and lower mantle. In this case, the lower mantle would appear to be chondritic, at least with respect to rare earth elements.

It is important to remember the assumptions that went into this calculation, in particular, that there are only 3 reservoirs of significance for the rare earths: the crust, the depleted mantle, and primitive mantle. If some other reservoir with a significant mass of rare earths and ϵ_{Nd} very different from 0 exists, then the calculated volume of the depleted mantle could be significantly larger or smaller than calculated above. Two reservoirs in particular cause concern in this respect: the first is the subcontinental lithosphere and the second is the region of the deep mantle that gives rise to mantle plumes (discussed below). At present, the mass of rare earths in the subcontinental lithosphere does not seem to be large enough to invalidate the assumptions made. The mantle plume source region

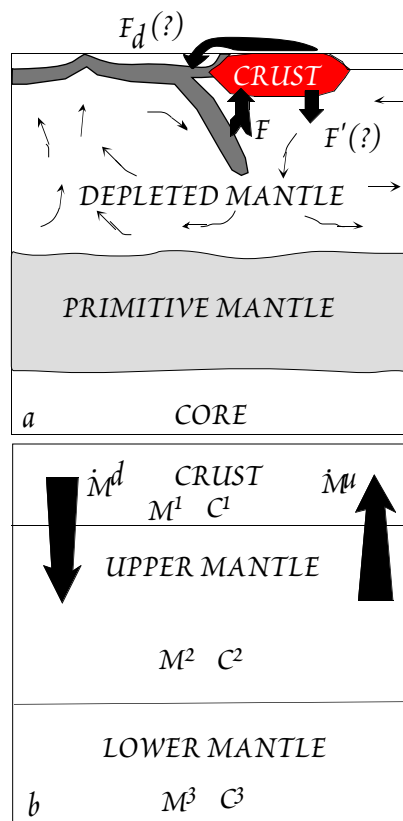


Figure 11.21. The three reservoir model of the mantle. The depleted mantle is the source of MORB and has $\epsilon_{\text{Nd}} = +10$, the lower mantle is primitive and has bulk Earth characteristics, e.g., $\epsilon_{\text{Nd}} = 0$.

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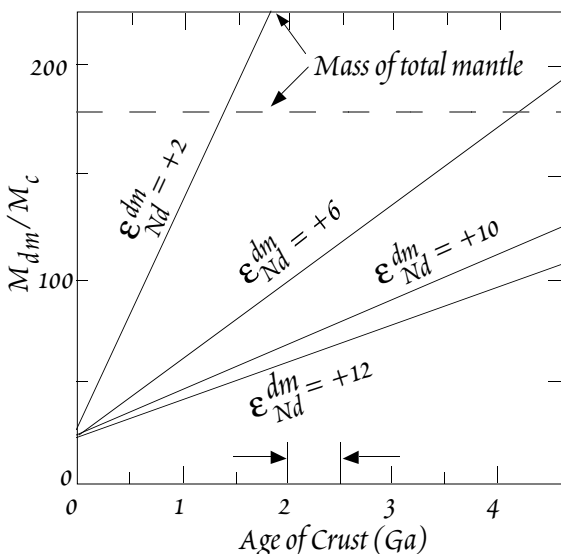


Figure 11.22. The relationship between ratio of mass of the depleted mantle to mass of the continental crust as a function of mean age of the crust calculated from equation 18.6 using various values of ϵ_{Nd} for the depleted mantle. The arrows at the bottom enclose the range of probable values for the mean age of the crust.

is also often assumed to be small, but this need not be the case. The present plume flux has been estimated by Sleep (1990) to be about 2.56×10^{17} g/yr (assuming an average excess temperature for plumes of 225° C). If material resides in some plume source layer (such as D'') for 10^9 yr for rising in a mantle plume, and if the plume flux is constant, then the mass of this plume source layer must be 2.5×10^{23} kg. This is ten times the mass of the crust. Thus if Sm and Nd concentrations in plumes are as much as 10% of the crustal concentration and this is included in the mass balance calculations above, the mass of the depleted mantle could be nearly twice as large as allowed by DePaolo's calculation. Thus these mass balance calculations must be viewed with some skepticism.

Nd isotope systematics are thus consistent with a fairly simple model of the mantle evolution: generation of the continental crust has depleted a third or more of the mantle. Some recycling of continental crust to the mantle can readily account for the apparent linear growth of ϵ_{Nd} in the mantle through time. Although difficult to document because initial Sr isotope ratios are poorly preserved due to the mobility of Rb and Sr, Sr isotope systematics appear to be consistent with this model, as

are Hf isotope systematics (though Hf isotopes suggest higher rates of recycling). However, Pb isotope systematics of the mantle and crust are not consistent with this simple picture, and hint at a much more complex evolution.

Pb isotope ratios do not seem to be consistent with such simple evolutionary models. As we pointed out in Chapter 8, Pb isotope ratios of MORB plot to the right of the Geochron, implying μ ($^{238}U/^{204}Pb$) has increased in the depleted mantle. From the incompatibilities of U and Pb, we would have expected this ratio to have decreased. Furthermore, a mass balance problem may exist since both the upper crust and the mantle have more radiogenic Pb than the bulk Earth, which must lie on the Geochron, and it is unclear whether this can be balanced by unradiogenic Pb from the lower crust alone.

Th isotope ratios in mid-ocean ridge basalts may point the way to a solution of the dilemma posed by Pb isotope ratios. As we saw in Chapter 8, the $^{230}Th/^{232}Th$ ratio in the young basalts is directly proportional to the $^{238}U/^{232}Th$ (κ) ratio in the mantle at the time the basalts were generated. Since this value of κ is derived from Th isotope ratios, we'll designate it as κ_{Th} . On the other hand, the ratio of radiogenic ^{208}Pb to ^{206}Pb is proportional to the time-integrated $^{238}U/^{232}Th$ (κ) ratio. Let's explore this a bit further.

We can write a radiogenic growth equation for both ^{208}Pb and ^{206}Pb :

$$^{208}Pb/^{204}Pb = ^{208}Pb/^{204}Pb_i + ^{232}Th/^{204}Pb(e^{\lambda_2 t} - 1) \tag{11.11}$$

rearranging:

$$^{208}Pb/^{204}Pb - ^{208}Pb/^{204}Pb_i = ^{232}Th/^{204}Pb(e^{\lambda_2 t} - 1) \tag{11.12}$$

The term on the left is the radiogenic ^{208}Pb , which we will designate as $^{208}Pb^*$. Thus:

$$^{208}Pb^*/^{204}Pb = ^{232}Th(e^{\lambda_2 t} - 1) \tag{11.13}$$

Designating the radiogenic ^{206}Pb as $^{206}Pb^*$, and analogous equation may be written for ^{206}Pb :

$$^{206}Pb^*/^{204}Pb = ^{238}U/^{204}Pb(e^{\lambda_8 t} - 1) \tag{11.14}$$

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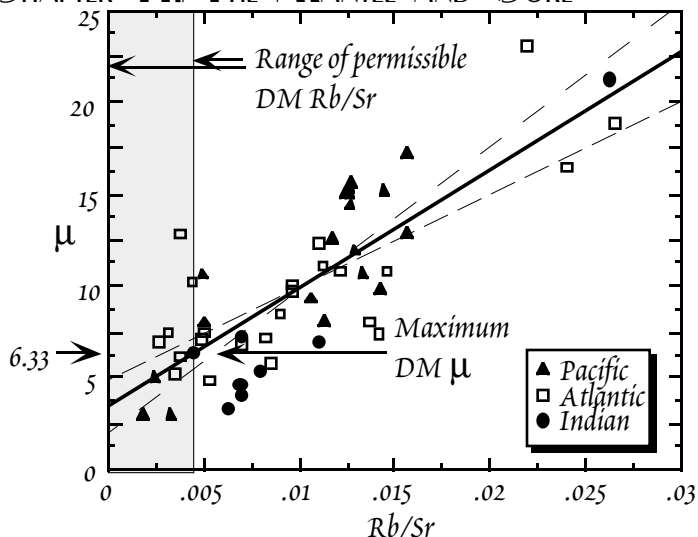


