

3.1 Cosmochemical Estimates of Mantle Composition

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3.1.1	Introduction and Historical Remarks	1
3.1.2	The Composition of Earth's Mantle as Derived from the Composition of the Sun	2
3.1.3	The Cosmochemical Classification of Elements and the Chemical Composition of Chondritic Meteorites	4
3.1.4	The Composition of the PM Based on the Analysis of the Upper Mantle Rocks	6
3.1.4.1	Rocks from the Mantle of Earth	6
3.1.4.2	The Chemical Composition of Mantle Rocks	7
3.1.4.2.1	Major-element composition of Earth's PM	10
3.1.4.2.2	Comparison with other estimates of PM compositions	13
3.1.4.2.3	Abundance table of the PM	13
3.1.4.3	Nonchondritic Models for the PM	18
3.1.4.4	Is the Upper Mantle Composition Representative of the Bulk Earth Mantle?	19
3.1.5	Comparison of the PM Composition with Meteorites	20
3.1.5.1	Refractory Lithophile Elements	20
3.1.5.2	Refractory Siderophile Elements	23
3.1.5.3	Magnesium, Silicon, and Chromium	23
3.1.5.4	The Fe Content of Earth	25
3.1.5.5	Moderately Volatile Elements	26
3.1.5.5.1	Origin of depletion of moderately volatile elements	29
3.1.5.5.2	Time of depletion of moderately volatile elements	30
3.1.5.6	HSE in Earth's Mantle	31
3.1.5.7	Late Veneer Hypothesis	31
3.1.6	The Isotopic Composition of Earth	32
3.1.6.1	Major Elements	32
3.1.6.2	Minor and Trace Elements	33
3.1.7	Summary	35
References		35

3.1.1 Introduction and Historical Remarks

In 1794, the German physicist E.F.F. Chladni published a small book in which he proposed the extraterrestrial origin of meteorites. The response was skepticism and disbelief. In the age of enlightenment, rocks could not simply fall from heaven. Only after additional witnessed falls of meteorites did scientists begin to take Chladni's hypothesis seriously. The first chemical analyses of meteorites were published by the English chemist E. Howard in 1802 and, shortly afterward, by M.E. 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: C, O, Na, Mg, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, and Sn (Burke, 1986). A popular hypothesis, which arose after the discovery of the first asteroid Ceres on 1 January 1801 by Piazzi, held that meteorites came from a single disrupted planet in the asteroid belt between Mars and Jupiter. In 1847, the French geologist A. Boisse (1810–96) proposed an elaborate model, in an attempt 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, that is, eucrites or meteoritic basalts. About 20 years later, G.-A. Daubrée (1814–96) 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 Earth was composed of a similar sequence of concentric layers (see Burke, 1986; Marvin, 1996).

At the beginning of the twentieth century, W.D. Harkins at the University of Chicago thought that meteorites would provide a better estimate for Earth's bulk composition than the terrestrial rocks collected at the surface, as one has access only to the 'mere skin' of Earth. Harkins tried 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 Harkins 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, closely resembling corresponding ratios of the average solar system based on presently known elemental abundances in the Sun and in CI meteorites (see [Burke, 1986](#)).

If Earth resembles the meteorite planet in composition, it should have a similar high bulk Fe content, which requires that the major fraction of Fe is concentrated in Earth's interior. The presence of a central metallic core to Earth was suggested by Emil Wiechert in 1897. Its existence was firmly established using information from seismic wave propagation by Richard D. Oldham in 1906 and was accurately located at a depth of 2900 km by Beno Gutenberg in 1913. In 1926, a liquid outer core was finally accepted, and the high density of the core and the high abundance of Fe and Ni in meteorites led very early to the suggestion that Fe and Ni are the dominant elements in Earth's core ([Brush, 1980](#); see [Chapter 3.16](#)).

[Goldschmidt \(1922\)](#) introduced his zoned Earth model. Seven years later, he published details ([Goldschmidt, 1929](#)). Goldschmidt thought that Earth was initially completely molten and separated on cooling into three immiscible liquids, leading to the final configuration of a core of FeNi overlain by sulfide liquid and covered by an outer shell of silicates.

Outgassing during melting 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 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 the absorption line spectroscopy of the solar photosphere. In a review article in 1941, [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."

Despite the vast amount of additional chemical data on terrestrial and meteoritic samples and despite significant improvements in the accuracy of solar abundance determinations, the basic picture as outlined by Russell has not changed. In the following sections, the validity of Russell's assumption will be demonstrated and some refinements in the estimate of Earth's

composition and the relationship to meteorites and the Sun are described.

3.1.2 The Composition of 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 volatiles. 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, *c.* 150 000 000 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 inner asteroid belt. There are no systematic variations with distance from the Sun, either in the chemistry of the inner planets, such as Mercury, Venus, Earth, and Mars; the Moon; and Vesta (the fourth largest asteroid) or in any other property ([Palme, 2000](#)). The high S content in the surface rocks of Mercury as determined by MESSENGER does not argue for a strong decline in volatiles with increasing distance from the Sun ([Nittler et al., 2011](#)). One reason is the substantial radial mixing of materials formed at various heliocentric distances during the formation of the terrestrial planets. In current models of planet formation, Earth is made by collisions of a few dozen Moon- to Mars-sized embryos, small planets that had accreted within a million years from local feeding zones. The growth of Earth and the other inner planets took tens of millions of years and the materials from various heliocentric distances contributed to the growth of the planets (e.g., [Canup and Agnor, 2000](#); [Chambers, 2001](#); [O'Brien et al., 2006](#); [Wetherill, 1994](#)).

The abundances of all major and many minor and trace elements in the Sun are known from the absorption line spectroscopy of the solar photosphere. Accuracy and precision of these data have continuously improved over the last 70 years. In a recent compilation of the solar abundances by [Asplund et al. \(2009\)](#), there are 32 elements listed with uncertainties below 12%. The more accurate the solar abundances are, the better they fit with the abundances of CI chondrites, a small group of meteorites that appear closest in composition to the Sun. There are now 40 elements with a Si-normalized photospheric/CI chondrite abundance ratio between 0.9 and 1.1 ([Lodders et al., 2009](#)). A first approximation to the composition of the bulk Earth is, therefore, to assume that Earth has the average solar system composition for rock-forming elements, that is, excluding highly volatile elements such as H, N, C, O, and noble gases ([Table 2](#)).

The six most abundant rock-forming elements in the Sun are Si (100), Mg (104), Fe (86), S (43), Al (8.4), and Ca (6.2) with appropriate fractions of oxygen. The numbers in parentheses are atoms (the number of Si atoms has been set arbitrarily to 100; data from [Lodders et al., 2009](#)). Geophysical

measurements indicate that Earth's core accounts for 32.5% of Earth's mass (Anderson and Kovach, 1967). Assuming that the core contains only Fe, Ni and S allows the composition of the silicate fraction of Earth to be calculated by mass balance. This is the composition of the bulk silicate Earth (BSE) or Earth's primitive mantle (PM). The term primitive indicates that this is the composition of Earth's mantle before crust and core formation.

If only these six rock-forming elements made up the BSE along with the oxygen associated with them by stoichiometry, then as with negligible amounts of zerovalent Fe (i.e., Fe⁰) and Fe³⁺ in the BSE, the sum of their 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 the solar abundance ratios into eqn [1], for example, Si/Mg, Ca/Mg, and Al/Mg, (Lodders et al., 2009) one obtains:

$$\text{MgO} = 38.12 - \text{FeO}/2.623 \quad [2]$$

(MgO and FeO in wt%).

This equation is valid for the mantle of any planet with CI chondritic bulk composition. The maximum MgO content of a completely reduced, FeO-free mantle is 38.12%. This number decreases slightly when minor elements are considered. Enrichment in refractory elements will also produce lower MgO contents. With increasing FeO, MgO will decrease, and the lowest achievable MgO content for a planet with CI composition and without a core is 24.3% MgO.

So far, only the composition of the mantle has been considered, and the only element that is not quantitatively contained in the mantle is Fe. It is distributed between the core and mantle according to

$$\text{Fe}_{\text{core}} \times X_{\text{core}} + \text{Fe}_{\text{mantle}} \times (1 - X_{\text{core}}) = \text{Fe}_{\text{bulk Earth}} \quad [3]$$

the corresponding mass balance for Mg, assuming a Mg-free core, is

$$\text{Mg}_{\text{mantle}} \times (1 - X_{\text{core}}) = \text{Mg}_{\text{bulk Earth}} \quad [4]$$

where X_{core} is the mass fraction of the core in a planet ($0 \leq X_{\text{core}} \leq 1$).

Writing eqn [2] in a different form

$$\text{Mg}_{\text{mantle}} = 22.99 - \text{Fe}_{\text{mantle}} \times 0.2958 \quad [5]$$

and assuming a CI chondritic bulk Earth Fe/Mg weight ratio (Lodders et al., 2009):

$$(\text{Fe}/\text{Mg})_{\text{bulk}} = (\text{Fe}/\text{Mg})_{\text{CI}} = 1.93 \quad [6]$$

gives four eqns [3–6] with 6 unknowns (Fe_{bulk} , Mg_{bulk} , $\text{Fe}_{\text{mantle}}$, $\text{Mg}_{\text{mantle}}$, Fe_{core} , and X_{core}).

This leads to an equation for the oxidized iron in the silicate mantle ($\text{Fe}_{\text{mantle}}$) as the function of the iron content in the core (Fe_{core}) and the mass fraction of the core (X_{Fe}):

$$\text{Fe}_{\text{mantle}} = (44.37 \times (1 - X_{\text{core}}) - \text{Fe}_{\text{core}} \times X_{\text{core}}) / (1.571 \times (1 - X_{\text{core}})) \quad [7]$$

($\text{Fe}_{\text{mantle}}$ and Fe_{core} in wt%).

This equation is valid for any planet with a volatile-free CI chondritic bulk composition and a metal core. The Fe content of the core depends also on Ni and S. The partitioning of Si into the core requires very reducing conditions, that is, low FeO contents in the mantle (<1%), pressure effects not considered.

Equation [7] is graphically displayed in Figure 1. Three cases are considered:

1. The core contains only metallic Fe (solid lines in Figure 1). The maximum core size is about 31% with an FeO-free mantle and a corresponding MgO mantle content of 38%.
2. The core contains an FeNi alloy and the bulk Earth has a chondritic bulk Fe/Ni ratio. Increasing the core fraction increases the Fe of the core until the Fe/Ni reaches the chondritic ratio of 17%. The resulting FeO and MgO contents are shown as dashed lines in Figure 1. At Earth's core size of 32.5%, about 3% FeO and 37% MgO are calculated for the mantle.
3. The core contains Fe, Ni, and S. Calculating the S content from the CI Fe/S ratio leads to about 8% S for the bulk planet. If S and Ni are entirely concentrated in the core, the Fe content of a 32.5% core is 50%, the rest is Ni and S. None of the terrestrial planets have such a high S content, reflecting the general depletion of volatile elements in the inner solar system. To better study the influence of S, the calculated S content of the bulk Earth has been reduced by 80%, which leads to a bulk Earth S content of 1.6%. The resulting mantle composition is shown in Figure 1 as a dotted line

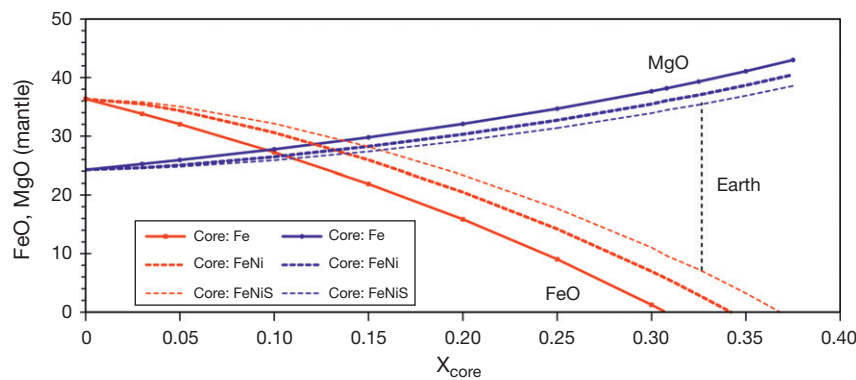


Figure 1 The anticorrelation of FeO and MgO in planetary mantles as the function of the core size (by mass, at zero pressure) for volatile-free bulk CI-chondritic planets, according to eqn [7]. For the case of a S-containing core, only 20% of the solar S is used for the bulk planet and all S is in the core.

Table 1 Composition of Earth's mantle assuming the average solar system element ratios for the whole Earth except for S (20% of the solar S)

	<i>Earth's mantle: solar model^a</i>	<i>Earth's mantle: based on the composition of the upper mantle rocks^b</i>
MgO	35.34	36.77
SiO ₂	50.93	45.40
FeO	7.29	8.10
Al ₂ O ₃	3.60	4.52
CaO	2.90	3.62
Total	100	98.41

^aAssuming a core containing all Ni and S, with 20% of the CI abundance of S (see text).^bFrom Table 3.

and is listed in Table 1. With 7.29% FeO and 35.34% MgO, this composition comes close to the PM derived from the upper mantle rocks (see Table 3 in Section 3.1.4.2.1).

The important conclusion is that by assuming solar element ratios among rock-forming elements in the bulk Earth, the calculated mantle composition is in basic agreement with the mantle composition derived from the upper mantle rocks. Thus, the bulk Earth has basically a chondritic bulk composition. On a finer scale, there are, however, differences between the calculated mantle composition of the solar model and the mantle composition derived from the analyses of mantle rocks that make a strictly solar model of Earth unlikely: (1) 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 Earth. (2) The Si/Mg ratio of Earth's mantle is different from the solar ratio, because Earth's core contains several percent of Si, as will be discussed below. Adding this to the subchondritic Si/Mg of the mantle leads to a chondritic or solar Si/Mg ratio for the bulk Earth. (3) Minor and trace element data indicate that Earth is significantly depleted in volatile elements when compared to solar abundances. As pointed out above, the S content of the core assuming the solar composition model for Earth is unrealistically high. Therefore only 20% of the total endowment of S has been used. (4) As will be seen below, the bulk Earth Fe/Mg ratio is about 10% above the CI chondritic ratio (O'Neill and Palme, 2008). In order to assess the significance of these differences properly, some understanding of the variability of the chemical compositions of chondritic meteorites is required.

3.1.3 The Cosmochemical Classification of Elements and the Chemical Composition of Chondritic Meteorites

The thermal evolution of the planetesimals accreted in the very early stages of the solar system depends on the timescale of accretion (beginning and duration) and the amount of short-lived radioactive nuclei they incorporate, primarily ²⁶Al with a half-life of 710 000 years and some ⁶⁰Fe ($T_{1/2} = 2.62$ My). In some cases, there was sufficient heat available to melt and differentiate planetesimals completely, forming a metal core and a silicate mantle, while in other cases, records of even modest heating were absent because accretion started late when the radioactive nuclei had largely decayed.

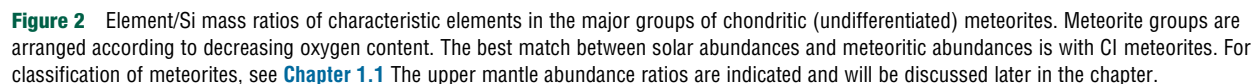
Undifferentiated meteorites derived from unmelted parent bodies are called *chondritic meteorites*. Their chemical composition is close to the solar composition, after allowing for depletion of the volatile elements. Textures of chondritic meteorites have been more or less modified by thermal metamorphism and/or aqueous alteration in the parent body. Chemically, chondritic meteorites are characterized by limited ranges of Mg/Si, approximately from 0.7 to 0.9, and Fe/Si, approximately from 1.2 to 1.7. The high values are close to the ratios measured in the solar photosphere (0.91 for Mg/Si and 1.81 for Fe/Si). This transforms to roughly the same numbers of atoms for Mg, Si, and Fe and indicates the absence of the two major planetary fractionation processes, namely, partial melting, leading to planetary crusts with high Al/Mg and Si/Mg ratios, and, probably also triggered by partial melting, metal separation, that is, core formation.

The roughly solar composition of chondritic meteorites is, however, only a first-order observation. Nebular processes, primarily fractionation during condensation and/or aggregation, have produced some compositional variation in the chemistry of chondritic meteorites. The extent to which individual elements are affected by these processes depends mainly on their volatility under early solar nebula conditions. Nebular volatilities of elements are quantified by condensation temperatures formally calculated for a gas of solar composition under the assumption of complete chemical equilibrium (see Lodders, 2003; Wasson, 1985). In Table 2, elements are grouped according to their condensation temperatures. In addition, the geochemical character of each element is indicated, that is, whether it is lithophile or siderophile and/or chalcophile. In Figure 2, the abundances of several elements with different cosmochemical characteristics in the various groups of chondritic meteorites and in the Sun have been plotted. All

Table 2 Cosmochemical classification of elements

<i>Cosmochemical components</i>	<i>Elements</i>	
	<i>Lithophile (silicate + oxides)</i>	<i>Siderophile + chalcophile (sulfide + metal)</i>
Refractory $T_c = 1850\text{--}1355$ K	Zr, Hf, Sc, Y, Gd, Tb, Dy, Ho, Er, Tm, Lu, Th, Al , U, Nd, Sm, Ti , Pr, La, Ta, Nb, Ca , Yb, Ce, Sr, Ba, Be, V, Eu	Re, Os, W, Ir, Mo, Ru, Pt, Rh
Main component $T_c = 1355\text{--}1250$ K	Mg, Si, Cr	Ni, Co, Fe, Pd
Moderately volatile $T_c = 1250\text{--}250$ K	Mn , Li, K, Na , Cl, B, Rb, Cs, F, Zn	P, As, Au, Cu, Ag, Sb, Ga, Ge, Bi, Pb, Te, Sn, Se, S
$T_c(\text{S}) > 664$ K	Br, I, Tl	Cd, In, Tl, Hg
$T_c(\text{S}) < 664$ K		
Highly volatile (not fully condensed in CI chondrites)	O, N, Xe, Kr, Ar, C, Ne	

Elements in order of decreasing 50% condensation temperatures (T_c) at a pressure of 10^{-4} bar (Lodders, 2003); major and minor elements in bold face; for example, $T_c(\text{S})$, 50% condensation temperature of S.



1. The refractory component (see [Table 2](#)) comprises the elements with the highest condensation temperatures. There are two groups of refractory elements, the *refractory lithophile* elements (RLE) condensing in Al-, Ca-, Ti-oxides, and silicates and the *refractory siderophile* elements (RSE) condensing as refractory metal grains (e.g., [Berg et al., 2009](#) and references). The refractory component accounts for about 5% of the total condensable matter. Variations in the refractory element abundances of bulk meteorites reflect the incorporation of variable fractions of a refractory Al, Ca-rich component. The ratios among RLE are constant in all types of chondritic meteorites to within about 5% in most cases. The total variation of refractory element concentrations is about a factor of 2, as shown in [Figure 2](#), where Al represents the refractory component.
2. The *common lithophile* elements Mg and Si represent the main silicate component of condensable matter. They condense as Mg silicates with Cr in solid solution. Together with iron (metallic and oxidized), Mg silicates account for more than 90% of the mass of the objects of the inner solar

3. In a gas of solar composition, all iron condenses as FeNi alloy including Co and Pd 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. The well-known decrease in Fe/Si ratios ([Figure 2](#)) from H through L to LL chondrites is a good example. A similar, but less pronounced effect is seen within the groups of carbonaceous chondrites (CC), where Fe/Si decreases from CI to CV chondrites ([Figure 2](#)). There are also rare groups of meteorites with significant excess in Fe (not shown in [Figure 2](#)), the CH and CB chondrites ([Chapter 1.1](#)). These meteorites often are assumed to have formed not from the solar nebula but by later condensation from large impact vapor clouds. In all cases considered, siderophile element abundances, such as Ni, Co, Ir, etc., vary in parallel with the Fe abundance.

4. The *moderately volatile elements* comprise lithophile, siderophile, and/or chalcophile elements. This group of elements may be further subdivided into elements condensing between Mg silicates and troilite (FeS) and elements condensing at temperatures below FeS and Hg, with the lowest condensation temperature of elements that fully condense in CI meteorites (Lodders, 2003). However, the solar abundance of Hg is only poorly known and its CI chondritic abundance is also quite uncertain (Lauretta et al., 2001; Table 2). In general, abundances of moderately volatile elements when normalized to average solar abundances decrease in most groups of chondritic meteorites with decreasing condensation temperatures, that is, the more volatile an element is, the lower is its normalized abundance (Palme et al., 1988). The three elements Na, Zn, and S represent moderately volatile elements in Figure 2. Significant variations are seen among the different chondrite groups, the Zn/Si ratio varies by a factor of 10. It is remarkable that only depletions of moderately and highly volatile elements are observed in chondritic meteorites, never enrichments (Palme et al., 1988). The lithophile and siderophile elements of this group are fully condensed in CI chondrites.
5. The group of *highly volatile elements* with condensation temperatures below Hg (250 K) includes the atmophile elements H, He, C, O, Ne, Ar, Kr, and Xe. These elements are depleted in all groups of meteorites, even in CI meteorites (see Palme et al., 2012, Chapter 2.2).

As can be seen in Figure 2, the CI chondrites with their most prominent member the Orgueil meteorite, have, for most elements shown here, the same abundance ratios as the Sun. The agreement between the composition of the Sun and CI meteorites holds for most elements heavier than oxygen and with the exception of noble gases (Palme et al., 2012, Chapter 2.2). Differences among the various types of chondritic meteorites include differences in chemical composition (Figure 2), mineralogy, texture, and degree of oxidation. In recent years, new chondrite groups have been discovered (see Chapter 1.1). Only the most important groups are shown here. The compositional variations observed among chondritic meteorites can be explained in terms of the five components discussed above.

The element Al in Figure 1 is a representative of the refractory component. All types of CC are enriched in refractory elements, whereas the ordinary (OC) and enstatite chondrites (EC) are depleted. The variations in Mg/Si (Figure 2) are smaller and may be the result of preferred accumulation or loss of Mg-rich olivine as discussed above. The variations in Fe/Si ratios reflect variable incorporation of metallic iron into a chondrite parent body. The variations in the moderately volatile elements Na, Zn, and S among chondrite groups are large and demonstrate the uniqueness of CI chondrites as best representing solar abundances. The decrease in O/Si ratios (Figure 2) indicates an increasingly reducing environment from CC through OC to EC. The average fayalite content of olivine (or ferrosilite content of orthopyroxene) in these meteorites decreases in the same sequence. The large variations in the composition of the olivine in unequilibrated chondrites do not allow an ambient oxygen fugacity to be defined.

