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1. On the extract of the chart of the nuclides below, identify the mode of origin (S, R, or P process) of the stable isotopes of W, Re, Os, and Ir by writing S, R or P in the box for each (remember, some nuclides can be created by more than one process). Identify those isotopes you feel should be most abundant and those least abundant. On the chart below, mass numbers are given for only the stable isotopes. As a start, assume the S-process path starts at ^{181}Ta . Assume the unstable isotopes will decay before capturing a neutron during the S-process.

- One calcium-aluminum inclusion in the *Allende* meteorite has $\delta^{26}\text{Mg}$ values which imply a $^{26}\text{Al}/^{27}\text{Al}$ ratio of 0.46×10^{-4} at the time of its formation. A second inclusion apparently formed with a $^{26}\text{Al}/^{27}\text{Al}$ ratio of 1.1×10^{-4} . The half-life of ^{26}Al is 7.2×10^5 years. Assuming both these inclusions formed from the same cloud of dust and gas and that the $^{26}\text{Al}/^{27}\text{Al}$ ratio in this cloud was uniform, what is the time interval between formation of the two inclusions?
- Assuming that the oxygen in CV chondrites is a mixture of oxygen having an oxygen isotope composition lying on the terrestrial fractionation line in Figure 10.29 and pure ^{16}O , how much ^{16}O would have to be added to oxygen lying on the terrestrial fractionation line to reproduce their oxygen isotopic composition?
- Using the partition coefficients in Table 7.5, estimate the fraction of plagioclase that would have to fractionally crystallize from a lunar magma ocean to produce the Eu anomaly of KREEP shown in Figure 10.38. (*Hint: concern yourself only with the Eu/Sm ratio.*)
- Make a plot of the log of the fraction of Os condensed from a gas of “solar” composition as a function of temperature (e.g., a plot similar to Figure 10.34). Assume a total pressure of 10^{-4} atm, ΔH_v° of 738 kJ/mol, ΔS_v° of 139 J/mol, and the solar system abundances in Table 10.2. Assume the solid is pure Os metal. (*Hint: about 50% will be condensed at 1737 K.*)

Chapter 11

Geochemistry of the solid Earth

11.1 INTRODUCTION

Having considered the Earth's formation in the last chapter, let's now use the tools of geochemistry we acquired in the first eight chapters to consider how the Earth works. The Earth, unlike many of its neighbors, has evolved over its long history and it remains geologically active. Four and a half billion years later, it is very different place than when it was first formed. Certainly one of the main objectives of geochemistry is to understand this activity and unravel this history.

The solid Earth consists of three distinct layers: crust, mantle, and core. As Table 11.1 shows, these layers become progressively denser with depth, reflecting a stable density stratification of the planet (one shared by the other terrestrial planets). Unfortunately, only the shallowest of these layers, the crust, is accessible to direct study. The crust may well be the most interesting part of the planet, but it represents less than half a percent of its mass. Even most of the crust is out of reach; the deepest boreholes drilled in the continental crust, which is 35 km thick on average, are only 12 km deep; the deepest borehole in oceanic crust, which is on average 7 km thick, is only 1.5 km deep. Thus study of the solid Earth necessarily relies on indirect approaches and on rare samples of deeper material brought to the surface through geologic processes.

We'll begin by considering the geochemistry of the mantle because it represents the

largest fraction of the Earth, both by mass (67%) and volume (88%). Although remote, the mantle is important for a number of reasons. For one, the crust has been formed from it. For another, convection within the Earth's mantle drives most tectonic activity that affects us on the surface, including plate motions, earthquakes, and volcanoes. We'll next consider the core. As we found in the previous chapter, the core formed quite early – more or less simultaneously with formation of the Earth itself. While we do have a few samples of the Earth's mantle, we have none at all from the core, so its composition and history must be inferred entirely indirectly. Lastly, we'll consider the Earth crust – the part of the Earth we inhabit and are most familiar with. The crust, particularly the continental crust, is the most varied, and arguably the most interesting, part of our planet. We'll find that the continental crust, unlike the core which is as old as the Earth itself, has grown through geologic time through magmatism. The crust, particularly the continental crust, is where the geologic history of the planet is preserved.

11.2 THE EARTH'S MANTLE

Parts of the mantle are occasionally thrust to the surface as so-called alpine peridotites; fracture zones in the oceanic crust also occasionally expose mantle rocks. And volcanic eruptions sometimes carry small pieces of the mantle to the surface as *xenoliths*. Nevertheless, much

Table 11.1 Volumes and masses of the Earth's shells.

	Thickness (km)	Volume 10^{12} km^3	Mean density kg/m^3	Mass 10^{24} kg	Mass percent
Atmosphere				0.000005	0.00009
Hydrosphere	3.80	0.00137	1026	0.00141	0.024
Crust	17	0.0087	2750	0.024	0.4
Mantle	2883	0.899	4476	4.018	67.3
Core	3471	0.177	10915	1.932	32.3
Whole Earth	6371	1.083	5515	5.974	100.00

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, electrical conductivity, and seismic velocity. Another indirect method of study is examination of volcanic rocks produced by partial melting of the mantle. Finally, cosmochemistry provides an important constraint on the composition of the Earth.

The mantle was once viewed as being homogenous, 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.

The crust has been created by extraction of partial melts from the mantle (i.e., volcanism), a process that has continued over the Earth's entire history. For the major elements, crust formation affects the composition of the mantle only slightly because the volume of the crust is so small. For example, if the SiO_2

concentration in the mantle were originally 45%, extraction of continental crust containing an average of 60% from that mantle would reduce the SiO_2 concentration in the mantle only to 44.6%. Of course, extraction of partial melt undoubtedly has changed the major element composition of the mantle *locally*, as we will see in subsequent sections of this chapter. Furthermore, the concentrations of highly incompatible elements in the mantle have changed significantly as a result of formation of the crust. The idea that the core and the mantle segregated very early and the crust formed subsequently gives rise to the notion of a *primitive mantle* composition. This composition is the composition of the mantle before the crust was extracted from it. It is identical to the composition of the crust plus the mantle. Thus, the terms *primitive mantle composition* and *bulk silicate Earth composition* (BSE) are synonymous. One of the objectives of this chapter will be to estimate this composition.

In attempting to assess this composition, we have essentially three kinds of constraints. The first is *geophysical*: geophysical measurements of moment of inertia and seismic wave velocities allow us to constrain the density, compressibility, and rigidity of the mantle, which in turn constrains its composition. The second is *cosmochemical*: the Earth formed from the solar nebula, which has a chondritic composition for condensable elements, and therefore the composition of the Earth should relate in some rational way to the composition of chondrites. Finally, the mantle can be directly sampled locally where it is tectonically exposed or where small pieces are carried to the surface by volcanic eruptions and indirectly through volcanism. Most lavas erupted on the surface of the Earth are basalts and they are products of partial melting of the

mantle. The composition of the mantle thus must be such that it yields basaltic magma upon melting. There is, however, a caveat: only the uppermost mantle is sampled by volcanism and tectonism. Even the most deeply generated magmas, kimberlites, come from the upper few hundred km of the mantle, which is nearly 3000 km deep.

11.2.1 Structure of the mantle and geophysical constraints on mantle composition

Geophysical measurements constrain the physical properties of the Earth and its interior, and therefore constrain its composition. One set of constraints comes from the velocities with which seismic waves travel through the Earth. There are two kinds of seismic body waves: *compressional* or p-waves, in which particle motion is parallel to wave motion, and *shear* or s-waves, in which particle motion is perpendicular to wave motion. P-waves can travel through all media, they are the familiar sound waves in air, but s-waves can only travel through solids. Indeed, the absence of s-wave arrivals in a zone between about 100° and 180° from an earthquake epicenter, the so-called s-wave shadow zone, provided the original and still most compelling evidence that the outer core is liquid. The velocity with which seismic waves travel depends on the square root of the ratio of the elastic modulus to density. For s-waves this is:

$$v_s = \sqrt{\frac{\mu}{\rho}} \quad (11.1)$$

where ρ is density and μ is the rigidity modulus, defined as the ratio of shear stress to shear strain. For p-waves the velocity is given by:

$$v_p = \sqrt{\frac{\kappa + \frac{4}{3}\mu}{\rho}} \quad (11.2)$$

where κ is the bulk modulus. κ is defined as:

$$\kappa = -V \left(\frac{\partial P}{\partial V} \right)_s \quad (11.3)$$

κ is very nearly the inverse of the compressibility, which we defined in eqn. 2.12. The only

difference is that in eqn. 2.12 we specified constant temperature in the differential term and here we are specifying constant entropy. This makes things slightly easier for the present problem because the temperature of the Earth would continually increase downward as a result of adiabatic compression, even if there were no other sources of heat in the Earth's interior. Here, we allow for that adiabatic temperature increase. Density, rigidity modulus, and compressibility all depend on the phases constituting a material rather than just composition. However, assuming equilibrium conditions prevail, only one phase assemblage will be possible for a given composition, pressure, and temperature.