Figure 11.24. Correlation of Rb/Sr and μ ($^{238}\text{U}/^{204}\text{Pb}$) in MORB. Solid line is a regression line, dashed lines represent errors on the regression. The value of Rb/Sr in the depleted mantle must be lower than 0.0045, based on Sr isotope evolution. From the correlation, this implies $\mu < 6.33$. From White (1993).

$$\frac{^{208}\text{Pb}^*}{^{206}\text{Pb}^*} = \frac{^{208}\text{Pb}/^{204}\text{Pb} - 29.476}{^{206}\text{Pb}/^{204}\text{Pb} - 9.307} \quad 11.16$$

From the $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ ratio, we can calculate a time-averaged κ , which we denote as κ_{Pb} , by rearranging equation 11.15:

$$\kappa_{\text{Pb}} = \frac{^{208}\text{Pb}^* (e^{\lambda_{\text{st}}t} - 1)}{^{206}\text{Pb}^* (e^{\lambda_{\text{st}}t} - 1)} \quad 11.17$$

where t is now set to 4.55 Ga, the age of the Earth.

Galer and O’Nions (1985) compared values of κ_{Pb} with κ_{Th} in MORB. They found that the values of κ_{Th} averaged about 2.5, whereas the time-integrated ones averaged about 3.7. The value of κ in *Orgueil* (CI-1) is about 3.8, which they took as the primitive mantle value. The time-integrated value is barely lower than the primitive mantle value, and much higher than the present value. From this they concluded that Pb now in the depleted mantle could not have resided there for very long. In other words, the depleted mantle appears to be open to the flow of Pb, with both inputs and outputs. They calculated the residence time of Pb in the depleted mantle, the average time spent in the depleted mantle by an atom of Pb, to be about 600 million years.

As we saw earlier in this chapter, there is reason to believe the terrestrial value of κ may be somewhat higher than that in *Orgueil*, perhaps 4 or 4.2. However, with additional data, it appears the average value of κ_{Th} in MORB is lower than 2.5, perhaps about 2.2 (Figure 11.23). The residence time for Pb calculated using these parameters is about 1 Ga, which is still short compared to the age of the Earth.

Dividing 11.13 by 11.14, we have:

$$\frac{^{208}\text{Pb}^*}{^{206}\text{Pb}^*} = \frac{^{232}\text{Th}(e^{\lambda_{\text{st}}t} - 1)}{^{238}\text{U}(e^{\lambda_{\text{st}}t} - 1)} \quad 11.15$$

For any fixed time the exponential term is a constant, so that $^{208}\text{Pb}^*/^{204}\text{Pb}^*$ is proportional to the average κ over that time. Taking the initial isotope ratios to be the meteoritic values (i.e., Canyon Diablo troilite), we can calculate $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ as:

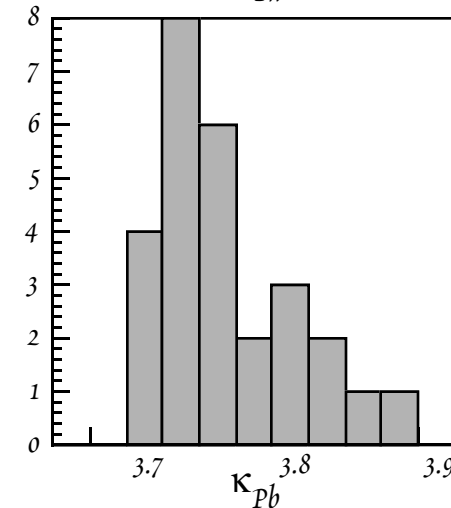
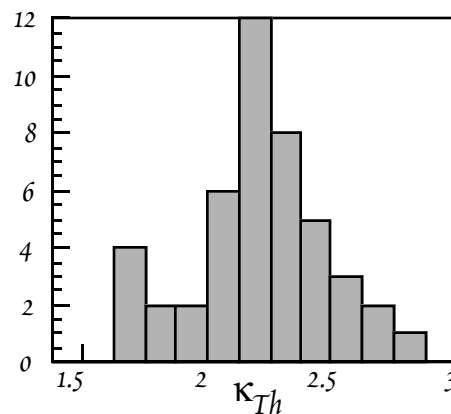


Figure 11.23. Comparison of κ_{Pb} and κ_{Th} in MORB. κ_{Pb} is the time-integrated value of κ calculated from Pb isotope ratios. κ_{Th} is the present value, calculated from the $^{230}\text{Th}/^{232}\text{Th}$ ratio. The time integrated value is much higher than the present value, implying Pb now in the depleted mantle could not have resided there for long.

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White (1993) addressed the question of the $^{238}\text{U}/^{204}\text{Pb}$ (μ) ratio in the depleted mantle, and concluded it was less than about 6, which is lower than the bulk Earth value of about 8. Unlike κ , μ cannot be calculated directly. It can, however, be constrained in several ways. Figure 11.24 illustrates one example. The Rb/Sr ratio in MORB is strongly correlated with μ . From the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in MORB, the maximum Rb/Sr ratio in the depleted mantle can be constrained to be less than 0.0045. Based on the correlation, the value of μ in the depleted mantle must be less than 6.33. The low present μ in the MORB contrasts with the time-integrated one deduced from the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio, the latter being about 9. This difference also leads to the conclusion that the Pb now in the depleted mantle could not have resided there for very long.

These results suggest a very different model for evolution of the upper mantle than the one based on Nd isotope ratios discussed above. They suggest that radiogenic isotope ratios and concentrations of incompatible elements are controlled not simply by the degree of depletion resulting from partial melting, but by the ratio of the flows into and out of the mantle. In other words, the mantle appears to be a *kinetically* controlled system rather than a thermodynamically controlled one. The large scale reservoirs on the surface of the Earth, such as the oceans and the atmosphere, are known to be kinetically controlled in this same sense. So this result should not be too surprising. It appears that the compositions of all large chemical systems on the Earth are controlled, at least in part, by kinetic factors.