In the following section, the composition of Earth's mantle from the chemical analyses of the upper mantle rocks will be derived. The resulting mantle composition will then be compared with the composition of chondritic meteorites. In order to avoid circular arguments, as few assumptions will be used as possible based on the above cosmochemical observations. However, some assumptions are essential, and these will be clearly indicated.

3.1.4 The Composition of the PM Based on the Analysis of the Upper Mantle Rocks

3.1.4.1 Rocks from the Mantle of Earth

Earth's principal division into core, mantle, and crust is the result of two fundamental processes: (1) the formation of a metal core early in Earth's history (see Chapter 3.16) and (2) the formation of the continental crust by partial melting of the silicate mantle. This process has occurred with variable intensity throughout Earth's history (see Chapter 4.1). Conceptually, the least fractionated rocks of Earth would be those that have suffered core formation (this seems unavoidable), but have not been affected by the extraction of partial melts during crust formation. These rocks would have the composition of the PM, that is, the mantle before the onset of melting. Such rocks are typically high in MgO and low in Al₂O₃, CaO, TiO₂, and other elements incompatible with mantle minerals. Fortunately, samples can be collected at Earth's surface with compositions that come close to the composition of the PM. Such samples are not known from the surfaces of the Moon, Mars, and the asteroid Vesta, making it much more difficult to reconstruct the bulk composition of these planets.

Rocks and rock fragments from Earth's mantle occur in a variety of geologic settings as discussed in detail by O'Neill and Palme (1998) (see also, Chapters 3.4 and 3.5): (1) as the mantle sections in ophiolites representing suboceanic lithosphere; (2) as massive peridotites, variously known as Alpine, orogenic, or simply high-temperature peridotites; (3) as abyssal peridotites, dredged from the ocean floor – the residue from melt extraction of the oceanic crust; (4) as spinel (rarely garnet) peridotite xenoliths from alkali basalts, mostly from the subcontinental lithosphere but with almost identical samples from suboceanic lithosphere; and (5) as garnet peridotite xenoliths from kimberlites and lamproites – these fragments sample to deeper levels in the subcontinental lithosphere and are restricted to ancient cratonic regions. In addition, diamonds sometimes contain inclusions of deep mantle minerals, including those formed in the lower mantle or relicts thereof, but the rarity and unusual mode of occurrence of such samples warns against their being regarded as representative.

Typical mantle peridotites contain more than 50% olivine, variable amounts (depending on their history of melt extraction and refertilization) of orthopyroxene (opx) and clinopyroxene (cpx), 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 (see [Chapter 3.2](#)). Another obvious reason for believing that these rocks come from the mantle is that the constituent minerals of the xenoliths have chemical compositions that show that the rocks have equilibrated at upper mantle pressures and temperatures. In the case of the xenoliths, their ascent to Earth's surface was so fast that the minerals had no time to adjust to the lower pressure and temperature of 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 40–60 km. Garnet lherzolites, which sample the mantle down to a depth of about 200 km and a temperature of 1400 °C, are much rarer (see [Chapter 3.5](#)).

Early compositional data on peridotites have been summarized by [Maaløe and Aoki \(1977\)](#). A comprehensive review of the data on mantle peridotites published to the mid-1990s was given by [O'Neill and Palme \(1998\)](#). Since then, there has been

an explosion of chemical analyses of mantle peridotites, both xenoliths ([Chapter 3.5](#)) and massive peridotites ([Chapter 3.4](#)), from many geographical settings, which have confirmed the compositional trends identified by [Maaløe and Aoki \(1977\)](#) and [O'Neill and Palme \(1998\)](#).

3.1.4.2 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 SiO₂ from 43 to 46 wt%, remarkably constant abundances of FeO (8 ± 1 wt %), Cr₂O₃ (0.4 ± 0.1 wt%), and Co (100 ± 10 ppm). The bulk-rock Mg#s ($100 \times \text{Mg}/(\text{Mg} + \text{Fe})$, in atoms) are generally ≥ 0.89 . The comparatively high contents of Ni (2200 ± 500 ppm), a siderophile element, and of Ir (3.2 ± 0.3 ppb), a compatible highly siderophile element (HSE), are also diagnostic of mantle rocks. In [Figure 3](#), the bulk-rock concentrations of SiO₂, CaO, and Al₂O₃ versus MgO for peridotites from the Central Dinaric Ophiolite Belt (CDOB) in Yugoslavia, a typical occurrence of

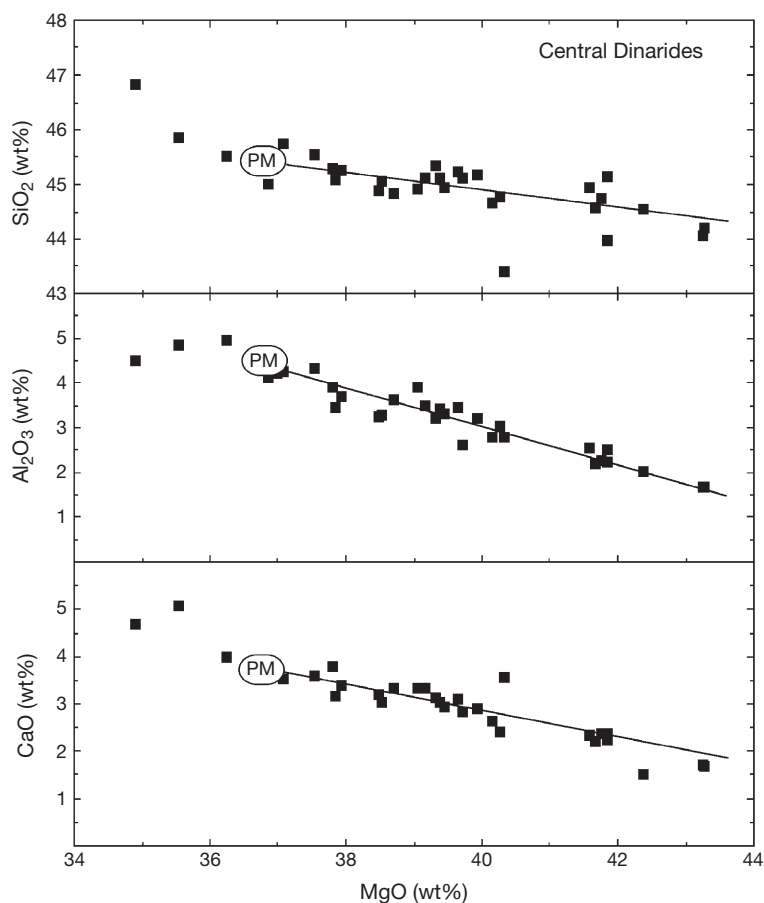


Figure 3 Correlations of SiO₂, Al₂O₃, and CaO with MgO for a suite of mantle samples from the Central Dinaric Ophiolite Belt (CDOB) in Yugoslavia, a typical occurrence of mantle rocks associated with ophiolites. The samples are recovered from an area comprising a large fraction of the former Yugoslavia ([Lugovic et al., 1991](#)). The abundances of the refractory elements CaO and Al₂O₃ are negatively correlated with MgO, indicating the preferred partitioning of these elements into the partial melt. The effect for SiO₂ is comparatively small. These correlations are characteristics of a large number of occurrences of mantle xenoliths and massive peridotites (see [BVSP, 1981](#); [McDonough, 1990](#); [McDonough and Sun, 1995](#); [O'Neill and Palme, 1998](#)). The PM indicates the composition of the PM derived in this chapter.

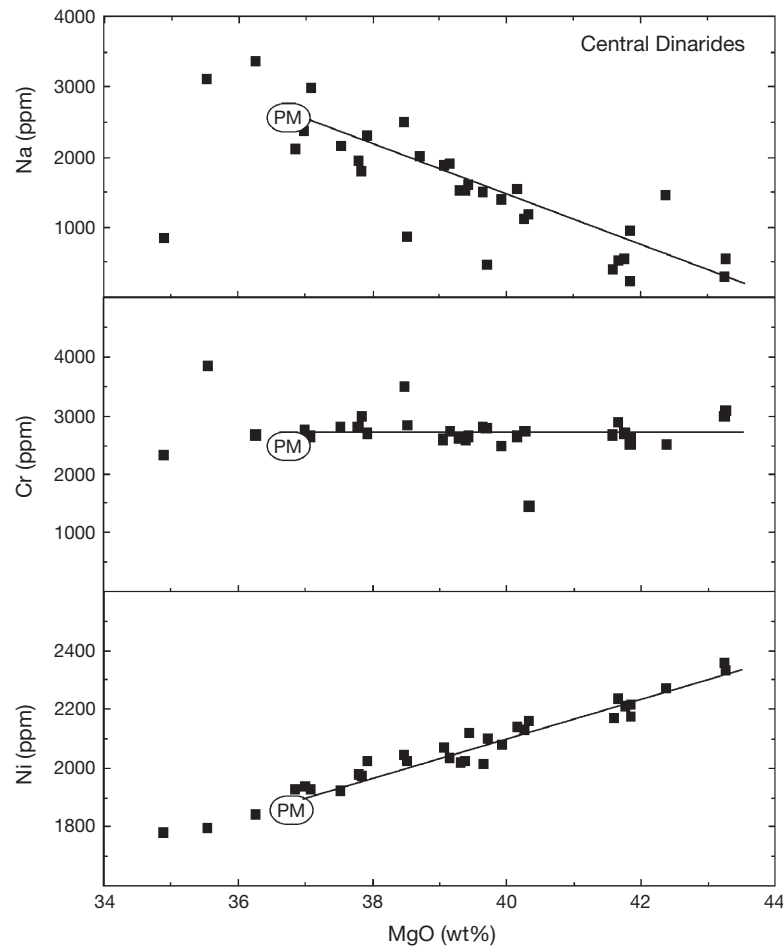


Figure 4 Na, Cr, and Ni form from the same suite of rocks as in [Figure 3](#). Na is incompatible with mantle minerals, Ni is compatible, and Cr partitions equally between melt and residue.

mantle rocks associated with ophiolites, have been plotted. The samples are recovered from an area comprising a large fraction of the former Yugoslavia ([Lugovic et al., 1991](#)). The abundances of the refractory elements CaO, Al_2O_3 and also of Ti, Sc, and the heavy rare earth elements (HREE) 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 3](#)). There is a comparatively small increase of 3.5% in SiO_2 over the same range. In [Figure 4](#), Na, Cr, and Ni versus MgO for the same suite of mantle rocks have been plotted. The increase of Na is about twice that of Ca and Al. The Cr concentrations are constant, independent of MgO, while Ni concentrations are positively correlated with MgO.

The samples of massive peridotites and of spinel and garnet lherzolite xenoliths from worldwide localities are plotted on the same or on very similar correlations as those shown here for the CDOB samples ([BVSP, 1981](#); [McDonough, 1990](#); [McDonough and Sun, 1995](#); [O'Neill and Palme, 1998](#); [Chapters 3.4 and 3.5](#)). Particularly noteworthy is that trends for xenoliths and massive peridotites are statistically indistinguishable ([McDonough and Sun, 1995](#); [Chapter 3.4](#)). An example is given in [Figure 5](#) where FeO versus MgO plots for samples from two massive peridotites, the CDOB and Zabargad Island in the Red Sea

are compared with xenoliths data from two localities, the Vitim (Baikal region, Russia) and the Hessian Depression (Germany). Two important conclusions can be drawn from this figure: (1) the FeO contents are on average independent of MgO and (2) the average FeO content is the same in all four localities. The two statements can be generalized. On the left side of [Figure 6](#), the average FeO contents of samples from 11 suites of xenoliths are compared with those of ten suites of massif peridotites. Each of the points in [Figure 6](#) represents the average of at least six, and in most cases more than ten, samples (see [O'Neill and Palme, 1998](#), for details). The errors assigned to the data points in [Figure 6](#) 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 3](#)).

The 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

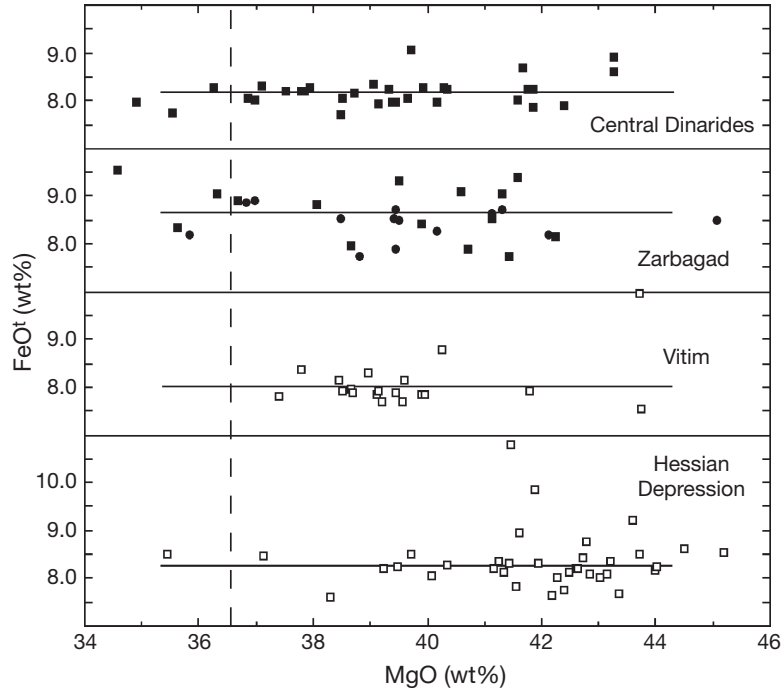


Figure 5 The FeO contents of the samples from the same suites as in [Figures 3 and 4](#), samples from Zabargad Island, and samples from two suites of xenoliths from the Vitim (Baikal region) and the Hessian Depression (Germany). The FeO contents are, similar to Cr in [Figure 4](#), independent of the fertility of the mantle rocks reflected in their MgO contents. Reproduced from O'Neill HStC and Palme H (1998) *Composition of the silicate Earth: Implications for accretion and core formation*. In: Jackson I (ed.) *The Earth's Mantle: Structure, Composition and Evolution – The Ringwood Volume*, pp. 3–126. Cambridge: Cambridge University Press.

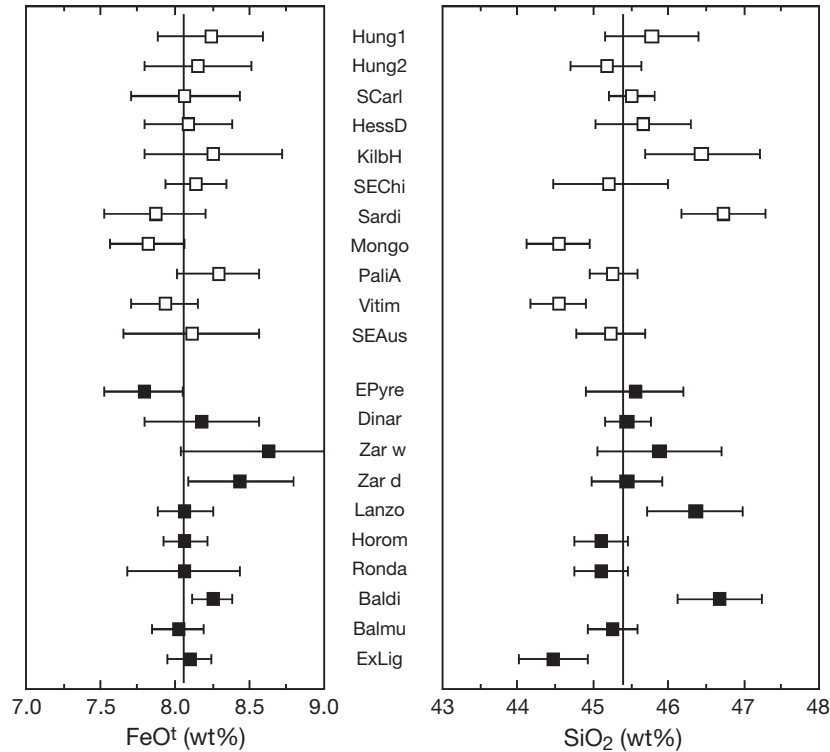


Figure 6 Average FeO (all Fe assumed as FeO) and SiO₂ contents in various suites of xenoliths (open symbols) and massive peridotites (full symbols). All suites give the same FeO value within 1 σ (standard deviation). An average PM FeO content of $8.07 \pm 0.06\%$ is calculated from these data (see O'Neill and Palme, 1998). The SiO₂ concentrations are somewhat more variable as SiO₂ depends on MgO (see [Figure 2](#)). Reproduced from O'Neill HStC and Palme H (1998) *Composition of the silicate Earth: Implications for accretion and core formation*. In: Jackson I (ed.) *The Earth's Mantle: Structure, Composition and Evolution – The Ringwood Volume*, pp. 3–126. Cambridge: Cambridge University Press.

melting. Most peridotites are, however, depleted to various extents in incompatible elements, that is, they have lower contents of CaO, Al_2O_3 , Na_2O , etc., than a fertile mantle would have, as shown in **Figures 3** and **4**. By contrast, an element compatible with olivine, such as Ni, increases with increasing MgO contents (**Figure 4**). Thus, the trends in **Figures 3** and **4** have been interpreted as reflecting various degrees of melt extraction (Frey et al., 1985; Nickel and Green, 1984). Following this reasoning, the least depleted peridotites, that is, the highest in CaO and Al_2O_3 should be the closest in composition to the PM.

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 Cr-diopside suite of dikes, which are then folded back into the peridotite as the 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 Cr-diopside suite, that is, in cpx and opx 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, melt extraction should only cause linear relationships for compatible and slightly incompatible elements. Partial melting experiments and corresponding calculations show that for most incompatible elements, such trends should not be linear (see O'Neill and Palme, 1998, Figure 2.12). Although the banding may not be as obvious in xenoliths as in the massive peridotites, since it operates over length scales greater than that 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 elements such as Th, U, Nb, and light rare earth elements (LREE), and these elements cannot be used to distinguish melt extraction trends from those caused by modal banding.

In summary, then, the trends of CaO, Al_2O_3 , and Na, (**Figures 3** and **4**), and also TiO_2 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 several processes—melt extraction, followed by one or more of refertilization, metamorphic modal banding, and 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 Al_2O_3 than that inferred for the PM. Thus, those peridotites richest in incompatible elements may not be the best representatives of PM and instead some other method of reconstructing the PM composition must be used. Here, a new procedure for calculating the composition of PM that is independent of the apparent linear correlations discussed above is described. The method was first introduced by O'Neill and Palme (1998).

3.1.4.2.1 Major-element composition of Earth's PM

The two elements Ca and Al are RLE. The assumption is usually made that all RLE are present in Earth's PM 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, Earth's mantle abundances of RLE have been assumed to occur in chondritic relative proportions in the PM, 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 $(\text{RLE}/\text{Mg})_{\text{N}}$, is a measure of the concentration level of Earth's refractory component. A single factor of $(\text{RLE}/\text{Mg})_{\text{N}}$ valid for all RLE is a basic assumption in this procedure and will be calculated from mass balance considerations.

In the first step, the FeO^{t} (total Fe as FeO, which is a very good approximation for mantle rocks) and MgO contents are estimated from two empirical constraints:

1. As discussed above, FeO^{t} is remarkably constant worldwide, in massive peridotites and in alkali basalt-derived lherzolite xenoliths (**Figures 5** and **6**), and moreover, it does not depend on MgO contents for reasonably fertile samples ($\text{MgO} < 42 \text{ wt\%}$). 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. 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 $\pm 0.5 \text{ wt\% FeO}^{\text{t}}$ for the least depleted samples, but the mean values are remarkably coherent (**Figure 6**). By averaging, O'Neill and Palme (1998) obtained $\text{FeO}^{\text{t}} = 8.10 \text{ wt\%}$, with a standard error of the mean of $0.05 \text{ wt\%}$. This topic has been revisited by compiling studies from the literature published since 1990. From 32 studies of xenoliths, we obtained $\text{FeO}^{\text{t}} = 8.10 \pm 0.06 \text{ wt\%}$, and for 17 studies of massive peridotites, $\text{FeO}^{\text{t}} = 8.10 \pm 0.05 \text{ wt\%}$, in complete agreement with the earlier values and attesting to the essential similarity of peridotite compositions worldwide. Next, the MgO content is constrained from the observation that molar $\text{Mg}/(\text{Mg} + \text{Fe}^{\text{t}})$ (i.e., bulk-rock Mg#s) ought not to be affected by modal segregation, since mineral Mg#s are nearly the same in olivine and in pyroxenes. This is shown not only by experimental phase equilibrium studies, but also by many empirical studies reporting both whole rock (WR) and olivine compositions in spinel peridotites (e.g., Ionov and Hofmann, 2007). From 19 such studies, including both xenolith and massive peridotite suites, 391 coupled WR and olivine analyses in which

olivine compositions were reported as homogeneous have been found. Regression of these data gave $Mg\#(WR) = 0.9997 Mg\#(ol)$, with a standard error of ± 0.0003 . Consequently, olivine compositions provide a reliable guide to WR $Mg\#$ in spinel peridotites. Histograms of olivine compositions in spinel lherzolites from a wide variety of environments show a distribution characterized by a sharp increase in frequency at an $Mg\#$ of 0.890 (see Figure 7). At higher $Mg\#$ s, the frequency of samples follows an approximately uniform distribution. Given that the uncertainty with which olivine $Mg\#$ s are determined in individual samples is typically about 0.001, the overall shape of the distribution is reasonably well modeled by a half Gaussian centered at $Mg\#$ of 0.890 with a standard deviation of 0.001, joined onto an approximately uniform distribution at a higher $Mg\#$ (Figure 7). This distribution can be interpreted as follows. The PM has a $Mg\#$ of 0.890 ± 0.001 , with a few samples at lower $Mg\#$ due notionally to the melt infiltration or metasomatism. Melt extraction, which increases $Mg\#$, accounts for the many samples at higher $Mg\#$. Hence,

$$MgO = (FeO^t \times 0.5610 \times mg\#) / (1 - mg\#) \quad [8]$$

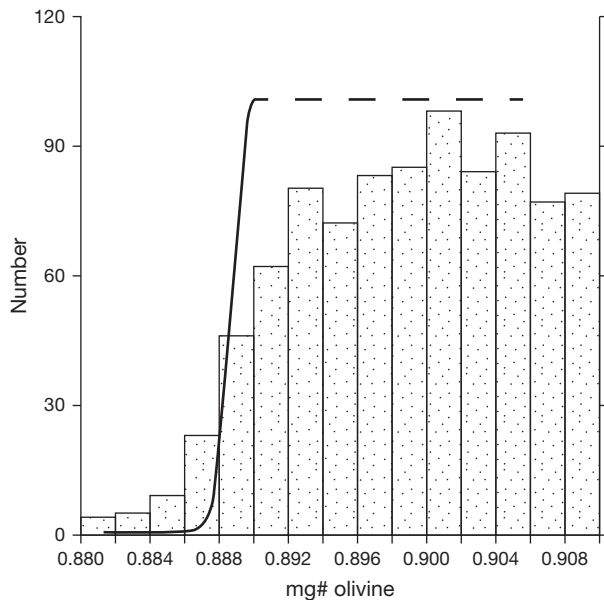


Figure 7 Histogram of olivine $Mg\#$ (molar $Mg/(Mg + Fe)$) in spinel peridotite xenoliths, compiled from the Geochemistry of Rocks of the Oceans and Continents (GEOROC) database (<http://georoc.mpch-mainz.gwdg.de>, Sarbas and Nohl, 2008). The data were filtered to exclude olivines with < 0.25 wt% NiO or with > 0.25 wt% CaO, giving 1317 samples, of which 44 have $Mg\# < 0.880$ and 373 have $Mg\# > 0.910$, which are not plotted. The distribution resembles a half Gaussian centered at $Mg\#$ of 0.890 with a standard deviation of 0.001 (solid curve), joined onto uniform distribution at higher $Mg\#$ (dashed line). The distributions are drawn with maximum frequencies of 100 samples. The important feature of the distribution is the large jump in frequency at $Mg\# = 0.890$, which is interpreted to be the primitive mantle value. The tendency to report chemical analyses of all unusual samples in a xenolith suite but only representative analyses of the dominant types would bias the distribution by overemphasizing the number of Fe-enriched samples with $Mg\# < 0.890$.