We can independently constrain density, and its variation through the Earth, in another way. The density of the Earth is, of course, simply its mass divided by its volume. The latter has been known since the Greek mathematician Eratosthenes determined the Earth's radius in the third century BC. The mass of the Earth was first estimated from the strength of its gravitational field by Isaac Newton in the 17th century and refined by Henry Cavendish in the 18th century. Using the most recent determinations of these parameters, we can calculate a mean density for the Earth of 5515 kg/m³. Comparing this value with the value of typical crustal rocks, which are in the range of 2000–3000 kg/m³, immediately leads to the conclusion that density must be greater in the Earth's interior.

Let's now see how we can combine density and seismic wave velocity variations to provide further constraints. First, we know that density is inversely related to volume:

$$\frac{d\rho}{\rho} = -\frac{dV}{V} \quad (11.4)$$

We can now rewrite eqn. 11.3 in terms of density rather than volume as:

$$\kappa = -\rho \left(\frac{\partial P}{\partial \rho} \right)_s \quad (11.5)$$

Then we note that pressure will vary with radial distance from the center of the Earth as:

$$\frac{dP}{dr} = -\rho(r)g(r) \quad (11.6)$$

where $g(r)$ is the gravitational acceleration at radial distance r . We can combine these equations to write:

$$\left(\frac{\kappa}{\rho}\right) = g(r)\rho(r)\frac{dr}{d\rho} \quad (11.7)$$

Interestingly, it is readily shown that the term on the left can be derived from the seismic wave velocities:

$$\left(\frac{\kappa}{\rho}\right) = V_P^2 - \frac{4}{3}V_s^2 \quad (11.8)$$

The acceleration of gravity at radial distance r is given by:

$$g(r) = \frac{G}{r^2} \int 4\pi\rho(r)r^2 dr \quad (11.9)$$

Combining eqns. 11.7 through 11.9, we have:

$$\frac{d\rho(r)}{dr} = \frac{G}{r^2} \frac{\rho(r)}{V_P^2 - \frac{4}{3}V_s^2} \int 4\pi\rho(r)r^2 dr \quad (11.10)$$

Equation 11.10 describes how density changes in a self-compressing, but otherwise uniform sphere and is known as the *Adams-Williamson Equation*. It allows us to predict the density of an infinitesimally small layer at distance r_1 from seismic velocities, provided we know the density at an adjacent layer, r_2 . Since we can directly measure density at the surface, we can begin there and work our way through the Earth calculating density variation.

Yet another parameter, the Earth's *moment of inertia*, also allows us to constrain how density changes with depth. The moment of inertia for a rotating sphere of uniform density is simply:

$$I = \frac{2}{5}mr^2 \quad (11.11)$$

where m is mass and r is radius. For a spherical body whose density is a function of depth, the moment of inertia is:

$$I = \int \frac{4}{3}\pi r^4 \rho(r) dr \quad (11.12)$$

The situation for the Earth is slightly more complex since it is not strictly spherical.

Rather, as a consequence of centrifugal force, it is an oblate spheroid with its equatorial radius slightly greater than polar radius. The gravitational interaction between the slightly flattened Earth and the Moon results in a gravitational torque which causes the Earth's rotational vector to itself slowly rotate, or *precess*. From the rate of this precession, about one rotation per 25,000 years, a moment of inertia of $8.07 \times 10^{37} \text{ kg/m}^2$ can be calculated.

Any density distribution we obtain using seismic velocities and the Adams-Williamson equation can also be used to calculate a moment of inertia, which should agree with that measured from precession. The two do not agree if we take the Earth to be a self-compressing sphere, for the simple reason that there are density discontinuities in the Earth that result from compositional changes, such as at the core-mantle boundary, as well as phase changes. The problem then is to produce a density model for the Earth that accounts for both observed seismic wave velocities and moment of inertia. The generally accepted model that accomplishes this is called the *Preliminary Reference Earth Model* or *PREM* (Dziewonski and Anderson, 1981). PREM is based on many decades of seismic records. The term *preliminary* clearly implies further refinements are expected, but no revisions have been made since the model was agreed upon in 1981. In part, this is because geophysicists have tended to focus on local deviations from PREM rather than further refine the spherically symmetric model, but it also means that the PREM model is actually reasonably mature. Density and seismic wave velocities of the PREM model are shown in Figure 11.1.

11.2.2 Cosmochemical constraints on mantle composition

In Chapter 10 we considered the composition of that part of our cosmic environment accessible to sampling: meteorites, the solar surface (deduced from optical spectra and solar wind particles), Mars, and the Moon. The meteorite data provide first-order constraints on the formation and composition of the Earth. Since the mantle comprises roughly 99% of the silicate part of the Earth, these constraints also apply to the mantle. Two important cos-

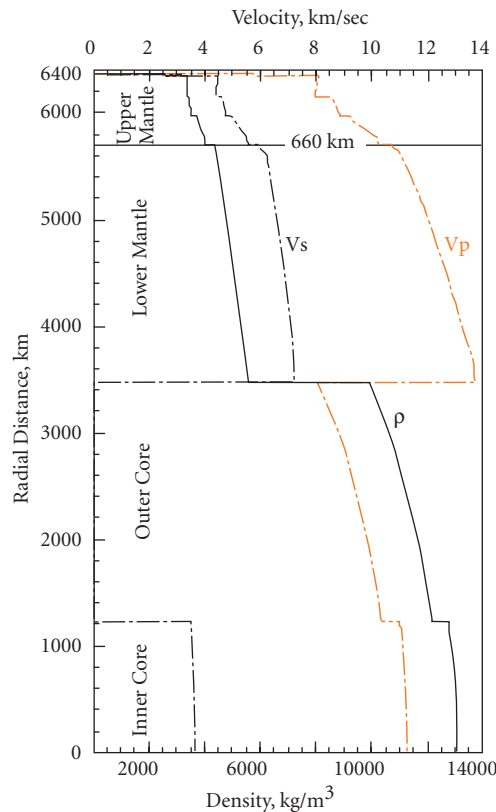


Figure 11.1 The PREM model of seismic velocities and density variation through the Earth.

mochemical assumptions guide our thinking about the composition of the Earth: (1) *the entire solar system formed at one time from a nebula of gas and dust*, (2) *the composition of this nebula was similar to that of CI chondrite for the condensable elements*. The last statement should not be construed to mean that all bodies that formed from this nebula are necessarily of chondritic composition. Indeed, we will see that the Earth's composition differs from chondritic in significant ways.

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 lasted 10^8 or more years); the second assumption certainly holds to a first approximation, but 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 exception 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 homogenous as a result. Processes occurring within the nebula resulted in chemical variation that in turn produced a range of compositions of chondritic parent bodies.

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 planets and asteroids occurred within roughly 10^8 years of the beginning of the solar system (which we take to be the formation of its oldest objects, the CAIs found in chondrites).
4. Asteroids and the terrestrial planets underwent differentiation in which iron metal and silicate segregated. Based on the age of differentiated meteorites, and on W isotope ratios of iron meteorites in particular, the process began very early – within a few million years at most of the beginning of the solar system.
5. The final stages of the formation of planetary assembly involved energetic collisions of large bodies. In the case of the Earth–Moon system, this culminated in a collision that released vast amounts of energy. A consequence of this was a magma ocean on the Moon and, most likely, the Earth as well.