If there is a flux of Pb and other elements into the depleted mantle, where is this Pb coming from? The continental crust can be easily ruled out as having inappropriate Pb isotope composition. A lower "primitive mantle", originally suggested by Galer and O'Nions (1985), can also be ruled out. White (1993) concluded mantle plumes were supplying this Pb. There are several reasons to believe this is the case. First, they have the appropriate isotopic composition. Second, only about 10% of the total plume flux is required to supply the necessary Pb to the depleted mantle. Third, if the suppositions that the depleted mantle occupies the uppermost mantle and that plumes come from deeper are correct, then plumes must transit the upper mantle, providing the opportunity to deliver Pb and other incompatible elements to it. Finally, numerous studies, particularly by J. G. Schilling and coworkers, have shown that plumes do mix with the depleted mantle. For example, Figure 11.25 shows the variation in Sr isotopes along the northern Mid-Atlantic Ridge. Regions of high $^{87}\text{Sr}/^{86}\text{Sr}$ extend hundreds of km outward from Iceland and Azores, reflecting mixing of these mantle plumes with the asthenosphere.

It is presumably this plume flux that buffers the ϵ_{Nd} of the depleted mantle as well. As we shall see below, mantle plumes may contain a significant component of recycled oceanic and continental crust. In a sense then, continental recycling may contribute to the flux of material into the depleted

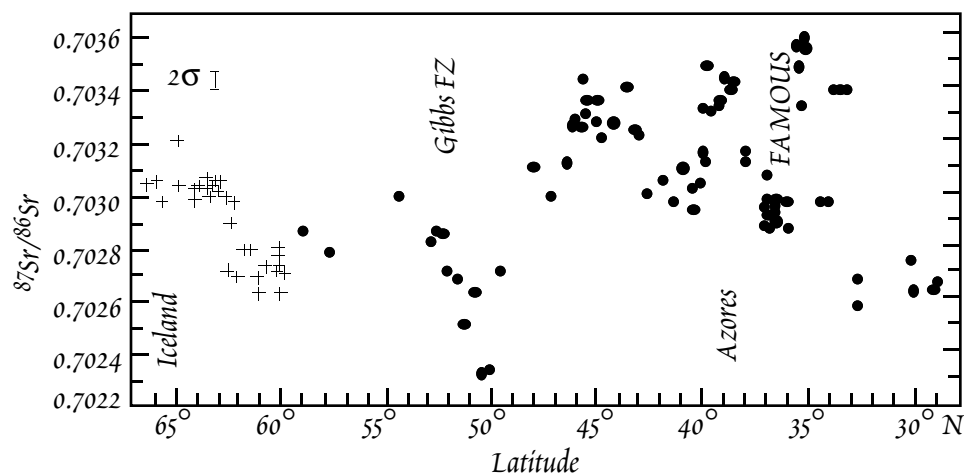


Figure 11.25. Sr isotope variations along the Mid-Atlantic Ridge. After White et al. (1976).

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upper mantle, although indirectly.

GEOCHEMICAL EVOLUTION OF MANTLE PLUME RESERVOIRS

As Figures 11.14 through 11.17 demonstrate, the geochemistry of OIB is more variable than that of MORB. Oceanic island volcanism is thought to be the surface manifestation of mantle plumes. Mantle plumes are columns of buoyant mantle that rise from the deep mantle. Exactly how deep is uncertain. Fluid dynamic experiments and numerical simulations indicate that they must arise from a thermal boundary layer (a region where heat is transported conductively rather than convectively). The only certain thermal boundary layer in the mantle is the base: the core-mantle boundary. If the thermodynamics of the phase change at 660 km prevents convection across the 660 km discontinuity, then it would be a thermal boundary layer as well. Thus plumes come either from the core-mantle boundary or the 660 km discontinuity. At present, most geophysicists and geochemists suspect it is the former.

There are clear systematic relationships in the geochemistry of plumes. White (1985) found that OIB could be divided into 4 distinct groups based on their Sr, Nd and Pb isotopic compositions. Thus though there are many mantle plumes and each is to some degree geochemically unique, there appear to be a much smaller number of geochemical reservoirs from which plumes are drawn. These groups, named St. Helena, Society, Kerguelen, and Hawaii for a type island, show distinctive correlations between isotope ratios or have distinctive isotopic compositions. For example, OIB of the St. Helena group, which encompasses the Austral Islands (Pacific), the Comores (Indian), and Ascension (Atlantic) as well as St. Helena (Atlantic), have Sr and Nd isotope ratios that plot below the main array (Figure 11.26), and their Pb isotopic compositions are very radiogenic. Indeed, all basalts with very radiogenic Pb ($^{206}\text{Pb}/^{204}\text{Pb} > 20$) plot within or close to the St. Helena field on a Sr-Nd isotope diagram. Similarly, islands of the Society group, which include the Azores (Atlantic), the Marquesas (Pacific), and Samoa (Pacific) as well as the Societies (Pacific), define a shallower Sr-Nd isotope correlation than do basalts from Kerguelen group islands, which include Tristan da Cunha (Atlantic), and Juan Fernandez (Pacific) as well as Kerguelen (Indian). The Kerguelen group OIB always have less radiogenic Pb than the Society group. Zindler and Hart (1986) subsequently renamed these groups as HIMU (St. Helena), EM I (Kerguelen), EM II (Societies), and these names are now more commonly used than the originals. The term HIMU comes from high- μ , as these basalts are characterized by high $^{206}\text{Pb}/^{204}\text{Pb}$. The term EM is an abbreviation for 'Enriched Mantle'. In addition,

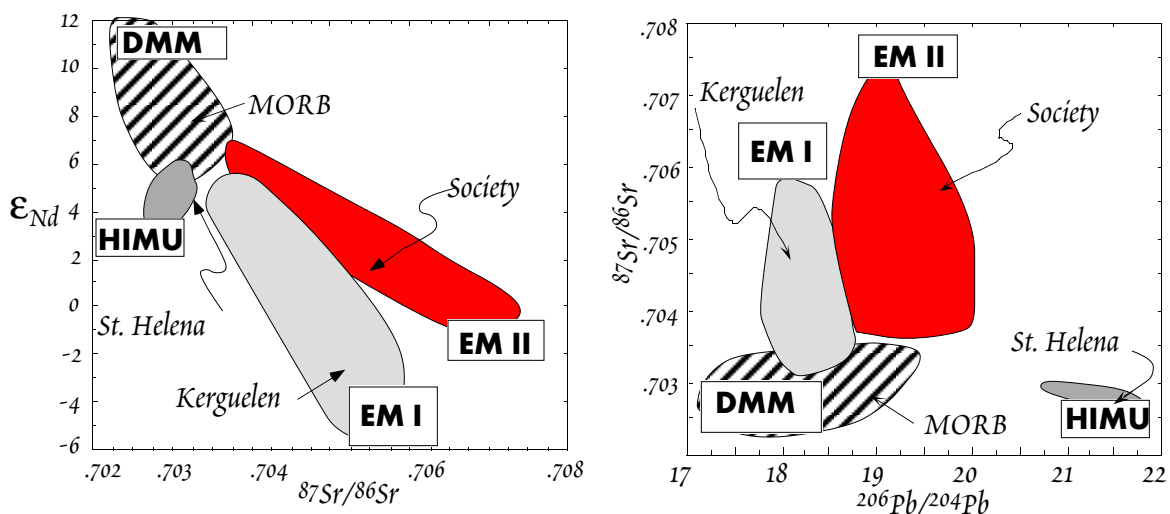


Figure 11.26. Isotopic classes of oceanic basalts of White (1985) and end-member compositions of Zindler and Hart (1986).

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White (1985) identified MORB as a distinct isotopic class, with which Zindler and Hart (1986) associated the component DMM (Depleted MORB Mantle).