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

2. 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 (H, C, N, and associated O) are removed. These elements are O, Mg, Al, Si, S, Ca, Fe, and Ni. Of these, Ni and S are heavily depleted in the PM by concentration in Earth's core; their abundances are also well constrained by the empirical data from peridotites (see below). The amount of O is fixed by the stoichiometry of the relevant oxide components, hence:

$$MgO + Al_2O_3 + SiO_2 + CaO + FeO^t = 98.41 \text{ wt\%} \quad [9]$$

The uncertainty is probably only $\pm 0.04\%$. This constraint is very robust because the abundances of the minor components that constitute 1.34% of the missing 1.59% (i.e., Na_2O , TiO_2 , Cr_2O_3 , MnO , and NiO , plus the excess O in Fe_2O_3) vary little among reasonably fertile peridotites, and all other components (H_2O , CO_2 , 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 SiO_2 is also relatively insensitive to the melt extraction and modal segregation processes. The SiO_2 concentration from SiO_2 versus MgO trends at 36.77% MgO given by O'Neill and Palme (1998) was 45.4 ± 0.3 wt% from spinel lherzolite suites worldwide. As for FeO^t , we have revisited this estimate using data published since 1992 on 32 xenolith suites, which gave 45.3 ± 0.1 wt%, and 17 massive peridotite suites, which gave 45.6 ± 0.2 wt%, identical to the previous value.

With these estimates of MgO , FeO^t , SiO_2 , and the minor and trace elements, the amounts of CaO plus Al_2O_3 in the PM are given by the difference:

$$CaO + Al_2O_3 = 100 - 36.77 - 8.10 - 45.40 - 1.59 = 8.14 \text{ wt\%} \quad [10]$$

Since Ca and Al are both RLE, the CaO/Al_2O_3 ratio is constrained at the chondritic value of 0.813. Unfortunately, Ca is rather more variable than other RLE in chondrites, probably due to some mobility of Ca in the most primitive varieties (like Orgueil); hence, this ratio is not known as well as one might like. A reasonable uncertainty is ± 0.03 . Then, $Al_2O_3 = 8.14 / (1 + 0.813) = 4.49$ wt% and $CaO = 3.65$ wt%. The method could be easily adapted to a nonchondritic CaO/Al_2O_3 ratio if a nonchondritic model for Earth were assumed. Simply calculating the CaO at 36.77 wt% MgO from the same 32 xenolith and 17 massive peridotite suites used to update the estimates of FeO^t and SiO_2 gives 3.77 ± 0.04 , and 3.90 ± 0.04 wt%, respectively, and 4.33 ± 0.04 and 4.33 ± 0.05 wt% for Al_2O_3 . The CaO is slightly higher and Al_2O_3 slightly lower, giving $CaO/Al_2O_3 = 0.885$, or 9% greater than the chondritic ratio, in agreement, qualitatively, with Palme and Nickel (1985).

If the assumption of the constant chondrite-normalized RLE ratios in Earth is accepted, the abundances of CaO and Al_2O_3 constrain all other RLE. The ratio of the RLE in the PM relative to CI chondrites is, with the CI chondritic Al and Ca contents (Palme et al., 2012, Chapter 1.1), 2.83 and normalized to Mg , $(RLE/Mg)_N = 1.22 \pm 0.10$.

Putting the algorithm in the form of a simple equation makes the effects of the uncertainties transparent. The final result for CaO, Al_2O_3 and the $(\text{RLE}/\text{Mg})_{\text{N}}$ ratio is particularly sensitive to the chosen value of Mg#; it is therefore important in deriving the PM composition from empirical data to use the information on Mg# distributions. We calculate through propagation of errors that uncertainties in $\sigma(\text{SiO}_2) = \pm 0.3 \text{ wt\%}$, $\sigma(\text{FeO}^{\text{t}}) = \pm 0.05 \text{ wt\%}$, and $\sigma(\text{Mg\#}) = \pm 0.001$ give a realistic uncertainty in $(\text{RLE}/\text{Mg})_{\text{N}}$ 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.

In Figure 8, the major element composition (+NiO) of a suite of peridotites from the Tariat region (Mongolia) reported by Ionov and Hofmann (2007) have been plotted. All data are normalized to the PM composition derived here and given in Table 3 (for Ni see Table 4). Some of these rocks are surprisingly fertile, closely approaching the PM composition. All xenoliths are larger than 10 cm in diameter and show on average little or no metasomatic imprint (Ionov and Hofmann, 2007).

The samples are arranged in order of increasing MgO contents. As discussed in an earlier section, FeO is basically constant, SiO_2 decreases very slightly, NiO increases in parallel with MgO, and CaO and Al_2O_3 strongly decrease. Out of the 43 xenoliths, there is only one with lower MgO and higher CaO and Al_2O_3 than the PM, probably containing an excess of cpx, apparently a rare case. The large number of rocks that closely approach the PM composition is unusual compared to other suites of peridotitic rocks.

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., Boyd, 1989). Most of these xenoliths are extremely depleted; extrapolation of the trends back to the PM MgO of 36.77% gives similar concentrations of SiO_2 , FeO , 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 primitive mantle and comparison with estimates from the literature

	<i>This work</i>	<i>Ringwood (1979)</i>	<i>Jagoutz et al. (1979)</i>	<i>Wänke et al. (1984)</i>	<i>Palme and Nickel (1985)</i>	<i>Hart and Zindler (1986)</i>	<i>McDonough and Sun (1995)</i>	<i>Allège et al. (1995)</i>
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	3.97	4.1	4.8	4.06	4.4	4.09
SiO_2	45.40 ± 0.30	45.1	45.2	45.6	46.2	46.0	45.0	46.12
CaO	3.65 ± 0.31	3.1	3.50	3.5	4.4	3.27	3.5	3.23
FeO^{t}	8.10 ± 0.05	8.0	7.82	7.5	7.7		8.1	7.49
Total	98.41 ± 0.10	97.6	98.8	97.5	98.6		98.8	98.7
$(\text{RLE}/\text{Mg})_{\text{N}}$	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
Mg#	0.890 ± 0.001	0.895	0.897	0.897	0.891		0.893	0.900

Mg#, molar $\text{Mg}/(\text{Mg} + \text{Fe})$; FeO^{t} , all Fe as FeO ; $(\text{RLE}/\text{Mg})_{\text{N}}$, RLE normalized to Mg and CI chondrites.

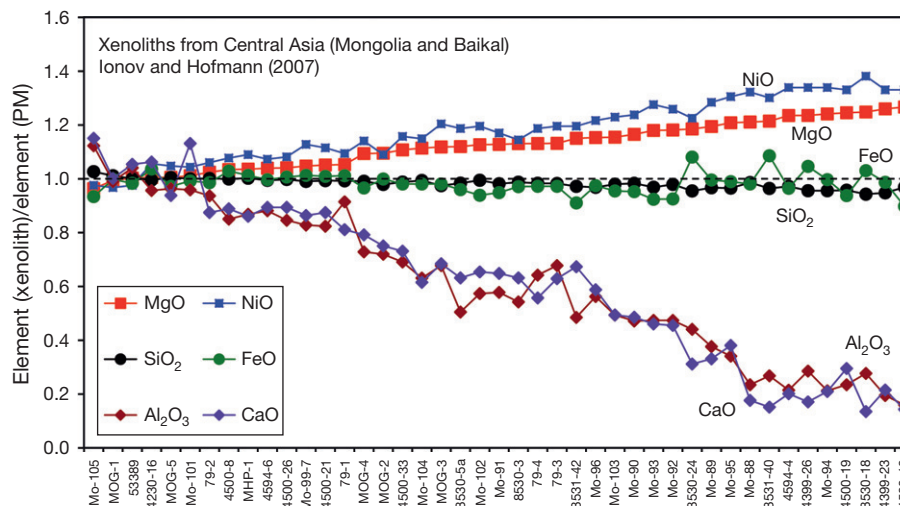


Figure 8 Chemical compositions of a suite of peridotites from the Tariat region (Mongolia) using data of Ionov and Hofmann (2007), normalized to the primitive mantle and arranged in order of increasing MgO. Some of these rocks are surprisingly fertile, closely approaching the primitive upper mantle composition.

3.1.4.2.2 Comparison with other estimates of PM compositions

Ringwood (1977) 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 partial melting). 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 rather fertile spinel lherzolite xenoliths as representing the PM. 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 the less incompatible Al_2O_3 , which in turn has a steeper slope than the fairly compatible Sc. 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 Al 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 in the above sections.

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 Nd and Ca 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 a Mg/Al ratio of 10.6 (Table 3).

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 Earth's mantle to calculate the bulk chemical composition of the upper mantle. McDonough and Sun (1995) used plots of Ca/Yb, Sc/Yb, and Sm/Yb of fertile lherzolites (MgO <40.5 wt%) against MgO to determine the value of MgO at which the RLE ratios best match the chondritic ratios. They found a value of 37.7 wt% MgO, slightly higher than the MgO content derived here, with a correspondingly lower value of $(\text{RLE}/\text{Mg})_{\text{N}}$ of 1.17, and an implied Mg# of 0.893.

All these estimates lead to roughly similar PM compositions. However, Lyubetskaya and Korenaga (2007) reassessed the peridotite database assembled by McDonough and Sun (1995), also using the assumption of chondritic RLE ratios. They reported significantly higher MgO of 38.8 wt%, with $(\text{RLE}/\text{Mg})_{\text{N}}$ of 0.89, implying contrary to all other estimates that the PM is depleted in RLE relative to Mg. That such a large difference could be obtained from the same data as used by McDonough and Sun (1995) is also disconcerting, but can be

explained by the method used by Lyubetskaya and Korenaga (2007) as follows. Firstly, like McDonough and Sun (1995), they filtered the data to exclude highly metasomatized samples with $(\text{La}/\text{Yb})_{\text{CI}} > 2$ to remove those most affected by metasomatism. This choice of $(\text{La}/\text{Yb})_{\text{CI}}$ ratio is arbitrary and is questionable given that melt extraction must produce residual compositions with $(\text{La}/\text{Yb})_{\text{CI}} < 1$ (mostly <1). They then found a least-squares trend line through the data in logarithmic coordinates, using orthogonal regression, an approach to multiple regression for data with errors in all variables suggested by Pearson (1901). Although widely recognized as the mathematical progenitor of principal component analysis, this approach has been little used for least-squares data fitting because it implies that the relative magnitudes of the error on variables are determined by the orientation of the trend line, which is not physically reasonable. In this regard, the data fitting method of Lyubetskaya and Korenaga (2007) therefore seems inferior to the simpler one of McDonough and Sun (1995) and turns out to be more sensitive to outliers and is badly influenced by metasomatized samples with $2 < (\text{La}/\text{Yb})_{\text{CI}} > 1$. In their second stage, Lyubetskaya and Korenaga (2007) attempt to find the point along the trend line at which the RLE approach chondritic relative abundances closest in the least-squares sense, with the data now in linear form. When this is done, the solution is found to be almost identical to that of McDonough and Sun (1995), which is not surprising given that the same data were used. However, Lyubetskaya and Korenaga (2007) bias the result by using a Monte Carlo method to remove solutions >5% from the CI model, producing an average solution skewed toward higher MgO and lower RLE abundances. The wealth of new data on mantle peridotites published since McDonough and Sun (1995) in any case makes their database obsolete.

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 about 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 about 10% encompass all other estimates.

3.1.4.2.3 Abundance table of the PM

In Table 4, the element abundances in Earth's PM have been listed. The CI chondrite abundances are given for comparison (Palme et al., 2012, Chapter 1.2). In this compilation, chondritic ratios of RLE are used. The depletion of highly incompatible elements, either by removal of a small melt fraction early in the history of Earth or by loss of these elements through collisional erosion prior to final accretion, is therefore not considered. This is discussed in Section 3.1.4.3.

Major elements and associated errors are from the previous section (Table 3). Trace element abundances are from O'Neill and Palme (1998) and from Palme and O'Neill (2003) and additional data from more recent studies. The changes that have been made since 2003 are described below. The abundances of RLE shown Table 4 are calculated by multiplying the CI abundances by 2.83, as explained in the above section. The two exceptions are V and Nb. Both elements may in part be concentrated in the core. Small changes of RLE are the

Table 4 Composition of the primitive mantle of Earth assuming chondritic RLE ratios

<i>Z</i>	<i>Elem</i>	<i>CI</i>	<i>SD</i>	<i>Earth's mantle</i>	<i>SD</i>	<i>Comments for Earth's mantle abundances</i>	<i>References</i>
1	H (%)	1.97	10	0.012	20	Mass balance	ON98, com
3	Li (ppm)	1.45	10	1.6	20	Data on mantle rocks	Ja79, Ry87, Se00, Se04, com
4	Be (ppm)	0.0219	7	0.062	10	RLE, PM/CI = 2.83	
5	B (ppm)	0.775	10	0.26	40	B/K = $1.0 \pm 3 \times 10^{-3}$	Ch94
6	C (%)	3.48	10	0.010	u	Mass balance	Zh93
7	N (%)	0.295	15	0.0002	u	Mass balance	ON98
8	O (%)	45.90	10	44.33	2	Stoichiometry, with $\text{Fe}^{3+}/\sum \text{Fe} = 0.03$	Ca94
9	F (ppm)	58.2	16	25	40	F/K = 0.09 ± 0.03 , F/P = 0.3 ± 0.1	Pa03, com
11	Na (ppm)	4962	9	2590	5	vs. MgO	ON98
12	Mg (%)	9.54	4	22.17	1	Major element (see text)	th.w.
13	Al (%)	0.840	6	2.38	8	Major element (see text)	th.w.
14	Si (%)	10.70	3	21.22	1	Major element (see text)	th.w.
15	P (ppm)	985	8	87	15	P/Nd = 65 ± 10	McD85, La92
16	S (%)	5.35	5	0.020	40	vs. MgO, komatiites	ON91, com
17	Cl (ppm)	698	15	30	40	Mass balance	Ja95, com
19	K (ppm)	546	9	260	15	Mean of K/U and K/La	ON98, com
20	Ca (%)	0.911	6	2.61	8	Major element (see text)	th.w.
21	Sc (ppm)	5.81	6	16.4	10	RLE, PM/CI = 2.83	
22	Ti (ppm)	447	7	1265	10	RLE, PM/CI = 2.83	
23	V (ppm)	54.6	6	86	5	vs. MgO	ON98
24	Cr (ppm)	2623	5	2520	10	vs. MgO	ON98
25	Mn (ppm)	1916	6	1050	10	vs. MgO	ON98
26	Fe (%)	18.66	4	6.30	1	Major element (see text)	ON98, th.w.
27	Co (ppm)	513	4	102	5	vs. MgO	ON98
28	Ni (%)	1.091	7	0.186	5	vs. MgO	ON98
29	Cu (ppm)	133	14	20	50		ON91, com
30	Zn (ppm)	309	4	53.5	5	vs. MgO	ON98
31	Ga (ppm)	9.62	6	4.4	5	vs. MgO	ON98, WE09
32	Ge (ppm)	32.6	9	1.2	20	vs. SiO ₂	ON98
33	As (ppm)	1.74	9	0.068	30	As/Pb = 0.37 ± 0.10 in OFB	Je12, com
34	Se (ppm)	20.3	7	0.076	u	Cl-ratio S/Se = 2635	com
35	Br (ppm)	3.26	15	0.075	50	Cl/Br = 400 ± 50	Ja95, com
37	Rb (ppm)	2.32	8	0.605	10	Rb/Sr = 0.029 ± 0.002 (Sr isotopes), Rb/Ba = 0.09 ± 0.02	Ho83
38	Sr (ppm)	7.79	7	22.0	5	RLE, PM/CI = 2.83	
39	Y (ppm)	1.46	5	4.13	10	RLE, PM/CI = 2.83	
40	Zr (ppm)	3.63	5	10.3	10	RLE, PM/CI = 2.83	
41	Nb (ppm)	0.283	10	0.595	20	Nb/Ta = 14.0 ± 0.3	Mu03, com
42	Mo (ppm)	0.961	10	0.047	40	Mo/Ce = 0.027 ± 0.012	Si90, Fi95
44	Ru (ppm)	0.690	5	0.0074	20	HSE	Be06, com
45	Rh (ppm)	0.132	5	0.0012	20	HSE	FG11, com
46	Pd (ppm)	0.560	4	0.0071	20	HSE	Be06, com
47	Ag (ppm)	0.201	9	0.006	50	Ag/Cu = $2.9 \pm 0.5 \times 10^{-4}$ in OFB	th.w., com
48	Cd (ppm)	0.674	7	0.035	20	Cd vs Ca in mantle rocks	WE09, com
49	In (ppm)	0.0778	5	0.018	20	In vs. Ca in mantle rocks	WE09, com
50	Sn (ppm)	1.63	15	0.14	30	Sn/Sm = 0.32 ± 0.06	Jo93
51	Sb (ppm)	0.145	14	0.0054	40	Sb/Pb = 0.029 ± 0.011 in OFB	Je12, com
52	Te (ppm)	2.28	7	0.009	u	S/Te = 23500 (CI)	th.w., com
53	I (ppm)	0.53	20	0.007	u	Mass balance	ON98, com
55	Cs (ppm)	0.188	6	0.018	50	Cs/Ba = 1.1×10^{-3} in the mantle, 3.6×10^{-3} in the crust	McD92
56	Ba (ppm)	2.42	5	6.85	15	RLE, PM/CI = 2.83	
57	La (ppm)	0.2414	3	0.6832	10	RLE, PM/CI = 2.83	
58	Ce (ppm)	0.6194	3	1.7529	10	RLE, PM/CI = 2.83	
59	Pr (ppm)	0.09390	3	0.2657	15	RLE, PM/CI = 2.83	
60	Nd (ppm)	0.4737	3	1.341	10	RLE, PM/CI = 2.83	
62	Sm (ppm)	0.1536	3	0.4347	10	RLE, PM/CI = 2.83	
63	Eu (ppm)	0.05883	3	0.1665	10	RLE, PM/CI = 2.83	
64	Gd (ppm)	0.2069	3	0.5855	5	RLE, PM/CI = 2.83	

(Continued)

Table 4 (Continued)

<i>Z</i>	<i>Elem</i>	<i>CI</i>	<i>SD</i>	<i>Earth's mantle</i>	<i>SD</i>	<i>Comments for Earth's mantle abundances</i>	<i>References</i>
65	Tb (ppm)	0.03797	3	0.1075	15	RLE, PM/CI = 2.83	
66	Dy (ppm)	0.2558	3	0.7239	10	RLE, PM/CI = 2.83	
67	Ho (ppm)	0.05644	3	0.1597	15	RLE, PM/CI = 2.83	
68	Er (ppm)	0.1655	3	0.4684	10	RLE, PM/CI = 2.83	
69	Tm (ppm)	0.02609	3	0.07383	15	RLE, PM/CI = 2.83	
70	Yb (ppm)	0.1687	3	0.4774	10	RLE, PM/CI = 2.83	
71	Lu (ppm)	0.02503	3	0.07083	15	RLE, PM/CI = 2.83	
72	Hf (ppm)	0.1065	3	0.3014	10	RLE, PM/CI = 2.83	
73	Ta (ppm)	0.015	10	0.043	5	RLE, PM/CI = 2.83	
74	W (ppm)	0.096	10	0.012	30	Ta/W = 3.4	Kö11, com
75	Re (ppm)	0.0400	5	0.00035	20	HSE	Be06, com
76	Os (ppm)	0.495	5	0.0039	15	HSE	Be06, com
77	Ir (ppm)	0.469	5	0.0035	10	HSE	Be06, com
78	Pt (ppm)	0.925	5	0.0076	20	HSE	Be06, com
79	Au (ppm)	0.148	12	0.0017	30	HSE	FG11, com
80	Hg (ppm)	0.35	50	0.006	u	Hg/Se = 0.075	th.w., com
81	Tl (ppm)	0.140	11	0.0041	25	Tl/Pb = 0.022 ± 0.005 in OFB	Je12, com
82	Pb (ppm)	2.62	8	0.185	10	²³⁸ U/ ²⁰⁴ Pb = 8.5 ± 0.5, 206/204 = 18, 207/204 = 15.5, 208/204 = 38	Ga96
83	Bi (ppm)	0.110	9	0.003	u	Bi/Pb = 0.02	th.w., com
90	Th (ppm)	0.0300	7	0.0849	15	RLE, PM/CI = 2.83	
92	U (ppm)	0.00810	7	0.0229	15	RLE, PM/CI = 2.83	

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, [Palme et al., 2012, Chapter 1.2](#). References: Be06 – [Becker et al., \(2006\)](#); BV81 – [BVSP \(1981\)](#); Ca94 – [Canil et al. \(1994\)](#); Ch94 – [Chaussidon and Jambon \(1994\)](#); Fi95 – [Fitton \(1995\)](#); FG11 – [Fischer-Gödde et al. \(2011\)](#); Ga96 – [Galer and Goldstein \(1996\)](#); Ho83 – [Hofmann and White \(1983\)](#); Ja95 – [Jambon et al. \(1995\)](#); Je12 – [Jenner and O'Neill \(2012\)](#); Jo93 – [Jochum et al. \(1993\)](#); Kö11 – [König et al. \(2011\)](#); La92 – [Langmuir et al. \(1992\)](#); McD85 – [McDonough et al. \(1985\)](#); McD92 – [McDonough et al. \(1992\)](#); Mu03 – [Münker et al. \(2003\)](#); ON91 – [O'Neill \(1991a\)](#); ON98 – [O'Neill and Palme \(1998\)](#); Ry87 – [Ryan and Langmuir \(1987\)](#); Se04 – [Seitz et al. \(2004\)](#); Si90 – [Sims et al. \(1990\)](#); WE09 – [Witt-Eickchen et al. \(2009\)](#); Zh93 – [Zhang and Zindler \(1993\)](#).

result of new CI abundances. The uncertainties of the RLE are at least 8%, reflecting the combined uncertainties of the scaling element and the Al content plus the CI error. This leads to uncertainties of 10% or more for many of the RLE. The relative abundances of the RLE are, however, better known, if CI chondritic ratios among RLE 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](#)).