11.2.3 Observational constraints on mantle composition

Figure 11.1 implies that the uppermost mantle should consist of rock having a density of around 3400 kg/m^3 and p-wave velocities of about 8 km/sec . Rocks having these properties are occasionally exposed at the surface in alpine massifs or collision zones, in fracture zones along mid-ocean ridges, and in sections

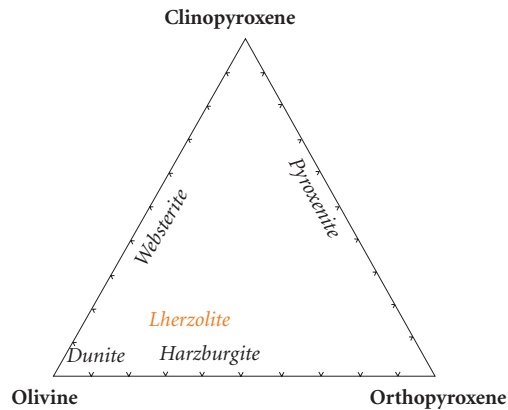


Figure 11.2 Ternary diagram illustrating ultramafic rock nomenclature based on minerals present.

of obducted oceanic crust called ophiolites. These rocks are invariably Mg- and Fe-rich silicates. In addition, rocks having these properties are sometimes found as xenoliths in lavas; they are also Mg- and Fe-rich silicate rocks that consist dominantly of olivine and pyroxenes. Chondrites, of course, are also Mg- and Fe-rich and consist dominantly of olivine and pyroxenes, so it would seem that such rocks meet both geophysical and cosmochemical constraints for mantle composition. The term *ultramafic* is applied to silicate rocks rich in magnesium and iron, which typically consist of olivine and pyroxenes (but hydrated ultramafic rocks can be dominated by minerals such as serpentine or talc). *Peridotite* is a rock dominated by olivine (*peridot* is the gem name for olivine). If the olivine exceeds 90% of the rock, it is termed a *dunite* (Figure 11.2). 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. Figure 11.3 shows the compositions of ultramafic xenoliths found in the volcanic rocks of Kilbourne Hole, New Mexico. The most common types are lherzolites. This suggests we should be focusing our attention on lherzolite as mantle

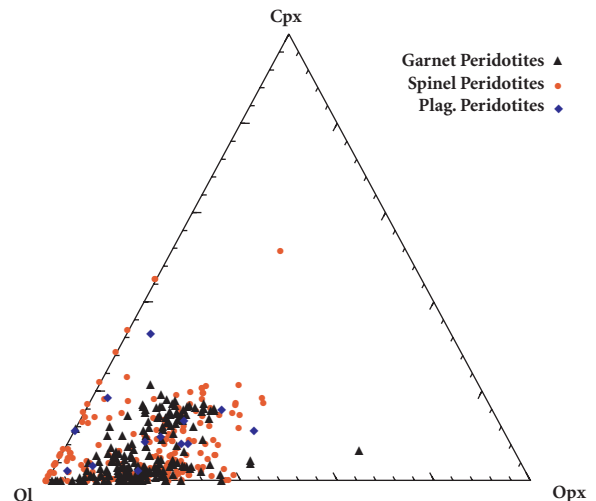


Figure 11.3 Modal mineralogy of peridotite xenoliths in the Deep Lithosphere Database of EarthChem (www.earthchem.org) projected onto the ol-opx-cpx plane.

material. Lherzolite also has appropriate density and seismic velocities to be mantle material. Furthermore, upon partial melting at high pressures it produces basaltic magma. Ringwood (1975) coined the term “pyrolite”, meaning pyroxene-olivine rock, for the lherzolitic composition matching geophysical and cosmochemical constraints.

Pyrolite is not unique as a mantle candidate, and some had argued that the mantle, or at least the upper mantle, consists dominantly of *eclogite*. Eclogite consists of garnet and a Na- and Al-rich pyroxene called omphacite, and is the mineralogy of basalt at high pressure. It can produce basaltic magma upon partial melting, but must melt much more extensively than lherzolite to do so. Eclogite does not match the chondritic composition sufficiently well, and is considerably rarer as xenoliths than peridotites. Furthermore, seismic anisotropy* observed in some parts of the upper mantle suggests the mantle is olivine-rich. However, Anderson (e.g., Anderson, 1989) has argued for an upper

* Seismic anisotropy refers to seismic waves traveling faster in one direction than another, and is related to crystal properties. Anisotropy occurs in orthorhombic olivine, but since garnet has a cubic (isotropic) structure, seismic velocity is equal in all crystallographic directions. Seismic anisotropy only occurs when crystallographic axes of individual grains tend to align, as can arise from flow associated with convection.

mantle consisting of olivine-bearing eclogite, for which he coined the term *piclogite* (an olivine-rich basalt is called a picrite; piclogite would be the high pressure equivalent of picrite). 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. We'll adopt Ringwood's term, *pyrolite*, as the rock that constitutes the mantle. In a subsequent section, we'll consider various estimates of its chemical composition.

11.2.4 Mantle mineralogy and phase transitions

11.2.4.1 Upper mantle phase changes

Figure 11.1 shows that a number of discontinuities exist in the density and seismic velocity profiles of the Earth. Some of these are clearly compositional changes, such as the shallowest discontinuity which is the crust–mantle boundary, and the core–mantle boundary. Others represent phase changes that are isochemical, or nearly so. The most prominent is the inner core–outer core boundary, which is principally a solid–liquid phase change. The discontinuities within the mantle now all appear to be *primarily* phase changes, but some still argue they may be compositional boundaries as well.

In the upper 200 km or so of the mantle, the only important phase changes are the nature of the aluminous phase (Figure 11.4), which changes from plagioclase to spinel (MgAl_2O_4) and then to garnet with increasing pressure.

The garnet lherzolite 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 $\text{M}_2(\text{MSi,Al}_2)\text{Si}_3\text{O}_{12}$ 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 anions such as oxygen are more compressible than are cations such as silicon. When compressed, more oxygens can

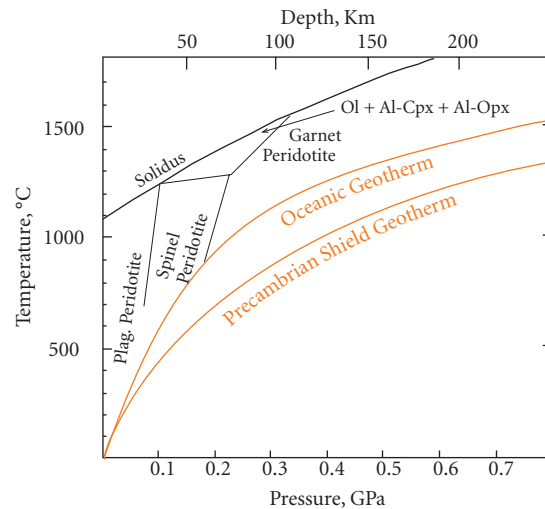


Figure 11.4 Upper mantle phase diagram.

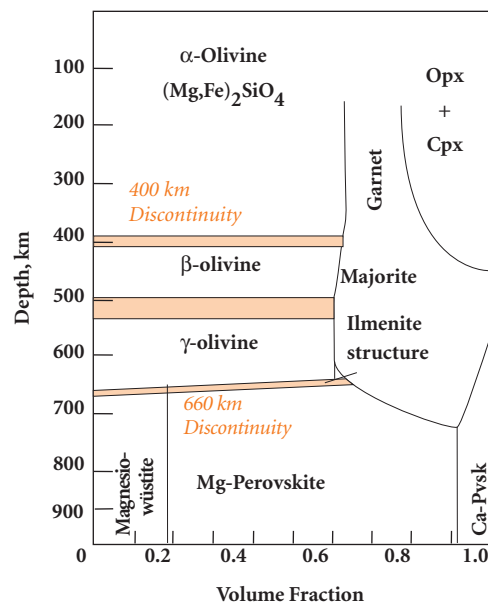


Figure 11.5 Mineral assemblages in the upper 1000 km of the mantle. Ringwood (1991). With permission from Elsevier.

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 11.5). The phase change results in a roughly 10% increase in density of the “pyroxene” component.

11.2.4.2 The transition zone

Between 400 and 670 km depth, seismic velocities increase more rapidly than elsewhere (Figure 11.1); this depth interval is called the transition zone. At about 400 km, or 14 GPa, olivine undergoes a structural change from the low-pressure or α form, to the β form, also known as *wadsleyite*. In contrast to the pyroxene-to-majorite phase change, this phase boundary is relatively sharp, with a transition interval of 9–17 km. It 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. More properly it has been given the name *ringwoodite*, which occurs naturally 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 begins 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.

As Figure 11.1 shows, a sharp and large increase in seismic velocity occurs at around 660 km depth or roughly 24 GPa; this is called the *660 seismic discontinuity*. This depth marks the beginning of the lower mantle. In the past, there was debate as to whether this discontinuity is a chemical boundary or a phase change. There is now complete agreement that it is *primarily* a phase change. At this depth γ -olivine reorganises to form $(\text{Mg,Fe})\text{SiO}_3$ in the perovskite structure and $(\text{Mg,Fe})\text{O}$

magnesiowüstite (perhaps more properly called ferripericlase), with the Fe going preferentially in the magnesiowüstite. This phase change results in a density increase of about 11%. The $(\text{Mg,Fe})\text{SiO}_3$ perovskite* has the chemical stoichiometry of pyroxene, but the silicons are in octahedral coordination. The structure, illustrated in Figure 11.6, is similar to that of the “high-temperature” cuprate superconductors discovered in the 1980s.

