

2.01

Cosmochemical Estimates of Mantle Composition

H. Palme

Universität zu Köln, Germany

and

Hugh St. C. O'Neill

Australian National University, Canberra, ACT, Australia

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2.01.1 INTRODUCTION AND HISTORICAL REMARKS

In 1794 the German physicist Chladni published a small book in which he suggested the extraterrestrial origin of meteorites. The response was skepticism and disbelief. Only after additional witnessed falls of meteorites did

scientists begin to consider Chladni's hypothesis seriously. The first chemical analyses of meteorites were published by the English chemist Howard in 1802, and shortly afterwards by Klaproth, a professor of chemistry in Berlin. These early investigations led to the important conclusion that meteorites contained the same elements that were known from analyses of

terrestrial rocks. By the year 1850, 18 elements had been identified in meteorites: carbon, oxygen, sodium, magnesium, aluminum, silicon, phosphorous, sulfur, potassium, calcium, titanium, chromium, manganese, iron, cobalt, nickel, copper, and tin (Burke, 1986). A popular hypothesis, which arose after the discovery of the first asteroid Ceres on January 1, 1801 by Piazzi, held that meteorites came from a single disrupted planet between Mars and Jupiter. In 1847 the French geologist Boisse (1810–1896) proposed an elaborate model that attempted to account for all known types of meteorites from a single planet. He envisioned a planet with layers in sequence of decreasing densities from the center to the surface. The core of the planet consisted of metallic iron surrounded by a mixed iron–olivine zone. The region overlying the core contained material similar to stony meteorites with ferromagnesian silicates and disseminated grains of metal gradually extending into shallower layers with aluminous silicates and less iron. The uppermost layer consisted of metal-free stony meteorites, i.e., eucrites or meteoritic basalts. About 20 years later, Daubrée (1814–1896) carried out experiments by melting and cooling meteorites. On the basis of his results, he came to similar conclusions as Boisse, namely that meteorites come from a single, differentiated planet with a metal core, a silicate mantle, and a crust. Both Daubrée and Boisse also expected that the Earth was composed of a similar sequence of concentric layers (see Burke, 1986; Marvin, 1996).

At the beginning of the twentieth century Harkins at the University of Chicago thought that meteorites would provide a better estimate for the bulk composition of the Earth than the terrestrial rocks collected at the surface as we have only access to the “mere skin” of the Earth. Harkins made an attempt to reconstruct the composition of the hypothetical meteorite planet by compiling compositional data for 125 stony and 318 iron meteorites, and mixing the two components in ratios based on the observed falls of stones and irons. The results confirmed his prediction that elements with even atomic numbers are more abundant and therefore more stable than those with odd atomic numbers and he concluded that the elemental abundances in the bulk meteorite planet are determined by nucleosynthetic processes. For his meteorite planet Harkins calculated Mg/Si, Al/Si, and Fe/Si atomic ratios of 0.86, 0.079, and 0.83, very closely resembling corresponding ratios of the average solar system based on presently known element abundances in the Sun and in CI-meteorites (see Burke, 1986).

If the Earth were similar compositionally to the meteorite planet, it should have a similarly high iron content, which requires that the major fraction of iron is concentrated in the interior of

the Earth. The presence of a central metallic core to the Earth was suggested by Wiechert in 1897. The existence of the core was firmly established using the study of seismic wave propagation by Oldham in 1906 with the outer boundary of the core accurately located at a depth of 2,900 km by Beno Gutenberg in 1913. In 1926 the fluidity of the outer core was finally accepted. The high density of the core and the high abundance of iron and nickel in meteorites led very early to the suggestion that iron and nickel are the dominant elements in the Earth’s core (Brush, 1980; see Chapter 2.15).

Goldschmidt (1922) introduced his zoned Earth model. Seven years later he published details (Goldschmidt, 1929). Goldschmidt thought that the Earth was initially completely molten and separated on cooling into three immiscible liquids, leading on solidification to the final configuration of a core of FeNi which was overlain by a sulfide liquid, covered by an outer shell of silicates. Outgassing during melting and crystallization produced the atmosphere. During differentiation elements would partition into the various layers according to their geochemical character. Goldschmidt distinguished four groups of elements: siderophile elements preferring the metal phase, chalcophile elements preferentially partitioning into sulfide, lithophile elements remaining in the silicate shell, and atmophile elements concentrating into the atmosphere. The geochemical character of each element was derived from its abundance in the corresponding phases of meteorites.

At about the same time astronomers began to extract compositional data from absorption line spectroscopy of the solar photosphere, and in a review article, Russell (1941) concluded: “The average composition of meteorites differs from that of the earth’s crust significantly, but not very greatly. Iron and magnesium are more abundant and nickel and sulfur rise from subordinate positions to places in the list of the first ten. Silicon, aluminum, and the alkali metals, especially potassium, lose what the others gain.” And Russell continued: “The composition of the earth as a whole is probably much more similar to the meteorites than that of its ‘crust’.” Russell concludes this paragraph by a statement on the composition of the core: “The known properties of the central core are entirely consistent with the assumption that it is composed of molten iron—though not enough to prove it. The generally accepted belief that it is composed of nickel–iron is based on the ubiquitous appearance of this alloy in metallic meteorites,” and, we should add, also on the abundances of iron and nickel in the Sun.

Despite the vast amount of additional chemical data on terrestrial and meteoritic samples and

despite significant improvements in the accuracy of solar abundances, the basic picture as outlined by Russell has not changed. In the following sections we will demonstrate the validity of Russell's assumption and describe some refinements in the estimate of the composition of the Earth and the relationship to meteorites and the Sun.

2.01.2 THE COMPOSITION OF THE EARTH'S MANTLE AS DERIVED FROM THE COMPOSITION OF THE SUN

The rocky planets of the inner solar system and the gas-rich giant planets with their icy satellites of the outer solar system constitute the gross structure of the solar system: material poor in volatile components occurs near the Sun, while the outer parts are rich in water and other volatile components. The objects in the asteroid belt, between Mars at 1.52 AU and Jupiter at 5.2 AU (1 AU is the average Earth–Sun distance, ca. 1.5×10^8 km), mark the transition between the two regimes. Reflectance spectroscopy of asteroids shows bright silicate-rich, metal-containing objects in the inner belt and a prevalence of dark icy asteroids in the outer parts (Bell *et al.*, 1989). Apart from the structure of the asteroid belt, there is little evidence for compositional gradients within the inner solar system as represented by the terrestrial planets and the asteroids. There are no systematic variations with distance from the Sun, either in the chemistry of the inner planets, Mercury, Venus, Earth, Moon, Mars, and including the fourth largest asteroid Vesta, or in any other property (Palme, 2000). One reason is the substantial radial mixing that must have occurred when the terrestrial planets formed. In current models of planet formation, the Earth is made by collisions of a hundred or more Moon- to Mars-sized embryos, small planets that formed within a million years from local feeding zones. The growth of the Earth and the other inner planets takes tens of millions of years, and material from various heliocentric distances contributes to the growth of the planets (e.g., Wetherill, 1994; Canup and Agnor, 2000; Chambers, 2001). Hence, no large and systematic changes in chemistry or isotopic composition of planets are to be expected with increasing heliocentric distance. The composition of the Earth will therefore allow conclusions regarding the formation and the origin of a large fraction of matter in the inner solar system, in particular when considering that the Earth has more than 50% of the mass of the inner solar system. One should, however, keep in mind that the inner solar system comprises only a very small fraction of the total solar system which extends beyond the orbit of

Pluto (39.5 AU) out to some 500 AU. This region is now called Kuiper belt, a disk of comets orbiting the Sun in the plane of the ecliptic. Lack of a chemical gradient in the inner solar system (2 AU) therefore, does, not allow any conclusions regarding the entire solar system.

The abundances of all major and many minor and trace elements in the Sun are known from absorption line spectrometry of the solar photosphere. Accuracy and precision of these data have continuously improved since the early 1930s. In a compilation of solar abundances, Grevesse and Sauval (1998) list the abundances of 41 elements with estimated uncertainties below 30%. A first approximation to the composition of the bulk Earth is to assume that the Earth has the average solar system composition for rock-forming elements, i.e., excluding extremely volatile elements such as hydrogen, nitrogen, carbon, oxygen, and rare gases.

The six most abundant, nonvolatile rock-forming elements in the Sun are: Si (100), Mg (104), Fe (86), S (43), Al (8.4), and Ca (6.2). The numbers in parentheses are atoms relative to 100 Si atoms. They are derived from element abundances in CI-meteorites which are identical to those in the Sun except that CI-abundances are better known (see Chapter 1.03). From geophysical measurements it is known that the Earth's core accounts for 32.5% of the mass of the Earth. Assuming that the core contains only iron, nickel, and sulfur allows us to calculate the composition of the silicate fraction of the Earth by mass balance. This is the composition of the bulk silicate earth (BSE) or the primitive earth mantle (PM). The term primitive implies the composition of the Earth's mantle before crust and after core formation.

As the mantle of the Earth contains neither metal nor significant amounts of Fe^{3+} , the sum of all oxides (by weight) must add up to 100%:

$$\text{MgO} + \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{CaO} + \text{FeO} = 100 \quad (1)$$

By inserting into (1) average solar system abundance ratios, e.g., Si/Mg, Ca/Mg, and Al/Mg (see Chapter 1.03), one obtains

$$2.62 \times \text{MgO} + \text{FeO} = 100 \quad (2)$$

Considering that iron is distributed between mantle and core, the mass balance for iron can be written as

$$\text{Fe}_{\text{core}} \times 0.325 + \text{Fe}_{\text{mantle}} \times 0.675 = \text{Fe}_{\text{total}} \quad (3)$$

and similarly for magnesium, assuming a magnesium-free core,

$$\text{Mg}_{\text{mantle}} \times 0.675 = \text{Mg}_{\text{total}} \quad (4)$$

By assuming that sulfur is quantitatively contained in the core and accounting for nickel in the core ($\text{Fe}_{\text{total}}/\text{Ni} = 17$), the amount of iron

Table 1 Composition of the mantle of the Earth assuming average solar system element ratios for the whole Earth.

	<i>Earth's mantle solar model</i>	<i>Earth's mantle based on composition of upper mantle rocks^a</i>
MgO	35.8	36.77
SiO ₂	51.2	45.40
FeO	6.3	8.10
Al ₂ O ₃	3.7	4.49
CaO	3.0	3.65

^a See Table 2.

in the core, Fe_{core} , is calculated to be 75%. From Equations (2) to (4) and by using the solar abundance ratio for Fe_{total}/Mg_{total} , the hypothetical composition of the Earth's mantle is obtained as given in Table 1. The Earth's mantle composition derived from the analyses of actual upper mantle rocks, as described in the next section, is listed for comparison.

The remarkable result of this exercise is that by assuming solar element abundances of rock-forming elements in the bulk Earth leads to a mantle composition that is in basic agreement with the mantle composition derived from upper mantle rocks. On a finer scale there are differences between the calculated mantle composition of the solar model and the mantle composition derived from the analyses of mantle rocks that makes a solar model of the Earth unlikely: (i) the Ca/Mg and Al/Mg ratios of mantle rocks are significantly higher than in the Sun, reflecting a general enhancement of refractory elements in the Earth; (ii) the Mg/Si ratio of the Earth's mantle is different from the solar ratio; and (iii) minor and trace element data indicate that the Earth is significantly depleted in volatile elements when compared to solar abundances. Hence, the sulfur content of the core assuming the solar composition model for the Earth is grossly overestimated. In order to assess the significance of these differences properly, some understanding of the variability of the chemical composition of chondritic meteorites is required.

2.01.3 THE CHEMICAL COMPOSITION OF CHONDRITIC METEORITES AND THE COSMOCHEMICAL CLASSIFICATION OF ELEMENTS

The thermal history of planetesimals accreted in the early history of the solar system depends on the timescale of accretion and the amount of incorporated short-lived radioactive nuclei, primarily ^{26}Al with a half-life of 7.1×10^5 years. In some cases there was sufficient heat to completely

melt and differentiate the planetesimals into a metal core and a silicate mantle, while in other cases even the signatures of a modest temperature increase is absent. *Undifferentiated meteorites* derived from unmelted parent bodies are called *chondritic meteorites*. Their chemical composition derives from the solar composition more or less altered by processes in the early solar nebula, but essentially unaffected by subsequent planetary processes. Their textures, however, may have been modified by thermal metamorphism or aqueous alteration since their formation from the nebula. Chemically, chondritic meteorites are characterized by approximately similar relative abundances of silicon, magnesium, and iron indicating the absence both of metal separation (which would lead to low Fe/Si in residual silicates) and of partial melting, which would produce low Mg/Si melts and high Mg/Si residues. The roughly solar composition is, however, only a first-order observation. Nebular processes, primarily fractionation during condensation and/or aggregation, have produced a rather wide range of variations in the chemistry of chondritic meteorites. The extent to which individual elements are affected by these processes depends mainly on their volatility under nebular conditions. Nebular volatilities are quantified by condensation temperatures formally calculated for a gas of solar composition (see Wasson, 1985). In Table 2, elements are grouped according to their condensation temperatures. In addition, the geochemical character of each element is indicated, i.e., whether it is lithophile or siderophile and/or chalcophile. Based on condensation temperatures the elements may be grouped into five categories that account for variations in the bulk chemistry of chondritic meteorites (Larimer, 1988).

(1) The refractory component comprises the elements with the highest condensation temperatures. There are two groups of refractory elements: the *refractory lithophile* elements (RLEs)—aluminum, calcium, titanium, beryllium, scandium, vanadium, strontium, yttrium, zirconium, niobium, barium, REE, hafnium, tantalum, thorium, uranium, plutonium—and the *refractory siderophile* elements (RSEs)—molybdenum, ruthenium, rhodium, tungsten, rhenium, iridium, platinum, osmium. The refractory component accounts for ~5% of the total condensable matter. Variations in refractory element abundances of bulk meteorites reflect the incorporation of variable fractions of a refractory aluminum, calcium-rich component. Ratios among refractory lithophile elements are constant in all types of chondritic meteorites, at least to within ~5%.

(2) The *common lithophile* elements, magnesium and silicon, condense as magnesium silicates with chromium and lithium in solid solution. Together with metallic iron, magnesium

Table 2 Cosmochemical and geochemical classification of the elements.

	Elements	
	<i>Lithophile (silicate)</i>	<i>Siderophile + chalcophile (sulfide + metal)</i>
Refractory	$T_c = 1,850\text{--}1,400\text{ K}$ Al, Ca, Ti, Be, Ba, Sc, V, Sr, Y, Zr, Nb, Ba, REE, Hf, Ta, Th, U, Pu	Mo, Ru, W, Re, Os, Ir, Pt
Main component	$T_c = 1,350\text{--}1,250\text{ K}$ Mg, Si, Cr, Li	Fe, Ni, Co, Pd
Moderately volatile	$T_c = 1,230\text{--}640\text{ K}$ Mn, P, Na, B, Rb, K, F, Zn	Au, As, Cu, Ag, Ga, Sb, Ge, Sn, Se, Te, S
Highly volatile	$T_c < 640\text{ K}$ Cl, Br, I, Cs, Tl, H, C, N, O, He, Ne, Ar, Kr, Xe	In, Bi, Pb, Hg

T_c —condensation temperatures at a pressure of 10^{-4} bar (Wasson, 1985; for B, Lauretta and Lodders, 1997).

silicates account for more than 90% of the mass of the objects of the inner solar system. Variations in Mg/Si ratios among meteorites may be ascribed to separation of early condensed magnesium-rich olivine (forsterite with an atom ratio of Mg/Si = 2), either by preferred accretion of forsterite (high Mg/Si reservoir) or loss of an early forsterite component (low Mg/Si reservoir).

(3) In a gas of solar composition all iron condenses as an *FeNi alloy*, which includes cobalt and palladium with similar volatilities. Parent bodies of chondritic meteorites have acquired variable amounts of metallic FeNi. Some separation of metal and silicate must have occurred in the solar nebula, before aggregation to planetesimals had occurred.

(4) The *moderately volatile elements* are in order of decreasing condensation temperature: gold, manganese, arsenic, phosphorus, rubidium, copper, potassium, sodium, silver, gallium, antimony, boron, germanium, fluor, tin, selenium, tellurium, zinc, and sulfur (50% condensation temperatures; Wasson, 1985). The condensation temperatures range between those of magnesium silicates and FeS. All elements of this group are trace elements except the minor element, sulfur, which condenses by the reaction of gaseous S_2 with solid iron metal. The trace elements are condensed by dissolution into already condensed major phases such as silicates, metal, and sulfides. In general, abundances of moderately volatile elements normalized to average solar abundances decrease in most groups of chondritic meteorites with decreasing condensation temperatures, i.e., the more volatile an element is, the lower is its normalized abundance (Palme *et al.*, 1988).

(5) The group of *highly volatile elements* with condensation temperatures below that of FeS

includes the lithophile elements—chlorine, bromine, iodine, caesium, thallium—the chalcophile elements—indium, bismuth, lead, mercury—and the atmophile elements—hydrogen, carbon, oxygen, neon, argon, krypton, xenon. The lithophile and siderophile elements of this group are fully condensed in CI-chondrites, whereas the atmophile elements are depleted in all groups of meteorites, even in CI-meteorites relative to solar abundances (see Chapter 1.03).

Figure 1 plots the abundances of several elements in the various groups of chondritic meteorites and in the Sun. All abundances are normalized to silicon. One group of meteorites, the CI-chondrites, with its most prominent member the Orgueil meteorite, has, for most elements shown here, the same abundance ratios as the Sun (Figure 1). The agreement between the composition of the Sun and CI-meteorites holds for most elements heavier than oxygen and with the exception of rare gases (see Chapter 1.03). Differences among the various types of chondritic meteorites include differences in chemical composition (Figure 1): mineralogy, texture, and degree of oxidation. More recently, new chondrite groups have been discovered (see Chapter 1.05). Only the most important groups are shown here. The compositional variations observed among chondritic meteorites may be explained in terms of the five components mentioned above.