Abundances of nonrefractory incompatible lithophile elements (K, Rb, Cs, etc.) or partly siderophile/chalcophile incompatible elements (W, Sb, Sn, etc.) are calculated from correlations with RLE of similar compatibility. This approach was first used by [Wänke et al. \(1973\)](#) to estimate the abundances of volatile and siderophile elements such as K or W in the Moon. The K 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 W 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, that is, 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 dataset (see [O'Neill and Palme, 1998](#), for details).

A good example is the Sm versus Sn correlation 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 Sn relative to CI chondrites in Earth's mantle. The origin of this depletion is twofold: (1) a general depletion of moderately volatile elements in Earth (see below) and (2) some partitioning of siderophile element Sn into the core of Earth. Many of the abundances of moderately volatile lithophile, siderophile, and chalcophile elements listed in [Table 4](#) were calculated from such correlations with RLE of similar compatibility. Well-known examples are K/U, K/La, W/Th, P/Nd, Rb/Ba, etc. (see [O'Neill and Palme, 1998](#) and [Palme and O'Neill, 2003](#) for details).

Further comments on the PM abundance of elements marked *com* in the last column of Table 4 are given here.

3.1.4.2.3.1 K

Potassium is a key element because all of the amount of ^{40}Ar in the atmosphere, produced by decay of ^{40}K and mantle degassing, establishes a lower limit not only for degassing of the mantle, but also for the possible depletion of incompatible elements in nonchondritic Earth models (O'Neill and Palme, 2008). First, consider the K abundance under the assumption of chondritic ratios of all RLE. During mantle melting, K is midway in incompatibility between two RLE, U and La, therefore its abundance is established from averaging the chondrite-normalized K/La and K/U ratios. With $\text{K/La} = 280 \pm 70$ and $\text{K/U} = 14\,050 \pm 3860$, respectively, in ocean floor basalts (OFB) from Jenner and O'Neill (2012), this gives 260 ppm K, which is the same value given previously by O'Neill and Palme (1998) and Palme and O'Neill (2003). Arevalo et al. (2009) found a significantly higher K/U ratio of $\sim 20\,000$ in OFB but from a much smaller database. For comparison, the K/La and K/U ratios in the bulk continental crust from Rudnick and Gao (2003) are 750 and 11 500, respectively; the latter ratio is much nearer to the OFB ratio, indicating that K is probably nearer in compatibility to U than La during extraction of the continental crust. Fortuitously, this crustal K/U ratio also translates to 260 ppm K in a PM with chondritic RLE.

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. With 260 ppm K in the PM, the amount of ^{40}Ar produced from ^{40}K over the age of 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. In the chondritic RLE model, this is taken to be the fraction of the mantle that has degassed. Alternatively, if Earth is depleted in incompatible RLE, for example, by collisional erosion (O'Neill and Palme, 2008), this constrains the maximum extent of the depletion.

3.1.4.2.3.2 H

It is assumed that the H in the PM is associated with O, forming an H_2O component. Under the assumption that Earth has chondritic RLE, the PM abundance of H_2O is derived as follows. 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 50% degassed mantle, it would imply a PM abundance of 850 ppm. However, H_2O , unlike Ar, is recycled into the mantle by subduction of the oceanic crust, such that mid-ocean ridge basalts (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 1100 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 $\pm 20\%$. Alternatively, a nonchondritic Earth model might assume that the U and La abundances in the mantle were only about half that expected from the chondritic model (O'Neill and Palme 2008). Hence, the K content would be ~ 130 ppm, such that the ^{40}Ar in the atmosphere corresponds to degassing of the entire mantle, not just 50% of it.

The amount of H_2O in the hydrosphere would therefore imply 425 ppm in the PM; together with the 200 ppm from the degassed mantle and the 0.5 wt% in the continental crust, the PM abundance would then be 675 ppm. Similar reasoning would reduce the amounts of other highly incompatible elements in the PM.

3.1.4.2.3.3 Li

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 to 2.07 ppm with an average of 1.52 ppm. Newer data by Seitz et al. (2004) are within the same range. We are taking here an average as 1.6 ppm Li.

3.1.4.2.3.4 Halogens (F, Cl, Br, and I)

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 halogens. F/K and F/P ratios in basalts are reasonably constant (Sigvaldason and Oskarsson, 1986; Smith et al., 1981) 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 Cl 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 Cl in the rocks of the continental crust is only a few hundred ppm (Gao et al., 1998; Wedepohl, 1995) and can therefore be neglected. The amount of Cl recycled back into the depleted mantle is more difficult to estimate, as the Cl 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 Cl is so incompatible that all the Cl in the MORB source mantle is from recycling and that MORB is assumed to be a 10% partial melt fraction). This gives a total Cl content of 30 ppm for PM.

The Cl/Br ratio of seawater is 290, but that of evaporites is considerably higher (>3000), such that the exospheric ratio is about 400 ± 50 . The ratio in MORB and other basalts is the same (Jambon et al., 1995). Iodine in 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 I comes from 50% of the mantle. MORB have ~ 8 ppb I (Déruelle et al., 1992), implying ~ 1 ppb in the depleted (degassed) mantle, for a PM abundance of 7 ppb.

3.1.4.2.3.5 S and Se

The abundance of S in the PM is not well constrained. Samples from peridotite massifs have in general much higher S contents (200–300 ppm) than xenoliths (<50 ppm) with notable exceptions, such as xenoliths from the Kilbourne Hole. The reason for this large variation is not understood (e.g., [Lorand, 1990](#); [Lorand et al., 2003](#); [O'Neill, 1991a](#)). The low S contents of xenoliths could be the result of oxidation of sulfides during weathering or alternatively the loss of S during eruption ([O'Neill et al., 1995](#)). Magmatic signatures can be excluded ([Lorand et al., 2003](#)). We believe that the higher S content of massive peridotites better represent the PM than the xenoliths data and use a value of 200 ppm from [O'Neill \(1991a\)](#). [McDonough and Sun \(1995\)](#) give a value of 250 ppm within the uncertainty of the concentration used here. The Se mantle content is similarly uncertain. There is a large variability in Se contents of peridotites, but no correlation with S ([Lorand et al., 2003](#)). We assume here the CI chondritic S/Se ratio of 2635 ([Palme et al., 2012, Chapter 1.2](#)), which is close to the ratio of 2540 of CI chondrites given by [Dreibus et al. \(1995\)](#).

3.1.4.2.3.6 Cu and Ag

The abundance of Cu in the depleted mantle raises a particular problem. Unlike other moderately compatible elements, there is a difference in the Cu abundances of massive peridotites compared to many, but not all, of the xenolith suites from alkali basalts. The Cu/MgO correlations in massive peridotites consistently extrapolate to values around 30 ppm at 36% MgO, whereas those for the xenoliths usually extrapolate to <20 ppm, albeit with much scatter. A correlation of Cu with S is found for peridotites from Iherzolite massifs, with the notable exception of samples from Zabargad island (see [Schmidt et al., 2000, Figure 2](#)). Cu in xenoliths is not correlated with S, and its abundance in the xenoliths and also inferred from correlations in basalts and komatiites point to a substantially lower abundance of about 20 ppm ([O'Neill, 1991a](#)). We have adopted this latter value. [McDonough and Sun \(1995\)](#) use a value of 39 ppm. Ag abundances were derived in [Palme and O'Neill \(2003\)](#) from Ag/Na ratios, but new data for Ag show that this element correlates very well with Cu in basalts ([Jenner and O'Neill, 2012](#)) with $\text{Ag/Cu} = 2.9 \pm 0.5 \times 10^{-4}$, implying an increase in the PM value from 4 to 5.8 ppb. However, [Gao et al. \(1998\)](#) report $\text{Ag/Cu} \sim 20 \times 10^{-4}$ in continental crust.

3.1.4.2.3.7 Nb

[Wade and Wood \(2001\)](#) have suggested that Nb, potentially the most siderophile of the RLE, is depleted in the PM by partial extraction into the core. Using a Nb/Ta from [Münker et al. \(2003\)](#) of 14.0 ± 0.3 (CI Nb/Ta is 19.9) yields a Nb abundance of 0.595 ppm, compared to 0.800 calculated with the CI ratio.

3.1.4.2.3.8 As, Sb, and Tl

These elements pose difficulties because, like Pb, they appear to be greatly enriched in the continental crust relative to rare earths of similar incompatibility (Ce, Pr, and Ce, respectively) in OFB and ocean island basalts (OIB). A compelling reason is that their mobility in fluids enriches them in subduction-zone

magmas ([Noll et al., 1996](#)), enhancing the net transfer to the crust compared to the fluid-immobile REE. As and Tl show excellent correlations with Pb in OFB, and Sb/Pb is also reasonably constant ([Jenner and O'Neill, 2012](#)). The average ratios from these data with standard deviations are as follows: $\text{As/Pb} = 0.37 \pm 0.10$, $\text{Sb/Pb} = 0.029 \pm 0.011$, and $\text{Tl/Pb} = 0.022 \pm 0.005$. The upper crustal averages from [Hu and Gao \(2008\)](#) are very scattered but overlap with these ratios ($\text{As/Pb} = 0.34 \pm 0.33$, $\text{Sb/Pb} = 0.041 \pm 0.043$, and $\text{Tl/Pb} = 0.040 \pm 0.040$). Although the enrichment of all these elements in the continental crust means that this reservoir dominates PM contents, the large uncertainty in these ratios dictates that PM values of As, Sb, and Tl are estimated from the more precise basalt data only. This implicitly assumes that these elements are not on average fractionated from Pb during their transfer to the continental crust. Further work is needed to test this assumption.

3.1.4.2.3.9 Cd and In

[Witt-Eickchen et al. \(2009\)](#) have shown that the nominally chalcophile elements Cd and In are quantitatively concentrated in cpx of the upper mantle rocks and that the mantle contents can be calculated from correlations with Yb or Ca in cpx or in bulk-rock samples. An example is given in [Figure 9](#) where In contents on bulk-rock powders are compared with bulk-rock data obtained from reconstruction of bulk-rock compositions using In data on individual mineral phases. The agreement of the two datasets indicates the absence of other carrier phases for In, such as, for example, sulfides. From the correlation of In with CaO, the In mantle abundance can be obtained (see [Witt-Eickchen et al., 2009](#) for details). The results agree well with estimates from In/Tm and Cd/Tm in OFB ([Jenner and O'Neill, 2012](#)).

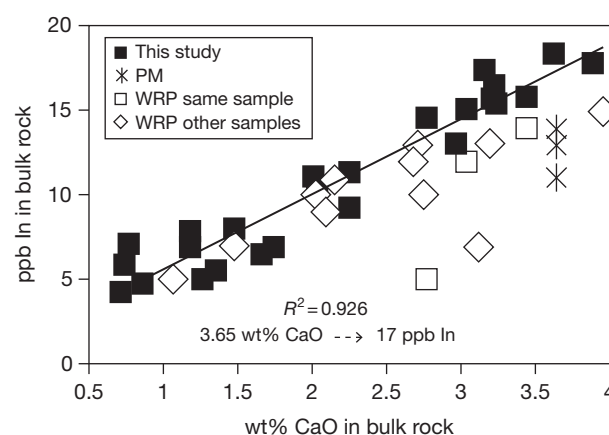


Figure 9 Correlation of In in whole rock powder (WRP) of mantle rocks and in reconstructed bulk from mineral analyses (full squares, 'this study'). The only important host phase for Ca and In in these rocks is clinopyroxene (cpx). The In mantle abundance is obtained from the correlation at the PM CaO content. Reproduced from Witt-Eickchen G, Palme H, O'Neill HStC, and Allen CM (2009) The geochemistry of the volatile trace elements As, Cd, Ga, In and Sn in the Earth's mantle: New evidence from in situ analyses of mantle xenoliths. *Geochimica et Cosmochimica Acta* 73: 1755–1778.

3.1.4.2.3.10 Te

Te is a chalcophile element (Hattori et al., 2002), but is not correlated with other chalcophile elements or anything else. Empirically, Te appears to be quite compatible. Morgan (1986) found 12.4 ± 3 ppb for fertile spinel lherzolite xenoliths (previously published in the Basaltic Volcanism Study Project (BVSP, 1981)), 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 island arc basalts but with samples from Loihi extending to 29 ppb. These MORB data confirm the earlier data of Hertogen et al. (1980), who analyzed five MORB with Te from 1 to 5 ppb and two outliers with 17 ppb, which also had elevated Se. The important point is that Te in peridotites is often higher than in basalts, plausibly explained by the retention in a residual sulfide phase. Thus, future work on Te needs to address the composition of mantle sulfides. If Te/S were chondritic, the PM with 200 ppm S would have 9 ppb Te. This has been adopted as the default value, as to use anything else would have interesting but unwarranted cosmochemical implications.

3.1.4.2.3.11 W

The W abundance was calculated from a Ta/W ratio of 3.4 by König et al. (2011). Jenner and O'Neill (2012) found a mean W/Th ratio for OFB glasses of 0.146 ± 0.04 and a W/Ba ratio of 0.0018 ± 0.0005 . With the Ba and Th data of Table 4, one calculates 12.3 and 12.4 ppb W, in perfect agreement with the Ta/W ratio of König et al. (2011).

3.1.4.2.3.12 Re, Os, Ir Pt, Au, Ru, Rh, and Pd

New data from Becker et al. (2006) on upper mantle rocks were used to define the abundances of HSE. The six platinum group elements (Os, Ir, Pt, Ru, Rh, and Pd) and Re and Au are collectively termed HSE. The basis for estimating HSE abundances in Earth's mantle is the relatively uniform distribution of Ir in mantle peridotites that was found very early. Morgan et al. (2001) estimated 3.2 ± 0.2 ppb Ir as the global upper mantle average. Becker et al. (2006) noticed constant Ir contents (3.5 ppb) in the upper mantle rocks at Al_2O_3 concentrations above 2%. Spettel et al. (1991) found, however, a mean value of 4.9 ppb for nine xenoliths from Antarctica, whereas xenoliths from other localities were within the 3 ppb range. Iridium, Os, and Ru are not affected by partial melting. Their concentrations are independent of the degree of partial melting, whereas Re, Pt, Rh, Pd, and Au are weakly to strongly incompatible with mantle mineralogy. They are enriched in partial melts, and their abundances have to be scaled to other elements sensitive to melt extraction, such as Al_2O_3 (see Walker, 2009, and references therein). In Table 4, the upper mantle abundances of Os, Ir, Ru, Pt, Pd, and Re from Becker et al. (2006) are listed. The Au and Rh abundances were taken from a large number of peridotites analyzed by Fischer-Gödde et al. (2011). Similar to the analyses of Pattou et al. (1996) and Schmidt et al. (2000), these authors found some enhancement of Rh relative to Ir, but the excess is smaller than the excesses of Ru and Pd (Becker et al., 2006; Pattou et al., 1996; Schmidt et al., 2000).

3.1.4.2.3.13 Hg

Very few pertinent data exist, and the high-temperature geochemical properties of Hg are very uncertain. Flanagan et al. (1982) measured Hg in a variety of standard rocks, including basalts. Hg 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. Ag). 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 Hg is completely chalcophile in its geochemical properties, a crustal ratio of $\text{Hg}/\text{Se} = 0.075$ from Gao et al. (1998) is obtained; on the further assumption that this ratio is conserved during mantle melting, this gives Hg = 6 ppb.

3.1.4.2.3.14 Bi

Although Bi^{3+} has an ionic radius similar to La^{3+} , its incompatibility in OFB is better matched by Tb (Jenner and O'Neill, 2012), confirming the finding of Hertogen et al. (1980) that Bi in MORB is quite constant at 6–9 ppb. Bi in spinel lherzolites is 1–2 ppb (BVSP, 1981). However, the abundance of Bi in the upper continental crust is distinctly elevated, like for As, Sb, Tl, and Pb. New analyses by Hu and Gao (2008) of the upper continental rocks confirm the considerable scatter of Gao et al. (1998), with $\text{Bi}/\text{Pb} = 0.019 \pm 0.020$. Nevertheless, this ratio is close to that observed in the OFB glasses of Jenner and O'Neill (2012), of 0.017 ± 0.008 , which implies 3 ppb Bi.

3.1.4.3 Nonchondritic Models for the PM

The PM composition given in Table 4 is evaluated from the assumption of chondritic relative abundances of all the RLE, with the absolute amounts of all RLE constrained by Ca and Al, the two RLE that are also major elements. It is, however, becoming increasingly apparent that this 'chondritic assumption' might not be correct, which will be discussed further below. O'Neill and Palme (2008) presented a simple heuristic model for a nonchondritic PM that was based on three assumptions: (1) the total material lost during collisional erosion was 10%, (2) the maximum extent of depletion of highly incompatible elements was a factor of 2, and (3) the Sm/Nd ratio was 6% above the chondritic ratio to explain the $^{142}\text{Nd}/^{144}\text{Nd}$ anomaly (Boyet and Carlson, 2005, 2006).

Major elements are not affected, because the method used to establish the PM abundances of Mg, Si, Fe, and Ca + Al is not based on the 'chondritic assumption.' The compatible and mildly incompatible minor and trace elements (such as Na, V, Cr, Mn, Ni, Zn, or In) are estimated empirically and likewise do not depend on this assumption. The most incompatible elements, including the three radiogenic heat-producing elements K, Th, and U, are reduced by a factor of 2, as are other elements related to these highly incompatible RLE, notably Pb and W. The implications from the ^{40}Ar constraint that the mantle is nearly all degassed mean that the elements concentrated into the crust and exosphere, including H (discussed

above) and the heavy halogens, Cl, Br, and I, would also be reduced by a factor of 2. The abundances of the elements of intermediate incompatibility (e.g., F, P, Mo, and Sn) are then reduced between these limits.

3.1.4.4 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. The superchondritic Mg/Si ratio of the upper mantle is well established and has been discussed by many authors (e.g., Jagoutz et al., 1979; Ringwood, 1979; Section 3.1.5.3).

A chemical layering may have occurred either as a direct result of inhomogeneous accretion without subsequent mixing (e.g., Turekian and Clark, 1969), which has not to our knowledge been suggested in recent times, or by some process akin to crystal fractionation from an early magma ocean. 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).

Three kinds of evidence have been put forward in support of a lower mantle with a different composition from the upper mantle. The first is the apparent lack of a match between the seismic and other geophysical properties observed for the lower mantle and the laboratory-measured properties of the lower mantle minerals (MgSiO₃-rich perovskite and magnesio-wüstite) in an assemblage with the upper mantle composition (meaning, effectively, with the upper mantle's Mg/Si and Mg/Fe ratios). Although this approach continues to be advocated by some mineral physicists, increasing awareness of the complexities of the problem, as regards not only to the dependence of physical properties on second-order compositional effects (e.g., the influence of other major elements such as Al and Ca, and Fe³⁺/Fe²⁺ ratios), but also the complexities of fitting data to equations of state at lower mantle temperatures and pressures (e.g., Kennett and Jackson, 2009), advises caution. A recent review of the subject (Chapter 3.2) concluded that present evidence "lends considerable support to the minimalist assumption that the bulk composition of the lower mantle greatly resembles that of the upper mantle." A similar conclusion was reached in an earlier review by Jackson and Rigden (1998). Another popular hypothesis, a hidden layer deep in the mantle, enriched in incompatible elements, is inconsistent with the heat flux carried by mantle plumes (Campbell and O'Neill, 2012).

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, which 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 CC.

The geochemical evidence against gross compositional layering of the mantle seems conclusive. Kato et al. (1988) and Corgne et al. (2005) have shown from experimental studies that fractional crystallization of high-pressure phases from a hypothetical magma ocean would disturb many of the ratios of RLE away from chondritic values. For example, high field strength elements (HFSE) like Ti, Zr, and Hf are preferentially hosted in MgSiO₃ perovskite, such that fractional crystallization of this phase would result in Sm/Zr and Sm/Hf ratios markedly lower than the chondritic ratios observed in the common varieties of basalts. Although this might be compensated by simultaneous fractionation of CaSiO₃ perovskite, which preferentially hosts REE over the HFSE (e.g., Corgne et al., 2005), this would require multiple saturation of the magma ocean in both phases in the right proportion. Whether both MgSiO₃ and CaSiO₃ coexist on the liquidus at some pressure pertinent to the lower mantle is perhaps not definitively ruled out by current knowledge of the phase relations of PM compositions (e.g., Andraut et al., 2011; Fiquet et al., 2010), but appears unlikely given the large temperature interval between solidus and liquidus (>500 K) reported in these studies. Whereas the effect of collisional erosion is difficult to detect because elements are fractionated according to the same low-pressure processes that produce the crust, perovskite fractionation of sufficient magnitude to alter the Mg-Si-Fe abundances of the upper mantle, on which are PM composition is based, should leave a distinctive signature.