High-pressure experiments carried out with a 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 (GPa) = $27.6 - 0.0025T$ (°C); e.g., Chopelas *et al.*, 1994), so that it will occur at somewhat shallower depths in hot regions, such as areas of mantle upwelling, and at greater depths in cooler regions, such as subducted lithosphere,

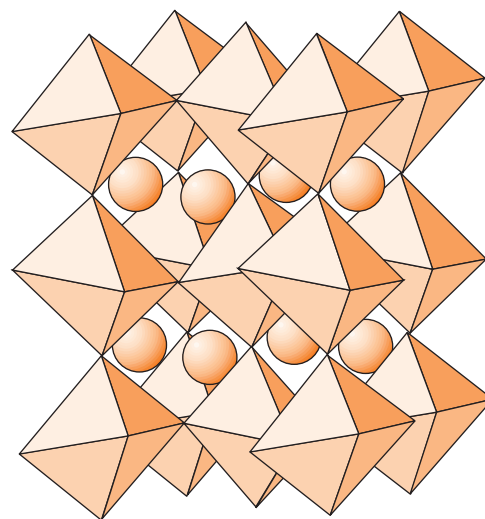


Figure 11.6 The structure of MgSiO_3 perovskite. The structure consists of corner-sharing SiO_6 octahedra with Mg^{2+} in dodecahedral sites. Poirier (1991). Reprinted with the permission of Cambridge University Press.

* We will refer to this phase as Mg-perovskite. This mineral does not have a formal name since it has not been found in nature, although it can be synthesized in the laboratory. $(\text{Mg,Fe})\text{SiO}_3$ accompanied by $(\text{Mg,Fe})\text{O}$ phases have been found in inclusions in diamond. Since this is the expected lower mantle phase assemblage, these diamonds probably originated at or below 660 km. However, the actual $(\text{Mg,Fe})\text{SiO}_3$ phase now present in the inclusion is pyroxene. The interpretation is that the original Mg-perovskite has retrograded to pyroxene as a consequence of pressure reduction.

though since the Clapeyron slope is shallow, the effect is small. The effect 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. The negative Clapeyron slope is probably not sufficient to prevent motion across this boundary, however. Indeed, this is just what seismic tomographic images show: slabs seem to encounter resistance at 660 km, but most ultimately manage to sink through the boundary.

11.2.4.3 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. Although a few small inclusions in diamond containing lower mantle assemblages have been found, these do not provide significant compositional constraints; so the nature of the lower mantle and its composition must be inferred indirectly. The principal constraint on its composition is seismic velocities and density. The assumption that the Earth is approximately chondritic forms another constraint. It is generally agreed that the lower mantle is similar in compositional to the upper mantle, composed dominantly of SiO_2 , MgO , and FeO with lesser amounts of CaO , Al_2O_3 , TiO_2 , and so on, but some disagreement remains as to whether it might be slightly richer in FeO and SiO_2 than the upper mantle. For example, Lee *et al.* (2004) concluded a molar $\text{Mg}/(\text{Mg}+\text{Fe})$ ratio of about 0.85 for the lower mantle is a better fit to seismic observations than the upper mantle value of 0.9. However, Mattern *et al.* (2005) have concluded that the density and elastic properties of lower mantle phases 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. If chemical layering exists in the mantle, it cannot presently be detected with confidence.

Mg-perovskite and magnesio-wüstite remain the principal phases to depths of 2700 km or

so. There had been some debate about how Al_2O_3 is accommodated in lower mantle minerals. The most recent experiments, however, suggest that while a separate aluminous phase may form at relatively low pressures (25–30 GPa, corresponding to the region of 600–800 km), Mg-perovskite apparently accepts all available Al_2O_3 in its structure at pressures above about 35 GPa (e.g., Kesson *et al.*, 1994). On the other hand, 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 . For a “pyrolite” mantle, the phase assemblage will be 65–80% Mg-perovskite, 15–30% magnesio-wüstite, and about 5% Ca-perovskite. Mg-perovskite is thus the most abundant mineral in the Earth. The magnesio-wüstite/perovskite partition coefficient for Fe decreases with increasing pressure, so that the proportion of Fe in perovskite should increase somewhat with depth down to about 30 GPa (~900 km), and then is constant at greater pressure. At this depth, the mole fractions of Mg ($\text{Mg}/(\text{Mg}+\text{Fe})$) in Mg-perovskite and magnesio-wüstite ($(\text{Mg},\text{Fe})\text{O}$) for a pyrolite composition are about 0.94 and 0.80 respectively.

The deepest layers of the mantle are particularly interesting. The core-mantle boundary represents a profound change in physical state (solid to liquid), density, composition, oxygen fugacity, seismic velocity, and probably temperature. From a geochemical perspective, it is a fascinating region. Seismic investigations show that the lowermost 200 km or so of the mantle, called the D'' layer (pronounced “dee-double prime”), is a region of unusual and highly variable properties. There appears to be a roughly 1% increase in density at the top of this layer, and seismic wave velocities within this layer are notably anisotropic. The unusual properties of this layer have led to considerable speculation as to its nature.

Reproducing the temperature and pressure conditions of the deep mantle in the laboratory is challenging to say the least. Pressures reach 135 GPa and temperatures exceed 3000 K. However, these conditions can be reproduced using the diamond anvil high-pressure cell, albeit only on a scale of less than a millimeter. They can also be simulated using an *ab initio* approach, in which materials are

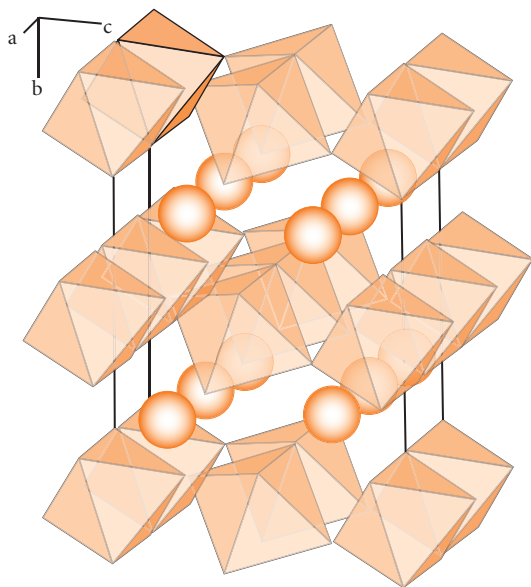


Figure 11.7 The post-perovskite structure of MgSiO_3 . The Si octahedra are organized into sheets, with Mg atoms (spheres) located between the sheets. Reprinted by permission from McMillan Publishers Ltd: After Oganov and Ono (2004).

simulated at the atomic level using computers. Recent experiments and *ab initio* simulations show that the structure of MgSiO_3 should transform from that of perovskite to a CaIrO_3 -like one in which the silica octahedra are organized into sheets as in Figure 11.7 (Murakami *et al.*, 2004; Oganov and Ono, 2004). This transformation should occur at about 125 GPa and 2500–3000 K, corresponding to a depth of about 2700 km, or close to the top of the D'' layer. The density increase in this phase transition is close to that predicted from seismic velocities: about 1%. The layered structure strongly suggests that this mineral should be seismically anisotropic. Thus the discovery of this phase seems to go a long way towards explaining the mystery of D''.

11.3 ESTIMATING MANTLE AND BULK EARTH COMPOSITION

11.3.1 Major element composition

We can draw several important conclusions from the geophysical properties of the mantle when we combine them with the laboratory

experiments of mineral physicists and petrologists. The first of these is that the material that best meets combined cosmochemical, geophysical, and mineral physics has the composition of *pyrolite*. Second, it appears that all seismic discontinuities can be explained by phase changes. Thus there is no compelling geophysical evidence that the mantle is compositionally layered (although we cannot rule it out). This does not, however, rule out the possibility of compositional heterogeneity in the mantle that is more randomly distributed. Consequently, we will assume that the composition of the upper mantle is also the composition of the whole mantle. As we noted at the beginning of Section 11.2, this composition will be the same as the *primitive mantle* and bulk silicate Earth compositions for major elements.

Table 11.2 compares several estimates for the major and minor element composition of the bulk silicate Earth with the composition of CI chondrites. Clearly, chondrites are much richer in siderophile elements (e.g., Fe, Ni) than all these estimated mantle compositions. The chondritic composition matches the upper mantle composition much better after a sufficient amount of the siderophile elements has been removed to form 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). The depletion in alkalis is also apparent by comparing Sr isotope ratios of the mantle and chondrites, as Gast demonstrated in 1960. 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. This depletion is thought to encompass all the moderately volatile elements. Many of the moderately volatile elements are siderophile or chalcophile, so their depletion in the mantle may also reflect extraction into the core.