In Figure 1 aluminum is representative of the refractory component. All types of carbonaceous chondrites are enriched in refractory elements, whereas ordinary and enstatite chondrites are depleted. Variations in Mg/Si (Figure 1) are smaller and may be the result of preferred accumulation or loss of olivine as discussed

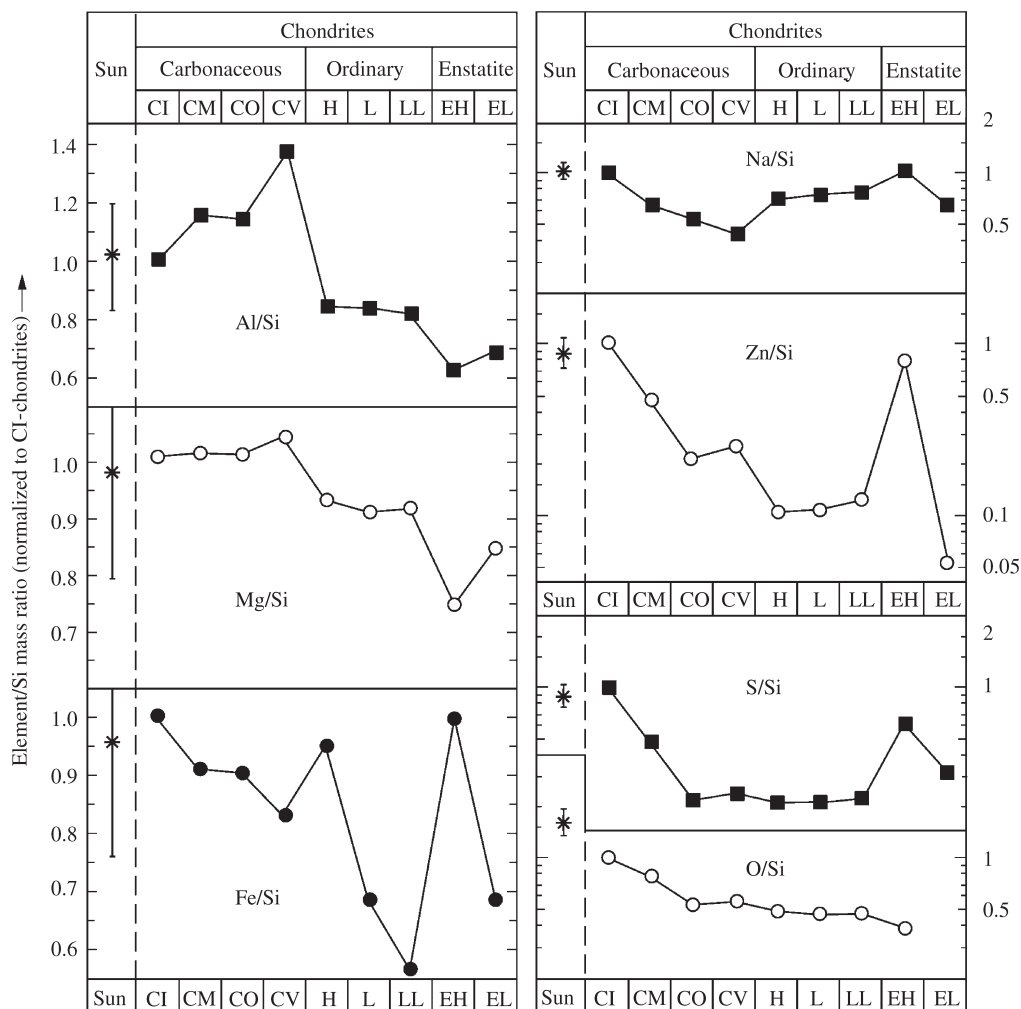


Figure 1 Element/Si mass ratios of characteristic elements in the major groups of chondritic (undifferentiated) meteorites. Meteorite groups are arranged according to decreasing oxygen content. The best match between solar abundances and meteoritic abundances is with CI-meteorites. For classification of meteorites, see Chapter 1.05.

above. The variations in Fe/Si ratios reflect variable incorporation of metallic iron into a chondrite parent body. Variations in the moderately volatile elements—sodium, zinc, and sulfur—are large and demonstrate the uniqueness of CI-chondrites as best representing solar abundances. The decrease in O/Si ratios (Figure 1) indicates average decreasing oxygen fugacities from carbonaceous through ordinary to enstatite chondrites. The average fayalite content of olivine (or ferrosilite content of orthopyroxene) decreases in the same sequence.

In the following section we will derive the composition of the mantle of the Earth from the chemical analyses of upper mantle rocks. The resulting mantle composition will then be compared with the composition of chondritic meteorites. In order to avoid circular arguments, we will use as few assumptions based on the

above cosmochemical observations as possible. However, some assumptions are essential, and these will be clearly indicated.

2.01.4 THE COMPOSITION OF THE PRIMITIVE MANTLE BASED ON THE ANALYSIS OF UPPER MANTLE ROCKS

2.01.4.1 Rocks from the Mantle of the Earth

The principal division of the Earth into core, mantle, and crust is the result of two fundamental processes. (i) The formation of a metal core very early in the history of the Earth. Core formation ended at ~30 million years after the beginning of the solar system (Kleine *et al.*, 2002). (ii) The formation of the continental crust by partial melting of the silicate mantle. This process has

occurred with variable intensity throughout the history of the Earth.

The least fractionated rocks of the Earth are those that have only suffered core formation but have not been affected by the extraction of partial melts during crust formation. These rocks should have the composition of the PM, i.e., the mantle before the onset of crust formation. Such rocks are typically high in MgO and low in Al_2O_3 , CaO, TiO_2 , and other elements incompatible with mantle minerals. Fortunately, it is possible to collect samples on the surface of the Earth with compositions that closely resemble the composition of the primitive mantle. Such samples are not known from the surfaces of Moon, Mars, and the asteroid Vesta. It is, therefore, much more difficult to reconstruct the bulk composition of Moon, Mars, and Vesta based on the analyses of samples available from these bodies.

Rocks and rock fragments from the Earth's mantle occur in a variety of geologic settings (e.g., see, O'Neill and Palme, 1998, Chapters 2.04 and 2.05): (i) as mantle sections in ophiolites representing suboceanic lithosphere; (ii) as massive peridotites, variously known as Alpine, orogenic, or simply high-temperature peridotites; (iii) as abyssal peridotites, dredged from the ocean floor—the residue from melt extraction of the oceanic crust; (iv) as spinel- (rarely garnet-) peridotite xenoliths from alkali basalts, mostly from the subcontinental lithosphere but with almost identical samples from suboceanic lithosphere; (v) as garnet peridotite xenoliths from kimberlites and lamproites—these fragments sample deeper levels in the subcontinental lithosphere and are restricted to ancient cratonic regions.

Typical mantle peridotites contain more than 50% olivine, variable amounts (depending on their history of melt extraction and refertilization) of orthopyroxene, clinopyroxene, plus an aluminous phase, whose identity depends on the pressure (i.e., depth) at which the peridotite equilibrated—plagioclase at low pressures, spinel at intermediate pressures, and garnet at high pressures. Peridotites have physical properties such as density and seismic velocity propagation characteristics that match the geophysical constraints required of mantle material. Another obvious reason for believing that these rocks come from the mantle is that the constituent minerals of the xenoliths have chemical compositions which show that the rocks have equilibrated at upper mantle pressures and temperatures. In the case of the xenoliths their ascent to the surface of the Earth was so fast that minerals had no time to adjust to the lower pressure and temperature on the Earth's surface. Most of the information used for estimating the chemical composition of the mantle is derived from spinel-lherzolite xenoliths originating from a depth of

40 km to 60 km. Garnet lherzolites, which sample the mantle down to a depth of ~ 200 km and a temperature of $1,400^\circ\text{C}$, are much rarer (see Chapter 2.05).

The early compositional data on peridotites have been summarized by Maaløe and Aoki (1977). A comprehensive review of more recent data on mantle rocks is given by O'Neill and Palme (1998).

2.01.4.2 The Chemical Composition of Mantle Rocks

The chemistry of the mantle peridotites is characterized by contents of MgO in the range of 35–46 wt.% and SiO_2 from 43 wt.% to 46 wt.%, remarkably constant abundances of FeO (8 ± 1 wt.%), Cr_2O_3 (0.4 ± 0.1 wt.%), and Co (100 ± 10 ppm). Bulk rock magnesium numbers ($100 \times \text{Mg}/\text{Mg} + \text{Fe}$, in atoms) are generally ≥ 0.89 . The comparatively high contents of nickel ($2,200 \pm 500$ ppm), a siderophile element, and of iridium (3.2 ± 0.3 ppb), a compatible highly siderophile element, are diagnostic of mantle rocks. Figure 2 plots the bulk rock concentrations of SiO_2 , Al_2O_3 , and CaO versus MgO for peridotites from the Central Dinaric Ophiolite Belt (CDOB) in Yugoslavia, a typical occurrence of mantle rocks associated with ophiolites. The samples are recovered from an area comprising a large fraction of the former Yugoslavia (Lugovic, 1991). The abundances of the refractory elements CaO, Al_2O_3 and also of Ti, Sc, and the heavy REE are negatively correlated with MgO. Both CaO and Al_2O_3 decrease by a factor of 2 with MgO increasing by only 15%, from 36% to 43% (Figure 2). There is a comparatively small decrease of 3.5% in SiO_2 over the same range. Figure 3 plots Na, Cr, and Ni versus MgO for the same suite of mantle rocks. The decrease of sodium is about twice that of calcium and aluminum. The chromium concentrations are constant, independent of MgO, while nickel concentrations are positively correlated with MgO.

Samples of massive peridotites and of spinel and garnet lherzolite xenoliths from worldwide localities plot on the same or on very similar correlations as those shown here for the CDOB samples (McDonough, 1990; BVSP, 1981; McDonough and Sun, 1995; O'Neill and Palme, 1998). It is particularly noteworthy that trends for xenoliths and massive peridotites are statistically indistinguishable (McDonough and Sun, 1995). An example is given in Figure 4, where FeO versus MgO plots for samples from two massive peridotites, the CDOB and Zabargad island in the Red Sea, are compared with xenolith data from two localities, Vitim (Baikal region, Russia) and the Hessian Depression (Germany). Two important

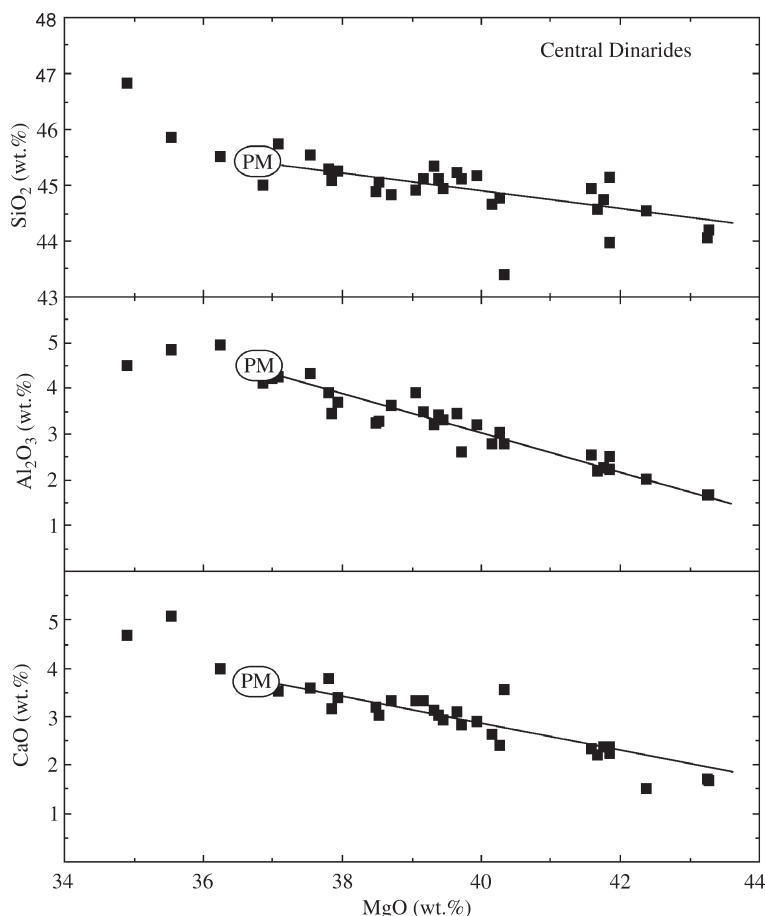


Figure 2 Correlations of SiO_2 , Al_2O_3 , and CaO with MgO for a suite of mantle samples from the CDOB in Yugoslavia, a typical occurrence of mantle rocks associated with ophiolites. The samples are recovered from an area comprising a large fraction of the former Yugoslavia (Lugovic, 1991). The abundances of the refractory elements CaO and Al_2O_3 are negatively correlated with MgO , indicating preferred partitioning of these elements into the partial melt. The effect for SiO_2 is comparatively small. These correlations are characteristic of a large number of occurrences of mantle xenoliths and massive peridotites (see McDonough, 1990; BVSP, 1981; McDonough and Sun, 1995; O'Neill and Palme, 1998). PM indicates the composition of the primitive mantle derived in this chapter.

conclusions can be drawn from this figure: (i) the FeO contents are independent of MgO in all occurrences of mantle rocks and (ii) the average FeO content is the same in all four localities. The two statements can be generalized. On the left side of Figure 5 average FeO contents of samples from 11 suites of xenoliths are compared with those of 10 suites of massif peridotites. Each of the points in Figure 5 represents the average of at least six, in most cases more than 10, samples (see O'Neill and Palme (1998) for details). The errors assigned to the data points in Figure 5 are calculated from the variations in a given suite. The range in average FeO contents from the various localities is surprisingly small and reflects the independence of FeO from MgO . Also, the average FeO contents are in most cases indistinguishable from each other. The average SiO_2 contents of the same suites plotted on the right side show a somewhat larger scatter,

reflecting the slight dependence of SiO_2 on MgO (see Figure 2).

Peridotites with the lowest MgO contents have, in general, the highest concentrations of Al_2O_3 , CaO , and other incompatible elements that preferentially partition into the liquid phase during partial melting. Such peridotites are often termed "fertile," emphasizing their ability to produce basalts on melting. Most peridotites are, however, depleted to various extents in incompatible elements, i.e., they have lower contents of CaO , Al_2O_3 , Na_2O , etc., than a fertile mantle would have, as shown in Figures 2 and 3. By contrast, an element compatible with olivine, such as nickel, increases with increasing MgO contents (Figure 3). Thus, the trends in Figures 2 and 3 have been interpreted as reflecting various degrees of melt extraction (Nickel and Green, 1984; Frey *et al.*, 1985). Following this reasoning, the least-depleted

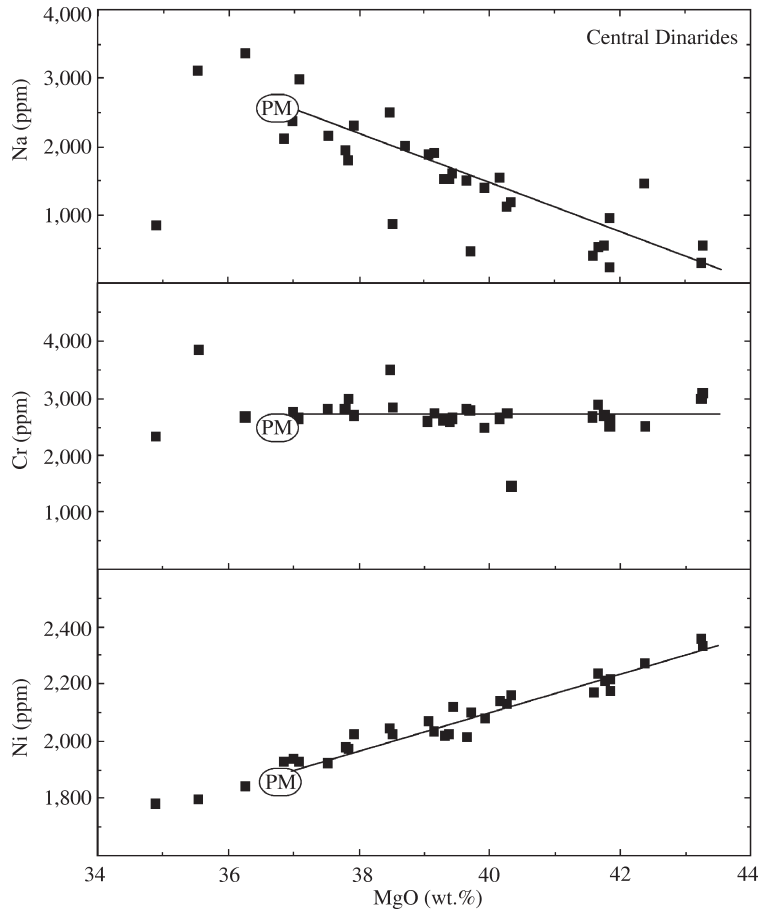


Figure 3 Na, Cr, and Ni for the same suite of rocks as in Figure 2. Na is incompatible with mantle minerals, Ni is compatible, and Cr partitions equally between melt and residue.

peridotites, i.e., highest in CaO and Al_2O_3 , should be the closest in composition to the primitive mantle.

In detail, however, the picture is not so simple. All mantle peridotites (whether massive peridotites or xenoliths) are metamorphic rocks that have had a complex subsolidus history after melt extraction ceased. As well as subsolidus recrystallization, peridotites have undergone enormous amounts of strain during their emplacement in the lithosphere. Massive peridotites show modal heterogeneity on the scale of centimeters to meters, caused by segregation of the chromium-diopside suite of dikes, which are then folded back into the peridotite as deformation continues. The net result is more or less diffuse layers or bands in the peridotite, which may be either enriched or depleted in the material of the chromium-diopside suite, i.e., in clinopyroxene and orthopyroxene in various proportions, \pm minor spinel, and \pm sulfide. This process should cause approximately linear correlations of elements versus MgO, broadly similar to, but not identical with, those caused by melt extraction. Indeed, there is

no reason for melt extraction to cause a linear relationship. Partial melting experiments and corresponding calculations show that for many elements, such trends should not be linear (see O'Neill and Palme, 1998, figure 2.12). Although the banding may not be so obvious in xenoliths as in the massive peridotites, since it operates over lengthscales greater than those of the xenoliths themselves (but it is nevertheless often seen, e.g., Irving (1980)), the similarity in the compositional trends between xenoliths and massive peridotites shows that it must be as ubiquitous in the former as it may be observed to be in the latter.