Weaver (1991) found that there were systematic variations in trace elements between these classes of plumes. This is illustrated in Figure 11.27.

Determining how these distinct geochemical reservoirs have evolved is among the most vexing problems in mantle geochemistry. The principal observation to be explained is that mantle plumes invariably have less depleted isotopic signatures than MORB, and the isotopic compositions of some indicate net enrichment in incompatible elements. Initially, mantle plumes were thought to consist of primitive mantle (e.g., Schilling, 1973). Mixing between primitive and depleted mantle can explain the Sr and Nd isotopic compositions of some plumes, but virtually none of the Pb isotope data can be explained this way, nor are the trace element compositions of OIB consistent with plumes being composed of primitive mantle. Indeed, although 'primitive mantle' has proved to be a useful hypothetical concept, no mantle-derived basalts or xenoliths have appropriate compositions to be 'primitive mantle'. It is possible, and perhaps likely, that no part of the mantle retains its original, primitive, composition.

Hofmann and White (1982) suggested mantle plumes obtain their unique geochemical signature through deep recycling of oceanic crust (Figure 11.28). Partial melting at mid-ocean ridges creates oceanic crust that is less depleted in incompatible elements than the depleted upper mantle. The oceanic crust is apparently inevitably subducted as virtually none is preserved at the surface, so it clearly is recycled back into the mantle. The question is what becomes of it? Hofmann and White noted that once oceanic crust reaches depths of about 90 km it converts to eclogite as is more dense than peridotite. Because it is rich in Fe, and garnet-forming components, it remains denser than peridotite at all depths greater than 90 km (except, perhaps, just at the 660 discontinuity due to the negative Clapeyron slope). Thus it will sink to the base of the convecting region. If the mantle is chemically stratified, with a Fe-rich lower mantle, the oceanic crust would sink to a thermal boundary layer at the 660 discontinuity. If the entire mantle convects as a single unit, that is if it is not chemically stratified, ocean crust will sink to base of the mantle, becoming embedded in thermal boundary layer there (D''). Hofmann and White originally suggested radioactive heating would ultimately cause it to become buoyant. It now seems more likely that heat conducted into it from below, from either the lower mantle or the core, may be more important. In any case, upon sufficient heating, it rises, melting near the surface to create intraplate volcanos.

Sediment appears often, if not always, to be subducted along with the oceanic crust (we will discuss the evidence for this in the next chapter). This subducted sediment would also contribute to incompatible element enrichment of plumes. Varying amounts, types, and ages of subducted sediment

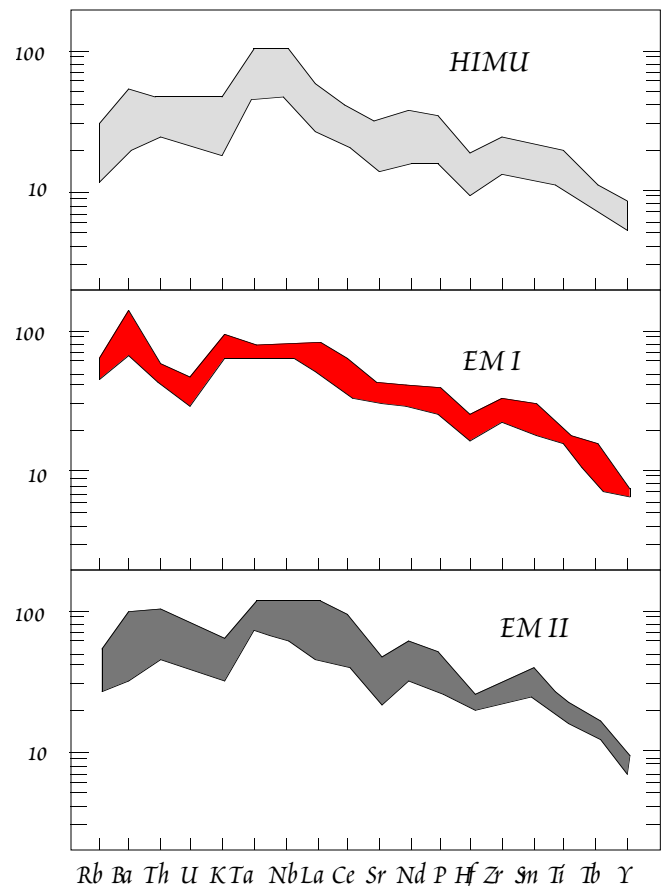


Figure 11.27. Spider diagrams showing differences in incompatible element enrichment among the various classes of oceanic basalts. After Weaver (1991).

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may be responsible for some of the geochemical variety displayed by plumes. Since sediment is ultimately derived from the continents, recycling of oceanic crust, continental crust, mantle plumes, and oceanic island basalts may all be part of a grand geochemical cycle. Tectonic erosion of continental crust in subduction zones and delamination of continental crust may be alternative mechanisms for deep recycling of continental crust.

Because the major element chemistry of OIB is often similar to that of MORB, it seems unlikely plumes could be composed entirely of recycled oceanic crust. Presumably they consist primarily of peridotite, with perhaps at most a few tens of percent oceanic crust. However, because the oceanic crust has much higher incompatible element concentrations than peridotite, it provides most of the isotopic and incompatible element "flavor" of plumes.

Trace elements provide some evi-

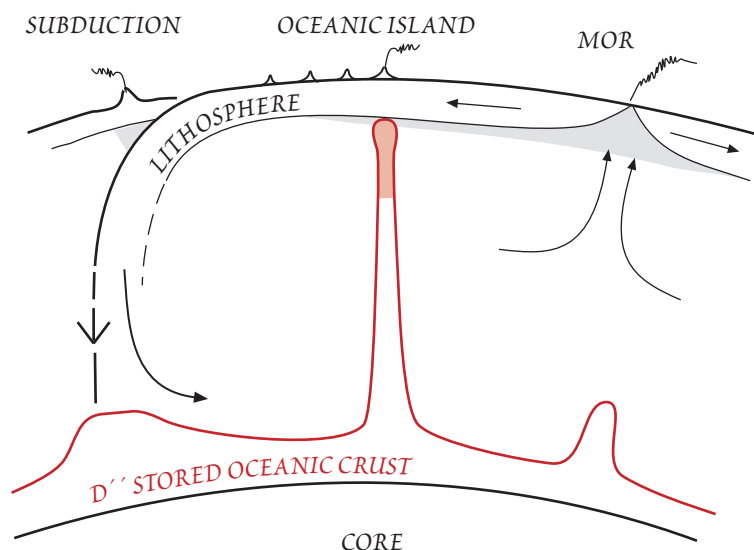


Figure 11.28. Cartoon illustrating the oceanic crustal recycling model of Hofmann and White (1982). Oceanic crust is transformed into eclogite and post-eclogite assemblages upon subduction. It separates from the less dense underlying lithosphere and sinks to the deep mantle where it accumulates. Eventually, it becomes sufficiently hot to form plumes that rise to the surface, producing oceanic island volcanism. After Hofmann and White (1982).

