

3.16 Compositional Model for the Earth's Core

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3.16.1	Introduction	559
3.16.2	First-Order Geophysics	559
3.16.3	Constraining the Composition of the Earth's Core	561
3.16.3.1	Observations from Meteorites and Cosmochemistry	562
3.16.3.2	Classification of the Elements	562
3.16.3.3	Compositional Model of the Primitive Mantle and the Bulk Earth	563
3.16.4	A Compositional Model for the Core	564
3.16.4.1	Major and Minor Elements	565
3.16.4.2	The Light Element in the Core	565
3.16.4.3	Trace Elements in the Core	568
3.16.5	Radioactive Elements in the Core	571
3.16.6	Timing of Core Formation	572
3.16.7	Nature of Core Formation	573
3.16.8	The Inner Core, its Crystallization, and Core–Mantle Exchange	574
3.16.9	Summary	574
Acknowledgments		575
References		575

3.16.1 Introduction

The remote setting of the Earth's core tests our ability to assess its physical and chemical characteristics. Extending out to half an Earth radii, the metallic core constitutes a sixth of the planet's volume and a third of its mass (see [Table 1](#) for physical properties of the Earth's core). The boundary between the silicate mantle and the core (CMB) is remarkable in that it is a zone of greatest contrast in Earth properties. The density increase across this boundary represents a greater contrast than across the crust-ocean surface. The Earth's gravitational acceleration reaches a maximum (10.7 m s^{-2}) at the CMB and this boundary is also the site of the greatest temperature gradient in the Earth. (The temperature at the base of the mantle ($\sim 2900 \text{ }^\circ\text{C}$) is not well established, and that at the top of the inner core is even less securely known ($\sim 3500\text{--}4500 \text{ }^\circ\text{C}$.) The pressure range throughout the core (i.e., 136 GPa to $>360 \text{ GPa}$) makes recreating environmental conditions in most experimental labs impossible, excepting a few diamond anvil facilities or those with high-powered, shock-melting guns (see [Chapter 3.15](#)). Thus, our understanding of the core is based on very few pieces of direct evidence and many fragments of indirect observations. Direct evidence comes from seismology, geodesy, geo- and paleomagnetism, and, relatively recently isotope geochemistry (see [Section 3.16.6](#)). Indirect evidence comes from geochemistry, cosmochemistry, and meteoritics; further constraints on the core system are gained from studies in experimental petrology, mineral physics, *ab initio* calculations, and evaluations of the Earth's energy budget (e.g., geodynamo calculations, core crystallization, heat flow across the core–mantle boundary). [Figure 1](#) provides a synopsis of research on the Earth's core, and the relative

relationship between disciplines. Feedback loops between all of these disciplines refine other's understanding of the Earth's core.

3.16.2 First-Order Geophysics

The Earth's three-layer structure (the core, the silicate shell (mantle and crust), and the atmosphere–hydrosphere system) is the product of planetary differentiation and is identified as the most significant geological process to have occurred since the formation of the Earth. Each layer is distinctive in its chemical composition, the nature of its phase (i.e., solid, liquid, and gas), and physical properties. Evidence for the existence and nature of the Earth's core comes from laboratory studies coupled with studies that directly measure physical properties of the Earth's interior including its magnetic field, seismological profile, and orbital behavior, with the latter providing a coefficient of the moment of inertia and a model for the density distribution in the Earth.

There is a long history of knowing indirectly or directly of the existence of Earth's core. Our earliest thoughts about the core, albeit indirect and unwittingly, may have its roots in our understanding of the Earth's magnetic field. The magnetic compass and its antecedents appear to be $\sim 2000 \text{ yr}$ old. F. Gies and J. Gies (1994) report that Chinese scholars make reference to a southpointing spoon, and claim its invention to ca. AD 83 (Han dynasty). A more familiar form of the magnetic compass was known by the twelfth century in Europe. With the discovery of iron meteorites followed by the suggestion that these extraterrestrial specimens came from the interior of fragmented planets in the late-nineteenth century came the earliest

models for planetary interiors. Thus, the stage was set for developing Earth models with a magnetic and metallic core. Later development of geophysical tools for peering into the deep Earth showed that with increasing depth the proportion of metal to rock increases with a significant central region envisaged to be wholly made up of iron.

A wonderful discussion of the history of the discovery of the Earth's core is given in the [Brush \(1980\)](#) paper. The concept of

a core perhaps begins with understanding the Earth's magnetic field. Measurements of the Earth's magnetic field have been made since the early 1500s. By 1600 the English physician and physicist, William Gilbert, studied extensively the properties of magnets and found that their magnetic field could be removed by heating; he concluded that the Earth behaved as a large bar-magnet. In 1832, Johann Carl Friedrich Gauss, together with Wilhelm Weber, began a series of studies on the nature of Earth's magnetism, resulting in the 1839 publication of *Allgemeine Theorie des Erdmagnetismus (General Theory of the Earth's Magnetism)*, demonstrating that the Earth's magnetic field was internally generated.