In addition, many peridotites bear the obvious signatures of metasomatism, which re-enriches the rock in incompatible components subsequent to depletion by melt extraction. Where this is obvious (e.g., in reaction zones adjacent to later dikes) it may be avoided easily; but often the metasomatism is cryptic, in that it has enriched the peridotite in incompatible trace elements without significantly affecting major-element chemistry (Frey and Green, 1974). Peridotites thus have very variable contents of highly incompatible trace

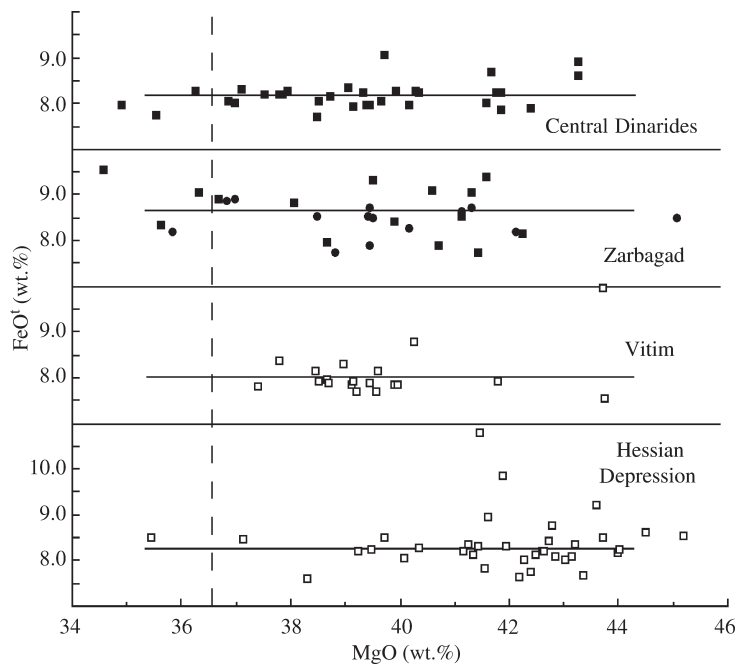


Figure 4 The FeO contents of samples from the same suites as in Figures 2 and 3, samples from Zabargad island and samples from two xenoliths suites from Vitim (Baikal region) and Hessian Depression (Germany). The FeO contents are, similar to Cr in Figure 3, independent of the fertility of the mantle rocks as reflected in their MgO contents (source O'Neill and Palme, 1998).

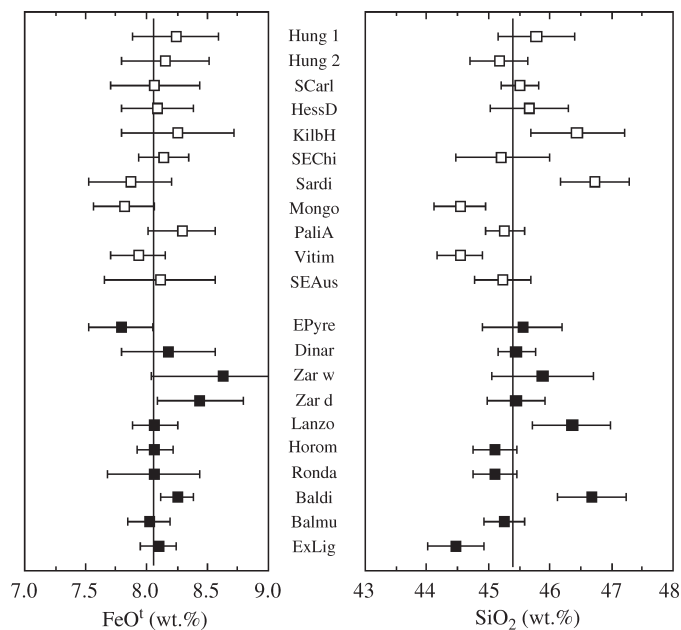


Figure 5 Average FeO (all Fe assumed as FeO) and SiO₂ contents in various suites of xenoliths (open symbols) and massive peridotites (full symbols). All suites give the same FeO value within 1 σ SD. An average PM FeO content of $8.07 \pm 0.06\%$ is calculated from these data (see O'Neill and Palme, 1998). The SiO₂ concentrations are somewhat more variable as SiO₂ depends on MgO (see Figure 2) (source O'Neill and Palme, 1998).

elements like thorium, uranium, niobium, and light REEs, and these elements cannot be used to distinguish melt extraction trends from those caused by modal banding.

In summary, then, the trends of CaO, Al₂O₃, and Na (Figures 2 and 3) and also TiO₂ and many other moderately incompatible trace elements (Sc, HREE) with MgO that appear approximately

linear in suites of massive peridotites or xenoliths, are due to a combination of two processes: melt extraction, followed by metamorphic modal banding; and possibly by metasomatism. This explains a number of features of these trends: the scatter in the data; the tendency to superchondritic Ca/Al ratios (Palme and Nickel, 1985; O'Neill and Palme, 1998, figure 1.13), and, importantly, the existence of peridotites with higher CaO or Al₂O₃ than that inferred for the PM. Thus, it is not possible simply to say that those peridotites richest in incompatible elements are closest to the PM, and instead some other method of reconstructing the PM composition must be used. Here we describe a new procedure for calculating the composition of PM that is independent of the apparent linear correlations discussed above. The method was first introduced by O'Neill and Palme (1998).

2.01.4.2.1 Major element composition of the Earth's primitive mantle

The two elements calcium and aluminum are RLEs. The assumption is usually made that all RLEs are present in the primitive mantle of the Earth in chondritic proportions. Chondritic (undifferentiated) meteorites show significant variations in the absolute abundances of refractory elements but have, with few exceptions discussed below, the same relative abundances of lithophile and siderophile refractory elements. By analogy, the Earth's mantle abundances of refractory lithophile elements are assumed to occur in chondritic relative proportions in the primitive mantle, which is thus characterized by a single RLE/Mg ratio. This ratio is often normalized to the CI-chondrite ratio and the resulting ratio, written as (RLE/Mg)_N, is a measure of the concentration level of the refractory component in the Earth. A single factor of (RLE/Mg)_N valid for all RLEs is a basic assumption in this procedure and will be calculated from mass balance considerations.

The FeO^t (total iron as FeO, which is a very good approximation for mantle rocks) and MgO contents are estimated from two empirical constraints.

(i) As discussed above, FeO^t is remarkably constant worldwide, in massive peridotites and in alkali-basalt-derived lherzolite xenoliths (Figures 4 and 5) and moreover it does not depend on MgO contents for reasonably fertile samples (MgO < 42 wt.%). This is expected, as FeO^t is not affected by melt extraction at low degrees of partial melting ($D_{\text{Fe}}^{\text{liq/sol}} \cong 1$), and is also insensitive to differing olivine/pyroxene ratios caused by modal segregation and remixing (see Chapter 2.08). As discussed above, O'Neill and Palme (1998)

considered data from 21 individual suites of spinel lherzolites. These individual suites usually show standard deviations of the order of ± 0.5 wt.% FeO^t for the least-depleted samples, but the mean values are remarkably coherent (Figure 5). By averaging O'Neill and Palme (1998) obtained FeO^t = 8.10 wt.%, with a standard error of the mean of 0.05 wt.%.

Next, the MgO content is constrained from the observation that molar Mg/(Mg + Fe^t) (i.e., bulk-rock Mg#) ought not to be affected by modal segregation, since mineral Mg#s are nearly the same in olivine and in pyroxenes (as shown by experimental phase equilibrium studies and empirical studies of coexisting phases in peridotites). Hence, (Mg#)_{ol} = (Mg#)_{bulk}, to a very good approximation, in spinel lherzolites. Extraction of partial melt causes an increase in Mg#, so that the most primitive samples should have the lowest Mg#. Histograms of olivine compositions in spinel lherzolites from a wide variety of environments show that the most fertile samples that have not been grossly disturbed by metasomatism have Mg#s from 0.888 to ~0.896. Since the uncertainty with which olivine Mg#s are determined in individual samples is typically ~0.001, we interpret this distribution as implying an Mg# for the primitive depleted mantle of 0.890, which value we adopt. Hence,

$$\text{MgO} = (\text{FeO}^t \times 0.5610 \times \text{Mg\#}) / (1 - \text{Mg\#}) \quad (5)$$

with 8.10 ± 0.05 wt.% FeO^t, and Mg# = 0.890 ± 0.001 , this gives MgO = 36.77 ± 0.44 wt.%.

(ii) The second step uses the cosmochemical observation that only seven elements make up nearly 99% of any solar or chondritic composition, if the light elements (hydrogen, carbon, nitrogen, and associated oxygen) are removed. These elements are oxygen, magnesium, aluminum, silicon, sulfur, calcium, iron, and nickel. In the PM, nickel and sulfur are not important, and in any case their abundances are well known. The amount of oxygen is fixed by the stoichiometry of the relevant oxide components; hence,

$$\begin{aligned} \text{MgO} + \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{CaO} + \text{FeO}^t \\ = 98.41 \text{ wt.\%} \end{aligned} \quad (6)$$

The uncertainty is probably only $\pm 0.04\%$. The robustness of this constraint arises because the abundances of minor components which constitute 1.34% of the missing 1.59% (i.e., Na₂O, TiO₂, Cr₂O₃, MnO, and NiO, plus the excess oxygen in Fe₂O₃) vary little among reasonably fertile peridotites, and all other components (H₂O, CO₂, S, K, O, and the entire remaining trace element inventory) sum to <0.15%.

Although not quite as invariant as the FeO^t content, the concentration of SiO₂ is also

relatively insensitive to melt extraction and modal segregation processes. The SiO_2 concentration from SiO_2 versus MgO trends at 36.77% MgO is 45.40 ± 0.3 wt.% (see, e.g., Figure 2) conforming to fertile spinel-lherzolite suites worldwide (Figure 5).

Since calcium and aluminum are both RLEs, the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio is constrained at the chondritic value of 0.813. Unfortunately, calcium is rather more variable than other RLEs in chondrites, probably due to some mobility of calcium in the most primitive varieties (like Orgueil); hence, this ratio is not known as well as one might like. A reasonable uncertainty is ± 0.003 (see Chapter 1.03). Then,

$$\text{Al}_2\text{O}_3 = (98.41 - \text{MgO} - \text{SiO}_2 - \text{FeO}^t) / (1 + 0.813) \quad (7)$$

With the concentrations of FeO , MgO , and SiO_2 given above, $\text{Al}_2\text{O}_3 = 4.49$ wt.%; hence, $\text{CaO} = 3.65$ wt.%. The RLEs/ Mg ratio, normalized to this ratio in CI-chondrites, is then 1.21 ± 0.10 , corresponding to an unnormalized ratio of RLE in the Earth to RLE in CI of 2.80. Hence, under the assumption of constant RLE ratios in the Earth, this constrains the abundances of all other RLEs.

Putting the algorithm in the form of a simple equation makes the effects of the uncertainties transparent. The main weakness of the method is that the final result for CaO , Al_2O_3 , and the $(\text{RLE}/\text{Mg})_N$ ratio is particularly sensitive to the chosen value of $\text{Mg}\#$. However, the values of CaO and Al_2O_3 look very reasonable when compared to actual analyses of least-depleted peridotite samples, and we calculate through propagation of errors that uncertainties in $\sigma(\text{SiO}_2) = \pm 0.3$ wt.%, $\sigma(\text{FeO}^t) = \pm 0.05$ wt.%, and $\sigma(\text{Mg}\#) = \pm 0.001$ give a realistic uncertainty in $(\text{RLE}/\text{Mg})_N$ of ± 0.10 , or $\pm 8\%$. The algorithm also gives $\text{Al}/\text{Si} = 0.112 \pm 0.008$ and $\text{Mg}/\text{Si} = 1.045 \pm 0.014$. The resulting major element composition of PM is given in Table 3.

While all spinel-lherzolite facies suites show remarkably similar compositional trends as a function of depletion, some garnet peridotite xenoliths in kimberlites and lamproites from ancient cratonic lithospheric keels show significantly different trends (e.g., see Boyd, 1989; Chapters 2.05 and 2.08). Most of these xenoliths are extremely depleted; extrapolation of the trends back to the PM MgO of 36.7% gives similar concentrations of SiO_2 , FeO^t , Al_2O_3 , and CaO to the spinel lherzolites (O'Neill and Palme, 1998); the difference in their chemistry is due to a different style of melt extraction, and not a difference in original mantle composition.

Table 3 Major element composition of the PM, and comparison with estimates from the literature.

	This work	Ringwood (1979)	Jagoutz et al. (1979)	Wänke et al. (1984)	Palme and Nickel (1985)	Hart and Zindler (1986)	McDonough and Sun (1995)	Allègre et al. (1995)
MgO	36.77 ± 0.44	38.1	38.3	36.8	35.5	37.8	37.8	37.77
Al_2O_3	4.49 ± 0.37	3.3	4.0	4.1	4.8	4.06	4.4	4.09
SiO_2	45.40 ± 0.30	45.1	45.1	45.6	46.2	46.0	45.0	46.12
CaO	3.65 ± 0.31	3.1	3.5	3.5	4.4	3.27	3.5	3.23
FeO^t	8.10 ± 0.05	8.0	7.8	7.5	7.7		8.1	7.49
Total	98.41 ± 0.10	97.6	98.7	97.5	98.6		98.8	98.7
$(\text{RLE}/\text{Mg})_N$	1.21 ± 0.10	1.02	$1.03 - 1.14$	$1.1 - 1.4$	$1.3 - 1.5$	$1.06 - 1.07$	1.17	$1.05 - 1.08$
$\text{Mg}\#$	0.890 ± 0.001	0.895	0.897	0.897	0.891		0.893	0.900

$\text{Mg}\#$ —molar $\text{Mg}/(\text{Mg} + \text{Fe})$; FeO^t —all Fe as FeO ; $(\text{RLE}/\text{Mg})_N$ —refractory lithophile elements normalized to Mg - and CI-chondrites.

2.01.4.2.2 Comparison with other estimates of PM compositions

Ringwood (1979) reconstructed the primitive upper mantle composition by mixing appropriate fractions of basalts (i.e., partial melts from the mantle) and peridotites (the presumed residues from the partial melts). He termed this mixture *pyrolite*. In more recent attempts the PM composition has generally been calculated from trends in the chemistry of depleted mantle rocks. Jagoutz *et al.* (1979) used the average composition of six fertile spinel lherzolites as representing the primitive mantle. This leads to an MgO content of 38.3% and a corresponding Al_2O_3 content of 3.97% for PM (Table 3).

In RLE versus MgO correlations, the slopes depend on the compatibility of the RLE with the residual mantle minerals. The increase of the incompatible TiO_2 with decreasing MgO is much stronger than that of less incompatible Al_2O_3 which in turn has a steeper slope than the fairly compatible scandium. The ratio of these elements is thus variable in residual mantle rocks, depending on the fraction of partial melt that had been extracted. As the PM should have chondritic ratios, Palme and Nickel (1985) estimated the PM MgO content from variations in Al/Ti and Sc/Yb ratios with MgO in upper mantle rocks. Both ratios increase with decreasing MgO and at 36.8% MgO they become chondritic, which was chosen as the MgO content of the PM. Palme and Nickel (1985), however, found a nonchondritic Ca/Al ratio in their suite of mantle rocks and concluded that aluminum was removed from the mantle source in an earlier melting event. O'Neill and Palme (1998) suggested that the apparent high Ca/Al ratios in some spinel lherzolites are the result of a combination of melt extraction, producing residues with higher Ca/Al ratios, and modal heterogeneities, as discussed above.

Hart and Zindler (1986) also based their estimate on chondritic ratios of RLE. They plotted Mg/Al versus Nd/Ca for peridotites and chondritic meteorites. The two refractory elements, neodymium and calcium, approach chondritic ratios with increasing degree of fertility. From the intersection of the chondritic Nd/Ca ratio with observed peridotite ratios, Hart and Zindler (1986) obtained an Mg/Al ratio of 10.6 (Table 2).

McDonough and Sun (1995) assumed 37.7% as upper mantle MgO content and calculated RLE abundances from Al_2O_3 and CaO versus MgO correlations.

Allègre *et al.* (1995) took the same Mg/Al ratio as Hart and Zindler (1986) and assumed an Mg/Si ratio of 0.945 which they considered to be representative of the least differentiated sample from the Earth's mantle to calculate the bulk chemical composition of the upper mantle.

All these estimates lead to roughly similar PM compositions. The advantage of the method presented here is that it is not directly dependent on any of the element versus MgO correlations and that it permits calculation of realistic uncertainties for the PM composition. With error bars for MgO, SiO_2 , and FeO of only $\sim 1\%$ (rel), most other estimates for MgO and FeO in Table 3 fall outside the ranges defined here, whereas the higher uncertainties of Al_2O_3 and CaO of $\sim 10\%$ encompass all other estimates.

2.01.4.2.3 Abundance table of the PM

In Table 4 we have listed the element abundances in the Earth's primitive mantle. The CI-chondrite abundances are given for comparison (see Chapter 1.03). Major elements and associated errors are from the previous section (Table 3). Trace element abundances are in many cases from O'Neill and Palme (1998). In some instances new estimates were made. The abundances of refractory lithophile elements (denoted RLE in Table 4) are calculated by multiplying the CI-abundances by 2.80, as explained above. The two exceptions are vanadium and niobium. Both elements may, in part, be partitioned the core. The errors of the other RLEs are at least 8%, reflecting the combined uncertainties of the scaling element and the aluminum content plus the CI-error. This leads to uncertainties of 10% or more for many of the RLEs. The relative abundances of the RLEs are, however, better known, in particular when CI-chondritic ratios among RLEs are assumed. In this case the uncertainty of a given RLE ratio may be calculated by using the uncertainties of the CI-ratios given in Table 4.

In estimating trace element abundances of the BSE, it is useful to divide elements into compatible and incompatible elements with additional qualifiers such as moderately compatible or highly incompatible. A measure of compatibility is the extent to which an element partitions into the melt during mantle melting, quantified by the solid/melt partition coefficient $D^{(\text{solid/melt})}$. As Earth's crust formed by partial melting of the mantle, the crust/mantle concentration ratio of an element is an approximate measure for its compatibility (see O'Neill and Palme, 1998). Crust/mantle ratios for 64 elements are listed in Table 5. The abundances of elements in the continental crust were taken from Chapter 3.01), while the PM abundances are from Table 4. The RLEs in Table 5 (in bold face) comprise a large range of compatibilities, from highly incompatible elements (thorium, uranium) to only slightly incompatible elements (scandium). Abundances of RLEs in the Earth's

Table 4 Composition of the PM of the Earth ($Z < 42$ in ppm, $Z \geq 42$ in ppb, unless otherwise noted).