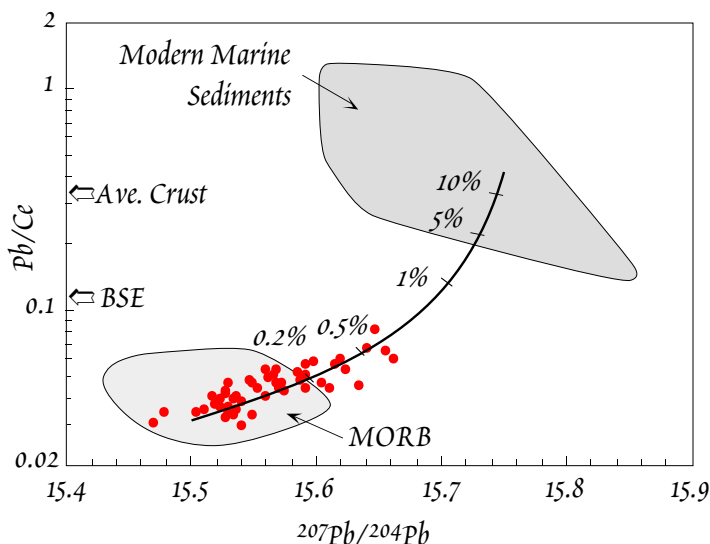


Figure 11.29. Pb/Ce and $^{207}\text{Pb}/^{204}\text{Pb}$ in basalts from the Societies Islands studied by White and Duncan (in press). A calculated mixing line between depleted mantle and sediment passes through the data. Also shown are estimated Pb/Ce ratios of average continental crust and bulk silicate Earth (BSE).

dence that some plumes contain a recycled sediment component. The Pb/Ce ratio is particularly useful indicator of the presence of sediment for several reasons. First, the Pb/Ce ratio is comparatively uniform in MORB and many OIB. Second, the Pb/Ce ratio is an order of magnitude higher in sediments than in the mantle (typically, Ce/Pb is greater than 0.3 in sediments and <0.04 in MORB). Third, sediments have two orders of magnitude higher concentrations of Pb (typically 20 ppm or more) than the mantle (less than 0.05 ppm), so that addition of even small amounts of sediment to mantle shifts the Pb/Ce ratio. Finally, the near constancy of Pb/Ce in most basalts suggests this ratio is not significantly changed in by magmatic processes such as partial melting and fractional crystallization. There is a strong correlation between isotope ratios and Pb/Ce

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in basalts from the Society Islands. As Figure 11.29 shows, the correlation is consistent with mixing between recycled sediment and mantle.

An alternative origin for mantle plumes was proposed by McKenzie and O'Nions (1983). They noted the common evidence for incompatible element enrichment in the subcontinental lithosphere (which we discuss in the next section) and suggested this material may occasionally become delaminated. Because it is cold, it would also sink to the deep mantle. As in the case of the Hofmann and White model, it would be stored in a thermal boundary layer, heated, and rise in the form of mantle plumes. However, recent studies have shown that the Os isotope composition of the subcontinental lithosphere is quite distinctive, and quite different from that of mantle plumes, as we shall see in the next section. This rather strongly suggests that "delaminated" subcontinental lithosphere does not contribute to mantle plumes. Because mantle plumes come in several geochemical varieties, it is possible that both mechanisms operate. Indeed, other as yet unknown processes may be involved as well.

Most oceanic islands show some variability in their isotopic compositions, defining elongated arrays on plots of isotope ratios. Such elongated arrays suggest mixing. This raises the rather obvious question of what is mixing with what. In a few cases, the Comores are a good example, the elongate arrays seems to reflect mixing between different plume reservoirs. The Comores data defines a trend in isotopic space that appears to be the result of mixing between an EM1 and a HIMU component. In other cases, such as the Galapagos, the plume is clearly mixing with the depleted upper mantle. However, in many cases, the cause of the isotopic variation is less clear.

Hart et al. (1992) plotted oceanic basalt isotope data in three dimensions, with axes of $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, and $^{206}\text{Pb}/^{204}\text{Pb}$ (Figure 11.30). Principal component analysis confirmed that 97.5% of the variance in the oceanic basalt isotope data could be accounted for by these ratios (leaving 2.5% to be accounted for by $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, and $^{176}\text{Hf}/^{177}\text{Hf}$). They found that most of the data plotted within a tetrahedron defined by the hypothetical end members EM1, EM2, HIMU, and DMM. They also noticed that many arrays were elongated toward the base of this tetrahedron on the DMM-HIMU join. From this they concluded that in many, if not most cases, mantle plumes appear to mixing with a previously unidentified component, which they named "FOZO" (an acronym for Focal Zone), that has the approximate isotopic composition of $^{87}\text{Sr}/^{86}\text{Sr} = 0.7025$, $\epsilon_{\text{Nd}} = +9$, and $^{206}\text{Pb}/^{204}\text{Pb} = 19.5$. They suggested that FOZO is the isotopic composition of the lower mantle and that plumes rising from the core mantle boundary entrain and mix with this lower mantle material. It is unclear, however, whether such a composition for the lower mantle can be fitted to reasonable isotopic mass balances for the Earth. A rather similar idea was presented by Farley et al. (1992), who point out that this additional component, which they called "PHEM", seems to be associated with high $^3\text{He}/^4\text{He}$. White (1995) concurred with these ideas, but argued that the $^{87}\text{Sr}/^{86}\text{Sr}$ of FOZO is higher, and the ϵ_{Nd}

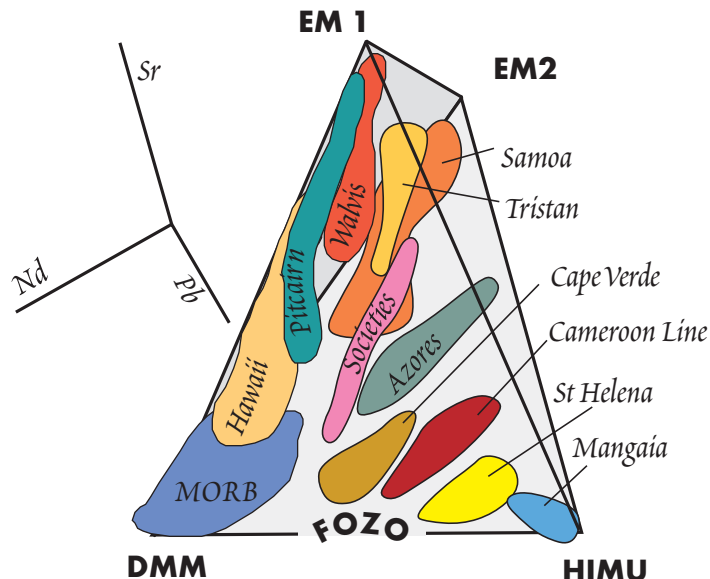


Figure 11.30. Three dimension plot of $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, and $^{206}\text{Pb}/^{204}\text{Pb}$. Most oceanic basalt data plot within a tetrahedron defined by the composition of EM1, EM2, HIMU, and DMM components. Oceanic islands and island chains tend to form elongate isotopic arrays, many of which seem to point toward a focal zone (FOZO) at the base of the tetrahedron. Adapted from Hart et al. (1992).

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lower, than estimated by Hart et al. (1992) and probably closer to the values chosen by Farley et al. (1992).