As discussed later the bulk of the silicate Earth is no longer considered to have strictly chondritic relative abundances of all the refractory elements. The most incompatible elements are depleted, based on evidence from ¹⁴²Nd (Boyet and Carlson, 2005). This does, however, not invalidate the above arguments, because the pattern of depletion is consistent with the extraction of partial melt under essentially low-pressure conditions, where the incompatible RLE are overwhelmingly hosted in cpx. The effect on the Sm/Nd ratio is much smaller than the effects calculated from perovskite removal, and the abundances of Sm, Hf, and Lu are barely affected (see Bouvier et al., 2008). The ubiquitous excess of ¹⁴²Nd in all accessible samples from the silicate Earth rather supports a uniform composition of the upper and lower mantle.

Finally, a largely 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 the whole mantle convection (Van der Hilst et al., 1997). Although slab penetration does require mass exchange between the upper and lower mantle, there may be deeper layers (D", large low shear velocity provinces) that are not involved in this circulation. The layers could affect the bulk mantle trace element budget but would not influence the major element composition of the mantle (see Chapter 3.2 and Campbell and O'Neill, 2012).

A compositionally uniform mantle is not consistent with the model of Javoy et al. (2010). Because the stable isotope composition of some elements, such as O, N, and Cr, but not Si (Fitoussi and Bourdon 2012) or Ti (Zhang et al., 2012), is the same in Earth and in EC, but different in other types of chondritic meteorites (see Section 3.1.6; Figure 23), Javoy et al. (2010) conclude that Earth is made of EC. As the difference between the composition of the PM and EC is very large (see Figure 15), Javoy et al. (2010) have to postulate a lower mantle higher in Si/Mg and lower in Al/Mg to balance the upper mantle composition and produce a bulk Earth with high Si and low refractory element contents, typical of EC. Complex processes are required to produce such a compositionally layered mantle. In addition, in present models of Earth formation, material formed at different heliocentric distances contributes to the growing Earth. Making Earth from a single type of meteorite is incompatible with these models. Also, EC have high concentrations of moderately volatile elements (Na, Mn, S, etc.). In the Javoy et al. (2010) model, these volatiles are lost during accretion. However, volatile elements gravitationally bound to the growing Earth cannot be easily lost. To the contrary, there is independent evidence that the depletion of volatile elements in planets and meteorites occurred very early, during formation of the first solids of the solar system, which would automatically disqualify the volatile-rich EC (see Section 3.5.5 for a detailed discussion). The isotopic similarity between EC and Earth is also limited. Apart from the differences in Si and Ti isotopes noted above, a recent study of Li isotopes in chondritic meteorites has shown that the BSE fits with CC, while OC and EC have significantly lower $\delta^7\text{Li}/^6\text{Li}$ values (Seitz et al., 2007). The Javoy et al. (2010) model therefore seems unlikely to us.

3.1.5 Comparison of the PM Composition with Meteorites

As pointed out above, many of the variations in chemical composition and oxidation state observed in chondritic meteorites must have been established very early, before the nebular components accreted to small planetesimals. As nebular fractionations have produced a variety of chondritic meteorites, understanding the whole spectrum of nebular fractionations is necessary in order to see if the proto-Earth material has been subjected to similar processes as those recorded in the chondritic meteorites. As Earth makes up more than 50% of the inner solar system, any nebular fractionation that affected Earth's composition must have been a major process in the inner solar system. The discussion of nebular fractionations in meteorites and in Earth with refractory elements begins and continues with increasingly more volatile components as outlined in Table 2.

3.1.5.1 Refractory Lithophile Elements

In Figure 10, the abundances of the four RLE Al, Ca, Sc, and V are shown in several groups of undifferentiated meteorites, Earth's upper mantle, and the Sun. The RLE abundances are divided by Mg, and this ratio is then normalized to the same ratio in CI chondrites. These $(\text{RLE}/\text{Mg})_N$ ratios are plotted in Figure 10.

The level of refractory element abundances in bulk chondritic meteorites varies by less than a factor of 2. CC have either CI-chondritic or higher Al/Mg ratios (and other RLE/Mg ratios), while Rumurutiites (very oxidized chondritic meteorites), OC, and EC are more or less depleted in refractory

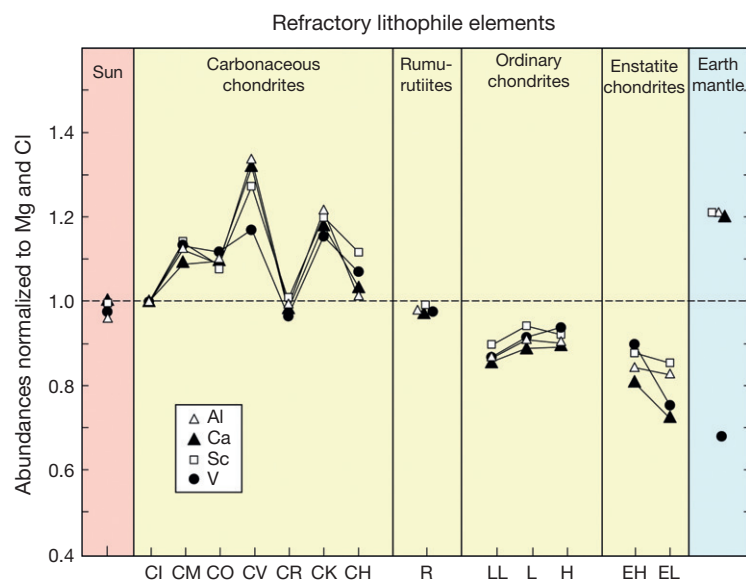


Figure 10 Element/Mg ratios normalized to CI chondrites of refractory lithophile elements (RLE) in various groups of chondritic meteorites. The carbonaceous chondrites (CC) are enriched in refractory elements, other groups of chondritic meteorites are depleted. The PM has enrichments within the range of CC. The figure is updated from O'Neill and Palme (1998). Data are from Wolf and Palme (2001), Wasson and Kallemeyn (1988). Included are Rumurutiites, a class of very oxidized chondritic meteorites (see Bischoff et al., 2011).

elements. The $(\text{RLE}/\text{Mg})_N$ ratio in Earth's mantle is different from the CI ratio but within the range of CC. The apparent depletion of V in Earth's mantle may have two possible causes or a combination of both. (1) V is one of the least refractory elements. It is significantly less enriched in CV chondrites compared to other RLE (Figure 10). Thus, V is a clear exception to the general rule of constant ratios among RLE. (2) V is slightly siderophile. Consequently, a certain fraction of V may have been sequestered in Earth's core (see succeeding texts).

Since neither Al, Ca, Sc, nor Mg are expected to partition into metallic Fe, even at very reducing conditions, the RLE/Mg ratios should be representative of the bulk Earth. Thus, relative to CI chondrites, the bulk Earth is enriched in refractory elements by a factor of 1.22 when normalized to Mg and by a factor of 1.41 when normalized to Si (see Figure 2). Normalization to Mg is preferred because some of Earth's Si may reside in the core (see below) making Si an uncertain reference element, when comparing Earth's abundances with meteorites. There is no evidence from iron meteorites or metal phases in meteorites that Mg partitions into metal, nor is such partitioning expected from thermodynamics. The RLE/Mg ratios of the bulk Earth are within the range of CC but very different from OC and EC – both groups are depleted in refractory elements (Figure 10). The small variations among RLE ratios within chondrite groups in Figure 10 reflect, with the exception of V, the limited accuracy of analyses and inhomogeneities in analyzed samples. Ratios among compatible RLE are constant within 5–10%. New high-precision analyses of RLE ratios indicate, in some cases, small variations of a few percent in different types of chondrites and Earth (e.g., Pack et al., 2007). Deviations from average chondritic ratios of RLE in bulk CC are becoming increasingly clear as measurement precisions improve.

Efremovka and Leoville and probably all members of the reduced subgroup of CV chondrites have reduced Ca/Al ratios of around one (Ahrens et al., 1973).

The REE pattern of Allende resembles the strongly fractionated REE pattern of a special group of Ca, Al-rich inclusion (see Stracke et al., 2012 and references). Thus, the RLE pattern of Allende is not strictly CI chondritic, that is, solar.

The constancy of compatible RLE ratios in Earth's mantle, discussed above, is documented in the most primitive samples from Earth's mantle. In Figure 11 (modified from Jochum et al., 1989), the PM-normalized abundances of 21 RLE from four fertile spinel lherzolites are plotted. These four samples closely approach in their bulk chemical composition the PM as defined in the previous section. The normalized abundance patterns of the heavy REE and of Ti, Zr, and Y are essentially the same. The three elements Ca, Al, and Sc (not shown in Figure 11) have the same PM-normalized abundances. Only strongly incompatible RLE, such as Th, Nb, La, and Ce, are depleted. This is consistent with the extraction of a small amount of a basaltic component under low-pressure conditions.

On a finer scale, there may be small deviations in RLE ratios from the current best estimates of the chondritic ratios, which would not be seen on Figure 9 where elements are plotted on a logarithmic scale. For example, the Y/Ho ratio of Earth is about 2% above the CI ratio (Pack et al., 2007).

A plot of Ti/Mg versus Al/Mg is shown in Figure 12. The Ti–Al relationship is not a straight line as for many other element ratios (see O'Neill and Palme, 1998). The most fertile, Al-rich peridotites have chondritic Al/Ti ratios. Because Ti is low in peridotites and difficult to precisely analyze, uncertainties in Ti are larger than for Al. It is also not clear if the differences in the Ti/Al ratios among the chondrite groups are real.

Chondritic relative abundances of strongly incompatible RLE (LREE, Nb, Ta, U, and Th) and their ratios to compatible RLE in Earth's mantle are more difficult to test. Simple crust–mantle mass balance arguments may be misleading, as shown below (see also Hofmann et al., 1986).

The smooth and complementary patterns of REE in the continental crust and the residual depleted mantle were long thought to be consistent with a PM REE pattern that is flat, that is, unfractionated when normalized to chondritic abundances. The positive $\epsilon^{143}\text{Nd}$ values (excess of $^{143}\text{Nd}/^{144}\text{Nd}$ relative to a chondritic evolution) of MORB reflected preferred incorporation of LREE into the continental crust, which is characterized by a complementary negative $\epsilon^{143}\text{Nd}$. Mass balance, particularly of ^{143}Nd , indicated that the enrichment of the continental

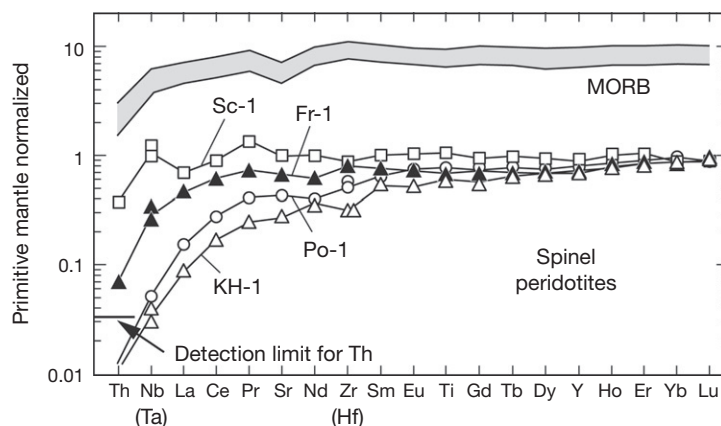


Figure 11 Abundances of RLE in fertile spinel lherzolite xenoliths from various occurrences. The compatible RLE have constant enrichment factors. The abundances decrease with increasing degree of incompatibility (from right to left), reflecting removal of very small degrees of partial melts. Adapted from Jochum KP, McDonough WF, Palme H, and Spettel B (1989) Compositional constraints on the continental lithospheric mantle from trace elements in spinel peridotite xenoliths. *Nature* 340: 548–550.

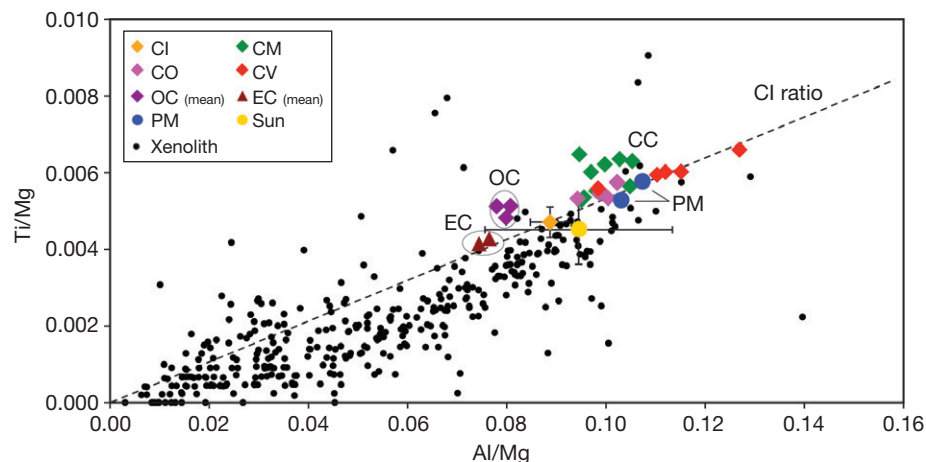


Figure 12 Al–Ti correlation in the upper mantle rocks and chondritic meteorites. The upper mantle rocks are represented by 365 xenoliths, data from the GEOROC (<http://georoc.mpch-mainz.gwdg.de>, Sarbas and Nohl, 2008). The Ti–Al relationship is not a straight line as for many other element ratios (see O'Neill and Palme, 1998). The most fertile, Al-rich peridotites have chondritic Al/Ti ratios. Because Ti is low in peridotites and difficult to analyze, uncertainties in Ti are generally larger than for Al. Small variations in Ti/Al ratios may be present in the various chondrite groups. For sources of data, see Figure 14.

crust corresponds to the depletion of about half the mantle, leading to the view that the other half of the mantle might be primitive (e.g., Wasserburg and DePaolo, 1979).

However, results from the application of the ^{146}Sm – ^{142}Nd isotope system (half-life of ^{146}Sm is 103 My) led to the conclusion that a large fraction, if not the whole of the silicate Earth, is nonchondritic in its Sm/Nd ratio, independent of LREE enrichment (Boyet and Carlson, 2005, 2006). These authors found that all terrestrial samples that were analyzed have $^{142}\text{Nd}/^{144}\text{Nd}$ ratios that are 20 ppm higher than in chondritic meteorites (see also Caro, 2011). The implication is that all terrestrial samples are derived from a source that was depleted in the more incompatible Nd relative to Sm very early in the history of Earth. For a depletion event at about 30 My, the depletion in Nd relative to Sm should be approximately 6% (i.e., $^{147}\text{Sm}/^{144}\text{Nd} = 0.21$, vs. the chondritic value of 0.1966) to satisfy the results (Boyet and Carlson, 2005). If the nonchondritic Sm/Nd ratio in the silicate Earth reflects the formation and subsequent burial and isolation of an early partial melt, then this early depletion event would have had a major effect on the abundances of all incompatible elements, particularly those more incompatible than Nd. Boyet and Carlson (2005, 2006) envision transport of the early partial melt to the core–mantle boundary deep in Earth, whereas O'Neill and Palme (2008) suggest removal of early formed crusts in Earth-forming embryos by collisional erosion, that is, removal of the outermost planetary layer by impacts. Warren (2008) suggested still another mechanism, the early loss of incompatible element-enriched melts by graphite-fueled explosive volcanism on 100 km-sized planetesimals, early building blocks of Earth. Some consequences of a PM depleted in highly incompatible RLE are described by O'Neill and Palme (2008) and Carlson and Boyet (2008).

The question arises how well do we really know the chondritic Sm/Nd ratio and is this ratio constant in all types of chondritic meteorites. Bouvier et al. (2008) have analyzed 32 chondrites and found an Sm/Nd ratio of $0.324 \pm 0.8\%$. Caro

and Bourdon (2010) define a chondritic ratio of 0.3237 with an uncertainty of 0.3%. Carlson and Boyet (2008) list further data on Sm/Nd of chondritic meteorites. Stracke et al. (2012) analyzed 39 bulk Allende samples, with about 0.6 g each, and found an average Sm/Nd ratio of $0.324 \pm 1.9\%$. Apparently the Sm/Nd ratio is chondritic and constant to within about 1%. The Allende data of Stracke et al. (2012) show also that other refractory element ratios are much less constant in this meteorite. For example, the standard deviation of Sm/Gd in the same suite of samples is 6.6% and the Tm/Lu ratio even has a standard deviation of 13.8%. The reason for this discrepancy is that bulk Allende has a nonchondritic pattern of REE with a signature, typical of group II Ca, Al-rich inclusions (Stracke et al., 2012). The group II pattern has, however, a chondritic Sm/Nd ratio but very nonchondritic Sm/Gd and Tm/Lu ratios. This confirms that the chondritic Sm/Nd ratio is well defined and that the difference to the Sm/Nd in the accessible silicate Earth is real. From this, it follows that the PM before extraction of the very first melt was probably chondritic (see Carlson and Boyet, 2008). A conclusion that is supported by the covariation of the present day $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ in terrestrial rocks centered around chondritic meteorites (Bouvier et al., 2008). The Allende example tells us however, that chondritic ratios Sm/Nd and Lu/Hf do not automatically imply that other refractory elements also occur in chondritic proportion.

The present evidence is compatible with the assumption that the RLE have similar PM chondrite-normalized abundances at least to within about 5%, with an enrichment factor of 1.22 (Mg normalized). This factor can be directly determined for the less incompatible refractory elements (e.g., Al) from the most fertile upper mantle rocks.

Evidence from ^{142}Nd indicates that highly incompatible refractory elements have been separated from compatible refractory elements early in the history of the solar system. The incompatible element component may be stored at the deep in Earth at the core–mantle boundary or it was lost earlier from Earth-forming planetesimals. The absolute level of RLE

in Earth's mantle is above that of CI chondrites, somewhere between type 2 (CM) and type 3 (CV and CO) CC, but very different from OC and EC, which are depleted in refractory elements (Figure 10).

Similar deficits in light REE abundances were reported by Caro et al. (2008) for the Moon and Mars based on ^{142}Nd analyses. These planets may have experienced similar histories as Earth.

3.1.5.2 Refractory Siderophile Elements

RSE comprise two groups of metals, the HSE Os, Re, Ru, Ir, Pt, and Rh with metal/silicate partition coefficients $>10^4$ and the two moderately siderophile elements Mo and W with partition coefficients $<10^4$ (Table 2). As the major fractions of these elements are in the core of Earth, it is not possible to establish independently whether the bulk Earth has chondritic ratios of RLE to RSE, that is, 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 13. The ratio of the RSE Ir to the non-RSE Au is plotted against the ratio of the RLE Al to the non-RLE Si. Figure 13 demonstrates that RLE and RSE are correlated in chondritic meteorites, and one may therefore assume that the bulk Earth RSE may be as enriched as the bulk Earth RLE. This is important as it allows the bulk Earth abundances of W, Mo, Ir, etc., to be calculated from the bulk Earth Al or Sc contents. However, as shown in a later section, Earth has excess Fe 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 HSE presently observed in Earth's mantle are probably of a different origin than the bulk of the refractory HSE, which are in the core. The present inventory of HSE in the PM will be discussed in a later section.

3.1.5.3 Magnesium, Silicon, and Chromium

The four elements Mg, Si, Fe, and O contribute more than 90% by mass to the bulk Earth. As stated above, Mg, Si, and Fe have approximately similar abundances (in atoms) in the Sun, in chondritic meteorites, and presumably also in the whole Earth. The roughly similar abundances of Mg and Si in Earth's PM derived here argues for cosmochemically primitive material, which should be representative of the whole mantle composition. In Figure 14, a Si/Mg versus Al/Mg plot for terrestrial rocks is shown. The upper mantle peridotites are represented by 365 xenolith analyses from the GEOROC data compilation (<http://georoc.mpch-mainz.gwdg.de>; Sarbas and Nohl, 2008). The trend with strongly increasing Al/Mg and weakly increasing Si/Mg has been discussed before. The position of the PM is indicated at the highest Al/Mg ratio of the mantle rocks, and it is evident that this is not far from the CI composition, which is close to the solar composition as shown in Figure 15 on an enhanced scale. In Figure 14, the results of the 6500 analyses of MORB glasses from GEOROC have also been plotted. The source region of MORB is generally considered to represent the PM after approximately 1% loss of a partial melt, which barely affects the major elements (e.g., Salters and Stracke, 2004). Results of partial melting experiments with PM-like compositions at 10 kbar and 1270 and 1390 °C are shown for comparison (Baker and Stolper, 1994). The composition of the continental crust is indicated (Chapter 4.1).

Rocks from other planets (the Moon, Mars, Venus, and Vesta) plot in the same area of Figure 14 as MORB. But since there are no Mg-rich rocks sampled from these planets, it is much more difficult to derive bulk compositions for them. The extrapolation is large, and the compositions of even primitive partial melts depend sensitively on minor and trace elements and the depths and extent of melting. For Earth we have by far the best estimate for the bulk composition of a differentiated planet.

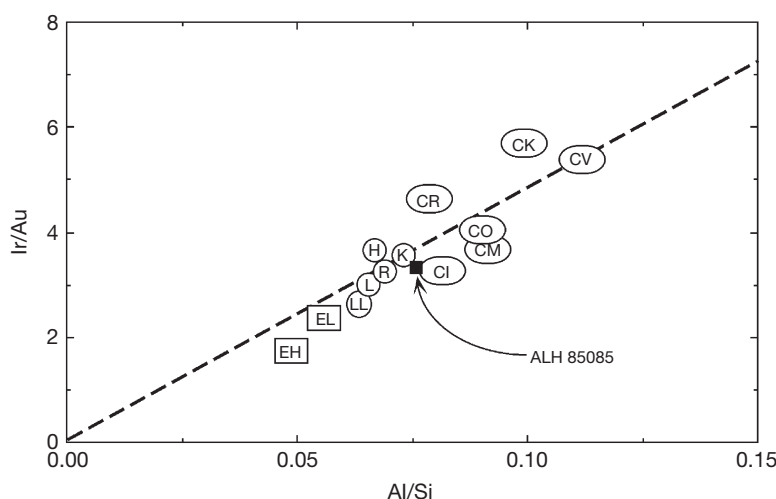


Figure 13 Ir/Au versus Al/Si in various types of chondritic meteorites. Ir is a refractory siderophile element (RSE), Al is an RLE. The figure shows the parallel behavior of RSE and RLE. Enstatite chondrites (EC) (EH and EL) are low in RSE and RLE, and CC (CM, CO, CR, CK, and CV) are high in both. Reproduced from O'Neill HStC and Palme H (1998) Composition of the silicate Earth: Implications for accretion and core formation. In: Jackson I (ed.) *The Earth's Mantle: Structure, Composition and Evolution – The Ringwood Volume*, pp. 3–126. Cambridge: Cambridge University Press.