<i>Z</i>	<i>Element</i>	<i>CI</i>	<i>SD</i>	<i>Earth's mantle</i>	<i>SD</i>	<i>Comment</i>	<i>References</i>
1	H (%)	2.02	10	0.012	20	Mass balance	ON98, com
3	Li	1.49	10	1.6	20	Data on mantle rocks	Ja79, Ry87, Se00, com
4	Be	0.0249	10	0.070	10	RLE	
5	B	0.69	13	0.26	40	$B/K = (1.0 \pm 0.3) \times 10^{-3}$	Ch94
6	C	32,200	10	100	u	Mass balance	Zh93
7	N	3,180	10	2	u	Mass balance	Zh93
8	O (%)	46.5	10	44.33	2	Stoichiometry, with $Fe^{3+}/\sum Fe = 0.03$	Ca94
9	F	58.2	15	25	40	$F/K = 0.09 \pm 0.03$, $F/P = 0.3 \pm 0.1$	com
11	Na	4,982	5	2,590	5	versus MgO	ON98
12	Mg (%)	9.61	3	22.17	1	Major element	th.w.
13	Al	8,490	3	23,800	8	Major element, RLE	th.w.
14	Si (%)	10.68	3	21.22	1	Major element	ON98, th.w.
15	P	926	7	86	15	$P/Nd = 65 \pm 10$	McD85, La92
16	S	54,100	5	200	40	versus MgO, komatiites	ON91
17	Cl	698	15	30	40	Mass balance	Ja95, com
19	K	544	5	260	15	Mean of K/U and K/La	ON98
20	Ca	9,320	3	26,100	8	Major element, RLE	th.w.
21	Sc	5,90	3	16.5	10	RLE	
22	Ti	458	4	1,280	10	RLE	
23	V	54.3	5	86	5	versus MgO	ON98
24	Cr	2,646	3	2,520	10	versus MgO	ON98
25	Mn	1,933	3	1,050	10	versus MgO	ON98
26	Fe (%)	18.43	3	6.30	1	Major element	ON98, th.w.
27	Co	506	3	102	5	versus MgO	ON98
28	Ni	10,770	3	1,860	5	versus MgO	ON98
29	Cu	131	10	20	50		ON91, com
30	Zn	323	10	53.5	5	versus MgO	ON98
31	Ga	9.71	5	4.4	5	versus MgO	ON98
32	Ge	32.6	10	1.2	20	versus SiO ₂	ON98
33	As	1.81	5	0.066	70	$As/Ce = 0.037 \pm 0.025$	Si90
34	Se	21.4	5	0.079	u	$Se/S = 2,528$, chondritic	Pa03
35	Br	3.5	10	0.075	50	$Cl/Br = 400 \pm 50$	Ja95, com

37	Rb	2.32	5	0.605	10	Rb/Sr = 0.029 ± .002 (Sr isotopes), Rb/Ba = 0.09 ± 0.02	Ho83
38	Sr	7.26	5	20.3	10	RLE	
39	Y	1.56	3	4.37	10	RLE	
40	Zr	3.86	2	10.81	10	RLE	
41	Nb (ppb)	247	3	588	20	RLE	com
42	Mo	928	5	39	40	Mo/Ce = 0.027 ± 0.12, Mo/Nb = 0.05 ± .015	Si90, Fi95
44	Ru	683	3	4.55	4	HSE, Ru/Ir = CI-chondrite	com
45	Rh	140	3	0.93	5	HSE, Rh/Ir = CI-chondrite	com
46	Pd	556	10	3.27	15	HSE, Pd/Ir = 1.022 ± 0.097, H-chondrite	Mo85, com
47	Ag	197	10	4	u	Ag/Na = $1.6 \pm 1.0 \times 10^{-6}$ in MORB, Iherzolites, crust	th.w., com
48	Cd	680	10	64	u	Cd/Zn = $1.2 \pm 0.5 \times 10^{-3}$	th.w., com
49	In	78	10	13	40	In/Y = $3 \pm 1 \times 10^{-3}$, spinel Iherzolites	Yi02, BV81
50	Sn	1.680	10	138	30	Sn/Sm = 0.32 ± 0.06	Jo93
51	Sb	133	10	12	u	Sb/Pb = 0.074 ± 0.031, Sb/Pr = 0.02 in mantle, 0.05 in crust	Jo97
52	Te	2,270	10	8	u	Te/S = Cl	th.w., com
53	I	433	20	7	u	Mass balance	ON98, com
55	Cs	188	5	18	50	Cs/Ba = 1.1×10^{-3} in mantle, 3.6×10^{-3} in crust	McD92
56	Ba	2,410	10	6,750	15	RLE	
57	La	245	5	686	10	RLE	
58	Ce	638	5	1,786	10	RLE	
59	Pr	96.4	10	270	15	RLE	
60	Nd	474	5	1,327	10	RLE	
62	Sm	154	5	431	10	RLE	
63	Eu	58.0	5	162	10	RLE	
64	Gd	204	5	571	10	RLE	
65	Tb	37.5	10	105	15	RLE	
66	Dy	254	5	711	10	RLE	

(continued)

Table 4 (continued).

Z	Element	CI	SD	Earth's mantle	SD	Comment	References
67	Ho	56.7	10	159	15	RLE	
68	Er	166	5	465	10	RLE	
69	Tm	25.6	10	71.7	15	RLE	
70	Yb	165	5	462	10	RLE	
71	Lu	25.4	10	71.1	15	RLE	
72	Hf	107	5	300	10	RLE	
73	Ta	14.2	6	40	10	RLE	
74	W	90.3	4	16	30	W/Th = 0.19 ± 0.03	Ne96
75	Re	39.5	4	0.32	10	Re/Os = 0.0874 ± 0.0027, H-chondrite	Wa02, com
76	Os	506	5	3.4	10	HSE, Os/Ir = 1.07 ± 0.014, H-chondrite	Ka89, com
77	Ir	480	4	3.2	10	av. PM analyses	Mo01, com
78	Pt	982	4	6.6	12	HSE, Pt/Ir, CI-chondrite	com
79	Au	148	4	0.88	11	HSE, Ir/Au = 3.63 ± 0.13, H-chondrite	Ka89, com
80	Hg	310	20	6	u	Hg/Se = 0.075	th.w., com
82	Tl	143	10	3	u	Tl/Rb = 0.005 in crust	He80, com
82	Pb	2,530	10	185	10	²³⁸ U/ ²⁰⁴ Pb = 8.5 ± 0.5, 206/204 = 18, 207/204 = 15.5, 208/204 = 38	Ga96
83	Bi	111	15	5	u	Bi/La = 8 × 10 ⁻³ in crust	th.w., com
90	Th	29.8	10	83.4	15	RLE	
92	U	7.8	10	21.8	15	RLE	

SD—standard deviation in %; RLE—refractory lithophile element; HSE—highly siderophile element; th.w.—this work; com—comments in text; u—uncertain, error exceeding 50%; CI—values, Chapter 1.03; References: BV81—BYSP (1981); Ca94—Canil *et al.* (1994); Cl94—Chaussidon and Jambon (1994); F95—Fitton (1995); Ga96—Galer and Goldstein (1996); He80—Hertogen *et al.* (1980); Ho83—Hofmann and White (1983); Ia79—Jagoutz *et al.* (1979); Ja95—Jambon *et al.* (1995); Jo93—Jochum *et al.* (1993); Jo97—Jochum and Hofmann (1997); Ka89—Kallamyn *et al.* (1989); La92—Langmuir *et al.* (1992); McD85—McDonough *et al.* (1985); McD92—McDonough *et al.* (1992); Mo01—Morgan *et al.* (2001); Mo85—Morgan *et al.* (1985); Ne96—Newsom *et al.* (1996); ON91—O'Neill (1991); ON98—O'Neill and Palme (1998); Pa03—Palme and Jones (2003); Ry87—Ryan and Langmuir (1987); Se00—Seitz and Woodland (2000); S90—Sims *et al.* (1990); Wa02—Walker *et al.* (2002); Zh93—Zhang and Zindler (1993); Yi02—Yi *et al.* (2000).

Table 5 Enrichment of elements in the bulk continental crust over the PM (abundances in ppb, except when otherwise noted, refractory lithophile elements are in bold face).

<i>Element</i>	<i>Mantle (PM)</i>	<i>Crust</i>	<i>Crust/Mantle</i>	<i>Element</i>	<i>Mantle (PM)</i>	<i>Crust</i>	<i>Crust/Mantle</i>
1 Ti	3	360	120.0	31 Dy	711	3,700	5.20
2 W	16	1,000	62.5	32 Ho	159	780	4.91
3 Cs	18	1,000	55.6	33 Yb	462	2,200	4.76
4 Rb (ppm)	0.605	32	52.9	34 Er	465	2,200	4.73
5 Pb	185	8,000	43.2	35 Y	4.37	20	4.58
6 Th	83.4	3,500	42.0	36 Tm	72	320	4.44
7 U	21.8	910	41.7	37 Lu	71.7	300	4.18
8 Ba (ppm)	6.75	250	37.1	38 Ti (ppm)	1,282	5,400	4.21
9 K (ppm)	260	9,100	35.0	39 Ga (ppm)	4.4	18	4.09
10 Mo (ppm)	39	1,000	25.6	40 In	13	50	3.85
11 Ta	40	1,000	25.0	41 Cu (ppm)	20	75	3.75
12 La	686	16,000	23.3	42 Al (%)	2.37	8.41	3.55
13 Be (ppm)	0.07	1.5	21.4	43 Au	0.88	3	3.41
14 Ag	4	80	20.0	44 V (ppm)	86	230	2.67
15 Ce	1,785	33,000	18.5	45 Ca (%)	2.61	5.29	2.03
16 Nb (ppm)	0.6	11	18.3	46 Sc (ppm)	16.5	30	1.82
17 Sn	138	2,500	18.1	47 Re	0.32	0.5	1.56
18 Sb	12	200	16.7	48 Cd	64	98	1.53
19 As	66	1,000	15.2	49 Zn (ppm)	53.5	80	1.50
20 Pr	270	3,900	14.4	50 Ge (ppm)	1.2	1.6	1.33
21 Sr (ppm)	20.3	260	12.8	51 Mn (ppm)	1,050	1,400	1.33
22 Nd	1,327	16,000	12.1	52 Si (%)	21.22	26.77	1.26
24 Hf	300	3,000	10.0	53 Fe (%)	6.3	7.07	1.12
25 Zr (ppm)	10.8	100	9.26	54 Se	79	50	0.63
26 Na (ppm)	2,590	23,000	8.88	55 Li (ppm)	2.2	1.3	0.59
25 Sm	431	3,500	8.12	56 Co (ppm)	102	29	0.28
27 Eu	162	1,100	6.79	57 Mg (%)	22.17	3.2	0.14
28 Gd	571	3,300	5.78	58 Cr (ppm)	2,520	185	0.073
29 B (ppm)	0.26	1.5	5.77	59 Ni (ppm)	1,860	105	0.056
30 Tb	105	600	5.71	60 Ir	3.2	0.1	0.031

Sources of data: mantle—Table 4; continental crust—Chapter 3.01.

mantle are calculated by scaling RLEs to aluminum and calcium, as discussed above.

Abundances of nonrefractory incompatible lithophile elements (potassium, rubidium, caesium, etc.) or partly siderophile/chalcophile elements (tungsten, antimony, tin, etc.) are calculated from correlations with RLE of similar compatibility. This approach was first used by Wänke *et al.* (1973) to estimate abundances of volatile and siderophile elements such as potassium or tungsten in the moon. The potassium abundance was used to calculate the depletion of volatile elements in the bulk moon, whereas the conditions of core formation and the size of the lunar core may be estimated from the tungsten abundance, as described by Rammensee and Wänke (1977). This powerful method has been subsequently applied to Earth, Mars, Vesta, and the parent body of HED meteorites. The procedure is, however, only applicable if an incompatible refractory element and a volatile or siderophile element have the same degree of incompatibility, i.e., do not fractionate from each other during igneous processes. In other words, a good correlation of the two elements over a wide

concentration range and over all the important differentiation processes that have occurred in the planet is required. In estimating abundances of trace elements from correlations, care must be taken to ensure that all important reservoirs are included in the data set (see O'Neill and Palme (1998) for details).

A particularly good example is the samarium versus tin correlation displayed in Figure 6 modified from figure 8 of Jochum *et al.* (1993). Both basalts, partial melts from the mantle, and mantle samples representing the depleted mantle after removal of melt plot on the same correlation line. From the Sm/Sn ratio of 0.32 obtained by Jochum *et al.* (1993), a mantle abundance of 144 ppb is calculated, reflecting a 35-fold depletion of tin relative to CI-chondrites in the Earth's mantle. The origin of this depletion is twofold: (i) a general depletion of moderately volatile elements in the Earth (see below) and (ii) some partitioning of the siderophile element tin into the core of the Earth. Many of the abundances of moderately volatile lithophile, siderophile, and chalcophile elements listed in Table 4 were calculated from such correlations with refractory lithophile elements of

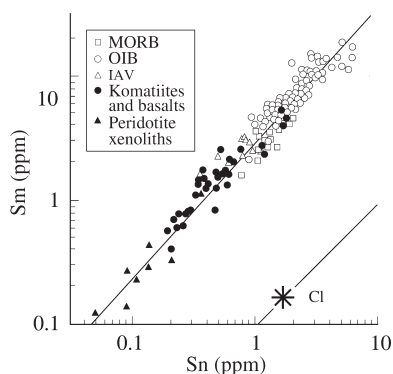


Figure 6 Correlation of Sm versus Sn in partial melts and residues of mantle melting. The constant Sm/Sn ratio suggests that this ratio is representative of the PM. Sn is depleted relative to CI-chondrites by a factor of 35. The knowledge of the abundance of the refractory element Sm in PM allows the calculation of the Sn PM abundance. Many of the PM abundances of siderophile and chalcophile elements are calculated from similar correlations (after Jochum *et al.*, 1993).

similar compatibility. Well-known examples are K/U, K/La, W/Th, P/Nd, Rb/Ba, etc.

The abundances of elements marked “com” in Table 4 are more difficult to estimate and require a more sophisticated approach. Detailed explanations on how the abundances are estimated are given below.

Hydrogen. The mass of the atmosphere is 5.1×10^{18} kg, of which 1.3% by mass is ^{40}Ar , derived from ^{40}K decay. The potassium content of the PM is 260 ppm; hence, the amount of ^{40}Ar produced from ^{40}K over the age of the Earth is calculated to 1.34×10^{17} kg. Thus, the amount of ^{40}Ar in the atmosphere corresponds to 0.5 of the amount produced in the PM, which is, therefore, taken to be the fraction of the mantle that has degassed. The amount of H_2O in the hydrosphere is 1.7×10^{21} kg (oceans, pore water in sediments, and ice). If this corresponds to the water originally contained in the degassed mantle, it would imply a PM abundance of 850 ppm. However, H_2O , unlike argon, is recycled into the mantle by subduction of the oceanic crust, such that MORB, products of the degassed mantle, contain ~0.2 wt.% H_2O . If MORB is produced by 10% partial melt and melting completely extracts H_2O , this corresponds to 200 ppm in the degassed mantle. Allowing 0.5 wt.% for the chemically bound water in the continental crust gives a total PM abundance of 1,100 ppm H_2O , or 120 ppm H. Since the exospheric inventory for H_2O is quite well constrained, the uncertainty of this estimate is only about $\pm 20\%$.

Lithium. Ryan and Langmuir (1987) estimate 1.9 ± 0.2 ppm Li for the PM based on the analyses of peridotites. As Li is sited in the major minerals of upper mantle rocks and behaves as moderately

incompatible, we have calculated bulk contents of spinel and garnet lherzolites from the mineral data of Seitz and Woodland (2000) which suggests an upper limit of 1.3 ppm for fertile mantle rocks. The range in unmetamorphosed fertile peridotites analyzed by Jagoutz *et al.* (1979) is somewhat higher, from 1.2 ppm to 2.07 ppm with an average of 1.52 ppm. We take here the average of all three estimates as 1.6 ppm Li.

Halides (fluorine, chlorine, bromine, and iodine). Fluorine as F^- substitutes readily for OH^- in hydroxy minerals, implying that it probably occurs in all “nominally anhydrous minerals” in the same way as OH^- . Fluorine is not significantly soluble in seawater. Both these properties make its geochemical behavior quite different from the other halides. F/K and F/P ratios in basalts are reasonably constant (Smith *et al.*, 1981; Sigvaldason and Oskarsson, 1986) with ratios of 0.09 ± 0.04 and 0.29 ± 0.1 , respectively. Both ratios yield the same value of 25 ppm for the PM abundance which is listed in Table 4. However, the F/K ratio in the continental crust appears distinctly higher and the F/P ratio lower (Gao *et al.*, 1998), indicating that the incompatibility of these elements increases in the order $\text{P} < \text{F} < \text{K}$.

Jambon *et al.* (1995) estimated the amount of chlorine in the “exosphere” to be 3.8×10^{19} kg, made up of 2.66×10^{19} kg in seawater, the rest in evaporites. If this is derived by depletion of 50% of the mantle (^{40}Ar argument), it corresponds to a contribution of 19 ppm from the depleted mantle. The average amount of chlorine in the rocks of the continental crust is only a few hundred ppm (Wedepohl, 1995; Gao *et al.*, 1998) and can therefore be neglected. The amount of chlorine recycled back into the depleted mantle is more difficult to estimate, as the chlorine in primitive, uncontaminated MORB is highly variable and correlates poorly with other incompatible elements (Jambon *et al.*, 1995). Adopting a mean value of 100 ppm and assuming 10% melting adds another 10 ppm (the assumption here is that chlorine is so incompatible that all the chlorine in the MORB source mantle is from recycling and that MORB is assumed to be a 10% partial melt fraction). This gives a total chlorine content of 30 ppm for PM.

The Cl/Br ratio of seawater is 290, but that of evaporites is considerably higher ($>3,000$), such that the exospheric ratio is $\sim 400 \pm 50$. The ratio in MORB and other basalts is the same (Jambon *et al.*, 1995). Iodine in the Earth is concentrated in the organic matter of marine sediments; this reservoir contains 1.2×10^{16} kg I (O'Neill and Palme, 1998), corresponding to 6 ppb if this iodine comes from 50% of the mantle. MORBs have ~ 8 ppb I (Déruelle *et al.*, 1992) implying ~ 1 ppb in the depleted (degassed) mantle, for a PM abundance of 7 ppb.

Copper. The abundance of copper in the depleted mantle raises a particular problem. Unlike other moderately compatible elements, there is a difference in the copper abundances of massive peridotites compared to many, but not all, of the xenolith suites from alkali basalts. The copper versus MgO correlations in massive peridotites consistently extrapolate to values of ~ 30 ppm at 36% MgO, whereas those for the xenoliths usually extrapolate to < 20 ppm, albeit with much scatter. A value of 30 ppm is a relatively high value when chondrite normalized ($(\text{Cu/Mg})_N = 0.11$), and would imply Cu/Ni and Cu/Co ratios greater than chondritic, difficult to explain, if true. However, the copper abundances in massive peridotites are correlated with sulfur, and may have been affected by the sulfur mobility postulated by Lorand (1991). Copper in xenoliths is not correlated with sulfur, and its abundance in the xenoliths and also inferred from correlations in basalts and komatiites points to a substantially lower abundance of ~ 20 ppm (O'Neill, 1991). We have adopted this latter value.