Table 11.2 Comparison of bulk silicate earth compositions.

	CI chondrites	CI chondritic mantle ¹	Hart and Zindler ²	McDonough and Sun ³	Palme and O'Neill ⁴	Lyubetskaya and Korenaga ⁵	O'Neill and Palme ⁶
SiO ₂	22.89	49.77	45.96	45.0	45.4	44.95	45.40
Al ₂ O ₃	1.60	3.48	4.06	4.45	4.49	3.52	4.29
FeO	23.71	6.91	7.54	8.05	8.10	7.97	8.10
MgO	15.94	34.65	37.78	37.8	36.77	39.95	36.77
CaO	1.30	2.83	3.21	3.55	3.65	2.79	3.52
Na ₂ O	0.671	0.293	0.332	0.36	0.33	0.30	0.281
K ₂ O	0.067	0.028	0.032	0.029	0.031	0.023	0.019
Cr ₂ O ₃	0.387	0.409	0.468	0.384	0.368	0.385	0.368
MnO	0.250	0.112	0.130	0.135	0.136	0.131	0.136
TiO ₂	0.076	0.166	0.181	0.20	0.21	0.158	0.183
NiO	1.371	0.241	0.277	0.25	0.24	0.252	0.237
CoO	0.064	0.012	0.013	0.013	0.013	0.013	0.013
P ₂ O ₅	0.212	0.014	0.019	0.021	0.20	0.15	0.015
Sum	69.79	100.0	100.0	100.2	99.8	100.0	99.3

¹ After removing volatiles and siderophile elements and some oxygen from the mantle to form the core. Hart and Zindler (1986).

² Hart and Zindler (1986).

³ McDonough and Sun (1995).

⁴ Palme and O'Neill (2003).

⁵ Lyubetskaya and Korenaga (2007).

⁶ Calculated from the equations of O'Neill & Palme (2008).

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 atmophile elements. Since the depletion in the highly volatile elements is a feature shared by all the terrestrial planets, it is probably due to temperatures in the inner solar system being too high for these elements to condense completely during the period that the planetesimals that ultimately formed the terrestrial planets were accreting. High temperatures achieved during formation of the Earth (due to release of gravitational energy during collisions), particularly as a result of the giant impact, may have also contributed to volatile loss.

Table 11.2 reflects a general agreement that at least the upper mantle is depleted in silicon relative to a "chondritic" mantle (whether this is true of the entire mantle is a question we will return to). The silicon depletion can be demonstrated in several ways. For example, Hart and Zindler (1986) showed that Mg/Si and Al/Si ratios of chondritic and terrestrial samples plot along separate arrays that intersect at the low-Si end of the chondritic range

(Figure 11.8). Hart and Zindler argued that the "meteorite array" reflects fractionation during processes occurring in the solar nebula or during planet formation (e.g., evaporation, condensation), whereas the "terrestrial array" reflects processes occurring in the Earth's mantle such as partial melting and crystallization.

Table 11.2 also shows that there is broad agreement among the most recent compositional estimates on the FeO concentration in the upper mantle. This reflects the observation that mantle peridotites have uniform concentrations of FeO of about $8 \pm 1\%$.

Let's consider how other elemental concentrations are estimated in one of the more recent studies, that of Palme and O'Neill (2003). They began by adopting an FeO concentration of 8.1%. According to them, the least modified peridotites have a MgO/(MgO+FeO) molar ratio (this ratio is referred to as the Mg-number, often written Mg#) of 0.89. Using that value and FeO of 8.1%, they calculated an MgO concentration for the mantle of 36.77%. They then examined the relationship of other oxides, such as SiO₂, CaO, and Al₂O₃, to MgO in peridotites. As

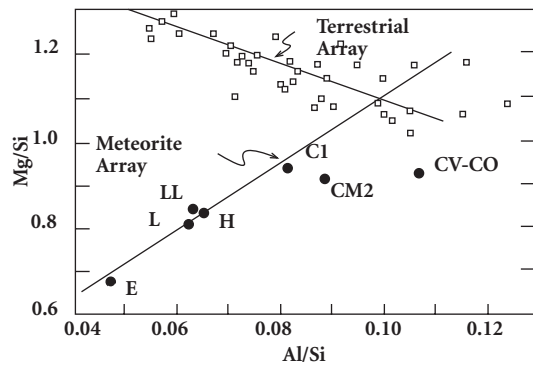


Figure 11.8 Variation of Mg/Si as a function of Nd/Si in terrestrial mantle xenoliths and meteorites. The data suggest the Earth is depleted in Mg and Si relative to chondrites. Hart and Zindler (1986). With permission from Elsevier.

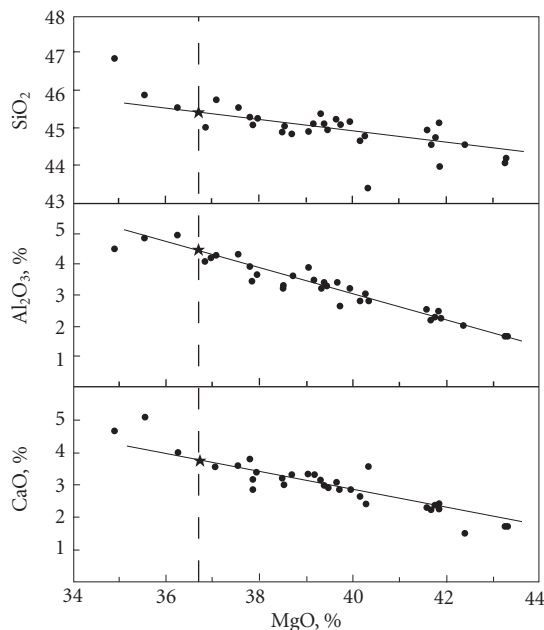


Figure 11.9 Correlation of SiO_2 , Al_2O_3 , and CaO with MgO in peridotites from the central Dinarides (Balkans). Stars indicate estimated mantle primitive compositions. Palme and O'Neill (2003). With permission from Elsevier.

Figure 11.9 shows, there is an inverse correlation, which is thought to result largely from melt extraction from these peridotites. Melt extraction leaves the residual peridotite richer in MgO, but poorer in SiO_2 , Al_2O_3 , and CaO.

If the MgO concentration of the undepleted mantle is known, the concentrations of these other oxides can be estimated from these correlations. Values deduced in this way correspond to Mg/Si and Ca/Al molar ratios of 0.94 and 1.1 respectively. The Mg/Si ratio is quite different from the CI chondrite ratio of 0.83, but in good agreement with the values of 0.95 and 0.94 estimated by Hart and Zindler (1986) and McDonough and Sun (1995), respectively, who used similar approaches.

The Ca/Al ratio agrees well with all other estimates for the Earth as well as with the CI chondrite value. The 50% condensation temperatures of these elements in a gas of solar composition at 10 Pa are: Al, 1650 K; Ca, 1518 K; Mg, 1340 K; and Si, 1311 K (Larimer, 1988). Lithophile elements with 50% condensation temperatures above that of Mg are generally present in constant proportions in chondritic meteorites. It would seem that temperatures in the solar nebula were never hot enough to fractionate these elements. Consequently, a widely held assumption is that these elements, referred to as *refractory lithophile elements*, should be present in the Earth and other planetary bodies in chondritic proportions. One of these elements is Ti, so using this logic, the Ti concentration can be estimated from the Ti/Al ratio in chondrites and the Al concentration deduced earlier. The remaining elements in Table 11.2 are either to varying degrees volatile (Na, K, Mn) and/or siderophile (Ni, Co, Cr), meaning they are concentrated in the Earth's core. Palme and O'Neill (2003) estimated concentrations of these elements from the correlations with MgO in peridotites. One exception is K. The K/U and K/La ratios in the mantle and crust show only limited variation. U and La are refractory lithophile elements, so Palme and O'Neill used these ratios to estimate K.