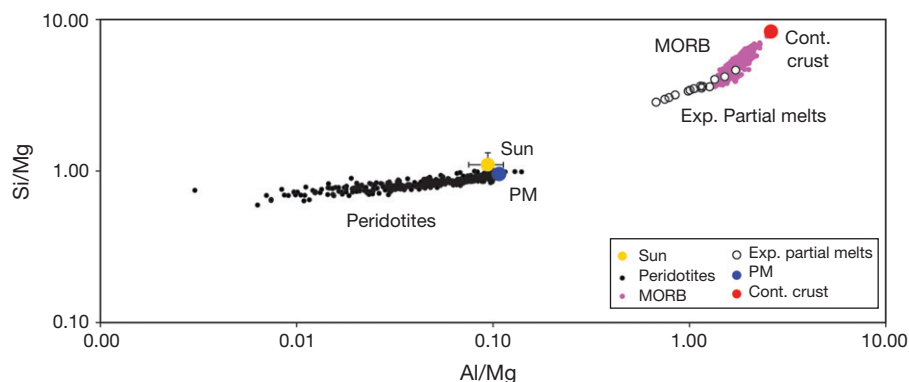


Figure 14 Si/Mg versus Al/Mg on a log-log scale. The upper mantle rocks are represented by 365 xenoliths data from the GEOROC (<http://georoc.mpch-mainz.gwdg.de>; Sarbas and Nohl, 2008). They are representative of peridotitic rocks from worldwide localities (Bodinier and Godard, 2003; Pearson et al., 2003). The PM composition is plotted at the high Al/Mg end (this work). The Sun is slightly above the PM composition (see text). The composition of 2912 mid-ocean ridge basalt (MORB) glasses is indicated (GEOROC, <http://georoc.mpch-mainz.gwdg.de>; Sarbas and Nohl, 2008). The results of partial melting experiments with PM-like compositions at 10 kbar and 1270 and 1390 °C are shown for comparison (Baker and Stolper, 1994). The composition of the continental crust is indicated (Chapter 4.1).

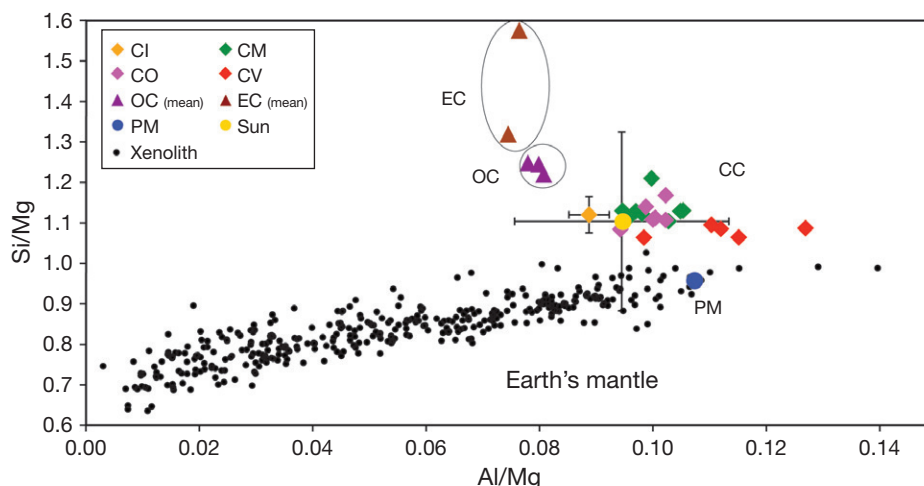


Figure 15 Si/Mg versus Al/Mg plot for the upper mantle rocks and chondritic meteorites. The PM compositions from this work are indicated. For EC and ordinary chondrites (OC), only averages are plotted (Wasson and Kallemeyn, 1988). The CC data are from Wolf and Palme (2001). They show a large spread in Al/Mg but have fairly constant Si/Mg ratios. Earth's mantle is clearly enriched in Al (and other refractory elements) and depleted in Si, relative to the Sun or CI meteorites. With 7% Si in the core, the bulk Earth composition would plot at the CI Si/Mg ratio (see text).

Figure 15 is a magnified version of Figure 14 on a linear scale. The primitive solar system materials, that is, chondritic meteorites, have also been plotted here. This figure makes it clear that Earth's mantle has an Al/Mg ratio within the range of CV chondrites, but the Si/Mg ratio is significantly below the ratios in chondritic meteorites. The 'nonmeteoritic' Si/Mg ratio of Earth's mantle has been extensively discussed in the literature. It is sometimes assumed that the bulk Earth has a CI-chondritic Si/Mg ratio and that the observed nonchondritic upper mantle ratio is balanced by higher than chondritic Si/Mg ratio in the lower mantle (e.g., Anderson, 1989). However, layered Earth models have become increasingly unlikely, as discussed above, and there is no reason to postulate a bulk Earth CI-Si/Mg ratio in view of the apparent variations of this

ratio in various types of chondritic meteorites. Ringwood (1989) suggested that the Si/Mg ratio of Earth's mantle is the same as that of the Sun, implying that CI chondrites have a nonsolar Si/Mg ratio. This is very unlikely in view of the excellent agreement between elemental abundances of CI chondrites and the Sun (Palme et al., 2012; Chapter 1.2). Other attempts to explain the low Si/Mg ratio of Earth's mantle include volatilization of Si from the inner solar system by high-temperature processing connected with the early evolution of the protosun and the solar nebula (Ringwood, 1979, 1991). Another possibility is partitioning of some Si into the metal core of Earth (e.g., Hillgren et al., 2000 and references therein). The latter proposition has the advantage that it would also reduce the density of the outer core, which is about 10% too

low for an FeNi alloy (Poirier, 1994). That Earth's core contains some Si is now assumed by most authors, but the amount is unclear. About 18% Si would be required to produce the 10% density deficit. 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 (2003) estimated a core composition with 6% Si and 1.9% S as light elements. Earlier models by Wänke (1981) had 12.5% Si in the core and 7.3% in the Allègre et al. (1995) model, respectively. In a recent accretion model for Earth by Rubie et al. (2011), Earth's core contains ~8 wt% Si. The isotopic composition of Si in Earth's mantle seems to support the presence of metallic Si in the core (see Section 3.1.6 on stable isotopes).

The effect of Si partitioning into the core can be readily seen in Figure 15. With 7.5% Si in the core, the bulk Earth Si/Mg ratio would exactly fit with the CI ratio of 1.12. The CI-chondritic Si/Mg ratio, the enhancement of refractory elements, and the depletion pattern of moderately volatile elements would then fit with the chemical characteristics of type 3 CC (see below).

A comparable, yet even more dramatic effect than for Si can be seen for Cr. The Cr content of the upper mantle rocks is fairly constant and independent of the Al/Mg ratio above about a ratio of 0.07 (Figure 16). Chondritic meteorites have a factor of 2 higher Cr/Mg ratios with little variation. The obvious explanation is that about 60% of the terrestrial Cr is in the core. The Cr deficit in Earth's mantle has been known for a long time and it has always been interpreted as indicating reducing conditions during formation of Earth's core, at least during its initial stage (O'Neill, 1991a; Ringwood, 1984; Wänke, 1981). Recent modeling of the accretion history of Earth including core formation also postulates accretion with

initially reduced materials to accommodate the low Cr in mantle rocks (Rubie et al., 2011; Wade and Wood, 2005).

3.1.5.4 The Fe Content of Earth

The bulk Fe content of Earth can be calculated from the FeO content of the PM and the Fe content of the core. A core with 75% Fe is obtained by assuming a CI-chondritic Fe/Mg ratio for the bulk Earth. After the addition of 5% Ni, 20% of the mass of the core would be left for the light element(s), which seems far too much. A higher Fe content of the core leads to higher bulk Earth Fe/Mg ratios. Anderson and Isaak (2002) estimate only 5% for the light element in the core, which would require an Fe content of the core of 90%. McDonough (2003) presents two models with 85.5 and 88.3% Fe in the core. The lower value leads to a bulk Earth Fe/Mg ratio of 2.11 and the higher content to 2.20 corresponding to 11 and 14% higher Fe/Mg ratios, respectively, than CI chondrites. We therefore conclude that Earth must have an Fe excess by at least 10%. Earlier, McDonough and Sun (1995) have emphasized that Earth has higher Fe/Al ratios than chondritic meteorites.

A comparison of the Fe content of the bulk Earth with chondritic meteorites shows that most other groups of chondrites have even lower Fe/Mg ratios than CI chondrites. Exceptions are H chondrites with similar Fe/Mg ratios as CI chondrites and EH chondrites with Fe/Mg ratios exceeding the CI ratio. However, when scaled to Si this excess disappears (see Figure 2). But the high Si/Mg ratios of EH chondrites disqualifies them as proto-Earth materials, as discussed before. See Javoy et al. (2010) for the opposite view.

Other groups of high-Fe meteorites are the CH and CB meteorites. These meteorites seem to have a more complex history involving evaporation and recondensation initiated by large impacts (Krot et al., 2003) and may thus reflect later more local events.

The growth of Earth by accumulation of Moon- to Mars-sized embryos could provide an explanation for the excess Fe

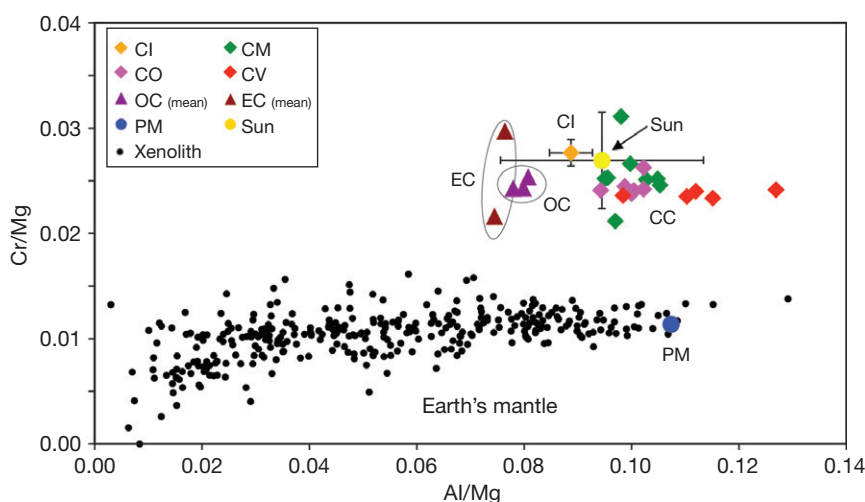


Figure 16 Cr/Mg versus Al/Mg in the upper mantle rocks and chondritic meteorites. The low Cr/Mg ratios of Earth's mantle reflect the presence of Cr in the core. This requires reducing conditions during core formation in the early history of Earth (see text). The sources of data are the same as in Figures 14 and 15.

in Earth. Large impacts will remove some material from Earth-making embryos. If these objects had a metal core, the silicate mantles will be preferentially eroded by impacts, which would lead to an increase in the bulk Fe/Mg bulk ratios of the embryos and consequently of Earth (O'Neill and Palme, 2008). The amount of dispersed material in a single impact is uncertain but may be several percent of the total mass involved in a collision (Canup and Agnor, 2000). The dispersed material not only must be removed from the planetesimal but also must leave the gravity field of the planet from which it was ejected, otherwise it will be reaccreted. To explain the high Fe content of Mercury, Benz et al. (1988) suggested that a large fraction of the mantle of Mercury had been removed by a late collision. Other potential effects of collisional erosion are described later.

3.1.5.5 Moderately Volatile Elements

The abundance of the moderately volatile Mn decreases continually from CI through CM, CO, and CV to the PM. Manganese is low in Earth because it is volatile not because it is siderophile, as described in more detail below. The spread in Mn/Mg in meteorites is much larger than that of Cr/Mg as shown in Figure 16 (the scale is different in Figures 16 and 17).

The solar and meteoritic abundances of Mn are different beyond analytical uncertainties, as shown in Figure 17. This is a rare case in view of the generally excellent agreement between solar and CI abundances and probably reflects problems with solar abundance determinations of Mn (Lodders et al., 2009).

In Figure 18, the moderately volatile elements of CV chondrites normalized to CI chondrites against condensation temperatures of Wasson (1985) have been plotted. A continuous depletion sequence with decreasing condensation temperatures is apparent. Lithophile, siderophile, and chalcophile moderately volatile elements show exactly the same behavior. The depletions increase with decreasing condensation temperatures, independent of the geochemical character of the elements. This behavior indicates that geochemical processes can

be excluded for explaining the depletion sequence, pointing instead to a volatility-related process, either evaporation or incomplete condensation. The latter possibility is more likely as there are no isotopic traces of evaporation of K and Rb (Humayun and Clayton, 1995; Nebel et al., 2011). Furthermore, evaporation will occur under oxidizing conditions favoring the loss of K and Na and producing a high Mn/Na ratio in residual phases (see O'Neill and Palme, 2008 for a detailed discussion). In a later section (Section 3.1.5.5.2) it will be shown that the Mn depletion must have occurred shortly after the formation of the solar system.

For elucidating volatile element behavior in Earth's composition, most of the elements plotted in Figure 18 are not useful, as siderophile and chalcophile moderately volatile elements may be additionally depleted by core formation. For the purpose of comparing moderately volatile elements between meteorites and Earth, only lithophile elements can be used.

In Figure 19 the concentrations of three lithophile elements (Mn, Na, and Zn) and the chalcophile element Se are shown in different types of chondritic meteorites. A characteristic feature of the chemistry of CC is the approximately similar depletion of Na and Mn in all types of CC, except CI. OC and EC are not or only slightly depleted in both elements, but their Zn contents are significantly lower than those of the CC. Earth fits qualitatively with the CC in having significant depletions of Mn and Na and a stronger depletion of Zn. The total depletion is stronger in Earth than in CV chondrites (see also McDonough, 2003).

Selenium has a similar condensation temperature as Zn and S. The Se (and S) content of Earth's mantle is, however, extremely low because a large fraction of the terrestrial Se is, together with S, in the core. In addition, the initial endowment in Earth in S and Se is, based on the abundances of other elements of comparable volatility, such as Zn, very low (Dreibus and Palme, 1996).

In Figure 20, the abundances of Al, Ca, Mg, Si, Cr, and of the three moderately volatile elements Mn, Na, and Zn are plotted in various groups of CC and in Earth. All elements are normalized to the refractory element Ti and to CI abundances.

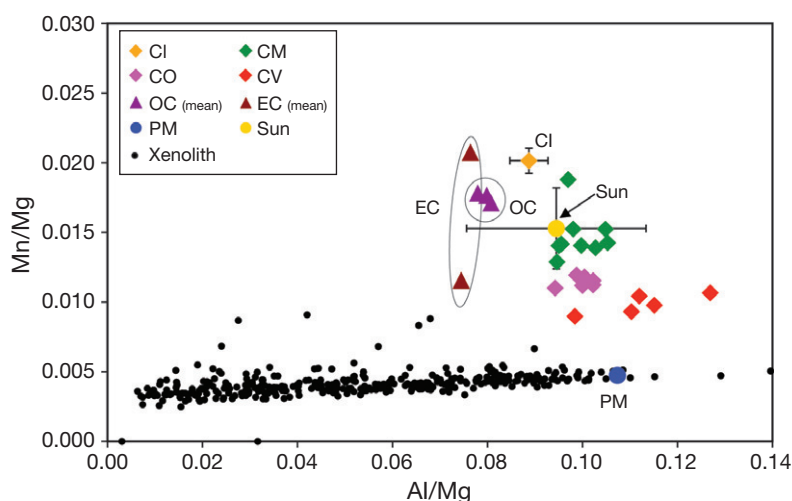


Figure 17 The Mn/Mg versus Al/Mg plot shows the continuous decrease of Mn/Mg from CI, through CM, CO, CV, to the PM, reflecting decreasing contents of moderately volatile elements. The Cr/Mg ratio in Figure 16 is much more constant and shows no volatility-related effects (notice the difference in the scale between this figure and Figure 16). The mismatch of the solar and CI Mn abundances is unusual (see discussion in Lodders et al., 2009).

By normalizing to Ti, 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 Mg, Si, and these moderately volatile elements. The sequence of

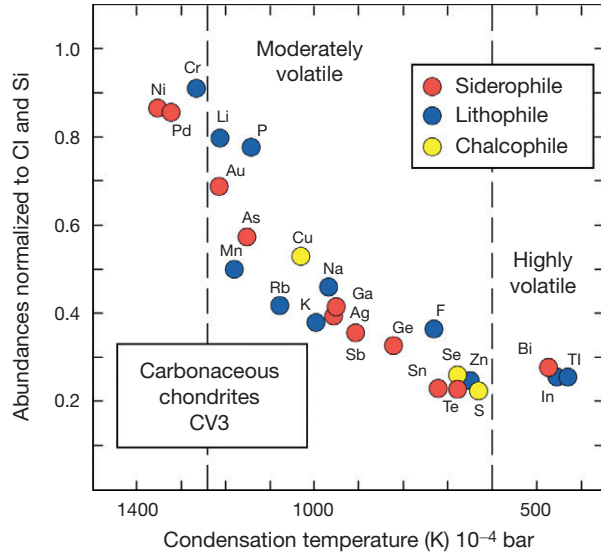


Figure 18 Abundances of volatile elements in CV3 chondrites (e.g., Allende) normalized to CI chondrites and Si. The normalization to Mg would give exactly the same picture. There is a continuous decrease of abundances with increasing volatility as measured by the condensation temperature. The sequence is independent of the geochemical characters of the elements indicating that volatility is the only relevant parameter in establishing this pattern. Here, condensation temperatures are from Wasson (1985). Adapted from Palme H (2000) Are there chemical gradients in the inner solar system. *Space Science Reviews* 92: 237–262, with kind permission from Springer Science and Business Media.

elements, their absolute depletions from Al to Zn, is basically in the order of decreasing condensation temperatures or increasing nebular volatility, the higher the volatility, the lower the abundance. Since we have argued above that the depletion trend in CC reflects nebular processes, it is concluded that this is also the dominant cause of the PM pattern.

In Figure 20, Earth's mantle seems to extend the trend of the moderately volatile elements to lower abundances, at least for Na, Mn, and Zn (Zn behaves as a lithophile element in Earth's mantle, see Dreibus and Palme, 1996). Several other volatile lithophile elements, such as Li, F, K, and Rb, show similar trends (not shown here). The CC trend of Fe is not extended to Earth, as most of the iron of Earth is in the core. The Mg abundance of Earth shows a slightly different trend. If the core had 7% Si (previous section) and if that would be added to the bulk Earth Si, then the bulk Mg/Si ratio of Earth would be the same as that of CC (Figure 15), and the Si abundance of Earth's mantle in Figure 20 would coincide with the Mg abundance.

The strong depletion of Cr (full symbol in Figure 20) reflects the partitioning of Cr into the core, discussed above. Extending the CC volatility trend to Earth leads to an estimated bulk Earth Cr content that is represented by an open symbol in Figure 20.

On the right hand side of Figure 20, the abundances of the same elements for average H chondrites from the compilation of meteorite data by Wasson and Kallemeyn (1988) and using the same normalization as for the CC in Figure 20 have been plotted. OC and EC have apparently very different chemical compositions when compared to CC: (1) the depletion of refractory elements in OC leads to the high abundances of Si and Mg in Figure 20, (2) Mg and Si are fractionated, and (3) Mn and Na are only slightly depleted (see Figure 2). EC show similar, though more enhanced compositional trends as OC (Figures 10, 16, and 17). In summary, Figure 20 demonstrates quite clearly that Earth mantle composition resembles trends

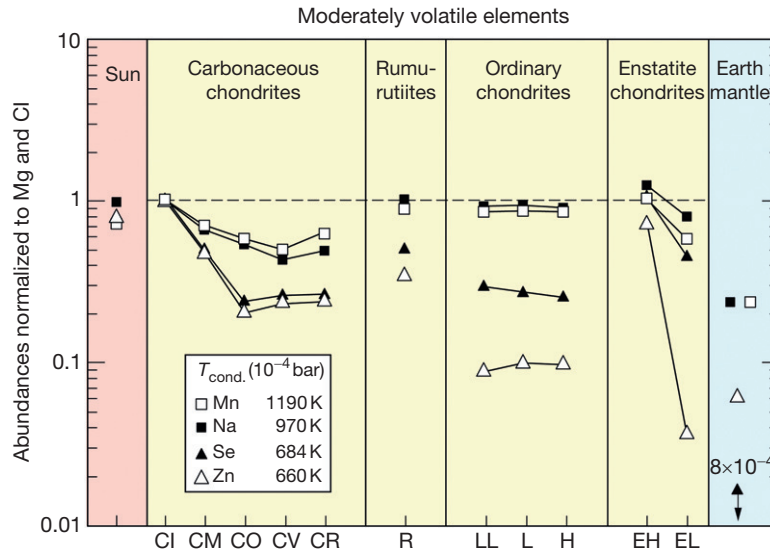


Figure 19 Four moderately volatile/Mg element ratios in various types of chondritic meteorites (three lithophile and one chalcophile element). All groups of chondritic meteorites are depleted in moderately volatile elements, none is enriched. The two elements Mn and Na are depleted in CC and in Earth but not in ordinary and enstatite chondrites. The depletion of Na and Mn in Earth is significantly stronger than in CV chondrites, although the chondritic Na/Mn ratio is more or less retained. The condensation temperatures are from Wasson (1985).