Niobium. Wade and Wood (2001) have suggested that niobium, potentially the most siderophile of the RLEs, is depleted in the PM by some extraction into the core. The depletion of niobium estimated from Nb/Ta would be $\sim 15 \pm 15\%$ (Kamber and Collerson, 2000). As an RLE, niobium would have a mantle abundance of 690 ppb. Considering that 15% is in the core reduces this number to 588 ppm, which is listed in Table 2.

Silver. The common oxidation state is Ag^{1+} , which has an ionic radius between Na^{1+} and K^{1+} , and nearer to the former. Rather gratifyingly, the ratio Ag/Na is quite constant between peridotites (BVSP), MORB and other basalts (Laul *et al.*, 1972; Hertogen *et al.*, 1980), and continental crust (Gao *et al.*, 1998) at $(1.6 \pm 1.0) \times 10^{-6}$, giving 4 ppb in the PM. Silver reported by Garuti *et al.* (1984) in massive peridotites of the Ivrea zone is much higher and does not appear realistic.

Cadmium. Cadmium appears to be compatible or very mildly incompatible, similar to zinc. Almost nothing is known about which minerals it prefers. From a crystal-chemical view, cadmium has similar ionic radius and charge to calcium, but a tendency to prefer lower coordination due to its more covalent bonding with oxygen (similar to zinc and indium). Cadmium in spinel lherzolites varies from 30 ppb to 60 ppb (BVSP) and varies in basalts from about 90 ppb to 150 ppb (Hertogen *et al.*, 1980; Yi *et al.*, 2000). Cd/Zn is $\sim 10^{-3}$ in peridotites (BVSP) and the continental crust (Gao *et al.*, 1998), and $\sim 1.5 \times 10^{-3}$ in basalts (Yi *et al.*, 2000). We adopt the mean of these ratios (1.2×10^{-3}).

Tellurium. Tellurium is chalcophile (Hattori *et al.*, 2002), but is not correlated with other

chalcophile elements, or anything else. Empirically, tellurium appears to be quite compatible. Morgan (1986) found 12.4 ± 3 ppb for fertile spinel-lherzolite xenoliths (previously published in BVSP), mainly from Kilbourne Hole, with somewhat lower values for more depleted samples. Yi *et al.* (2000) found 1–7 ppb for MORB, most OIB and submarine IAB, but with samples from Loihi extending to 29 ppb. These MORB data confirm the earlier data of Hertogen *et al.* (1980), who analyzed five MORBs with tellurium from 1 ppb to 5 ppb, and two outliers with 17 ppb, which also had elevated selenium. The important point is that tellurium in peridotites is often higher than in basalts, plausibly explained by retention in a residual sulfide phase. Thus, future work on tellurium needs to address the composition of mantle sulfides. If Te/S were chondritic, the PM with 200 ppm S would have 8 ppb Te. We have adopted this as the default value, as to use anything else would have interesting but unwarranted cosmochemical implications.

Mercury. Very few pertinent data exist, and the high-temperature geochemical properties of mercury are very uncertain. Flanagan *et al.* (1982) measured mercury in a variety of standard rocks, including basalts. Mercury in basalts is variable (3–35 ppb) and does not correlate with other elements. Garuti *et al.* (1984) report higher levels in massive peridotites (to 150 ppb, but mostly 20–50 ppb), of doubtful reliability (cf. silver). Wedepohl (1995) suggests 40 ppb in the average continental crust, but largely from unpublished sources. Gao *et al.* (1998) report ~ 9 ppb for the continental crust of East China. On the assumption that mercury is completely chalcophile in its geochemical properties, we obtain a crustal ratio of $\text{Hg/Se} = 0.075$ from Gao *et al.* (1998); on the further assumption that this ratio is conserved during mantle melting, this gives Hg = 6 ppb.

Thallium. Tl^{1+} has an ionic radius similar to Rb^{1+} . The crustal ratio Tl/Rb is quite constant at 0.005 (Hertogen *et al.*, 1980). Since $> 60\%$ of the Earth's rubidium is probably in the continental crust, and rubidium is reasonably well known from Rb/Sr isotope systematics, this ratio should supply a reasonable estimate for the PM.

Bismuth. Bi^{3+} has an ionic radius similar to La^{3+} , indicating that it may behave geochemically like this lightest of the REEs, i.e., highly incompatible. Bismuth in spinel lherzolites is 1–2 ppb, and is much less variable than lanthanum, with which it shows no correlation at all (BVSP). Nor does bismuth correlate with any other lithophile element. It is, however, noticeably higher in metasomatized garnet peridotites with elevated lanthanum. Bismuth in MORB is also quite constant at 6–9 ppb (Hertogen *et al.*, 1980), but much higher in the incompatible-element enriched BCR-1 (46 ppb). The crustal abundance

is distinctly elevated, and also unusually variable, with 90–1,400 ppb in various crustal units from East China units tabulated by Gao *et al.* (1998). Their mean is 260 ppb, with a Bi/La ratio of 0.008. This would imply PM bismuth of 5 ppb.

Highly siderophile elements. The six platinum-group elements (PGEs: osmium, iridium, platinum, ruthenium, rhodium, palladium) as well as rhenium and gold are collectively termed highly siderophile elements (HSEs). The basis for estimating HSE abundances in the Earth's mantle is the rather uniform distribution of iridium in mantle peridotites. Morgan *et al.* (2001) estimate 3.2 ± 0.2 ppb Ir. Data for other HSE show considerably larger scatter. As the $^{187}\text{Os}/^{186}\text{Os}$ ratios of upper mantle rocks are similar to H-chondrites but different from carbonaceous chondrites (Walker *et al.*, 2002), mantle abundances are estimated by assuming H-chondrite ratios among the HSEs. Kallemeyn and Wasson (1981) determined an Os/Ir ratio of 1.062 for CI-chondrites and a mean of 1.07 ± 0.04 for 19 carbonaceous chondrites, which is identical to the Os/Ir ratio of 1.072 ± 0.014 for 22 H-chondrites analyzed by Kallemeyn *et al.* (1989). For the calculation of the osmium mantle abundance we have used an Os/Ir ratio of 1.07, resulting in an osmium mantle content of 3.4 ppb. For platinum, rhodium, and ruthenium, CI-ratios with iridium were used (Table 4) as they are more accurately known than H-chondrite ratios. The Pd/Ir and Pd/Au ratios are different between CI-chondrites and H-chondrites. Morgan *et al.* (1985) determined an average Pd/Ir ratio of 1.02 ± 0.097 for 10 ordinary chondrites, leading to a PM concentration of 3.3 ppb. Kallemeyn *et al.* (1989) obtained a mean Ir/Au ratio of 3.63 ± 0.13 for H-chondrites. This value is near the CI-ratio of 3.24 calculated from the abundances in Table 4. The H-chondrite ratio leads to an upper mantle gold content of 0.88 ppb which is listed in Table 4.

2.01.4.3 Is the Upper Mantle Composition Representative of the Bulk Earth Mantle?

It has been proposed that there is a substantial difference in major element chemistry, particularly in Mg/Si and Mg/Fe ratios, between the upper mantle above the 660 km seismic discontinuity and the lower mantle below this discontinuity. A chemical layering may have occurred either as a direct result of inhomogeneous accretion without subsequent mixing, which has not to our knowledge been seriously suggested in recent times; or by some process akin to crystal fractionation from an early magma ocean, which has. The latter process would also imply gross layering of trace elements, and would invalidate the conclusions drawn here concerning PM

volatile and siderophile element abundances. For example, the nearly chondritic Ni/Co ratio observed in the upper mantle would be a fortuitous consequence of olivine flotation into the upper mantle (Murthy, 1991; see Chapter 2.10).

Three kinds of evidence have been put forward in support of a lower mantle with a different composition from the upper mantle. The first was the apparent lack of a match between the seismic and other geophysical properties observed for the lower mantle, and the laboratory-measured properties of lower mantle minerals (MgSiO₃-rich perovskite and magnesiowüstite) in an assemblage with the upper mantle composition (meaning, effectively, with the upper mantle's Mg/Si and Mg/Fe ratios). Jackson and Rigden (1998) reinvestigated these issues and conclude that there is no such mismatch (see Chapter 2.02).

The second line of evidence is that crystal fractionation from an early magma ocean would inevitably lead to layering. The fluid-dynamical reasons why this is not inevitable (and is in fact unlikely) are discussed by Tonks and Melosh (1990) and Solomatov and Stevenson (1993).

The third kind of evidence is that the upper mantle composition violates the cosmochemical constraints on PM compositions that are obtained from the meteoritic record. A detailed comparison of PM compositions with primitive meteorite compositions is given below and it is shown that the PM composition shows chemical fractionations that are similar to the fractionations seen in carbonaceous chondrites.

The geochemical evidence against gross compositional layering of the mantle seems to us conclusive. This evidence is the observation that the upper mantle composition as deduced from the depleted mantle/continental crust model conforms, within uncertainty, to the cosmochemical requirement of having strictly chondritic ratios of the RLEs. These ratios would not have survived large-scale differentiation by fractional crystallization. Experimental data (e.g., Kato *et al.*, 1988) show that Sm/Nd and Lu/Hf would not remain unfractionated if there had been any significant MgSiO₃-perovskite or majoritic garnet fractionation. The most precise line of argument comes from the observed secular evolution of ϵ_{Nd} and ϵ_{Hf} towards their present values in the depleted mantle reservoir. With chondritic ratios among hafnium, lutetium, neodymium, and samarium, the observed mantle array can be explained by assuming the depleted mantle to represent ancient garnet-bearing residues from normal mantle melting. Although perovskite fractionation during cooling of a magma ocean in the early history of the Earth could explain the Hf–Lu systematics, it would not account for the neodymium isotopic signature of the oceanic basalts (Blicher-Toft and Albarede, 1997).

Thus, there is neither evidence for nonchondritic bulk Earth RLE ratios nor for nonchondritic ratios in the upper or lower mantle.

Finally, a well-mixed compositionally uniform mantle is also supported by geophysical evidence (i.e., tomography), showing that slabs penetrate into the lower mantle, which would support whole mantle convection (Van der Hilst *et al.*, 1997; see Chapter 2.02).

2.01.5 COMPARISON OF THE PM COMPOSITION WITH METEORITES

As discussed earlier in the chapter, the existing models of the accretion of the Earth assume collisional growth by successive impacts of Moon- to Mars-sized planetary embryos, a process lasting for tens of millions of years and implying significant radial mixing (e.g., Chambers, 2001). The growth of the embryos from micrometer-sized dust grains to kilometer-sized planetesimals is completed in less than one million years, with material derived from local feeding zones. Meteorites are fragments of disrupted planetesimals that did not accumulate to larger bodies, perhaps impeded by the strong gravitational force of Jupiter. Thus meteorites may be considered to represent early stages in the evolution of planets, i.e., building blocks of planets.

As pointed out before, many of the variations in chemical composition and oxidation state observed in chondritic meteorites must have been established at an early stage, before nebular components accreted to small planetesimals.

As nebular fractionations have produced a variety of chondritic meteorites, it is necessary to study the whole spectrum of nebular fractionations in order to see if the proto-earth material has been subjected to the same processes as those recorded in the chondritic meteorites. As the Earth makes up more than 50% of the inner solar system, any nebular fractionation that affected the Earth's composition must have been a major process in the inner solar system. We will begin the discussion of nebular fractionations in meteorites and in the Earth with refractory elements and continue with increasingly more volatile components as outlined in Table 2.

2.01.5.1 Refractory Lithophile Elements

Figure 7 shows the abundances of the four refractory lithophile elements—aluminum, calcium, scandium, and vanadium—in several groups of undifferentiated meteorites, the Earth's upper mantle and the Sun. The RLE abundances are divided by magnesium and this ratio is then normalized to the same ratio in CI-chondrites. These $(\text{RLE}/\text{Mg})_{\text{N}}$ ratios are plotted in Figure 7 (see also Figure 1). The level of refractory element abundances in bulk chondritic meteorites varies by less than a factor of 2. Carbonaceous chondrites have either CI-chondritic or higher Al/Mg ratios (and other RLE/Mg ratios), while rumurutiites (highly oxidized chondritic meteorites), ordinary chondrites, acapulcoites, and enstatite chondrites are depleted in refractory elements. The $(\text{RLE}/\text{Mg})_{\text{N}}$ ratio in the mantle of the Earth is within the range of carbonaceous chondrites.

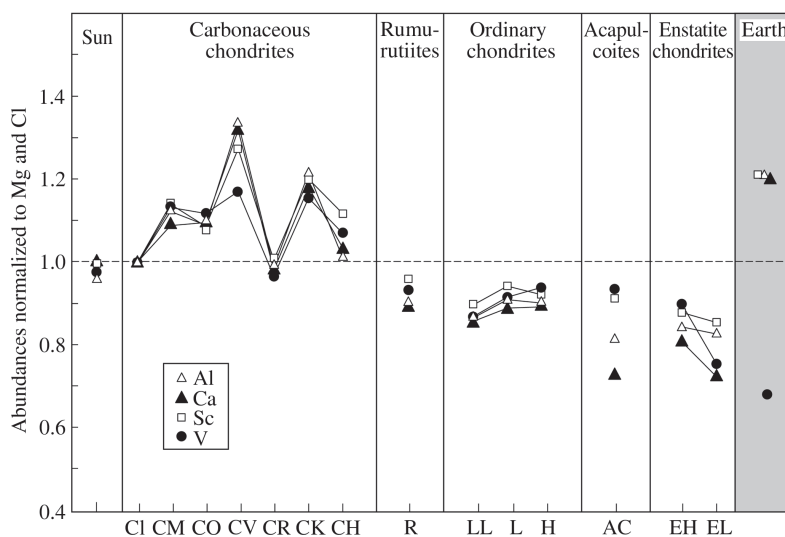


Figure 7 Element/Mg ratios normalized to CI-chondrites of RLEs in various groups of chondritic meteorites. The carbonaceous chondrites are enriched in refractory elements; other groups of chondritic meteorites are depleted. The PM has enrichments in the range of carbonaceous chondrites. The low V reflects removal of V into the core (source O'Neill and Palme, 1998).

The apparent depletion of vanadium in the Earth's mantle has two possible causes. (i) Vanadium is one of the least refractory elements. It is, e.g., significantly less enriched in CV-chondrites compared to other RLEs (Figure 7). Thus, vanadium is an exception to the general rule of constant ratios among RLEs. (ii) Vanadium is slightly siderophile. Consequently a certain fraction of vanadium is sequestered in the Earth's core (see below). Since neither aluminum, calcium, scandium, or magnesium are expected to partition into metallic iron, even at very reducing conditions, the RLE/Mg ratios should be representative of the bulk Earth. Thus, relative to CI-chondrites bulk Earth is enriched in refractory elements by a factor of 1.21 when normalized to magnesium, and by a factor of 1.41 when normalized to silicon, within the range of carbonaceous chondrites but very different from ordinary and enstatite chondrites. These chondrite groups are depleted in refractory elements (Figure 7). The small variations among RLE ratios in chondritic meteorites evident in Figure 7 probably reflect, with the exception of vanadium, the limited accuracy of analyses and inhomogeneities in analyzed samples. Whether there are minor variations ($<5\%$) in RLE ratios among chondritic meteorites is unclear. It cannot, however, be excluded based on available evidence.

The constancy of refractory element ratios in the Earth's mantle, discussed before, is documented in the most primitive samples from the Earth's mantle. Figure 8 plots (modified from Jochum *et al.*, 1989) the PM-normalized abundances of 21 refractory elements from four fertile spinel lherzolites. These four samples closely approach, in their bulk chemical composition, the primitive upper mantle as defined in the previous section. The patterns of most of the REEs (up to praseodymium) and of titanium, zirconium, and yttrium are essentially flat. The three

elements—calcium, aluminum, and scandium (not shown in Figure 8)—have the same PM-normalized ratios, i.e., they would plot at the level of ytterbium and lutetium in Figure 8. Only strongly incompatible elements—such as thorium, niobium, lanthanum, and caesium—are depleted. A very small degree of partial melting is sufficient to extract these elements from the mantle and leave the major element composition of the residual mantle essentially unaffected.

Chondritic relative abundances of strongly incompatible RLEs (lanthanum, niobium, tantalum, uranium, thorium) and their ratios to compatible RLEs in the Earth's mantle are more difficult to test. The smooth and complementary patterns of REEs in the continental crust and the residual depleted mantle are consistent with a bulk REE pattern that is flat, i.e., unfractionated when normalized to chondritic abundances. As mentioned earlier, the isotopic compositions of neodymium and hafnium are consistent with chondritic Sm/Nd and Lu/Hf ratios for bulk Earth. Most authors, however, assume that RLEs occur in chondritic relative abundances in the Earth's mantle. However, the uncertainties of RLE ratios in CI-meteorites do exceed 10% in some cases (see Table 4) and the uncertainties of the corresponding ratios in the Earth are in same range (Jochum *et al.*, 1989; Weyer *et al.*, 2002). Minor differences (even in the percent range) in RLE ratios between the Earth and chondritic meteorites cannot be excluded, with the apparent exception of Sm/Nd and Lu/Hf ratios (Blicher-Toft and Albarede, 1997).

That the assumption of chondritic relative abundances of refractory elements in the Earth is not without problems is demonstrated by the U/Nb ratio. Hofmann *et al.* (1986) showed that Nb/U is constant over several orders of magnitude of niobium or uranium concentrations in both MORBs and OIBs, with an Nb/U ratio of $\sim 47 \pm 10$, implying that niobium and uranium have similar incompatibilities during mantle melting, and that this ratio is also the ratio in the source of both MORBs and OIBs. However, because Nb and U are both RLEs, their ratio in the PM is assumed to be chondritic, i.e., 31.7. It turns out that the high ratio in the MORB and OIB source is compensated by a low ratio in the continental crust of ~ 10 , indicating that niobium and uranium did not behave congruently during the processes responsible for crust formation. Table 4 lists a niobium concentration for PM that is 15% below the average normalized RLE abundance of the PM, following the suggestion of Wade and Wood (2001) that some niobium has partitioned into the core. Although this would reduce the PM Nb/U ratio from 31.7 to 27.6, it would not affect conclusions regarding the complementary behavior of uranium and niobium during MORB

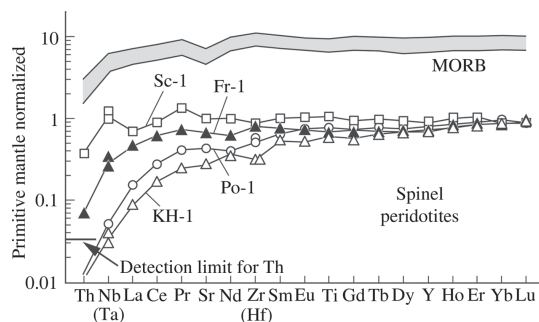


Figure 8 Abundances of RLEs in fertile spinel-lherzolite xenoliths from various occurrences. Compatible elements have constant enrichment factors. Abundances decrease with increasing degree of incompatibility, reflecting removal of very small degrees of partial melts (after Jochum *et al.*, 1989).

melting and crust formation. The lower than chondritic Nb/LRE ratio proposed for the Earth's mantle demonstrates how difficult it is to establish that an RLE ratio is indeed chondritic in the mantle. The 15% depletion of niobium relative to other RLE was only noticed from high accuracy studies of Nb/Ta abundances in mantle and crustal reservoirs (Münker *et al.*, 2003).