If Hart et al. (1992) are correct, this may explain why the isotopic composition of some volcanos, notably those of Hawaii and the Society Islands, change over time. Hawaiian volcanos commonly go through several evolutionary stages: a shield-building stage, during which the volcanic edifice is rapidly constructed and a relatively uniform tholeiitic basalt is erupted, followed by a late stage, during which eruption rates drop dramatically and composition shift to alkali basalt, and, following a significant hiatus in activity, a post-erosional stage in which small volumes of basanite and nephelinite are erupted. These latter magmas types are thought to be produced by small degrees of melting. Through this sequence, isotope ratios evolve, with $^{87}\text{Sr}/^{86}\text{Sr}$ decreasing and ϵ_{Nd} increasing (e.g., Chen and Frey, 1985).

White and Duncan (1996) observed a similar pattern in volcanos of the Society Islands. They argued that this evolution in isotopic composition reflects the passage of the volcano over a compositionally zoned mantle plume (Figure 11.31). The most incompatible element enriched material, which is also the hottest, is located in the center, and formed the core of the plume. This is surrounded by a sheath of material that is viscously entrained by the plume as it rises. It is cooler and also not as enriched in incompatible elements. When the volcano is over the core of the plume, the degree of melting is high, giving rise to tholeiitic basalt with high $^{87}\text{Sr}/^{86}\text{Sr}$ and high eruption rates during the shield building stage. When the volcano is over the sheath, the extent of melting is smaller, producing small volumes of nephelinite with low $^{87}\text{Sr}/^{86}\text{Sr}$.

There is also a geographic pattern to both the distribution of mantle plumes and their isotopic compositions. Mantle plumes appear to be preferentially located within regions of slow lower mantle seismic velocities, as may be seen in Figure 11.32. There are two areas where isotopic compositions are particularly extreme (e.g., high $^{87}\text{Sr}/^{86}\text{Sr}$), one in the southeastern Indian Ocean and South Atlantic, the other in the central South Pacific (Hart, 1984; Castillo, 1989). The anomaly in the Indian Ocean is called the DUPAL anomaly, while that in the South Pacific is called the SOPITA anomaly. Interestingly enough, both anomalies close to regions where lower mantle seismic velocities are particularly slow (Figure 11.32), which indicate low densities. The low density in turn implies that these are regions of high temperatures in the lower mantle. While the exact significance of this remains unclear, it does establish a connection with oceanic island volcanism and lower mantle properties, strengthening the plume hypothesis, and favoring a lower mantle origin for plumes.

There is still much to understand about the nature and evolution of the mantle. Many of the ideas presented here will undoubtedly evolve in the future and new studies pro-

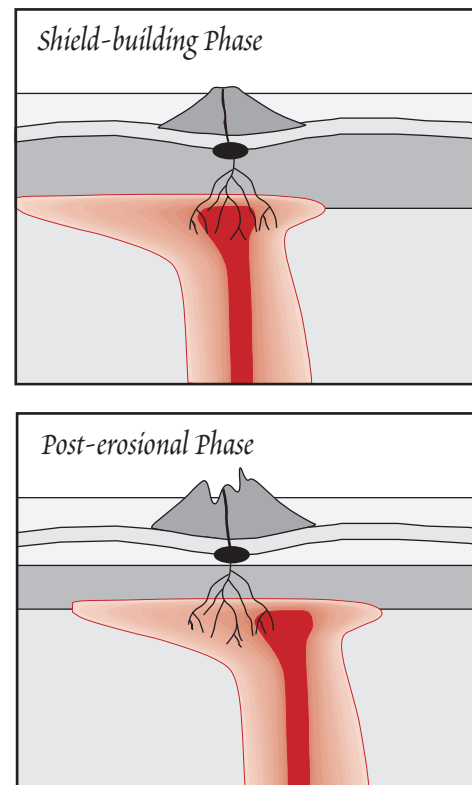


Figure 11.31. Cartoon of a model that explains why isotopic signatures of magmas become more "depleted" as volcanos evolve. During the "shield-building stage" the time of most vigorous growth, the volcano is located directly over the plume, and magmas are derived from the hot core of the plume, which has enriched isotopic signatures (high $^{87}\text{Sr}/^{86}\text{Sr}$, low ϵ_{Nd}). Because of lithospheric plate motion, the volcano will be located over the edge of the plume during later stages, such as in the post-erosional stage. During this stage magmas are derived from the viscously entrained sheath, which has more "depleted" isotopic signatures. After White and Duncan (1996).

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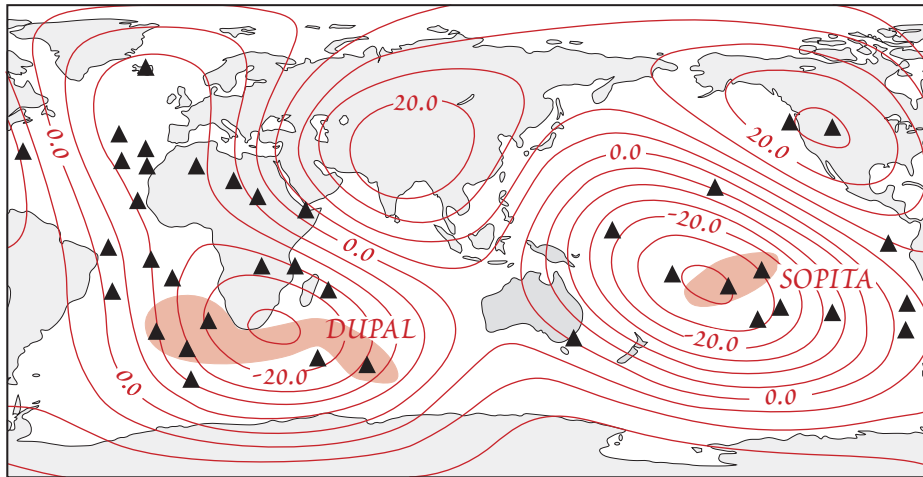


Figure 11.32. Map showing the distribution of mantle plumes (triangles), P-wave velocity anomalies (m/sec) averaged over the whole lower mantle (red lines), and location of the DUPAL and SOPITA isotope anomalies (pale red regions). Mantle plumes are located in regions of slow lower mantle seismic velocities, implying high temperatures. The DUPAL and SOPITA anomalies are located near seismic velocity minima. After Castillo (1989).

vide new insights into the workings of the mantle.

THE SUBCONTINENTAL LITHOSPHERE

Figure 11.33a shows Sr and Nd isotopic variations in continental basalts. The data span a much larger range than oceanic basalts. Some, but not all, of this variation reflects the effects of assimilation of continental crust on the isotopic signatures of the mantle-derived magmas. Assimilation effects can be avoided by considering only the data on peridotite xenoliths in continental basalts, the data for which is shown in Figure 11.33b. As may be seen, the range of values is reduced, but nevertheless much greater than that observed in oceanic basalts. One needs be cautious in directly comparing the heterogeneity observed in xenolith data to basalt data because the two represent different scales of sampling of the mantle. Basalts are created by melting of regions that have characteristic scales of tens of kilometers, and perhaps greater in some cases. The magma generation process undoubtedly averages out very small scale heterogeneities. Xenoliths, on the other hand, have characteristic dimensions of centimeters. Thus variations in isotope ratios in basalts reflect large scale heterogeneity in the mantle, while xenoliths reflect small scale heterogeneity. Despite this, it appears that the subcontinental lithosphere is more heterogeneous, even on relatively large scales, than is the suboceanic mantle.