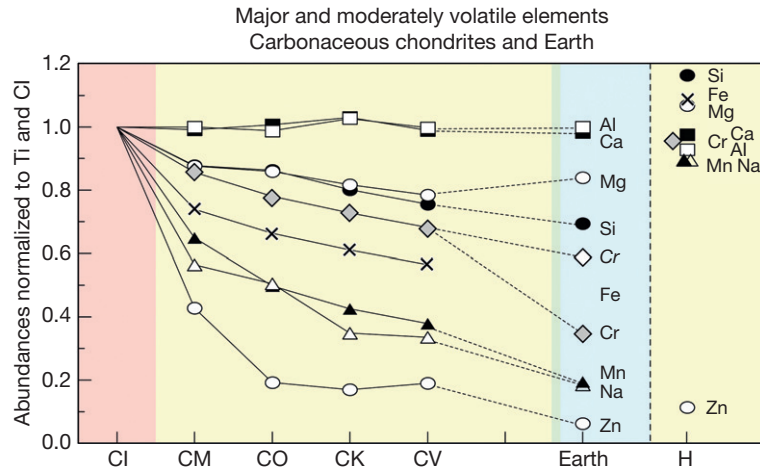


Figure 20 Major and moderately incompatible volatile elements in CC, H chondrites, and in Earth's mantle. All data are normalized to the RLE Ti. There is a single trend for RLE, Mg–Si, and moderately volatile elements. Earth may be viewed as an extension of the CC trend. The low Cr content in the present mantle (full symbol) is the result of Cr partitioning into the core. The open symbol is plotted at the extension of the CC trend. The data for OC are plotted for comparison. Similar chemical trends in CC and Earth are evident. H chondrites are very different. They show almost no depletion for Mn and Na. The Zn depletion is similar to that of CC, when normalized to Ti. Data from [Wolf and Palme \(2001\)](#) and [Wasson and Kallemeyn \(1988\)](#).

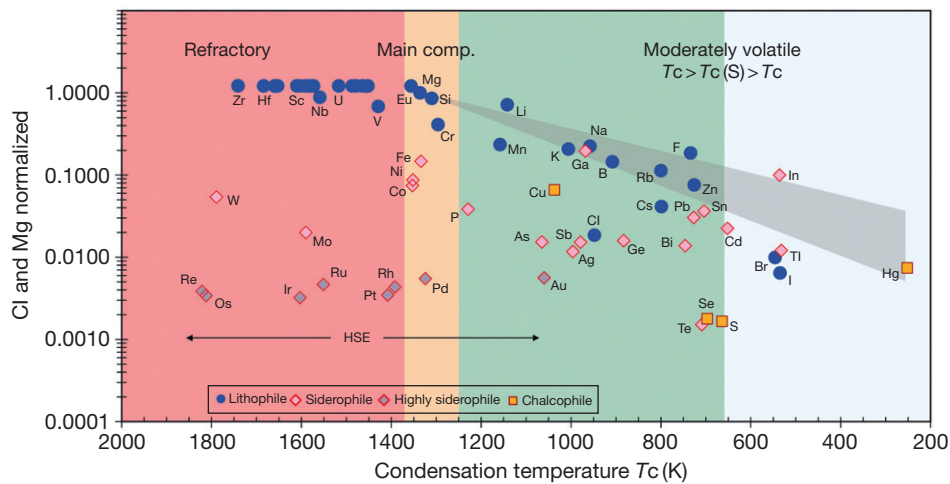


Figure 21 Cl- and Mg-normalized abundances of elements listed in [Table 4](#) are plotted against their condensation temperatures ([Lodders, 2003](#)). For most refractory elements between Sc and Eu (e.g., Al, Ti, Ca, and REE; see [Table 2](#)), element symbols are not given. Earth depletion trend for moderately volatile lithophile elements is indicated. The high abundance of In, an element with siderophile and chalcophile tendencies, is remarkable (see text).

in the chemistry of CC and that those trends are not compatible with the chemical composition of OC or EC.

In [Figure 21](#), Cl- and Mg-normalized abundances of all elements listed in [Table 4](#) except the ice-forming elements (H, C, N, and O) are plotted against the condensation temperatures of [Lodders \(2003\)](#).

The pattern is one in which RLE are uniformly enriched, except Nb and V which are partly in the core. Europium still belongs to the refractory elements despite its formally lower condensation temperature.

Here, the term 'moderately volatile' is used following [Lodders \(2003\)](#) to refer to all the elements that are calculated to condense from the solar nebula at temperatures below the Mg silicates and Fe metal, except the ice-forming elements (H, C, N, O, and the noble gases). The moderately volatile

elements are subdivided in elements condensing above the 50% condensation temperature of S, and those below. Sometimes, though, the elements condensing below S are termed 'highly volatile' (e.g., [Wasson, 1985](#)). But this introduces ambiguity because the 50% condensation temperatures of many of these elements are poorly known, as may be seen by comparing [Figure 18](#) (T_c from [Wasson, 1985](#)) with [Figure 21](#) (T_c from [Lodders, 2003](#)).

To a first approximation, a volatility trend of decreasing abundance with increasing volatility similar to that observed in the CC is apparent from elements that are geochemically not very highly incompatible (Li, Na, K, B, and F). Clearly, the trend can only be expected to be valid for lithophile elements because moderately volatile elements that are also siderophile and/or chalcophile are additionally depleted in the PM by core

formation. There are, however, many significant anomalies in the pattern. Two very well-determined elements, Zn and In, which might have been expected to become chalcophile under very reducing conditions, plot with the lithophile elements and do not show the extra depletions of other chalcophile elements like Cd, Pb, or Tl. Similarly, Ga, which is moderately siderophile, plots alongside Na, Mn, and K. Conversely, the heavy halogens (Cl, Br, and I) but not F are far more depleted than expected. Nitrogen is also greatly depleted in Earth compared to CC.

The lack of any clear volatility trend makes the interpretation of the significance of the Pb isotopic systematics of Earth problematic. The removal of Pb 50 My after the formation of the solar system is required to explain the Pb isotopic data of MORB. The loss of Pb from Earth's mantle has been variously ascribed to partitioning into sulfide (Wood and Halliday, 2005), removal by core-forming metal (Wood and Halliday, 2010) or additional losses due to its high volatility (Lagos et al., 2008).

The depletions of elements in Earth's mantle record the integral effects of both accretion and core formation. There are now many experimental determinations of metal/silicate partition coefficients as a function of pressure, temperature, oxygen fugacity, and silicate composition (e.g., Mann et al., 2009, 2012; Righter, 2003; Chapter 3.12). The application of these data to core formation modeling should allow a better understanding of the core formation. Modern theories of Earth formation imply a final status where tens of Moon-sized embryos form Earth by collisions. This may lead to the formation of several magma oceans, each leading to metal segregation (e.g., Rubie et al., 2011). The present discussion in the application of metal/silicate partition coefficients centers around the question of whether it is possible to fit all data to a single stage core formation. This seems to be difficult, however. The low abundances of Si, V, Cr, and Nb contents in Earth's mantle require an early stage of core formation under very reducing conditions. If these conditions had prevailed during all stages of accretion, the FeO content of Earth's mantle would have been much lower than presently observed. Newer models therefore begin with reducing conditions and end with oxidizing conditions (Rubie et al., 2011; Wade and Wood, 2005). The low concentrations of Cr, V, and sometimes Mn in Earth's mantle have been used earlier by Wänke (1981), Ringwood (1984), and O'Neill (1991a) to support heterogeneous accretion models, with early reduced, volatile poor material and later addition of oxidized, volatile rich components. A recent Pd–Ag isotope study by Schönbachler et al. (2010) comes to similar conclusions. There is also the possibility that the core formation occurred earlier in Earth-making embryos (Rubie et al., 2011).

There is ongoing research to define the conditions of core formation more precisely by considering as many elements as possible and their metal/silicate partition coefficients as a function of pressure, temperature, oxygen fugacity, and composition (Righter, 2003; Walter et al., 2000). However, this endeavor will also require a better understanding of the rather complex pattern of volatile-element depletion in Earth.

A particular problem is raised by the relative abundances of In and Zn. Both elements have well-defined concentrations in the mantle, with In slightly but resolvable less depleted than Zn, yet In is much more volatile than Zn under most

conditions (see discussion in Witt-Eickchen et al., 2009). In addition, data on metal/silicate partition coefficients of Zn and In show that In is under all circumstances more siderophile than Zn (Mann et al., 2009). Thus, if the core formation had affected In, its PM concentration would be even higher than presently observed in the mantle. In CV chondrites, the very volatile elements Bi, Tl, Te, In, and Cd are no more depleted than S (see Figure 18; Takahashi et al., 1978). In texturally primitive type 3 OC, elements with condensation temperatures below FeS show large variations, occasionally excesses (Keays et al., 1971), perhaps reflecting parent body mobilization. The behavior of these elements is not fully understood, neither in meteorites nor in Earth's mantle.

Besides the S, Se, and Te triplet, the HSE show the strongest depletion with roughly chondritic ratios (Figure 21). The significance of the HSE will be separately discussed below.

3.1.5.5.1 Origin of depletion of moderately volatile elements

The depletion of moderately and highly volatile elements is a characteristic feature of all inner solar system materials (excluding the CI parent body, if this is an inner solar system object). The degree of depletion of an element is a function of the nebular volatility but is independent of its geochemical character (see Figure 18). Thus, volatile element depletions are not related to geochemical processes such as partial melting and fractional crystallization or heating by impacts. The evaporation of volatiles from an undepleted reservoir is unlikely to have produced the observed depletions – (1) volatilization on a local scale would produce local enrichments through recondensation, but only depletions are observed in meteorites (Palme et al., 1988); (2) volatilization would lead to isotopic fractionations, but such fractionations are not observed even in rocks that are very low in volatile elements such as K and Rb (Humayun and Cassen, 2000; Nebel et al., 2011); and (3) the sequence of volatility-related losses of elements depends on oxygen fugacity. Volatilization will produce oxidizing conditions, while very reducing conditions prevailed during nebular condensation. A striking example for the different behavior during condensation and evaporation are the two moderately volatile elements Mn and Na, as discussed above. Both elements have similar condensation temperatures and their ratios are more or less chondritic in all undifferentiated meteorites despite significant variations in absolute concentrations as shown in Figures 19 and 20. These figures also show that the Mn/Na ratio of Earth's mantle is chondritic. Heating of meteorite samples to temperatures above 1000 °C for a period of days will inevitably lead to significant losses of Na and K but will not affect Mn abundances (e.g., Wulf et al., 1995). The chondritic Na/Mn ratio of Earth must, therefore, be attributed to nebular fractionations of proto-Earth material (O'Neill and Palme, 1998, 2008). If some Mn had partitioned into the core, as is sometimes assumed, the chondritic Mn/Na ratio of 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 Mn and Na, with that of CC implies that the proto-Earth material underwent similar fractionation processes as CC. The anomalously greater depletion of the most

incompatible elements such as the heavy halogens stands out as a feature not found in any chondrite group.

3.1.5.5.2 Time of depletion of moderately volatile elements

The Rb/Sr ratio of CI chondrites (0.296) is about ten times higher than the Rb/Sr of Earth (0.028), a result of the low abundance of the moderately volatile element Rb in Earth. If the depletion of moderately volatile elements had occurred by heating during accretion of Earth, one would expect much higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from the decay of ^{87}Rb than the lowest terrestrial ratios indicate. The growth of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from its initial values in Ca, Al inclusions (in CV meteorites) to the lowest ratios inferred for Earth requires about 20 My given an environment with a CI or solar Rb/Sr ratio (Halliday and Porcelli, 2001). This requires Rb fractionation at the very beginning of the solar system, either by incomplete condensation or by evaporation. A precise time is difficult to obtain, as the lowest terrestrial $^{87}\text{Sr}/^{86}\text{Sr}$ is not really known.

A better estimate for the time of depletion of moderately volatile elements may be obtained from ^{53}Mn , which decays with a 3.7 My half-life to ^{53}Cr . Trinquier et al. (2008) determined the Cr isotopic composition of primitive meteorites and differentiated planets and planetesimals. Figure 22 is a modified version of their Figure 7. Bulk OC and CC appear to form a single isochron, which also comprises differentiated inner solar system objects.

The age given by the Mn–Cr isochron is 4567.3 ± 1.9 Ma, close to the time of formation of the solar system. At this time, the moderately volatile Mn was separated from the nonvolatile Cr, and no later equilibration of the Cr isotopes from systems with different Mn/Cr ratios must have occurred. Earlier studies by Shukolyukov and Lugmair (2006) and Moynier et al.

(2007) gave similarly old ages, except for a shift in the initial $\epsilon^{53}\text{Cr}$ of the Shukolyukov and Lugmair (2006) data due to different normalization, as discussed in Trinquier et al. (2008). Qin et al. (2010) found, however, less variation in ^{53}Cr among chondritic meteorites. Nevertheless, these authors report a combined chondrite isochron of 4566.4 ± 2.2 Ma. The details of these isochrons may not be fully understood, but Earth seems to have a $\epsilon^{53}\text{Cr}$ at the lower end of the chondrites close to CV chondrites (Figure 22).

The Mn/Cr ratio of the PM of Earth is 0.417 (see Table 4), similar to the ratio in CV chondrites (0.42), despite a significantly lower Mn/Mg ratio in the PM (Figure 17). The higher than expected Mn/Cr ratio of the PM is the result of the presence of about 60% of Earth's Cr inventory in the core (Figure 16).

The bulk Earth Mn/Cr ratio also depends on the amount of Mn in the core, which is not expected to be large. Manganese is less siderophile than Cr (e.g., Mann et al., 2009). Furthermore, Mn and other volatile elements were absent during the early stages of accretion, when conditions are reducing enough for Cr to partition into the core (e.g., Rubie et al., 2011; Schönbachler et al., 2008, 2010). We thus conclude that the Mn content in the core is low, in agreement with McDonough (2003). The basically CI chondritic Na/Mn ratio of Earth's mantle is in agreement with the absence of a major fraction of Mn in the core, as Na does not partition into metal.

The Mn/Cr ratios of Earth's PM and the bulk Earth assuming a core with 500 ppm Mn are indicated in Figure 22. If it were assumed that the bulk Earth has the same $^{53}\text{Cr}/^{52}\text{Cr}$ ratio as the mantle, the bulk Earth would no longer plot on the chondrite isochron (Figure 22). This is unlikely, however, as it would imply a different initial $^{53}\text{Cr}/^{52}\text{Cr}$ for Earth, compared to chondrites, Mars, and Vesta (Trinquier et al., 2008). If the bulk Earth point is forced to lie on the isochron, it has to have a lower $^{53}\text{Cr}/^{52}\text{Cr}$ ratio than the mantle (point A in Figure 22). The consequence is that the core has to have a lower Cr isotopic composition than the mantle to achieve the bulk Earth value at point A in Figure 22. Thus, some Cr must have partitioned into the metal core of Earth or in the cores of Earth-forming planetesimals during the lifetime of ^{53}Mn . Later through further growth of the mantle by addition of chondritic material, the present Cr isotopic composition of the mantle was established (see Palme et al., 2012, for details).

This model requires early depletion of Mn, within the first 2 My after the beginning of the solar system (see isochron age in Figure 22). Since Mn fits well with the general sequence of volatile element depletion in Earth, it is reasonable to assume that other volatiles such as the alkalis fractionated at the same time. This compact timescale is compatible with nebular dissipation at a time when moderately volatile elements were still to a large extent in the gas.

In summary, the early depletion of Mn from Earth or Earth-forming bodies supports the hypothesis that the volatile element depletion in the various solar system materials is a nebular event right at the beginning of the solar system as suggested by Palme et al. (1988), Humayun and Cassen (2000), and Nyquist et al. (2001). The same reasoning may apply to other volatile elements. Early formed solids did not acquire the full share of volatile elements because of dissipation

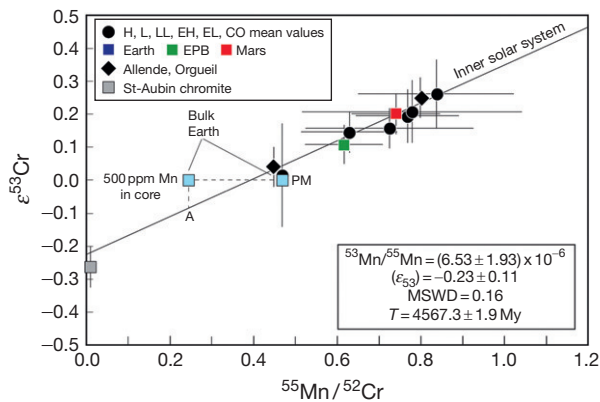


Figure 22 ^{53}Cr excess in bulk meteorites and bulk planets vs Mn/Cr ratios. CC, OC, and EC define an isochron that also passes through Mars and Vesta. The figure is adapted from Figure 7 in Trinquier et al. (2008), with the addition of the two points marked 'bulk Earth.' Qin et al. (2010) report a similar but less well-defined isochron. Earth's mantle lies in cases at the lower end. The Mn/Cr of the bulk Earth is off the isochron because the core is rich in Cr and probably low in Mn. If Earth is assumed to plot with other inner solar system materials, the bulk Earth should lie at point A, assuming a maximum of 500 ppm Mn in the core. This implies a different isotopic composition of the core and mantle. The present Earth's mantle is reached from a bulk Earth at A by later accretion of chondritic components (see Palme et al., 2012).

of the nebula during cooling (e.g., Wasson and Chou, 1974). The core formation must have begun at about the same time.

3.1.5.6 HSE in Earth's Mantle

The HSE Os, Ir, Pt, Ru, Rh, Pd, Re, and Au have a strong preference for the metal phase as reflected in their high metal/silicate partition coefficients of $>10^4$ at one bar pressure. Ratios of refractory HSE are approximately constant in chondritic meteorites, although newer high-precision data show that the variations in absolute and relative abundances are significantly above the analytical uncertainties (Fischer-Gödde et al., 2010; Horan et al., 2003). Some chondrites have high Os/Ir and simultaneously low Ru/Pt ratios contradicting simple volatility trends (see Horan et al., 2003 for a detailed discussion). Walker et al. (2002) found that the average Os/Re ratio in CC is 7 to 8% higher than that in OC and EC. Both elements, Os and Re, are refractory metals and there is no simple explanation for this difference. Fischer-Gödde et al. (2010) reported differences in Rh/Ir ratios between CC on one hand and OC and EC on the other hand. These examples demonstrate that the assumption of constant relative abundances of refractory elements in chondritic meteorites is not fully justified. This is similar to the variations seen in the RLE ratios in chondritic meteorites discussed earlier.

Two HSE, Pd and Au, are moderately volatile elements. Their abundances in chondrites are not constant. They follow the general trend of moderately volatile lithophile elements.

The HSE abundances in Earth's mantle are extremely low (Figure 21), about 0.2% of those estimated for the core, the major reservoir of the HSE in Earth. Most of the earlier HSE data on Earth's mantle samples come from the analyses of Ir that is sufficiently high in mantle rocks to allow the use of instrumental neutron activation analysis (e.g., Spettel et al., 1990). The Ir contents in spinel lherzolites from worldwide occurrences of xenoliths and massive peridotites are on average surprisingly uniform, although local exceptions are recorded. Jagoutz et al. (1979) listed 3.5 ppb for the PM corresponding to a CI-normalized abundance of 6.67×10^{-3} . Pattou et al. (1996) analyzed Pyrenean orogenic spinel lherzolites with an average Ir content of 3.0 ± 0.5 ppb, Morgan et al. (2001) estimated 3.2 ± 0.2 ppb for the PM. Becker et al. (2006) recommend an Ir mantle concentration of 3.5 ± 0.5 ppb obtained from high-precision analyses by isotope dilution on a large variety of mantle rocks. There are many more analyses with similar results in the literature. Nevertheless, there also seems to be some heterogeneity. Nine Antarctic spinel lherzolite xenoliths reported by Spettel et al. (1991) are uniformly enriched in Ir with an average Ir content of 4.92 ± 0.65 ppb. There are also reports of spinel peridotite xenoliths with lower Os that have been ascribed to a loss of the sulfide component either during weathering or more likely by dissolution into the host basalt (Handler et al., 1999).

Ratios among HSE in the upper mantle rocks are roughly chondritic, but on a finer scale, there are significant deviations, which are visible in Figure 21. Data by Pattou et al. (1996) on Pyrenean peridotites, analyses of abyssal peridotites by Snow and Schmidt (1998), results for lherzolites from Zabargad by Schmidt et al. (2000), and data on various mantle rocks by Rehkämper et al. (1997) indicate that higher than chondritic

Ru/Ir ratios are widespread and may be a characteristic of the whole upper mantle. Becker et al. (2006) confirmed the excess of Ru relative to Ir from a large number of analyses from different types of peridotites. A 30% enrichment of Ru relative to Ir and CI chondrites seems to be a characteristic signature of the upper mantle. A somewhat less pronounced enrichment was found for Rh in Pyrenean lherzolites (Pattou et al., 1996), in Zabargad rocks (Schmidt et al., 2000), and in peridotites with a variety of different origins (Fischer-Gödde et al., 2011).

The concentrations of Pd in the upper mantle rocks are also much more variable than those of the refractory siderophiles, with up to twice the CI chondritic Pd/Ir ratio (Pattou et al., 1996; Schmidt et al., 2000). Becker et al. (2006) reported similarly enhanced Pd/Ir ratios for their suite of mantle peridotites.

The element Au is more variable than Pd in the upper mantle rocks, presumably because Au is more soluble in silicate melts or more mobile in aqueous environments. It appears that the variations in Au are regional. Antarctic xenoliths analyzed by Spettel et al. (1991) have an average Au content of 2.01 ± 0.17 ppb, while seven xenoliths from Mongolia analyzed by the same authors have less than 1 ppb Au. The upper mantle abundance suggested by Fischer-Gödde et al. (2011) and listed in Table 4 is therefore quite uncertain.

The average upper mantle pattern of HSE clearly is different from any chondrite pattern, despite considerable scatter in both. Some similarity in the upper mantle pattern with lunar highland rocks is found (Fischer-Gödde and Becker, 2012). The significance of this observation is unclear. Walker (2009) has summarized the various hypotheses on the origin of HSE in the PM in some detail and comes to the conclusion that the most likely explanation is the addition of a late accreting component that arrived on Earth after the core formation has ceased. This hypothesis will be discussed in some more detail in the next section.