The Th/U ratio is of great importance in geochemistry, as uranium and thorium are major heat-producing elements in the interior of the Earth. In addition, the three lead isotopes— ^{206}Pb , ^{207}Pb , and ^{208}Pb —the decay products of the two uranium isotopes and of ^{232}Th are used for dating. The chondritic ratio of the two refractory elements, thorium and uranium, is not as well established as one would generally assume. Although a formal uncertainty of 15% is calculated for the Th/U ratio in CI-chondrites obtained from data in Table 4, the ratio is better known. Rocholl and Jochum (1993) estimate a chondritic Th/U ratio of 3.9 with an error of 5%. Based on terrestrial lead-isotope systematics, Allègre *et al.* (1986) concluded that the average Th/U ratio of the Earth's mantle is 4.2, significantly above the CI-chondritic ratio of 3.82 listed here (Table 4) or the chondritic ratio of 3.9 given by Rocholl and Jochum (1993). There is little evidence for such a high Th/U ratio, as, e.g., shown by Campbell (2002) who used a correlation of Th/U versus Sm/Nd to establish a Th/U ratio of ~ 3.9 at a chondritic Sm/Nd ratio.

In summary, it is generally assumed that all refractory lithophile elements are enriched in the Earth's mantle by a common factor of $2.80 \times \text{CI}$. This factor can be directly verified for the less

incompatible refractory elements by studying the most fertile upper mantle rocks, and there is indirect evidence that this factor is also valid for the highly incompatible refractory elements, although deviations from chondritic relative abundances of the order of 5–10% cannot be excluded for some elements. Nonchondritic refractory element ratios in various mantle and crustal reservoirs are interpreted in terms fractionation processes within the Earth. The absolute level of refractory elements, i.e., the refractory to nonrefractory element ratios in the Earth's mantle, is above that of CI-chondrites, somewhere between type 2 and type 3 carbonaceous chondrites, depending on magnesium or silicon normalization, but very different from ordinary chondrites.

2.01.5.2 Refractory Siderophile Elements

RSEs comprise two groups of metals: the HSEs—osmium, rhenium, ruthenium, iridium, platinum, and rhodium with metal/silicate partition coefficients $>10^4$ —and the two moderately siderophile elements—molybdenum and tungsten (Table 2). As the major fractions of these elements are in the core of the Earth, it is not possible to establish independently whether the bulk Earth has chondritic ratios of RLE to RSE, i.e., whether ratios such as Ir/Sc or W/Hf are chondritic in the bulk Earth. Support for the similar behavior of RLE and RSE in chondritic meteorites is provided by Figure 9. The ratio of the RSE, Ir, to the nonrefractory siderophile element, Au, is plotted against the ratio of the RLE, Al, to the nonrefractory lithophile element, Si. Figure 9 demonstrates that RLEs and RSEs are correlated

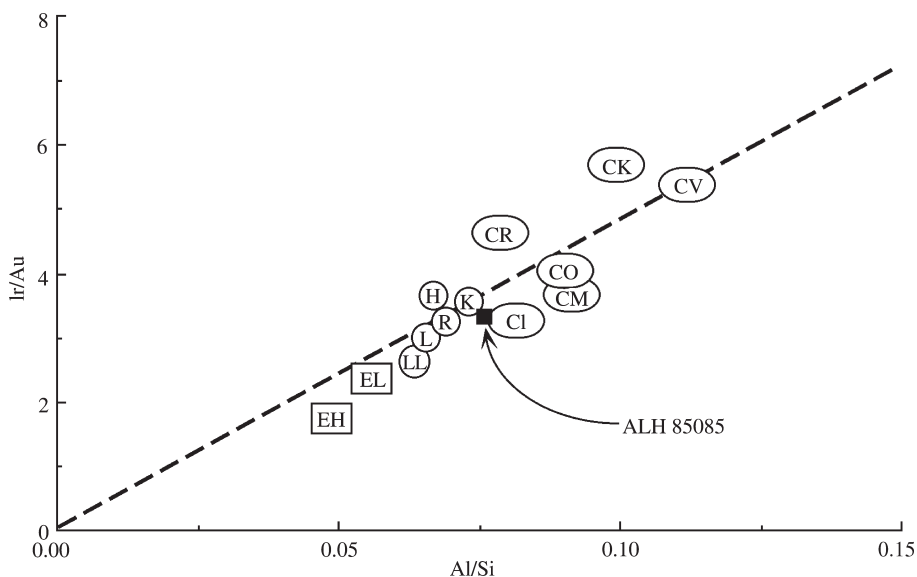


Figure 9 Ir/Au versus Al/Si in various types of chondritic meteorites. Ir is an RSE and Al is an RLE. The figure shows the parallel behavior of RSE and RLE. Enstatite chondrites (EH and EL) are low in RSE and RLE and carbonaceous chondrites (CM, CO, CR, CK, CV) are high in both (source O'Neill and Palme, 1998).

in chondritic meteorites, and one may therefore confidently assume that the bulk Earth RSEs behave similarly to the bulk Earth RLEs. This is important as it allows us to calculate bulk Earth abundances of tungsten, molybdenum, iridium, etc., from the bulk Earth aluminum or scandium contents. However, as shown in a later section, the Earth has excess iron metal, which provides an additional reservoir of siderophile elements. Thus, the RSE abundances calculated from RLE abundances provide only a lower limit for the RSE content of the bulk earth.

The refractory HSEs presently observed in the Earth's mantle are probably of a different origin than the bulk of the refractory HSEs which are in the core. This inventory of HSEs in the PM will be discussed in a later section.

2.01.5.3 Magnesium and Silicon

The four elements—magnesium, silicon, iron, and oxygen—contribute more than 90% by mass to the bulk Earth. As stated above, magnesium, silicon, and iron have approximately similar relative abundances (in atoms) in the Sun, in chondritic meteorites, and probably also in the whole Earth. On a finer scale there are, however, small but distinct differences in the relative abundances of these elements in chondritic meteorites. Figure 10 shows the various groups of chondritic meteorites in an Mg/Si versus Al/Si plot. As discussed before, the Earth's mantle has Al/Si and Al/Mg ratios within the range of

carbonaceous chondrites, but the Mg/Si ratio is slightly higher than any of the chondrite ratios. The “nonmeteoritic” Mg/Si ratio of the Earth's mantle has been extensively discussed in the literature. One school of thought maintains that the bulk Earth has to have a CI-chondritic Mg/Si ratio and that the observed nonchondritic upper mantle ratio is balanced by a lower than chondritic ratio in the lower mantle (e.g., Anderson, 1989). However, layered Earth models have become increasingly unlikely, as discussed before, and there is no reason to postulate a bulk Earth CI–Mg/Si ratio in view of the apparent variations of this ratio in various types of chondritic meteorites. Ringwood (1989) suggested that the Mg/Si ratio of Earth's mantle is the same as that of the Sun implying that CI-chondrites have a nonsolar Mg/Si ratio. This is very unlikely in view of the excellent agreement between elemental abundances of CI-chondrites and the Sun (Chapter 1.03). Other attempts to explain the high Mg/Si ratio of the Earth's mantle include volatilization of silicon from the inner solar system by high-temperature processing connected with the early evolution of the proto-sun and the solar nebula (Ringwood, 1979, 1991). Another possibility is loss of some silicon into the metal core of the Earth (e.g., Hillgren *et al.* (2000) and references therein). The latter proposition has the advantage that it would, in addition, reduce the density of the outer core, which is ~10% too low for an FeNi alloy (Poirier, 1994; see Chapters 2.14 and 2.15). That the Earth's core contains some silicon is now

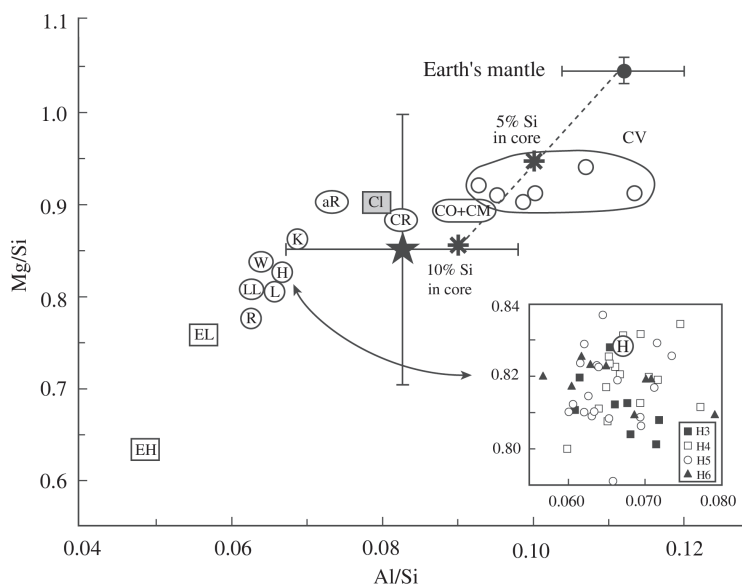


Figure 10 Mg/Si versus Al/Si for chondritic meteorites and the Earth's mantle. Carbonaceous chondrites are on the right side of the solar ratio (full star), ordinary and enstatite chondrites are on the left side, reflecting depletion of refractory elements. The Earth's mantle plots above CI-chondrites. Putting 5% Si into the core of the Earth leads to a PM composition compatible with CV-chondrites (after O'Neill and Palme, 1998).

assumed by most authors, but the amount is unclear. About 18% silicon is required to produce the 10% density reduction. This number is far too high as argued by O'Neill and Palme (1998), who concluded that other light elements must be involved in reducing the density of the core. The problem may be somewhat less severe in light of new density estimates of liquid FeNi alloys at high pressures and temperatures by Anderson and Isaak (2002) leading to a density deficit of only 5%. Based on these data McDonough (see Chapter 2.15) estimated a core composition with 6% silicon and 1.9% sulfur as light elements.

The effect of silicon partitioning into the core is shown in Figure 10. If the core has 5% silicon, the bulk Earth Mg/Si and Al/Si ratios would match with CV-chondrites which define a fairly uniform Mg/Si ratio of 0.90 ± 0.03 , by weight (Wolf and Palme, 2001). Such a composition is not unreasonable in view of the similarity in moderately volatile element trends of carbonaceous chondrites and the Earth, as shown below.

2.01.5.4 The Iron Content of the Earth

Figure 11 plots the Mg/Fe ratios of various chondrites against their Si/Fe ratios. Carbonaceous chondrites fall along a single correlation line, with the Earth plotting at the extension of the carbonaceous chondrite line in the direction of higher iron contents. The bulk Earth iron content used here was calculated by assuming a core content of 85%Fe + 5%Si. The rest, comprising 10%, is

made up of 5% Ni and some additional light element(s). Ordinary chondrites (H) and enstatite chondrites (EH and EL) do not plot on the same correlation line. If the upper mantle composition as derived here is representative of the bulk Earth's mantle, then the bulk Earth must have excess iron, at least 10% and more likely 20% above the iron content of CI-chondrites. Earlier McDonough and Sun (1995) have emphasized that the Earth has higher Fe/Al ratios than chondritic meteorites.

The growth of the Earth by accumulation of Moon- to Mars-sized embryos could provide an explanation for the excess iron in the Earth. Large impacts will remove some material from the Earth, preferentially silicates, if the Earth had a core at the time when the impact occurred. The amount of dispersed material is uncertain. It may be several percent of the total mass involved in a collision (Canup and Agnor, 2000). A model of collisional erosion of mantle has been proposed to explain the large metal fraction of Mercury by Benz *et al.* (1988). Because of the large size of the Earth, the colliding object must be very large or the collisional erosion occurred at a time when the Earth was not fully accreted, but nevertheless had an FeNi core. Some collisional erosion may also have occurred on the Moon- to Mars-sized embryos. The present excess of iron is then the integral effect over a long period of impact growth. Alternatively the high bulk Earth iron content would reflect the average composition of the "building blocks of the earth," i.e., the

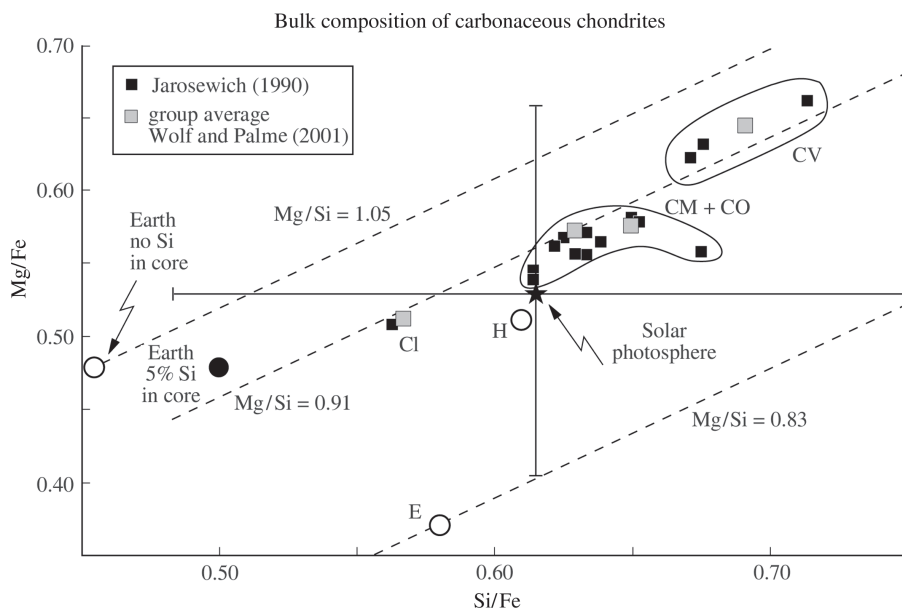


Figure 11 Mg/Fe versus Si/Fe for carbonaceous chondrites, the Sun and the Earth. Carbonaceous chondrites have constant Mg/Si ratios, but variable Fe contents. With 5% Si in the core the bulk Earth has the Mg/Si ratio of carbonaceous chondrites (see Figure 10). The bulk Earth has ~10% excess Fe compared to CI-chondrites (filled square—Jarosewich (1990) and gray square—group average Wolf and Palme (2001)).

Moon-sized embryos that produce the Earth through mutual collisions. Either the Fe/Mg ratios of these embryos were, on average, higher than the solar ratio or there were comparatively large variations in the Fe/Mg ratios of individual embryos, and a population with high Fe/Mg ratios was accidentally accumulated by the growing Earth. On the scale of meteorites, large variations in bulk iron contents are found, e.g., in the recently discovered group of CH-chondrites (not shown in Figure 1). These meteorites are compositionally and mineralogically related to carbonaceous chondrites (Bischoff *et al.*, 1993) and there is no doubt that the enrichment of iron is the result of nebular and not of planetary fractionations. It is, however, not clear if the large variations in metal/silicate ratios that occur on the scale of small parent bodies of chondritic meteorites would still be visible in the much larger Moon-sized embryos that made the Earth. The collisional erosion of silicates appears to us a more plausible possibility (Palme *et al.*, 2003).

2.01.5.5 Moderately Volatile Elements

The concentrations of four typical moderately volatile elements—manganese, sodium, selenium, and zinc—in the various classes of chondritic meteorites are shown in Figure 12, where elements are normalized to magnesium and CI-chondrites. Again there is excellent agreement between solar abundances and CI-meteorites. A characteristic feature of the chemistry of carbonaceous chondrites is the simultaneous depletion of sodium and manganese in all types of carbonaceous chondrites, except CI. Ordinary and enstatite chondrites are not or only slightly

depleted in both elements, but their zinc contents are significantly lower than those of the carbonaceous chondrites. The Earth fits qualitatively with the carbonaceous chondrites in having depletions of manganese, sodium, and zinc. Selenium has a similar condensation temperature to zinc and sulfur. The selenium content of the Earth's mantle is extremely low, because a large fraction of the terrestrial selenium is, together with sulfur, in the core. In addition, the initial endowment of sulfur and selenium is very low based on the low abundances of other elements of comparable volatility (Dreibus and Palme, 1996).

Figure 13 plots the abundances of aluminum, calcium, magnesium, silicon, chromium, and of the three moderately volatile elements—manganese, sodium, and zinc—in the various groups of carbonaceous chondrites and in the Earth. All elements are normalized to the refractory element titanium and to CI-abundances. By normalizing to titanium the increasing enrichment of the refractory component from CI to CV is transformed into a depletion of the nonrefractory elements. There is a single depletion trend for magnesium, silicon, and the moderately volatile elements. The sequence of elements, their absolute depletion from aluminum to zinc, is basically in the order of decreasing condensation temperatures or increasing nebular volatility; the higher the volatility, the lower the abundance. It thus appears that this trend is the result of processes that occurred in the solar nebula and not by igneous or metamorphic activities on a parent body (Palme *et al.*, 1988; Humayun and Cassen, 2000).

Figure 13 plots only the lithophile moderately volatile elements. However, in carbonaceous chondrites siderophile and chalcophile moderately

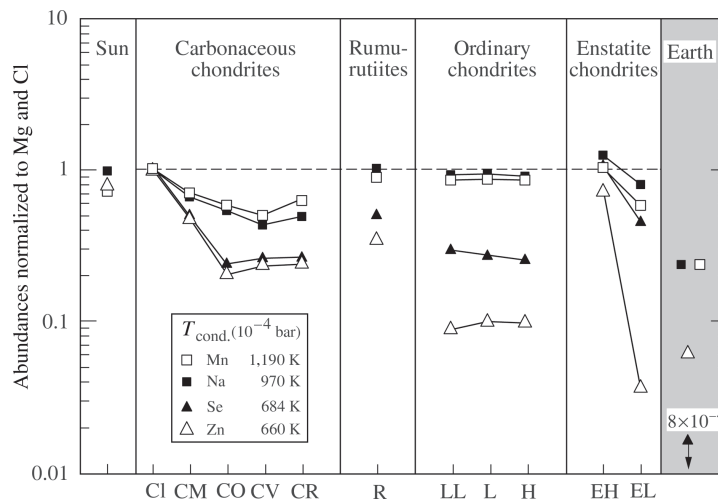


Figure 12 Moderately volatile/Mg ratios in various types of chondritic meteorites. All groups of chondritic meteorites are depleted in moderately volatile elements, none is enriched. The two elements Mn and Na are depleted in carbonaceous chondrites and in the Earth but not in ordinary and enstatite chondrites. The Earth is also depleted (source O'Neill and Palme, 1998).