It appears that the subcontinental mantle can be quite old, and often has the same age as the crust it underlies. Studies of xenoliths and inclusions in diamond from South African kimberlites suggests the mantle is 3–3.5 Ga old in this region, ages similar to that of the South African craton. The greater isotopic heterogeneity of the subcontinental lithosphere probably reflects its long term stability, which allows variations in parent-daughter ratios to be expressed in variations in radiogenic isotope ratios. Convective mixing in the suboceanic mantle will tend to destroy heterogeneity in the suboceanic mantle.

Though many xenoliths have isotopic compositions indicating incompatible element enrichment, others xenoliths show parts of the subcontinental lithosphere can be extremely incompatible element depleted. ϵ_{Nd} values of +500 have been recorded in garnets in eclogites from the Roberts Victor mine kimberlite. These eclogites appear to be rafts of subducted oceanic crust stranded in the subcontinental lithosphere over 3 Ga ago, an interpretation supported by highly variable oxygen isotope ratios in the eclogites. They apparently suffered extreme LRE depletion around that time, perhaps by a

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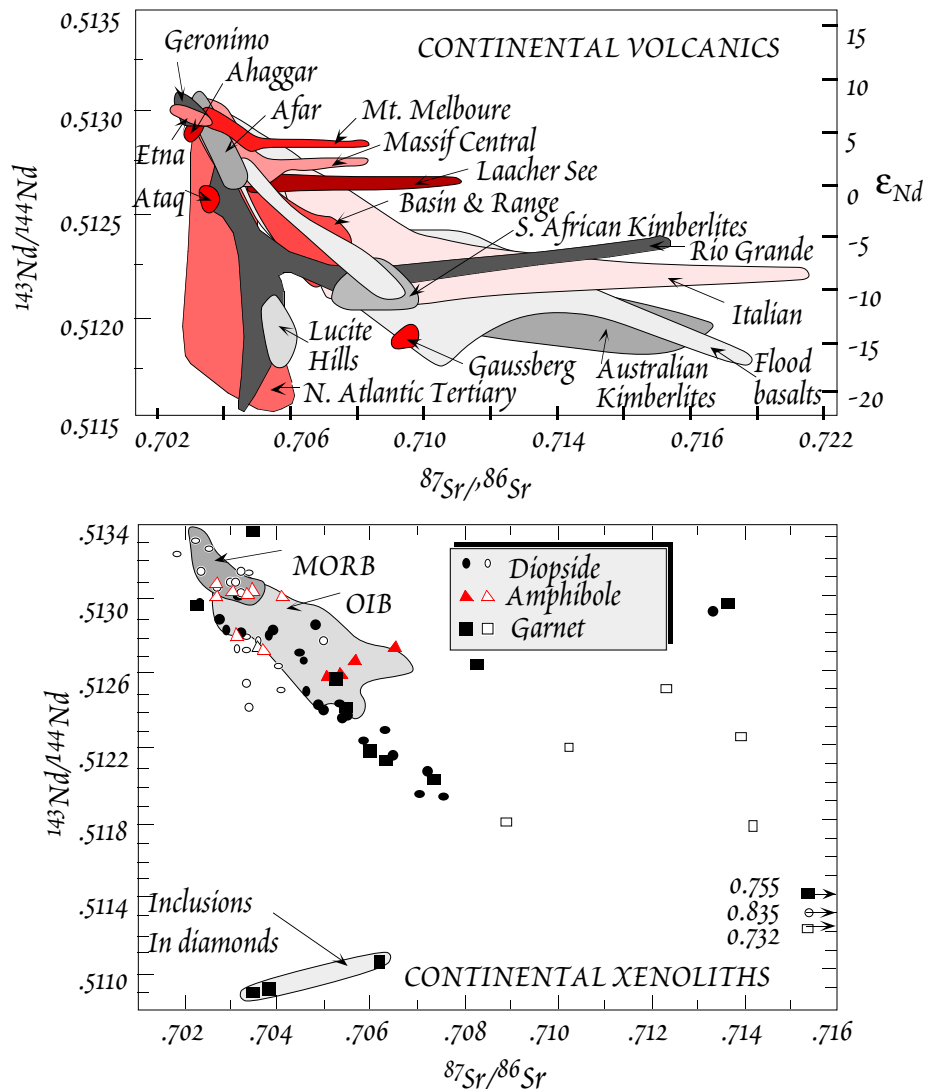


Figure 11.33. (a) top. Sr and Nd isotope ratios in continental basalts. (b) bottom. Sr and Nd isotope ratios in xenoliths in continental basalts. After Zindler and Hart (1986).

small degree of melting or dehydration after subduction. Much of the subcontinental lithosphere may consist of mantle from which partial melts have been extracted to form the continental crust. Interesting, when the upper mantle undergoes melting both the melt and residual solid will have a density that is less than the original material. This residue is less dense is because garnet, a very dense phase, is preferentially removed during melting. Thus both the crustal and mantle parts of the continental lithosphere have relatively low density, which may help to explain its stability.

If the subcontinental lithosphere is residual material from which melts have been extracted, why are xenoliths and basalts with “enriched” isotopic signatures so common? What process or processes could have produced this incompatible element enrichment of many parts of the subcontinental lithosphere? One possibility, first suggested by Brooks et al. (1976), is that partial melts from mantle plumes migrate upward into the lithosphere, where they freeze. The extent to which upwelling mantle can melting will depend on the depth to which it rises. Where continental lithosphere pre-

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vents plumes from rising above 200 km depth or so, the degree of melting is likely to be quite small, meaning the melts would be quite incompatible element enriched. These melts could then migrate upward into the lithosphere, reacting with it and enriching it in incompatible elements. Yet another possibility is that hydrous fluids released during dehydration of subducting oceanic lithosphere may migrate into the continental lithosphere and react with it (Hawkesworth, 1990). Judging from studies of island arc magmas (Chapter 12), such fluids appear to be particularly enriched in soluble incompatible elements, such as the alkalis and alkaline earths. These processes in which lithosphere reacts with melts or fluids is known as *mantle metasomatism**. Petrographic studies of some xenoliths clearly reveal features, such as the secondary growth of hydrous minerals such as phlogopite (Mg-rich mica) and richterite (an alkali-rich amphibole) indicative of such metasomatism.

Recent studies of Os isotope ratios in xenoliths from the subcontinental lithosphere have been particularly enlightening. Most xenoliths derived from below regions of old continental crust have low Os isotope ratios, which imply that low Re/Os ratios were established long ago. The low Re/Os ratios are consistent with the idea that this material undergone partial melting in the past, since Re is moderately incompatible, and would partition into the melt, while Os is highly compatible, and would remain in the solid. Despite their low $^{187}\text{Os}/^{188}\text{Os}$ ratios, many of these same xenoliths have quite low ϵ_{Nd} (Figure 11.34). The low ϵ_{Nd} suggests incompatible element enrichment, and hence would appear to be inconsistent with the high $^{187}\text{Os}/^{188}\text{Os}$ ratios (Figure 11.34). The explanation of this paradox appears to be that Os is was not affected by the metasomatism that enriched these regions in incompatible elements and decreased Sm/Nd ratios (e.g., Carlson and Irving, 1994). Apparently, neither Re nor Os are transported effectively by metasomatic fluids. If the fluids are aqueous, this is perhaps not surprising, since these elements have low solubilities under reducing conditions. If the fluids are silicate melts, it is unclear why they do not transport Re. The answer may have to do with dependence of the Re partition coefficient on composition and oxygen fugacity.