3.1.5.7 Late Veneer Hypothesis

Although HSE concentrations are low in Earth's mantle, they are not as low as one would expect from equilibrium partitioning between core-forming metal and residual mantle silicates. The low solubility of Ir and other HSE elements in silicate melts suggests extremely low metal/silicate partition coefficients of HSE (e.g., Borisov and Palme, 1997; Borisov et al., 1994; O'Neill et al., 1995; Walter et al., 2000). Murthy (1991) has therefore suggested that partition coefficients are dependent on temperature and pressure in such a way that at the high-P and high-T conditions where core formation may have occurred, the observed mantle concentrations of HSE would reflect metal/silicate equilibration. This hypothesis has been rejected on various grounds (O'Neill, 1992), and high-P and high-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., 2000). Mann et al. (2012) determined metal/silicate partition coefficients of Ru, Rh, Pd, Re, Ir, and Pt over a range of pressures (3.5–18 GPa) and temperatures (2423–2773 K). Although increasing pressure and temperature decreases the siderophilicity of the HSE, the pressure dependence is significantly smaller above pressures of about 5 GPa (Mann et al., 2012). A similar effect has

been observed for Ni and to a lesser degree for Co by [Kegler et al. \(2008\)](#). Thus, the decrease in metal/silicate partition coefficients with increasing depth in Earth is not sufficient to produce the present level of HSE by equilibrium partitioning. [Mann et al. \(2012\)](#) therefore conclude “that the major process that caused the observed near-chondritic HSE abundances of Earth’s mantle cannot be high-pressure, high-temperature metal/silicate equilibration during core formation.” The least siderophile of the HSE is Pd, which may not have been quantitatively extracted into Earth’s core, which would explain its overabundance in the mantle (see also [Righter et al., 2008](#)). This is, however, no explanation for the enhanced Ru (and Rh) in the PM ([Mann et al., 2012](#)).

Addition of a late accretionary component without subsequent metal separation has been widely used to explain the elevated concentrations of HSE in the mantle of Earth. The addition of a more or less chondritic veneer to Earth has been suggested by [Kimura et al. \(1974\)](#) and [Chou \(1978\)](#) and supported by the data of [Jagoutz et al. \(1979\)](#). The late veneer was assumed to be identified as CI chondrite material and thought to also have delivered water to Earth (e.g., [Drake and Righter, 2002](#); [Morbidelli et al., 2000](#)). However, [O’Neill \(1991a\)](#) argued that CI chondrites would deliver much more S to the mantle than is actually found, and he suggested a late veneer component of H chondritic composition, which would require a separate source for water. [Figure 21](#) shows that S, Se, and Te are more depleted in Earth’s mantle than the HSE. The late veneer hypothesis has gained additional support from the analyses of the Os isotopic composition of the mantle rocks. [Meisel et al. \(1996\)](#) determined the $^{187}\text{Os}/^{188}\text{Os}$ ratios of a suite of mantle xenoliths. Since Re is more incompatible during partial mantle melting than Os, 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 Lu, two proxies for Re, [Meisel et al. \(1996\)](#) determined an $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.1296 ± 0.0008 for the PM. This value is above the range of $^{187}\text{Os}/^{188}\text{Os}$ ratios of CC but within the range of OC. The basically chondritic $^{187}\text{Os}/^{188}\text{Os}$ in Earth’s mantle is a very strong argument in favor of the late veneer ([Walker, 2009](#) and references therein). [Fischer-Gödde and Becker \(2012\)](#) suggested that the HSE composition of the silicate Earth can be matched by a late veneer comprising $\sim 80\%$ volatile depleted CC-like material and of $\sim 20\%$ differentiated meteoritic metal, similar to what has been identified in ancient lunar impact rocks. The HSE pattern of the differentiated component is assumed to be similar to the HSE pattern of IVA iron meteorites. This requires, however, the addition of a metal mass corresponding to a core of a 2300 km diameter planetary body ([Fischer-Gödde and Becker, 2012](#)).

There is another problem with the arrival of a late chondritic component. [Dauphas et al. \(2004\)](#) reported a correlation of isotope anomalies of Ru and Mo primarily reflecting variations in the fraction of s-process components. Both elements show isotope anomalies in bulk meteorites, with the terrestrial Ru and Mo having larger s-process contributions than any other meteorite. This observation led [Dauphas et al. \(2004\)](#) to the conclusion that the late veneer material comes from the same source as the bulk Earth. This is because Mo is a moderately siderophile element entering Earth with the main mass of accretion, whereas the presently observed Ru in the PM is

thought to be delivered with a late chondritic veneer. [Burkhardt et al. \(2012\)](#) have recently confirmed these findings. This does not fit well with current accretion models of Earth, where independently formed embryos from different heliocentric distances contribute to the growth of Earth. There is no a priori reason why the isotopic signature of Ru in a very late accreting component should fit to the isotopic composition of Mo representing the mean of the composition of up to a hundred embryos.

3.1.6 The Isotopic Composition of Earth

3.1.6.1 Major Elements

The most abundant element in Earth (by atoms) is oxygen. In a diagram of $\delta^{17}\text{O}$ versus $\delta^{18}\text{O}$, the oxygen isotopic composition of terrestrial rocks plot along a line with a slope of 0.5, designated as the terrestrial fractionation line ([Figure 23](#)).

Most CC plot below and OC above the terrestrial mass fractionation line. EC, 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. Other groups of CC have different oxygen isotopic compositions. Interestingly, the largest variations in oxygen isotopes are found in the smallest meteorite components. Individual components of single CC span an extremely wide range in oxygen isotopes, such that the bulk meteorite value is of little significance (e.g., [Clayton, 1993](#); [Clayton and Mayeda, 1984](#)). Larger objects have smaller variations in oxygen isotopes. 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

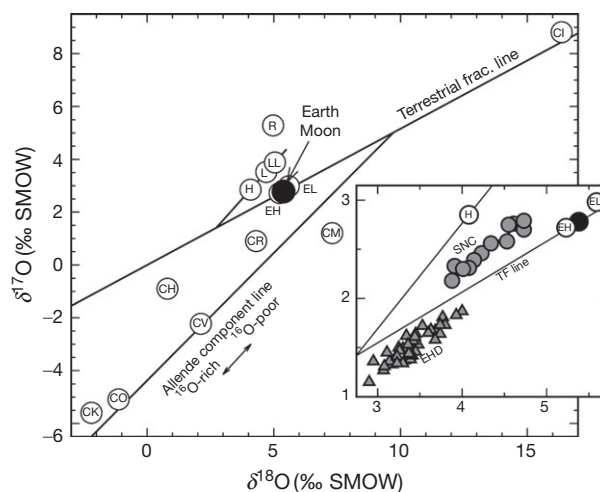


Figure 23 $\delta^{17}\text{O}$ versus $\delta^{18}\text{O}$ for chondritic meteorites. The OC (H, L, LL, and R) plot above the terrestrial fractionation line and the CC below. The most oxidized (CI) and the most reduced (E) chondrites also plot on terrestrial fractionation line. The larger bodies of the solar system, for which oxygen isotopes have been determined, Earth, the Moon, Mars (SNC meteorites), and Vesta (EHD meteorites), plot on or close to the terrestrial fractionation line, TFL. Reproduced from Lodders K and Fegley B Jr (1997) An oxygen isotope model for the composition of Mars. *Icarus* 126: 373–394.

same oxygen isotopic composition (Wiechert et al., 2001). And the oxygen isotopic composition of Mars and Vesta, two other large inner solar system bodies, are not very different from that of Earth and the Moon. During formation of high- and low-temperature components in meteorites, large variations in oxygen isotopic composition are recorded, while large bodies show a more uniform composition, presumably the result of the mixing of extremely heterogeneous components.

It has recently become apparent, however, that this planetary oxygen isotopic composition, typical of most of the material in the inner solar system differs from the solar wind as sampled by the Genesis mission (McKeegan et al., 2011). These results agree with the earlier measurements on lunar metals exposed to the solar wind (Hashizume and Chaussidon, 2005). Thus, an effective mechanism has to be found for fractionating average solar system oxygen isotopes to produce the oxygen isotopic compositions of the terrestrial planets and meteorite parent bodies (see Mittlefehldt et al., 2008 and references therein).

Whatever is causing the variable oxygen isotope composition of planetary objects, the available data clearly indicate that chondritic meteorites have drawn the oxygen from a different reservoir than has Earth.

Oxygen isotopic compositions are notoriously variable in meteorites, probably because of the reactions of solids with gases from different reservoirs. Recent high-precision isotope analyses have shown that there are also variations in the stable isotopic composition of nongaseous, solid rock-forming elements. These effects are a factor of 10 or more smaller than those of oxygen. An increasing number of papers report isotope anomalies in samples from meteorites and planets.

Poitrasson et al. (2004) published a paper claiming differences in the isotopic composition of Fe between Earth, the Moon, Mars, and Vesta of around 0.1‰ in $\delta^{57}\text{Fe}/^{54}\text{Fe}$. Weyer et al. (2005) reported differences in the isotopic composition of Fe between peridotites and terrestrial basalts, which they found indistinguishable from lunar basalts. These authors conclude that the initial Fe isotopic composition is the same within analytical uncertainties in all solar system materials. Schoenberg and von Blanckenburg (2006) found a larger spread in $\delta^{56}\text{Fe}/^{54}\text{Fe}$ of mantle rocks than Weyer et al. (2005), although on average terrestrial basalts still seem to have slightly higher $\delta^{56}\text{Fe}/^{54}\text{Fe}$ ratios than mantle rocks. Schoenberg and von Blanckenburg (2006) also concluded that Fe isotopes are uniform in all solar system materials. There is, however, agreement among various authors that Fe isotopes do not fractionate during metal/silicate fractionation, that is, core formation. This was concluded by Weyer et al. (2005) and experimentally verified up to pressures of 7.7 GPa by Poitrasson et al. (2009).

In contrast to Fe, Si isotopes fractionate when Si partitions into metal. Several authors have noticed a consistently heavier Si isotopic composition in terrestrial samples compared to differentiated and undifferentiated meteorites (Armstrong et al., 2011; Fitoussi et al., 2009; Georg et al., 2007), except for Chakrabarti and Jacobsen (2010) who did not see this difference. Shahar et al. (2009) have experimentally verified that the distribution of Si between Si-containing metal and silicate melt at 1 GPa and 1800 °C leads to a difference of about 2‰ in $\delta^{30}\text{Si}$ between metal and coexisting silicate phases. Assuming a chondritic Si isotopic composition for the bulk Earth, one can calculate the Si isotopic composition

of the core and mantle during core formation. Based on the difference in Si isotopes between Earth's mantle and chondrites, Fitoussi et al. (2009) estimate about 8% Si in the core, Armstrong et al. (2011) give a range of possible Si contents of 2.5 to 16.8%, consistent with the estimated Si core contents of 7.5%, by assuming a CC Si/Mg ratio in the bulk Earth. Whether there are small variations in Si isotopic composition among meteorites is presently unclear. The general increase in $\delta^{30}\text{Si}$ with the Mg/Si ratio of chondritic meteorites reported by Fitoussi et al. (2009) has not been confirmed by Armstrong et al. (2011). Both studies, however, find a significantly lighter Si isotopic composition of EC. Fitoussi and Bourdon (2012) find that the difference in $\delta^{30}\text{Si}$ between the present Earth's mantle and EC is too large to result from core formation in a proto-Earth with EC Si isotopes. This is remarkable because in many elements, EC closely match the isotopic composition of Earth (e.g., Javoy et al., 2010). The similarity of $\delta^{30}\text{Si}$ in Earth and the Moon (Fitoussi and Bourdon, 2012) requires that the Moon is predominantly made of Earth's mantle material after core formation (see O'Neill, 1991b).

A similar effect as for Si has been proposed for Cr by Moynier et al. (2011). That Earth has higher $\delta^{53}/^{52}\text{Cr}$ and $\delta^{50}/^{52}\text{Cr}$ ratios than any chondritic meteorite is interpreted by these authors as indicating fractionation of Cr isotopes during core formation. We have shown above that a major fraction of Earth's Cr is indeed in the core.

Wiechert and Halliday (2007) reported a very small difference in Mg isotopes between terrestrial mantle rocks and meteorites. Young et al. (2009) also found a small difference in $\delta^{25}\text{Mg}$ of about 0.05‰ between chondritic meteorites and upper mantle xenoliths. Schiller et al. (2010) used a larger dataset of terrestrial samples and concluded that the chondritic Mg isotopic composition is within the range of terrestrial Mg isotopes.

3.1.6.2 Minor and Trace Elements

Isotopic variations are found for many minor and trace elements. Particularly obvious are variable excesses of neutron-rich isotopes, such as ^{54}Cr , ^{50}Ti , ^{62}Ni , and ^{96}Zr , in bulk meteorites and planets. In a recent paper, Warren (2011) has shown that there is a distinct grouping of CC and non-CC in plots of neutron-rich isotopes. An example is shown in Figure 24 that is taken from the paper by Warren (2011). The excesses in ^{54}Cr and ^{50}Ti are significantly larger in CC than in OC, EC, or differentiated meteorites. Earth, Mars, and the Moon plot in all diagrams with the non-CC.

Qin et al. (2011) reported huge local, nanometer-sized excesses of ^{54}Cr in acid-resistant residue of the Orgueil meteorite. These authors estimated that the actual $^{54}\text{Cr}/^{52}\text{Cr}$ enrichments in the grains may be as high as 50 times solar. Such enhancements strongly favor a Type II supernova origin. Qin et al. (2011) further concluded that the variability in bulk $^{54}\text{Cr}/^{52}\text{Cr}$ between meteorite classes indicates a heterogeneous distribution of the ^{54}Cr carrier in the solar protoplanetary disk following a late supernova injection event. Dauphas et al. (2010) identified the carrier of ^{54}Cr anomalies in Orgueil as nanoparticles (<100 nm), most likely spinels with large enrichments in ^{54}Cr relative to the solar composition. Dauphas et al. (2010) also believe that the source of the large ^{54}Cr

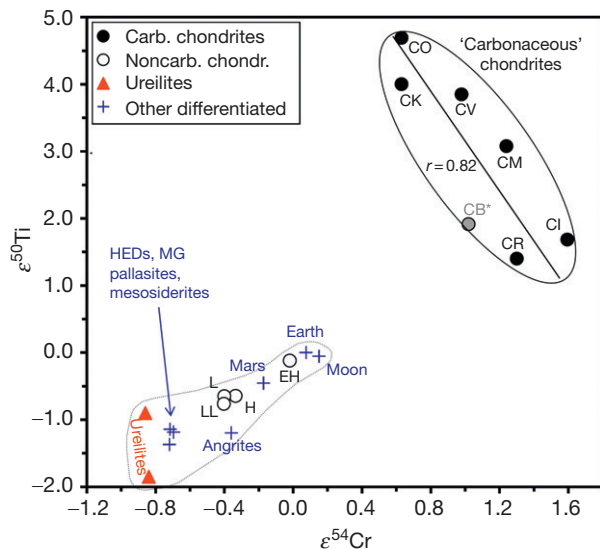


Figure 24 CC and most other planetary materials are clearly separated in a plot of two neutron-rich isotopes $\epsilon^{50}\text{Ti}$ versus $\epsilon^{54}\text{Cr}$. The generally higher fraction of neutron-rich isotopes in CC may indicate a larger heliocentric distance of the formation location of CC, which collected more supernova nanoparticles with extreme anomalies (Dauphas et al., 2010) than the inner solar system materials. Sources of data given in Warren (2011). Reproduced from Warren PH (2011) Stable-isotopic anomalies and the accretionary assemblage of the Earth and Mars: A subordinate role for carbonaceous chondrites. *Earth and Planetary Science Letters* 311: 93–100.

enrichments are grains condensed in supernovae outflows. Other neutron-rich isotopes also likely come as nanoparticles from the same source as ^{54}Cr -containing nanoparticles.

Variations in the s-process components were found earlier in chondritic meteorites. Schönbachler et al. (2005) separated phases in chondritic meteorites by stepwise dissolution enriched in s-process Zr and phases depleted in s-process Zr. These authors believe that s-process-rich presolar SiC grains that did not equilibrate with the rest of the meteorite are responsible for the variations. Similar observations were made on Os by Brandon et al. (2005). Bulk samples from Earth and from various types of meteorites are in all cases identical in their isotopic composition of Zr and Os. The s-process-depleted and s-processed-enriched phases must be present in bulk samples in exactly the same proportions. In primitive, unequilibrated meteorites, these two phases are still physically separable. This is not the case for Mo and Ru, which have measurable isotope variations on the bulk meteorite scale (Burkhardt et al., 2012; Chen et al., 2010; Dauphas et al., 2002). S-, r-, and p-process related bulk meteorite anomalies also have been documented in Ba, Nd, and Sm by Carlson et al. (2007) and Andreasen and Sharma (2007).

A comparison of the isotopic composition of chondritic meteorites and Earth is important for identifying the relationship between Earth and these primitive solar system objects. The bulk Earth composition deduced here shows distinct similarities with CV chondrites in the enrichment of refractory elements, in the Mg/Si ratio, and in the pattern of moderately volatile elements. But the similarity does not extend to isotopes. As shown in Figure 24, Earth is isotopically very different from CV chondrites, not only in Cr and Ti but also in O, Ni,

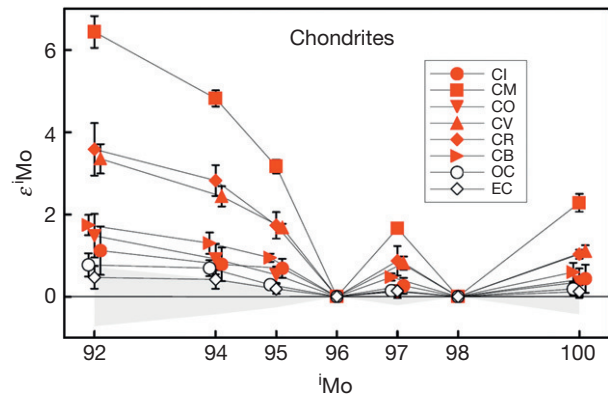


Figure 25 Mo isotope data for chondritic meteorites. The terrestrial Mo is the lowest in all isotopes, when normalized to ^{96}Mo . This excludes models where Earth is made from a mixture of various types of chondritic meteorites. Reproduced from Burkhardt C, Kleine T, Oberli F, Pack A, and Bourdon B (2012) Molybdenum isotope anomalies in meteorites: Constraints on solar nebula evolution and origin of the Earth. *Earth and Planetary Science Letters*, 312: 390–400.

Mo, and several other elements. The opposite effect is with EC that fit, in stable isotopes (except for Li and Si isotopes), reasonably well with Earth but are very different in chemistry as discussed above.

The decoupling of isotope effects with chemistry can be seen best from the position of pallasites in Figure 24 and similar plots by Warren (2011). Main group pallasites in Figure 24 fit with the non-CC, while the rare Eagle Station pallasites (ESP) plot with the CC with regard to its ^{54}Cr isotopic composition (Shukolyukov and Lugmair, 2006). ESP are not plotted in Figure 24 because there are no ^{50}Ti data. But in oxygen isotopes, Eagle Station also plots with CC (Clayton, 1993). This example demonstrates that cosmo- and geochemical processes may produce the same types of meteorites in different formation regions. Basic physicochemical processes are identical, whereas the contamination with tiny particles carrying nucleosynthetic anomalies may be very different. In this sense, we believe that Earth's accretion began under similar conditions under which type 3 CC formed, albeit from reservoirs with different isotopic compositions.

Stable isotopes also provide evidence that Earth is not simply a mixture of different types of chondritic meteorites. Figure 25 is a plot of Mo isotopes in various types of chondritic meteorites. The figure is from Burkhardt et al. (2012). All data are normalized to terrestrial Mo. In this figure, Earth clearly has an end-member composition, that is, one that cannot be produced by mixing various types of chondritic meteorites. Similar arguments can be applied for Ru isotopes as discussed by Burkhardt et al. (2012).

These arguments seem to exclude that meteorites are building blocks of the planets. Meteorites formed in an isotopically distinct nebular region, which is different from the formation region of the planets. Meteorites are not leftover pieces of the planet formation. They have their own characteristic formation regions, at least judging from the stable isotopes. Chemically, Earth and CC must have had a similar formation history.

The atmophile elements H, C, N, and the rare gases are strongly depleted in 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).

3.1.7 Summary

As regards the rock-forming elements, the bulk composition of Earth is basically chondritic (i.e., solar) with approximately equal abundances of Mg, Si, and Fe atoms. From a detailed comparison with chondritic meteorites, it is concluded that the bulk Earth composition is not CI chondritic (i.e., solar) but has similarities to the chemical composition of the CV group of CC:

1. Earth is similarly enriched in refractory elements as CV chondrites.
2. Assuming that Earth's core contains about 7% Si, yields a bulk Earth Mg/Si within the narrow range of CC but very different from OC and EC.
3. Earth and CC show similar patterns of the moderately volatile elements; in particular, both are depleted in Na and Mn to the same degree. EC and OC are also depleted in volatile elements, but their depletion patterns are very different.
4. Earth, chondritic meteorites, and other planets lie approximately on the same $^{53}\text{Cr}/^{52}\text{Cr}$ versus $^{55}\text{Mn}/^{52}\text{Cr}$ isochron, indicating that the depletion of Mn and probably of all other moderately volatile elements in Earth and in CC occurred shortly after the first solids had formed in the solar nebula, during the lifetime of the 3.7 My ^{53}Mn . There is little evidence for loss of volatile elements by later evaporation or impact heating.

There are also differences between the chemistry of type 3 CC and Earth:

1. The bulk Earth has excess Fe relative to the common groups of chondritic meteorites. Silicates may have been lost during collisional growth of Earth involving giant impacts.
2. Earth is more depleted in volatiles than type 3 CC, although the patterns are similar.
3. The terrestrial pattern of very volatile elements (In, Bi, and Cd) is different from chondritic meteorites, possibly reflecting processes during the initial differentiation of Earth.
4. CC have isotope anomalies in Cr, Ti, Ni, Zr, Ba, Nd, and Sm that are not observed in Earth. The stable isotopic composition of several elements in Earth is similar to OC and fits particularly well with EC, except for Li and Si.
5. The HSE in the mantle of Earth have been delivered by a late meteoritic component. Excesses in Pd, Ru, and Rh in the terrestrial pattern make it impossible to identify this component among known types of meteorites.

In summary, the composition of the PM derived here shows that Earth was assembled from material that shows many of the same chemical fractionation processes as the chondritic meteorites. These processes occurred at the initial stage of the solar system formation, under conditions thought to be present in the solar nebula. But the stable isotope record excludes

chondritic meteorites as the 'building blocks' of Earth. Meteorites formed in local environments separated from that part of the inner solar system where much of the material forming the terrestrial planets was sourced.

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