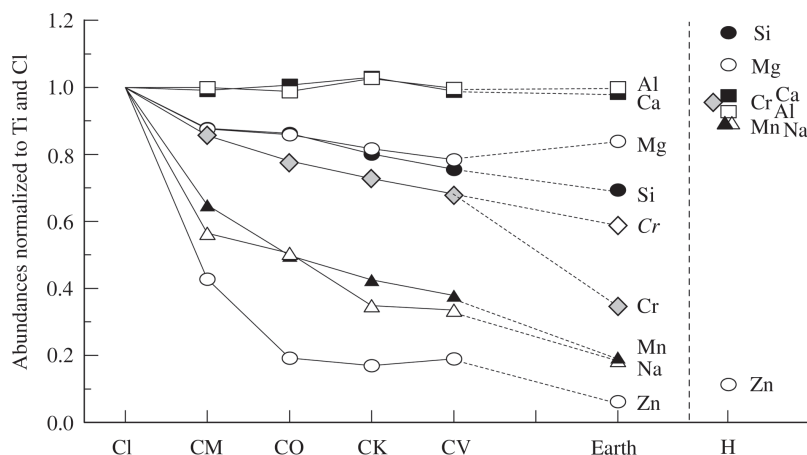


Figure 13 Major and moderately volatile elements in carbonaceous chondrites and in the Earth's mantle. All data are normalized to the RLE Ti. There is a single trend for RLE, Mg–Si, and moderately volatile elements. The Earth may be viewed as an extension of the carbonaceous chondrite trend. The low Cr content in the present mantle (full symbol) is the result of Cr partitioning into the core. The open symbol is plotted at the extension of the carbonaceous chondrite trend. Data for ordinary chondrites are plotted for comparison. Similar chemical trends in carbonaceous chondrites and the Earth are evident. H-chondrites are very different (sources Wolf and Palme, 2001; Wasson and Kallemeyn, 1988).

volatile elements show exactly the same behavior as lithophile elements as shown in Figure 14, where the ratio of moderately volatile elements in CV-chondrites to those in CI-chondrites is plotted against condensation temperature. The depletions increase with decreasing condensation temperatures independently of the geochemical character of the elements. For elucidating volatile element behavior in the Earth's composition, most of the elements plotted in Figure 14 are not useful, as siderophile and chalcophile moderately volatile elements may be depleted by core formation too. For the purpose of comparing moderately volatile elements between meteorites and the Earth, only lithophile elements can be used.

In Figure 13 the Earth's mantle seems to extend the trend of the moderately volatile elements to lower abundances, at least for sodium, manganese, and zinc (zinc behaves as a lithophile element in the Earth's mantle (see Dreibus and Palme, 1996)). The elements lithium, potassium, and rubidium which are not plotted here, show similar trends. The carbonaceous chondrite trend of iron is not extended to the Earth, as most of the iron of the Earth is in the core. The magnesium abundance of the Earth shows a slightly different trend. If the core had 5% silicon (previous section) and if that would be added to the bulk Earth silicon, then the bulk Mg/Si ratio of the Earth would be the same as that of carbonaceous chondrites (Figure 10) and the silicon abundance of the Earth's mantle in Figure 13 would coincide with the magnesium abundance.

The strong depletion of chromium (filled symbol in Figure 13) observed in the Earth's

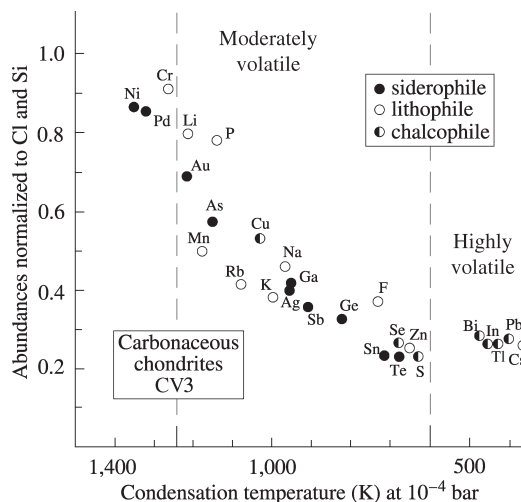


Figure 14 Abundances of volatile elements in CV3 chondrites (e.g., Allende) normalized to CI-chondrites and Si. There is a continuous decrease of abundances with increasing volatility as measured by the condensation temperature. The sequence is independent of the geochemical characters of the elements indicating that volatility is the only relevant parameter in establishing this pattern (source Palme, 2000).

mantle indicates that a significant fraction of chromium is now in the core of the Earth. Extending the carbonaceous chondrite volatility trend to the Earth leads to an estimated bulk Earth chromium content that is represented by an open symbol in Figure 13.

On the right-hand side of Figure 13 we have plotted the abundances of the same elements for

average H-chondrites according to the compilation of meteorite data by Wasson and Kallemeyn (1988) and using the same normalization as for the carbonaceous chondrites in Figure 13. Ordinary and enstatite chondrites have apparently very different chemical compositions when compared to carbonaceous chondrites: (i) the depletion of refractory elements in ordinary chondrites leads to the high abundances of silicon and magnesium in Figure 13; (ii) magnesium and silicon are fractionated; and (iii) magnesium and sodium are only slightly depleted (see Figure 12). Enstatite chondrites show similar, though more enhanced, compositional trends for ordinary chondrites (Figures 9, 11, and 12). In summary, Figure 13 demonstrates quite clearly that the Earth's mantle composition resembles trends in the chemistry of carbonaceous chondrites and that these trends are not compatible with the chemical composition of ordinary or enstatite chondrites.

Figure 15(a) plots CI and magnesium-normalized abundances of lithophile moderately volatile elements against their condensation temperatures. The trend of decreasing abundance with increasing volatility is clearly visible. As mentioned above only few elements can be used to define this trend; most of the moderately volatile elements are siderophile or chalcophile and their abundance in the Earth's mantle is affected by core formation.

The additional depletions of siderophile elements are shown in Figure 15(b). Gallium, the least siderophile of the elements plotted here falls on the general depletion trend. All other elements are more or less strongly affected by core formation. The abundances of these elements in the Earth's mantle provide important clues to the mechanism of core formation. For example, the similar CI-normalized abundances of cobalt and nickel (Figure 15(b)) are surprising in view of the large differences in metal/silicate partition coefficients (e.g., Holzheid and Palme, 1996). Core formation should remove the more strongly siderophile element nickel much more effectively than cobalt leaving a mantle with low Ni/Co behind. The stronger decrease in metal/silicate partition coefficients of nickel compared to cobalt with increasing temperature and pressure provides a ready explanation for the relatively high abundance of nickel and the chondritic Ni/Co ratio in the Earth's mantle and allows us to estimate the P - T conditions of the last removal of metal to the core (see Walter *et al.* (2000) and references therein; Chapter 2.10). The HSEs show the strongest depletion with a basically chondritic pattern. The significance of the HSEs will be discussed in more detail below.

Figure 15(c) shows chalcophile element abundances which are compared with the general depletion trend. The distinction between siderophile and chalcophile elements is not very clear.

Analyses of separate phases in meteorites have shown that the only element apart from sulfur that is exclusively concentrated, i.e., truly chalcophile, in sulfides is selenium. All other elements have higher concentrations in metal than in coexisting sulfide, with the possible exceptions of indium and cadmium, for which the data are not known. This is particularly true for molybdenum, silver, tellurium, and copper elements that are traditionally considered to be chalcophile (Allen and Mason, 1973). In the absence of metallic iron, however, some siderophile elements will become chalcophile and partition into sulfide, such as the elements plotted in Figure 15(c). The significance of the trends shown in Figure 15(c) is twofold: (i) the depletion of the three elements—sulfur, selenium, and tellurium—is stronger than that of the highly siderophile elements in Figure 15(b) and (ii) elements more volatile than sulfur and selenium are less depleted than are these elements (see below for more details).

2.01.5.5.1 *Origin of depletion of moderately volatile elements*

The depletion of moderately volatile elements is a characteristic feature of every known body in the inner solar system (with the exception of the CI parent bodies, if these are inner solar system objects). The degree of depletion of an element is a function of nebular volatility but is independent of its geochemical character, i.e., whether an element is lithophile, chalcophile or siderophile, or compatible or incompatible (see Figure 14). Thus, volatile element depletions are not related to geochemical processes such as partial melting or separation of sulfide or metal. Also evaporation, e.g., by impact heating, is unlikely to have produced the observed depletion of moderately volatile element. (i) Volatilization on a local scale would produce enrichments through recondensation, but only depletions are observed (Palme *et al.*, 1988). (ii) Volatilization would lead to isotopic fractionations. Such fractionations are not observed even in rocks that are very low in volatile elements (Humayun and Cassen, 2000). (iii) The sequence of volatility-related losses of elements depends on oxygen fugacity. Volatilization will produce oxidizing conditions while very reducing conditions prevail during nebular condensation. A striking example for the different behavior during condensation and evaporation are the two moderately volatile elements—manganese and sodium. Both elements have similar condensation temperatures and their ratios are chondritic in all undifferentiated meteorites despite significant variations in absolute concentrations of manganese and sodium in carbonaceous chondrites

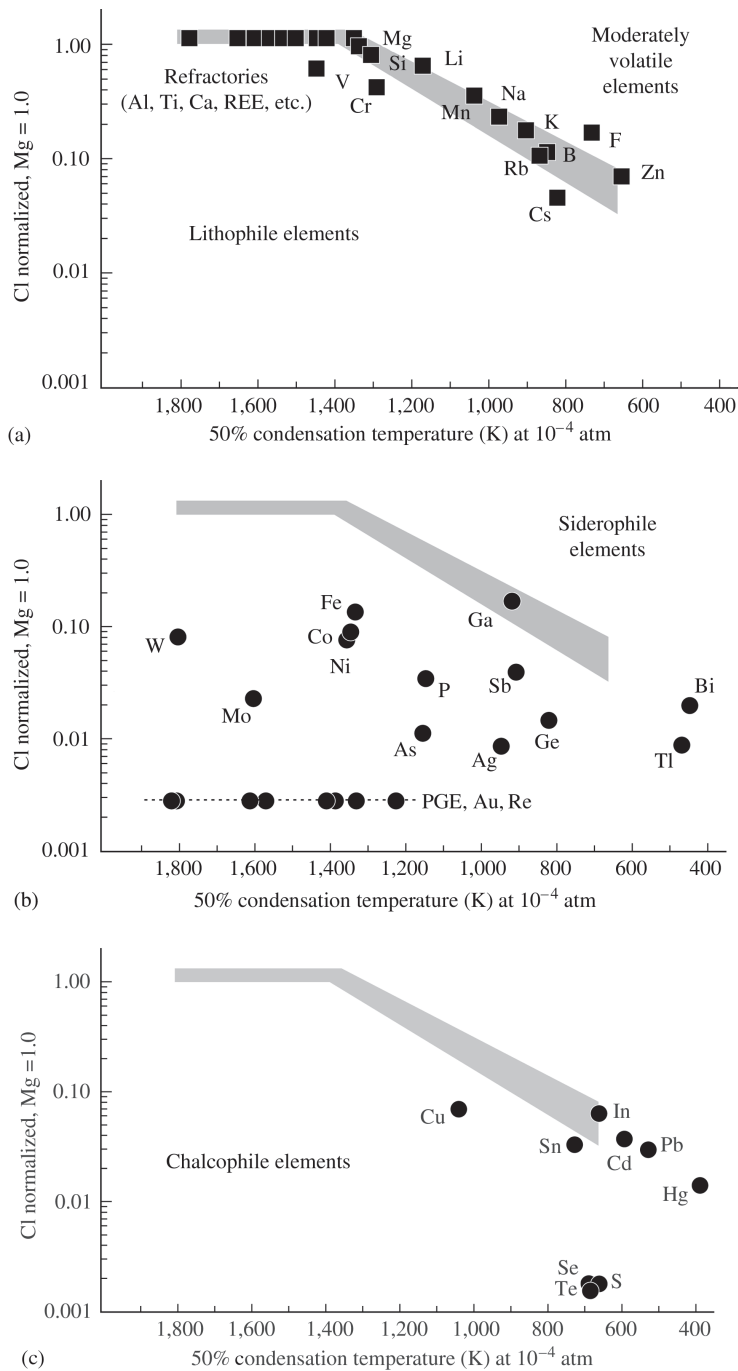


Figure 15 Abundances of moderately volatile elements in the Earth's mantle versus condensation temperatures: (a) lithophile elements define the volatility trend; (b) siderophile elements have variable depletions reflecting the process of core formation; and (c) chalcophile elements. The difference between siderophile and chalcophile elements is not well defined, except for S and Se. The large depletions of S, Se, and Te are noteworthy (see text) (after McDonough, 2001).

(Figures 12 and 16). The Mn/Na ratio of the Earth's mantle is also chondritic (Figures 12 and 16). Heating of meteorite samples to temperatures above 1,000 °C for a period of days will inevitably lead to significant losses of sodium and potassium but will not affect manganese

abundances (e.g., Wulf *et al.*, 1995). The chondritic Mn/Na ratio of the Earth must, therefore, be attributed to nebular fractionations of proto-earth material (O'Neill and Palme, 1998). If some manganese had partitioned into the core, as is often assumed, the chondritic Mn/Na ratio

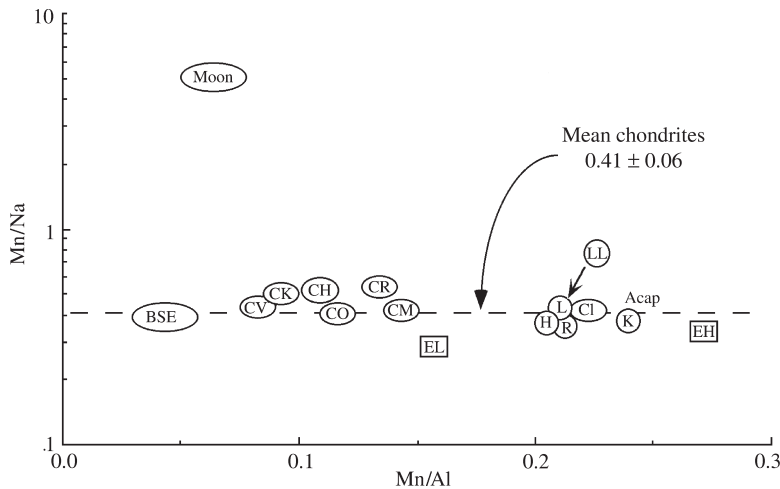


Figure 16 Mn/Na versus Mn/Al in chondritic meteorites. The two moderately volatile elements Na and Mn have the same ratio in all chondritic meteorites and in the primitive Earth's mantle, here designated as BSE. The low Mn/Al content of the Earth's mantle reflects enrichment of Al and depletion of Mn. Because of the chondritic Mn/Na ratio of the Earth's mantle, it is unlikely that a significant fraction of the Earth's inventory of Mn is in the core (source O'Neill and Palme, 1998).

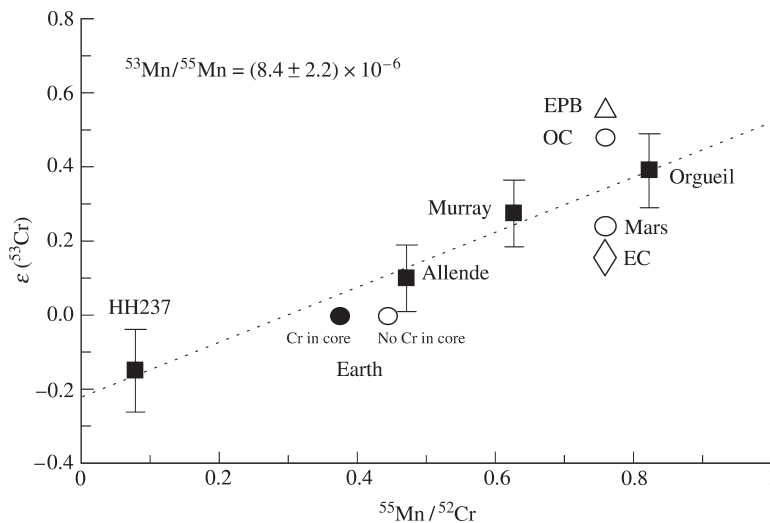


Figure 17 ^{53}Cr excess in bulk meteorites and bulk planets versus Mn/Cr ratios. The line through Orgueil, Allende, and Earth and the CH meteorite HH237 defines a $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $(8.40 \pm 2.2) \times 10^{-6}$. This is three million years earlier than the time of differentiation of Vesta (Lugmair and Shukolyukov, 1998). The $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of carbonaceous chondrites and the Earth could be interpreted as the time of Mn/Cr fractionation in the solar system. The fractionation of other moderately volatile elements may have occurred at the same time and by the same process.

of the Earth's mantle would be the fortuitous result of the reduction of an originally higher Mn/Na ratio to the chondritic ratio. The similarity of the terrestrial pattern of moderately volatile elements, including manganese and sodium, with that of carbonaceous chondrites implies that the proto-earth material underwent similar fractionation processes for carbonaceous chondrites.

The depletion of moderately volatile elements such as manganese, sodium, rubidium in the

Earth's mantle must have occurred very early in the history of the solar system. Figure 17 plots $^{53}\text{Cr}/^{52}\text{Cr}$ versus $^{55}\text{Mn}/^{52}\text{Cr}$ ratios of several chondritic meteorites and samples of differentiated planets. The data are taken from the work of Lugmair and Shukolyukov (1998) and Shukolyukov and Lugmair (2000, 2001). Samples from the metal-rich CH-chondrite HH237, the Earth, Allende (CV), Murray (CM), and Orgueil (CI) define an approximately straight line in Figure 17. If this line is interpreted as an isochron,

the time of Mn–Cr fractionation can be calculated from the slope. The slope in Figure 17 corresponds to a $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of $(7.47 \pm 1.3) \times 10^{-6}$. Nyquist *et al.* (2001) have determined chromium isotopes of individual chondrules with variable Mn/Cr ratios from the Bishunpur and Chainpur meteorites and they obtained “isochrons” in both cases with $^{53}\text{Mn}/^{55}\text{Mn}$ ratios of $(9.5 \pm 3.1) \times 10^{-6}$ for Bishunpur and $(9.4 \pm 1.7) \times 10^{-6}$ for Chainpur, respectively. These ratios are, within error limits, the same as indicated in Figure 17. Nyquist *et al.* (2001) believe that the time defined by the $^{53}\text{Mn}/^{55}\text{Mn}$ ratio of the chondrules date the Cr–Mn fractionation in the chondrule precursors. The fact that chondrules, bulk carbonaceous chondrites, and the Earth have, within error limits, the same $^{53}\text{Mn}/^{55}\text{Mn}$ ratio suggests that the Mn/Cr fractionation in these objects occurred at about the same time, at the beginning of the solar system.