The approach used by Lyubetskaya and Korenaga (2007) was similar to that of earlier studies in that they relied on correlations between elements in peridotites. However, they employed more sophisticated statistical techniques including principal component analysis and Monte Carlo simulations. Principal component analysis is based on correlations among variables (concentrations in this case) and attempts to define secondary variables, the "components", that predict the

behavior of the primary variables. They found that a single such component could predict 82% of the compositional variance. They interpreted this component as the effects of melt extraction, an interpretation consistent with earlier studies. As did earlier studies, they adopted the assumption that refractory lithophile elements are present in the Earth in chondritic relative proportions, but rather than adopt strict ratios, they incorporated that assumption into their statistical analysis as a “cost function”. As Table 11.2 shows, their results are broadly similar to earlier studies, but there are a few important differences. Their estimate of MgO is significantly higher than earlier ones and their estimated concentrations of refractory lithophile elements (Al, Ca, Ti) significantly lower. They also found that the Earth had lower concentrations of the incompatible elements Na, K, and P than estimated in earlier studies. This apparent depletion of incompatible elements in their study is intriguing and suggests some of the assumptions of earlier estimates of bulk Earth composition might be flawed. Another indication that this might be the case comes from an entirely different kind of evidence: Nd isotopic composition.

11.3.2 The ^{142}Nd conundrum

In Chapter 8 we noted that recent studies of the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio in chondrites and terrestrial materials provide evidence that the Sm/Nd ratio of the Earth, or at least the part accessible to sampling, is not chondritic. (Recall that ^{142}Nd is produced by α -decay of ^{146}Sm , which has a half-life of 68 Ma.) This is surprising to say the least, because it had been widely assumed that refractory lithophile elements are present in the Earth in chondritic relative proportions. For Sm and Nd, this appears to be a good assumption indeed. These two elements are very similar to each other, having identical configurations of bonding electron orbitals, and are both refractory lithophile elements. Indeed, Nd and Sm have 50% condensation temperatures of 1602 and 1590 K, respectively. It is difficult to see how processes operating in the solar nebula could have fractionated these elements significantly. The total range of high precision Sm/Nd ratio measurements in individual chondritic meteorites is only 3%, and mean values

for the different chondrite classes vary by only a tenth of that. This would seem to confirm that these elements were not fractionated in the solar nebula. Yet the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio of all modern terrestrial materials is different from that of chondrites (Figure 8.27), implying differences in $^{146}\text{Sm}/^{144}\text{Nd}$ ratios.

How might these isotopic differences come about? Three possible answers have been proposed. First, it is possible that the early solar system was isotopically heterogeneous. As we learned in Chapter 10, some isotopic heterogeneity existed in the early solar system, most notably for oxygen. More significantly, small variations in the isotopic composition of Nd and Sm have been found in chondrites (Andreasen and Sharma, 2006; Carlson *et al.*, 2007; Gannoun *et al.*, 2011; Qin *et al.*, 2011). Indeed, carbonaceous, ordinary, and enstatite chondrites each appear to have different $^{142}\text{Nd}/^{144}\text{Nd}$ despite identical Sm/Nd. Both ^{146}Sm and ^{144}Sm are p-process-only nuclides produced exclusively in supernovae explosions, while ^{142}Nd is primarily an s-process nuclide produced in red giants, with a small fraction (<5%) produced by the p-process. Incomplete mixing of material from different stars could thus result in variations in $^{142}\text{Nd}/^{144}\text{Nd}$ in the early solar system. However, Andreasen and Sharma (2006) and Qin *et al.* (2011) concluded that while the observed isotopic heterogeneity could explain $^{142}\text{Nd}/^{144}\text{Nd}$ variations observed among chondrites, it could not entirely explain the difference between the Earth and chondrites.

A second possibility was suggested by Boyet and Carlson (2005). They suggested that Earth underwent early differentiation forming an *early-enriched reservoir* (EER), such as a primordial crust that sank into the deep mantle and has not been sampled since. This differentiation might have occurred as a consequence of crystallization of a terrestrial magma ocean analogous to the lunar magma ocean. Alternatively, crystallization of the terrestrial magma ocean might have left a layer of residual melt, similar to the KREEP source on the Moon. Boyet and Carlson (2005) noted that if it were rich in Fe and Ti, as is the lunar KREEP reservoir, once crystallized, the EER could have sunk into the deep mantle, where it remains because of its high density. As Boyet and Carlson (2005) pointed out, this early-enriched reservoir must have formed in the

upper mantle. Below the 660 km discontinuity, Mg- and Ca-perovskite would crystallize and fractionate incompatible elements in a manner much different than observed.

A third possibility, “collisional erosion”, has been suggested by Caro *et al.* (2008) and O’Neill and Palme (2008). As we discussed in Chapter 10, planetary bodies are thought to form through the process of “oligarchic growth”. The initial stages of this process involve aggregations of dust-sized particles to form sand-sized particles, which in turn aggregate to form pebble-sized particles, and so on. The later stages of this process involve infrequent, energetic collisions between large bodies. Sufficient energy is released in these collisions that the growing planet extensively melts. Between collisions, one might reasonably expect a primitive basaltic crust to form through crystallization at the surface. Caro *et al.* (2008), O’Neill and Palme (2008), and Caro and Bourdon (2010) suggest that a substantial fraction of this crust was blasted away in these collisions, leaving the Earth depleted in elements that were concentrated in that crust: incompatible elements.

Common to both the second and third hypotheses is the idea that planetary melting and consequent differentiation began during, rather than after, planetary accretion. Both hypotheses rely on the idea of formation, through melting and fractional crystallization, of a primitive crust enriched in incompatible elements. Such a crust would have a low Sm/Nd ratio, leaving the remainder of the planet with a higher Sm/Nd ratio than the material from which it accreted. In the Boyet and Carlson (2005) hypothesis, this early crust sinks into the deep mantle where it remains as an isolated reservoir. In the collisional erosion hypothesis, this early crust is lost from the Earth. Several observations suggest the latter hypothesis is preferable.

The first of these observations is that the Moon appears to have $^{142}\text{Nd}/^{144}\text{Nd}$ ratios higher than chondritic. All lunar rocks are ancient, and consequently they have variable $^{142}\text{Nd}/^{144}\text{Nd}$ ratios. When these ratios are plotted against $^{147}\text{Sm}/^{144}\text{Nd}$ they display a correlation indicating the bulk Moon has $^{142}\text{Nd}/^{144}\text{Nd}$ about 17 ppm higher than the chondritic value – identical, within uncertainty, to the modern terrestrial value (Boyet and Carlson, 2007). The similarity of

$^{142}\text{Nd}/^{144}\text{Nd}$ in the Earth and Moon implies that the Sm/Nd fractionation must have occurred before the giant impact that formed the Moon. One reaches the same conclusion when one considers the timing of the Moon-forming event. Once corrected for the effects of cosmic rays, tungsten isotope ratios on the Moon are uniform and indistinguishable from those of the Earth, indicating that the Moon-forming event occurred at least 50 Ma and as much as 150 Ma after the start of the solar system (Figure 10.41; Touboul *et al.*, 2009). A fractionation event increasing the Sm/Nd ratio occurring this late would require unreasonably high Sm/Nd ratios to explain the $^{142}\text{Nd}/^{144}\text{Nd}$ of the Earth and Moon. Thus the early-enriched reservoir hypothesized by Boyet and Carlson must pre-date the giant impact. It is unlikely it could have survived this event without being remixed into the mantle (Caro and Bourdon, 2010).

Mars may also have the same $^{142}\text{Nd}/^{144}\text{Nd}$ as the Earth (Caro *et al.*, 2008), but this remains controversial. It is possible that higher than chondritic Sm/Nd ratios is a common feature of terrestrial planets.

Geophysical considerations also cast doubt on the existence of a highly incompatible element-enriched reservoir in the deep mantle. In order to explain the 6% increase in Sm/Nd ratio in the remaining mantle, this reservoir would have to contain at least 40% of the Earth’s inventory of highly incompatible lithophile elements. This group of elements includes the heat-producing elements K, U, and Th. Thus the early-enriched reservoir at the base of the mantle would be responsible for some 40% of the heat production in the Earth, and 70% or more of the heat production in the mantle, or some 9 terawatts (TW). If this were the case, the mantle should be heated mainly from below. As Davies (2009) points out, this would produce a very different style of convection than actually occurs. Convective layers heated mainly from below are dominated by plumes that initiate as instabilities at the base of the layer. While some plumes do form at the base of the mantle and rise through it, the dominant form of convection in the Earth’s mantle is plate tectonics, which is the kind of convection expected in systems heated from within (lava lakes, for example, convect in a way similar to plate tectonics). Furthermore, as Campbell and

O'Neill (2012) point out, the heat generated by this layer plus that flowing from the core to the mantle (5 to 12 TW) likely exceeds the amount of heat carried by mantle plumes.