Regardless of why it arises, these unusual Os-Nd isotope systematics provide the continental lithosphere with a distinctive isotopic signature, and geochemists a means of identifying continental lithosphere. In an earlier section, we discussed the hypothesis of

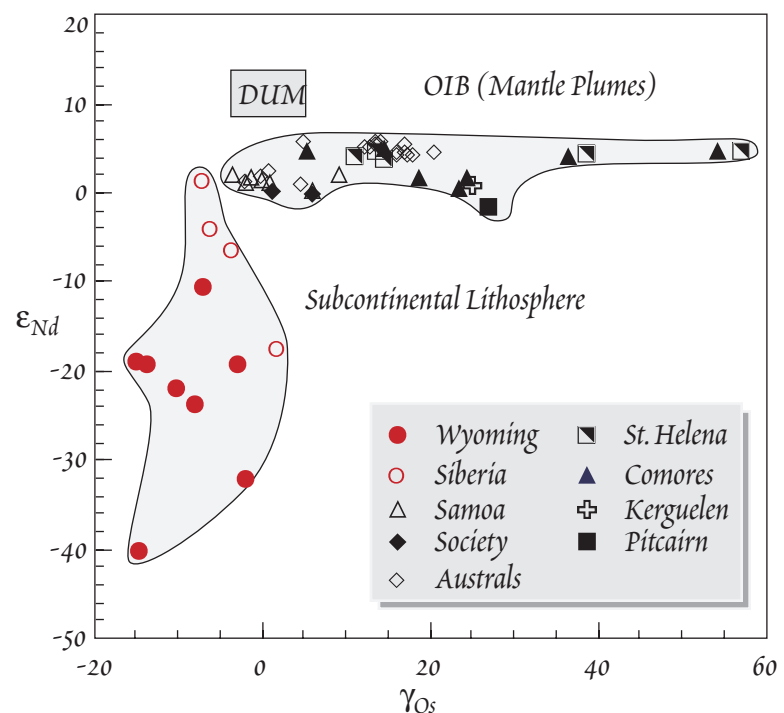


Figure 11.34. ϵ_{Nd} vs. γ_{Os} in xenoliths from the subcontinental lithosphere and oceanic island basalts. Despite low and variable ϵ_{Nd} , the subcontinental lithosphere appears to be characterized by systematically low γ_{Os} (γ_{Os} is the percent deviation of the $^{187}\text{Os}/^{188}\text{Os}$ ratio from the chondritic value).

* Metasomatism is defined in metamorphic petrology as a subsolidus process that results in a net change in the composition of the metamorphic rock. Usually this is accomplished by the flow of aqueous solutions through the rock. The term 'mantle metasomatism' is widely used to refer to reaction between rock and silicate liquid as well as between rock and aqueous solution.

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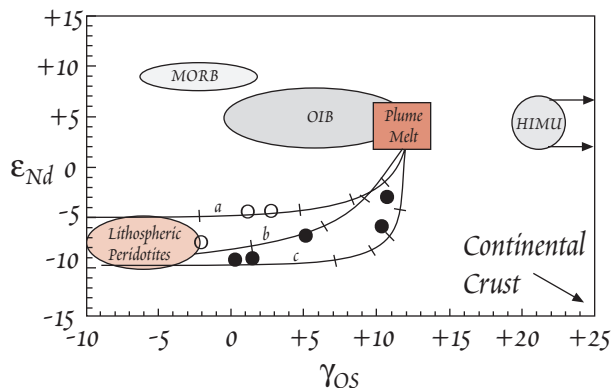


Figure 11.35. ϵ_{Nd} of picritic basalts from the Karroo flood basalts plotted against γ_{Os} . The fall between the fields. Three lines, illustrating 3 mixing models (different concentrations of Os and Nd in the end-members), connect the fields of xenoliths from the subcontinental lithosphere and oceanic island basalts (i.e., mantle plumes). The data fall close to these lines, suggesting they are mixtures of melts of lithosphere and a mantle plume. After Ellam et al. (1992).

America were rifting. These observations have given rise to the idea that continental flood basalts are produced when new mantle plumes arrive at the surface. Fluid dynamic experiments and simulations show that new plumes will have large bulbous heads. When the heads arrive in the upper mantle, they melt, producing a pulse of volcanism. Others, however, have argued on geochemical grounds that continental flood basalts are produced by melting of the continental lithosphere. Because mantle plumes and continental lithosphere have such different Os and Nd isotope signatures, Os-Nd systematics provide a means of discriminating between these possibilities. Because of the difficulties in determining Os isotope ratios in basalts, only one such study has been carried out thus far. In it, Ellam et al. (1992) found that the Karroo flood basalts, erupted in South Africa 190 million years ago, have Os and Nd isotope compositions that lie on mixing lines connecting mantle plume compositions and continental lithosphere compositions (Figure 11.35). Thus at least in this case, then both a mantle plume and continental lithosphere appear to have contributed to the magmas. The data also demonstrate the assimilation of continental crust cannot explain the low ϵ_{Nd} observed in these basalts.

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McKenzie and O'Nions that subcontinental lithosphere can delaminate and sink to the bottom of the mantle where it is incorporated into mantle plumes. The distinctive isotope signatures of mantle plumes on the one hand and subcontinental lithosphere on the other (Figure 11.34) is inconsistent with this hypothesis.

Continental flood basalts provide another interesting example. These are huge outpouring of basaltic lava that apparently occurred within relatively short time intervals, a few million years and possibly less in some cases. The great oceanic plateaus, such as Ontong-Java and Kerguelen are the marine equivalents. A number of continental floods basalts can be clearly associated with mantle plumes. For example, the Deccan Traps erupted 65 million years ago when India lay directly over the Reunion mantle plume, and the Parana in Brazil and Etendeka in Namibia were erupted 130 million years ago over the Tristan da Cunha mantle plume when Africa and South

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PROBLEMS

1. Assuming the Earth has a CI chondritic composition, and using the values for the mass of the core and the mass of the mantle in Table 11.1 and the partition coefficients in Table 11.4, calculate what the concentrations of Re, Ir, Mo, and Ag should be in the bulk silicate Earth if the core formed by an equilibrium process. Compare your results with the primitive mantle values in Table 11.3.
2. Calculate new bulk silicate Earth concentrations of Re, Ir, Mo, and Ag by adding 1% CI chondritic material to your results from Problem 1. Again compare these results with primitive mantle values of Table 11.3.
3. Assume that the bulk silicate Earth has a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.705, and Sr concentration of 20 ppm. Calculate the bulk silicate Earth Rb/Sr ratio.

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4. Suppose a rising mantle plume is 220° hotter than surrounding mantle and that the γ -olivine–Mg-perovskite transition occurs at 600 km depth in the surrounding mantle. Assume a homogeneous mantle density of 3.5 g/cc at 660 km and above. At what depth does the γ -olivine–Mg-perovskite transition occur within the mantle plume?
5. Whether the γ -olivine–Mg-perovskite transition is endothermic or exothermic will affect mantle convection (i.e., sinking of lithospheric slabs, rise of mantle plumes). Discuss why this is so, explaining the effects of both endothermic and exothermic phase transitions on rising mantle plumes and sinking lithospheric slabs.

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Geochemistry