In Figure 17, bulk ordinary chondrites (OCs) lie somewhat above the “isochron.” This may reflect a reservoir with a slightly different initial $^{53}\text{Cr}/^{52}\text{Cr}$ ratio. The Mn/Cr ratios of Mars and of the eucrite parent body in Figure 17 are assumed to be the same as those of ordinary chondrites. This is, however, quite uncertain, as the chromium contents estimated for Mars (based on SNC meteorites) and on Vesta (based on EPB meteorites) are model dependent. The position of the Earth in Figure 17 is critically dependent on the assumed Mn/Cr ratio of the bulk Earth. As mentioned above, we take the view here that the parallel behavior of sodium and manganese in the carbonaceous chondrites and in the Earth’s mantle follows from their empirically observed similar nebular volatilities in all groups of chondritic meteorites (Figure 16) and we assume that the Earth’s core is, therefore, free of manganese (O’Neill and Palme, 1998). In contrast, the strong decrease of chromium in the Earth’s mantle (see Figure 13) compared to CV-chondrites indicates that a certain fraction of chromium is in the Earth’s core. For calculating the bulk Earth chromium content, we have extrapolated the CV-trend for chromium in Figure 13 (open symbol). With this procedure the bulk Earth chromium point of Figure 17 lies within the error of the carbonaceous chondrite isochron.

In summary, it appears from Figure 17 that the bulk composition of the Earth is related to the carbonaceous chondrites, suggesting the same event of manganese depletion for carbonaceous chondrites and the Earth. This supports the hypothesis that the depletion of volatile elements in the various solar system materials is a nebular event at the beginning of formation of the solar system as suggested by Palme *et al.* (1988), Humayun and Cassen (2000), and Nyquist *et al.* (2001).

2.01.5.6 HSEs in the Earth’s Mantle

As discussed above, the HSEs—osmium, iridium, platinum, ruthenium, rhodium, palladium, rhenium, and gold—have a strong preference for the metal phase as reflected in their high metal/silicate partition coefficients of $>10^4$. Ratios among refractory HSEs are generally constant in chondritic meteorites to within at least 5%. There is, however, a notable exception. Walker *et al.* (2002) found that the average Re/Os ratio in carbonaceous chondrites is 7–8% lower than that in ordinary and enstatite chondrites. Both elements, osmium and rhenium, are refractory metals. They are, together with tungsten, the first elements to condense in a cooling gas of solar composition (Palme and Wlotzka, 1976). There is no apparent reason for the variations in Re/Os ratios. This example demonstrates that the assumption of constant relative abundances of refractory elements in chondritic meteorites may not be justified in all cases, although it is generally taken as axiomatic.

The HSE abundances in the Earth’s mantle are extremely low (Figure 15(b)), $\sim 0.2\%$ of those estimated for the core, the major reservoir of the HSEs in the Earth. Most of the HSE data on Earth’s mantle samples come from the analyses of iridium, which is sufficiently high in mantle rocks to allow the use of instrumental neutron activation analysis (e.g., Spettel *et al.*, 1990). The iridium contents in spinel lherzolites from worldwide occurrences of xenoliths and massive peridotites are, on average, surprisingly uniform. In particular, HSE abundances do not depend on the fertility of the mantle peridotite, except for rhenium (Pattou *et al.*, 1996; Schmidt *et al.*, 2000; Morgan *et al.*, 2001). The latter authors estimated an average PM iridium content of 3.2 ± 0.2 ppb, corresponding to a CI-normalized abundance of 6.67×10^{-3} . Other HSEs have similarly low CI-normalized abundances, as indicated by the approximately flat CI-normalized pattern of these elements that is generally observed, at least at the logarithmic scale at which these elements are usually displayed.

Some HSE ratios in upper mantle rocks often show significant deviations from chondritic ratios. For example, Schmidt *et al.* (2000) reported a 20–40% enhancement of ruthenium relative to iridium and CI-chondrites in spinel lherzolites from the Zabargad island. Data by Pattou *et al.* (1996) on Pyrenean peridotites, analyses of abyssal peridotites by Snow and Schmidt (1998), and data by Rehkämer *et al.* (1997) on various mantle rocks suggest that higher than chondritic Ru/Ir ratios are widespread and may be characteristic of a larger fraction, if not of the whole of the upper mantle. A parallel enrichment is found for rhodium in Zabargad rocks (Schmidt *et al.*, 2000). There are,

however, few data on rhodium and it remains to be seen if this is a general signature of upper mantle. Further clarification is needed to see if these nonchondritic ratios are a primary signature of the Earth's mantle or are the result of later alterations (e.g., Rehkämper *et al.*, 1999). This question has important consequences for the understanding of the origin of the highly siderophile elements in the Earth's mantle.

Two of the HSEs, palladium and gold, are moderately volatile elements. Their abundances in chondrites are not constant. To some extent, they follow the general trend of moderately volatile lithophile elements (see Figures 9 and 14). For example, Morgan *et al.* (1985) found an average Pd/Ir ratio of 1.02 ± 0.097 for 10 ordinary chondrites, whereas E-chondrites have significantly higher ratios as shown by Hertogen *et al.* (1983) who determined an average ratio of 1.32 ± 0.2 .

The concentrations of palladium in upper mantle rocks are also much more variable than those of the refractory siderophiles, with anomalously high Pd/Ir ratios with up to twice the CI-chondritic ratio (Pattou *et al.*, 1996; Schmidt *et al.*, 2000). These variations exceed those in chondritic meteorites considerably.

The high palladium content of some upper mantle rocks has led to a number of speculations attempting to explain the excess palladium. McDonough (1995) has suggested addition of outer core metal, high in nonrefractory palladium and low in refractory iridium. Other possibilities are discussed by Rehkämper *et al.* (1999), Schmidt *et al.* (2000), and Morgan *et al.* (2001). As the abundance of palladium in upper mantle rocks is so variable, we have chosen to calculate the average upper mantle palladium content from the H-chondrite Pd/Ir ratio of 1.022 ± 0.097 (Morgan *et al.*, 1985), as H-chondrite fit with osmium isotopes of Earth's mantle rocks as explained above (see Table 4 and explanations).

The element gold is even more variable than palladium in upper mantle rocks, presumably because gold is more mobile. It appears that variations in gold are regional. Antarctic xenoliths analyzed by Spettel *et al.* (1990) have an average gold content of 2.01 ± 0.17 ppb, while seven xenoliths from Mongolia analyzed by the same authors have less than 1 ppb Au. The average upper mantle abundance of gold is unclear. Morgan *et al.* (2001) suggested a very high value of 2.7 ± 0.7 ppb, based on extrapolation of trends in xenoliths. We take the more conservative view that the Ir/Au ratio in the upper mantle of the Earth is the H-chondrite ratio, which we take from Kallemeyn *et al.* (1989) as 3.63 ± 0.13 . This value is near the CI-ratio of 3.24 calculated from the abundances in Table 4.

This leads to an upper mantle gold content of 0.88 ppb which is listed in Table 4.

2.01.5.7 Late Veneer Hypothesis

Although HSE concentrations are low in the Earth's mantle, they are not as low as one would expect from equilibrium partitioning between core forming metal and residual mantle silicate, as emphasized by new data on metal/silicate partition coefficients for these elements (Borisov and Palme, 1997; Borisov *et al.*, 1994). Murthy (1991) suggested that partition coefficients are dependent on temperature and pressure in such a way that at the high P - T conditions where core formation may have occurred, the observed mantle concentrations of HSEs would be obtained by metal/silicate equilibration. This hypothesis has been rejected on various grounds (O'Neill, 1992), and high P - T experiments have not provided support for the drastic decrease of metal/silicate partition coefficients of HSE required by the Murthy model (Holzheid *et al.*, 1998).

Thus core-mantle equilibration can be excluded as the source of the HSEs in the Earth's mantle. It is more likely that a late accretionary component has delivered the HSEs to the Earth's mantle, either as single Moon-sized body which impacted the Earth after the end of core formation or several late arriving planetesimals. The impactors must have been free of metallic iron, or the metallic iron of the projectiles must have been oxidized after the collision(s) to prevent the formation of liquid metal or sulfide that would extract HSEs into the core of the Earth. The relative abundances of the HSEs in the Earth's mantle are thus the same as in the accretionary component, but may be different from those in the bulk Earth. The late addition of PGE with chondritic matter is often designated as the late veneer hypothesis (Kimura *et al.*, 1974; Chou, 1978; Jagoutz *et al.*, 1979; Morgan *et al.*, 1981; O'Neill, 1991). This model requires that the mantle was free of PGE before the late bombardment established the present level of HSEs in the Earth's mantle.

The late veneer hypothesis has gained additional support from the analyses of the osmium isotopic composition of mantle rocks. Meisel *et al.* (1996) determined the $^{187}\text{Os}/^{188}\text{Os}$ ratios of a suite of mantle xenoliths. Since rhenium is more incompatible during mantle partial melting than osmium, the Re/Os ratio in the mantle residue is lower and in the melt higher than the PM ratio. By extrapolating observed trends of $^{187}\text{Os}/^{188}\text{Os}$ versus Al_2O_3 and lutetium, two proxies for rhenium, Meisel *et al.* (1996) determined a $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.1296 ± 0.0008 for the primitive mantle. This ratio is 2.7% above that of carbonaceous

chondrites, but within the range of ordinary and enstatite chondrites (Walker *et al.*, 2002). Thus, the time-integrated Re/Os ratio of the Earth's primitive mantle is similar to that of H- and E-chondrites, but 7.6% higher than that of carbonaceous chondrites. The ordinary chondrite signature of the late veneer does not contradict the general similarity of Earth's mantle chemistry with the chemistry of carbonaceous chondrites, because the fraction of material added as late veneer material is less than 1% of the mantle, and the origin of this material may, therefore, be quite different from the source of the main mass of the Earth, according to popular models of the accretion of the inner planets (Wetherill, 1994; Chambers, 2001; Canup and Agnor, 2000). In any case, the precisely determined chondritic Re/Os ratio in the primitive mantle of the Earth is a very strong argument in favor of the late veneer hypothesis.

The small amount of the late veneer (<1% chondritic material) would not have had a measurable effect on the abundances of other elements besides HSEs, except for some chalcophile elements, most importantly sulfur, selenium and tellurium (Figure 15(c)). The amount of sulfur presently in the Earth's mantle (200 ppm, Table 4) corresponds to only 0.37% of a nominal CI-component, while the iridium content suggests a CI-component of 0.67%. O'Neill (1991) has, therefore, suggested that the late veneer was compositionally similar to H-chondrites which contain only 2% S (Wasson and Kallemeyn, 1988). Because H-chondrites have higher iridium (780 ppb) than CI-chondrites, the required

H-chondrite fraction would only be 0.41% based on iridium. This would correspond to 82 ppm S delivered by the late veneer to the mantle. In this case the Earth's mantle should have combined ~120 ppm S before the advent of the late veneer. If core formation in the Earth (or in differentiated planetesimals that accreted to form the Earth) occurred while the silicate portion was molten or partially molten, some sulfur must have been retained in this melt (O'Neill, 1991).

2.01.6 THE ISOTOPIC COMPOSITION OF THE EARTH

The most abundant element in the Earth is oxygen. In a diagram of $\delta^{17}\text{O}$ versus $\delta^{18}\text{O}$ the oxygen isotopic compositions of terrestrial rocks plot along a line with a slope of 0.5, designated as the terrestrial fractionation line in Figure 18. Most carbonaceous chondrites plot below and ordinary chondrites above the terrestrial mass fractionation line. Enstatite chondrites, extremely reduced meteorites with low oxygen content, and the most oxidized meteorites, CI-chondrites with magnetite and several percent of water, both plot on the terrestrial fractionation line (Figure 18). Other groups of carbonaceous chondrites have different oxygen isotopic compositions.

Variation in the oxygen isotopic composition of solar system materials has long been regarded as demonstrating the nonuniformity in isotopic composition of the solar system (e.g., Begemann, 1980). However, oxygen must be considered a

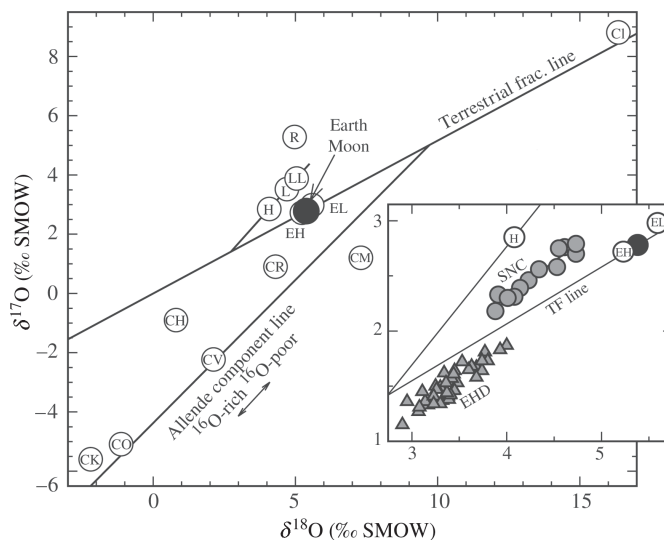


Figure 18 $\delta^{17}\text{O}$ versus $\delta^{18}\text{O}$ for chondritic meteorites. Ordinary chondrites (H, L, LL, and R) plot above the terrestrial fractionation line, and carbonaceous chondrites below. The most oxidized (CI) and the most reduced (E) chondrites also plot on terrestrial fractionation line. The larger bodies of the solar system, for which oxygen isotopes have been determined, Earth, Moon, Mars (SNC-meteorites), Vesta (EHD-meteorites), plot on or close to TFL (source Lodders and Fegley, 1997).

special case, because the major fraction of oxygen in the inner solar system was gaseous at the time of formation of solid objects, as oxygen is not fully condensed in any inner solar system material (see Figure 1). Gas–solid exchange reactions between individual meteoritic components with gases of different oxygen isotopic composition played an important role in establishing the variations (Clayton, 1993). The largest variations are found in the smallest meteorite inclusions. Individual components of carbonaceous chondrites span an extremely wide range in oxygen isotopes, such that the bulk meteorite value is of little significance (e.g., Clayton and Mayeda, 1984). The larger the object the smaller the variations in oxygen isotopes. The Earth and the Moon, the largest and the third largest body in the inner solar system for which oxygen isotopes are known, and which comprise more than 50% of the mass of the inner solar system, have exactly the same oxygen isotopic composition (Wiechert *et al.*, 2001). These two bodies may well represent the average oxygen isotopic composition of the bulk solar system, i.e., the Sun. The oxygen isotopic composition of Mars and Vesta, two other large inner solar system bodies, are not very different from that of Earth and Moon (Figure 18).

For most other elements there is no difference between the isotopic composition of carbonaceous chondrites and the Earth. As of early 2000s, only two exceptions, chromium and titanium, are known; for these two elements very small differences in the isotopic composition between carbonaceous chondrites and the Earth were found. Bulk carbonaceous chondrites have isotope anomalies in chromium and titanium. Isotopically unusual material may have been mixed to the CC-source after proto-earth material has accumulated to larger objects.

For chromium, the anomaly is only in ^{54}Cr and this effect is limited to carbonaceous chondrites (Rotaru *et al.*, 1992; Podosek *et al.*, 1997; Shukolykov and Lugmair, 2000). Titanium appears to be anomalous in ^{50}Ti and again the effect has only been found in carbonaceous chondrites (Niemeyer and Lugmair, 1984; Niederer *et al.*, 1985). In both cases the anomalies are larger in Ca, Al-inclusions of the Allende meteorite than in bulk meteorites.

The atmospheric elements hydrogen, carbon, nitrogen, and the rare gases are strongly depleted in the Earth compared to chondritic meteorites. Pepin (1989) concluded that it appears that “simple ‘veneer’ scenarios in which volatiles are supplied from sources resembling contemporaneous meteorite classes” cannot explain the observed isotopic compositions. It is, therefore, often assumed that the isotopic compositions of these elements were affected by the process

that led to their depletion (e.g., hydrodynamic escape) (Chapter 2.06).

2.01.7 SUMMARY

As regards the rock-forming elements, the bulk composition of the Earth is basically chondritic (i.e., solar) with approximately equal abundances of magnesium, silicon, and iron atoms. In detail, however, there are some variations in chemistry among chondritic meteorites, and from a detailed comparison with meteorites it is concluded that the bulk Earth composition has similarities with the chemical composition group of carbonaceous chondrites.

(i) The Earth and most groups of carbonaceous chondrites are enriched in refractory elements, other types of chondrites are depleted.

(ii) If the Earth’s metal core contains 5% Si, then the Earth and carbonaceous chondrites have the same CI Mg/Si ratios. Ordinary and enstatite chondrites have significantly lower ratios.

(iii) Although the depletions of moderately volatile elements in the Earth are larger than in any group of carbonaceous chondrites, the Earth and carbonaceous chondrites show similar patterns of depletion of the moderately volatile elements: in particular, both are depleted in the alkali elements and in manganese. Enstatite and ordinary chondrites are also depleted in volatile elements, but their depletion patterns are different and sodium and manganese are not depleted relative to silicon.

(iv) The Earth and carbonaceous chondrites lie on the same $^{53}\text{Cr}/^{52}\text{Cr}$ versus $^{53}\text{Cr}/^{55}\text{Mn}$ isochron, indicating that the depletion of manganese and probably of all other moderately volatile elements in the Earth and in carbonaceous chondrites occurred shortly after the first solids had formed in the solar nebula.

There are also some differences between the chemistry of carbonaceous chondrites and the Earth.

(i) The bulk Earth has excess iron, reflected in higher Fe/Mg ratios of bulk Earth than the common groups of chondritic meteorites. It is suggested that silicates were lost during the collisional growth of the Earth involving giant impacts.

(ii) The Earth has a different oxygen isotopic composition from most carbonaceous chondrites.

(iii) Carbonaceous chondrites have isotope anomalies in chromium and titanium that are not observed in the Earth.

As the Earth makes up more than 50% of the inner solar system, we conclude that carbonaceous chondrites and the Earth reflect the major fractionation processes experienced by the material of the inner solar system. Other types of meteorites reflect fractionation processes on a more local scale.

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