We conclude then that through the process of collisional erosion, the Earth lost a fraction of a primitive crust of roughly basaltic composition. For most of the major elements such as Si, Al, and Ca, this does not have a discernable effect on mantle or bulk Earth composition. Of those elements listed in Table 11.2, only K is affected significantly. The effect on incompatible trace elements is more significant, as we shall see in the following section.

11.3.3 Composition of the bulk silicate Earth

All previous efforts to estimate bulk Earth composition relied on the assumption that refractory lithophile elements are present in the Earth in chondritic relative proportions, but as we have just seen, the Earth's non-chondritic $^{142}\text{Nd}/^{144}\text{Nd}$ ratio means this assumption must be discarded or modified. O'Neill and Palme (2008) suggested a way to modify the chondritic assumption to account for erosional loss of a primitive crust, and we will follow their approach here. O'Neill and Palme (2008) begin by assuming that the growing proto-earth partially melted to produce a proto-crust of mass fraction f_{p-c}^1 . The concentration of an element, i , in the proto-crust is given by the batch melting equation (eqn. 7.42):

$$\frac{c_i^{pc}}{c_i^o} = \frac{1}{D_i + f_{p-c}^1(1 - D_i)} \quad (11.13)$$

where D_i is the bulk partition coefficient of i . They assume that some of this crust corresponding to a mass fraction f_{p-c}^2 is removed by erosion, along with a fraction of the residue of crust formation, f_{res}^2 . The depletion of element i in the bulk silicate Earth is then:

$$\frac{c_i^{BSE}}{c_i^o} = \frac{f_{p-c}^1(1 - D_i) + D_i(1 - f_{res}^2) - f_{p-c}^2}{(D_i + f_{p-c}^1(1 - D_i))(1 - f_{res}^2 - f_{p-c}^2)} \quad (11.14)$$

The unknowns in this equation are the three mass fraction terms and the partition coefficients. For the latter, O'Neill and Palme adopt the bulk partition coefficients for formation of the basaltic oceanic crust of Workman and

Hart (2005). The other unknowns can be constrained by geochemical considerations.

First, O'Neill and Palme (2008) note that the bulk Earth (including the core) Fe/Mg ratio is about 2.1, compared with the solar and chondritic value, which is about 1.9. Since Fe and Mg have similar volatility, one would expect the terrestrial ratio to be close to the solar one. Collisional erosion would increase the Fe/Mg ratio because the material eroded would come from the mantle and proto-crust, and not from the core (which they assume had already formed). On this basis, O'Neill and Palme estimate the mass fraction lost, $f_{p-c}^2 + f_{res}^2$, to be about 10%. A second constraint comes from the amount of ^{40}Ar in the atmosphere. Essentially all atmospheric ^{40}Ar has been produced by the decay of ^{40}K . The amount of K necessary to produce this Ar corresponds to a K concentration of 120 ppm, which is about half that estimated from K/U and K/La ratios under the assumption of chondritic refractory lithophile relative abundances. The maximum computed K loss occurs if the partition coefficient is 0, so provides a lower limit on c_K^{BSE} / c_K^o of 0.5 when $D_K = 0$. The third constraint comes from the observed difference in $^{142}\text{Nd}/^{144}\text{Nd}$ between the Earth and chondrites, implying a Sm/Nd ratio greater than chondritic. The difference in $^{142}\text{Nd}/^{144}\text{Nd}$ between the Earth and ordinary chondrites implies a terrestrial Sm/Nd ratio 6% greater than chondritic. Based on this, O'Neill and Palme (2008) concluded that $f_{p-c}^1 = 0.026$ and $f_{p-c}^2 = 0.014$. In other words, the proto-crust was about 2.6% of the mass of the Earth and about 0.014/0.026 = 54% of this crust was lost.

Enstatite chondrites appear to have a systematically higher $^{142}\text{Nd}/^{144}\text{Nd}$ than ordinary chondrites (despite having identical Sm/Nd ratios), and the difference in $^{142}\text{Nd}/^{144}\text{Nd}$ between the Earth and enstatite chondrites implies a terrestrial Sm/Nd ratio only 3% greater than chondritic. The enstatite chondrites are unique in having the same O isotopic composition as the Earth (Chapter 10); they thus may represent a better compositional model for the Earth. If we begin with enstatite chondrites instead of ordinary chondrites as a composition model for the Earth, then the terrestrial Sm/Nd ratio can be produced in the O'Neill and Palme calculations by adopting a slightly larger crust fraction,

3%, and a slightly smaller fraction of crust lost, 33%, that is, $f_{p-c}^1 = 0.03$ and $f_{p-c}^2 = 0.01$ ($f_{\text{res}} = 0.09$). This model also predicts a terrestrial Lu/Hf ratio that produces a $^{176}\text{Hf}/^{177}\text{Hf}$ ratio that falls within the $\epsilon_{\text{Nd}}-\epsilon_{\text{Hf}}$ terrestrial array (Figure 8.12). Nd isotope ratios also correlate with Sr isotope ratios in mantle material (Figure 8.11), but because Rb

is a moderately volatile element, the Rb/Sr ratio of the Earth cannot be predicted from this model alone. Instead, the $^{87}\text{Sr}/^{86}\text{Sr}-\epsilon_{\text{Nd}}$ correlation (Figure 8.11) can be used to constrain the terrestrial Rb/Sr ratio.

Table 11.3 compares bulk silicate Earth compositions estimated by McDonough and Sun (1995) and Lyubetskaya and Korenaga

Table 11.3 Bulk silicate Earth compositions.

	McDonough and Sun (1995)	Lyubetskaya and Korenaga (2007)	“Eroded Earth”		McDonough and Sun (1995)	Lyubetskaya and Korenaga (2007)	“Eroded Earth”
Li	1.60	1.60	1.52	Ag	0.008	0.004	0.004
Be	0.07	0.05	0.06	Cd	0.040	0.050	0.064
B	0.30	0.17	0.23	In	0.011	0.010	0.012
C	120.00	–	100.00	Sn	0.130	0.103	0.125
F	25.00	18.00	22.88	Sb	0.0055	0.0070	0.0089
Na	2670	2220	2590	Te	0.012	0.008	0.008
Mg	228000	234100	221700	I	0.010	0.010	0.001
Al	23500	18700	23500	Cs	0.021	0.016	0.015
Si	210000	210900	212200	Ba	6.60	5.08	5.03
P	90	66	76	La	0.648	0.508	0.555
S	250	230	200	Ce	1.68	1.34	1.53
Cl	17	1.4	8.5	Pr	0.254	0.203	0.235
K	240	190	226	Nd	1.25	0.99	1.16
Ca	25300	20000	25541	Sm	0.406	0.324	0.389
Sc	16	13	16	Eu	0.154	0.123	0.147
Ti	1205	950	1176	Gd	0.544	0.432	0.523
V	82	74	86	Tb	0.099	0.080	0.097
Cr	2625	2645	2520	Dy	0.674	0.540	0.666
Mn	1045	1020	1050	Ho	0.149	0.121	0.149
Fe	62600	62000	63000	Er	0.438	0.346	0.440
Co	105	105	102	Tm	0.068	0.054	0.068
Ni	1960	1985	1860	Yb	0.441	0.346	0.440
Cu	30	25	20	Lu	0.068	0.054	0.068
Zn	55	58	54	Hf	0.283	0.227	0.269
Ga	4.0	4.2	4.4	Ta	0.037	0.030	0.031
Ge	1.1	1.2	1.2	W	0.029	0.012	0.012
As	0.050	0.050	0.057	Re	0.0003	0.0003	0.0003
Se	0.075	0.075	0.079	Os	0.0034	0.0034	0.0034
Br	0.05	0.004	0.022	Ir	0.0032	0.0032	0.0032
Rb	0.60	0.46	0.47	Pt	0.0071	0.0066	0.0066
Sr	19.90	15.80	17.48	Au	0.0010	0.0009	0.0009
Y	4.30	3.37	4.12	Hg	0.0100	0.0060	0.0060
Zr	10.50	8.42	9.64	Tl	0.0035	0.0002	0.0024
Nb	0.66	0.46	0.45	Pb	0.150	0.144	0.120
Mo	0.050	0.030	0.034	Bi	0.0025	0.0040	0.0044
Ru	0.005	0.005	0.005	Th	0.080	0.063	0.063
Rh	0.0009	0.0009	0.0009	U	0.02	0.0173	0.0164
Pd	0.0039	0.0036	0.0033				

All concentrations in ppm. “Eroded Earth” is modified from Palme and O’Neill (2003) as described in the text.

(2007) with a composition computed using the approach described earlier, assuming a 3% Sm/Nd difference from chondritic, and where the c° values are taken from Palme and O'Neill (2003). For those elements where Workman and Hart (2005) did not give D values, bulk D values were estimated (e.g., Li, Na), or concentrations were adjusted appropriately based on Palme and O'Neill's original estimate. As an example of the latter, Palme and O'Neill estimated the As concentration from the observation that the As/Ce ratio in the Earth is 0.37. Using the revised Ce concentration of 1.53 ppm, which is 14% lower than Palme and O'Neill's (2003) value, the As concentration is calculated as 0.05 ppm, also 14% lower. Other concentrations, such as Cu and Zn, were derived by Palme and O'Neill (2003) by correlation with MgO, and as such are independent of the assumption of chondritic abundances of refractory lithophile elements and are taken unmodified from Palme and O'Neill (2003). K in Table 11.3 (and K₂O in Table 11.2) has been estimated using a revised estimate of the K/U ratio of the Earth of Arevalo *et al.* (2009) of 13,800, based largely on an upwardly revised K/U in MORB. The Pb concentration is constrained by Pb isotope systematics such that the U/Pb ratio should be 0.133.

The data in Table 11.3 correspond to $^{147}\text{Sm}/^{144}\text{Nd}$, $^{87}\text{Rb}/^{86}\text{Sr}$, and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios of 0.2024, 0.0764, and 0.03565, respectively, which in turn correspond to present-day $^{143}\text{Nd}/^{144}\text{Nd}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of 0.51282, 0.70404, and 0.28287, respectively. This implies $\epsilon_{\text{Nd}} = +3.6$ and $\epsilon_{\text{Hf}} = +6.4$ for the bulk silicate Earth. Exact values, however, must be viewed as uncertain. For example, Caro and Bourdon (2010) used the $^{142}\text{Nd}/^{144}\text{Nd}$ difference between the Earth and *ordinary* chondrites to infer that the terrestrial Sm/Nd ratio is 6% higher than chondritic. This implies $^{147}\text{Sm}/^{144}\text{Nd}$, $^{87}\text{Rb}/^{86}\text{Sr}$, and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios of 0.2082, 0.065, and 0.0375, respectively, corresponding to present-day $^{143}\text{Nd}/^{144}\text{Nd}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of 0.51299, 0.7030, and 0.28313, respectively ($\epsilon_{\text{Nd}} = +6.9$ and $\epsilon_{\text{Hf}} = +12$).

If the Boyet and Carlson (2005) hypothesis that an "early-enriched reservoir" is present as an isolated layer at the base of the mantle is correct, then the composition listed in Table 11.3 becomes the composition of the geo-

chemically "observable Earth", namely continental crust that has formed after 3.5 Ga and that part of the mantle that has contributed to volcanism after that time.

The revised composition of the Earth (or the observable part of it) listed in Table 11.3, particularly the lower incompatible element abundances, has profound implications for the mantle structure and convection. Higher incompatible element concentrations derived from the assumption of chondritic refractory lithophile element abundances led to the conclusion that only a relatively small fraction, half or less, of the mantle had been involved in continental crust creation, and that half or more of the mantle retained their original inventory of volatile elements such as Ar. These observations were used as an argument in favor of "primitive" lower mantle and for layered mantle convection. The revised estimates remove geochemical objections to whole mantle convection. The concentrations of the heat-producing elements K, U, and Th listed in Table 11.3 are substantially lower than previous estimates, meaning there is much less energy being generated in the mantle than previously believed. We will explore these implications further in a subsequent section.

Figure 11.10 shows the abundances of the elements in the silicate Earth relative to CI chondritic (i.e., solar system) concentrations as a function of their 50% condensation temperatures under conditions relevant to the solar nebula. The refractory lithophile elements are enriched in the Earth by factors ranging from 1.5 to 2.8. Other elements show more variable enrichments. In general, the volatile lithophile elements are depleted roughly as a function of their 50% condensation temperatures, consistent with inferences made by Paul Gast and others half a century ago. Yet there can be considerable differences in depletion for elements of similar volatility, such as Rb and Cs. Campbell and O'Neill (2012) suggest that this too is a result of collisional erosion. They argue that incompatible volatile elements, such as Cs, were concentrated in the crusts of the growing protoplanets that eventually coalesced to form the Earth, and were therefore more likely to be volatilized by impacts. We also see that many elements are more depleted in the silicate Earth than we would predict from their

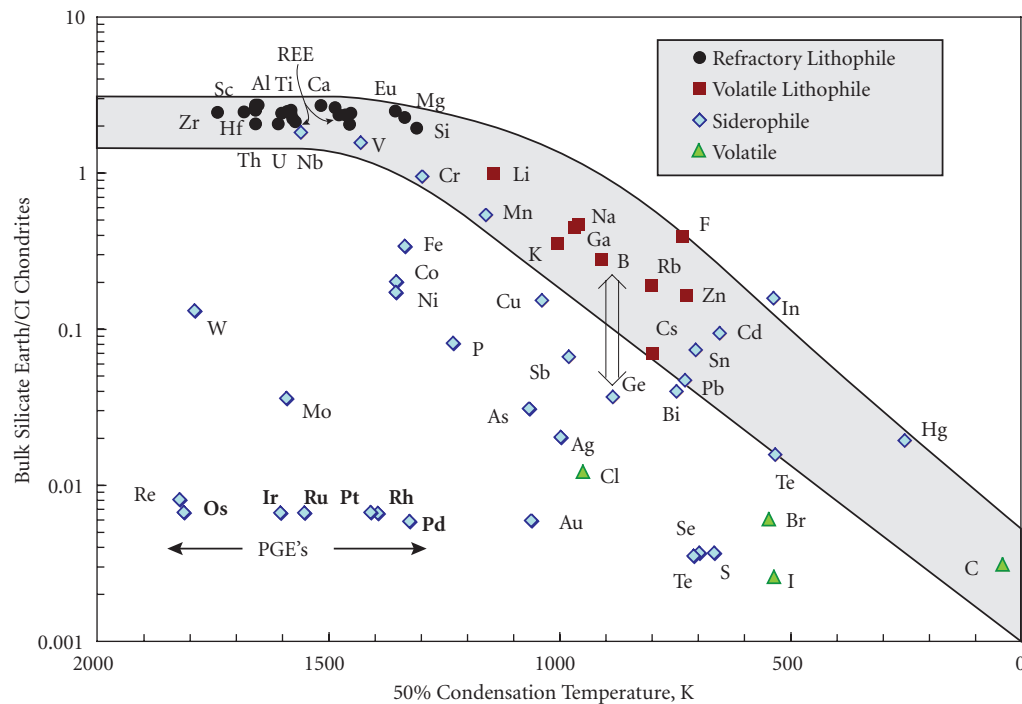


Figure 11.10 Abundances of the elements in the bulk silicate Earth (Table 11.3) relative to CI chondrite abundances as a function of 50% nebular condensation temperature (Lodders, 2003). Primary controlling factors are volatility and the siderophile or chalcophile nature of the element.

volatility. We can infer from this that these elements are concentrated in the core, whose composition we consider in the following section.

11.4 THE EARTH'S CORE AND ITS COMPOSITION

11.4.1 Geophysical constraints

That the Earth has an iron core is known even to schoolchildren. But how do we know this, since no one has ever seen or touched the core? Here again we turn to geophysics. Perhaps the first hint came when 17th-century physicist William Gilbert observed that the Earth's magnetic field was similar to a bar magnet. The plot thickened in 1634, so to speak, when Henry Gellibrand demonstrated temporal changes in the Earth's magnetic field. Further evidence emerged when measurement of the mass of the Earth indicated a high-density interior (section 11.2.1). Unequivocal evidence of this, however, did not emerge until two centuries later. As seismology advanced in the early 20th century, Inga

Lehmann found that the Earth had a core consisting of an outer layer that did not transmit s-waves, and therefore must be liquid, and an inner core that did, and therefore must be solid. Both the inner and outer core have lower seismic velocities than silicate, suggesting the core has higher density. Comparison of density solutions to the Adams-Williamson equation (eqn. 11.10) with the Earth's moment of inertia provided evidence that the Earth's high-density interior could not be simply a consequence of self-compression: the material in the core must have intrinsically higher density. At this point, we can turn to cosmochemistry to ask what heavy element is abundant enough to make up the core, which makes up 16% of the volume and 32% of the mass of the Earth. Looking at Table 11.2, one answer immediately emerges: iron. Iron has a lower melting point than peridotite, making it easy to explain the transition from solid mantle to liquid iron outer core. Iron is also a conductor, and can, when placed in motion, generate a magnetic field. Looking further at cosmic abundances and at Table 11.2, we see