With the nineteenth-century development of the seismograph, studies of the Earth's interior and core accelerated rapidly. In 1897 Emil Wiechert subdivided the Earth's interior into two main layers: a silicate shell surrounding a metallic core, with the core beginning at ~ 1400 km depth. This was the first modern model of the Earth's internal structure, which is now confirmed widely by many lines of evidence. Wiechert was a very interesting scientist; he invented a seismograph that saw widespread use in the early twentieth century, was one of the founders of the Institute of Geophysics at Göttingen, and was the PhD supervisor of Beno Gutenberg. The discoverer of the Earth's core is considered to be Richard Dixon Oldham, a British seismologist, who first distinguished *P* (compressional) and *S* (shear) waves following his studies of the Assam earthquake of 1897. In 1906 Oldham observed that *P* waves arrived later than expected at the surface antipodes of epicenters and recognized this as evidence for a dense and layered interior. Oldham placed the depth to the core–mantle boundary at 3900 km. Later, [Gutenberg \(1914\)](#) established the core–mantle boundary at 2900 km depth (cf. the modern estimate of 2891 ± 5 km depth; [Masters and Shearer, 1995](#)) and suggested that the core was at least partly liquid ([Gutenberg, 1914](#)). Subsequently, [Jeffreys \(1926\)](#) established that the outer core is liquid, and [Lehmann \(1936\)](#) identified the existence of a solid inner core using seismographic records of large earthquakes, which was later confirmed by [Anderson et al. \(1971\)](#) and [Dziewonski and Gilbert \(1972\)](#) using Earth's free-oscillation frequencies. Finally, [Washington \(1925\)](#) and contemporaries reported that an iron core would have a significant nickel content, based on analogies with iron meteorites and the cosmological abundances of these elements.

The seismological profile of the Earth's core ([Figure 2](#)) combined with the first-order relationship between density

Table 1 Physical properties of the Earth's core

		Units	Refs.
<i>Mass</i>			
Earth	5.9736E+24	kg	1
Inner core	9.675E+22	kg	1
Outer core	1.835E+24	kg	1
Core	1.932E+24	kg	1
Mantle	4.043E+24	kg	1
Inner core to core (%)	5.0%		
Core to Earth (%)	32.3%		
<i>Depth</i>			
Core–mantle boundary	3483 \pm 5	km	2
Inner–outer core boundary	1220 \pm 10	km	2
Mean radius of the Earth	6371.01 \pm 0.02	km	1
<i>Volume relative to planet</i>			
Inner core	7.606E+09 (0.7%)	km ³	
Inner core relative to the bulk core	4.3%		
Outer core	1.694E+11 (15.6%)	km ³	
Bulk core	1.770E+11 (16.3%)	km ³	
Silicate earth	9.138E+11 (84%)	km ³	
Earth	1.083E+12	km ³	
<i>Moment of inertia constants</i>			
Earth mean moment of inertia (<i>I</i>)	0.3299765	<i>Ma</i> ²	1
Earth mean moment of inertia (<i>I</i>)	0.3307144	<i>MR</i> ₀ ²	1
Mantle: <i>I</i> _m / <i>Ma</i> ²	0.29215	<i>Ma</i> ²	1
Fluid core: <i>I</i> _f / <i>Ma</i> ²	0.03757	<i>Ma</i> ²	1
Inner core: <i>I</i> _{ic} / <i>Ma</i> ²	2.35E–4	<i>Ma</i> ²	1
Core: <i>I</i> _{f+ic} / <i>M</i> _{f+ic} <i>a</i> _f ²	0.392	<i>Ma</i> ²	1

1:Yoder (1995), 2:Masters and Shearer (1995).

M is the Earth's mass, *a* is the Earth's equatorial radius, *R*₀ is the radius for an oblate spheroidal Earth, *I*_m is the moment of inertia for the mantle, *I*_f is the moment of inertia for the outer (fluid) core, *I*_{ic} is the moment of inertia for the inner core, and *I*_{f+ic}/*M*_{f+ic}*a*_f² is the mean moment of inertia for the core.

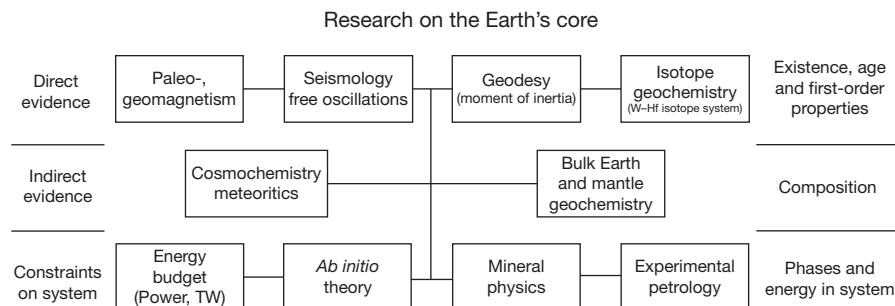


Figure 1 The relative relationship between disciplines involved in research on the Earth's core and the nature of data and information that come from these various investigations. Studies listed in the upper row yield direct evidence on properties of the core. Those in the middle row yield indirect evidence on the composition of the Earth's core, whereas findings from disciplines listed on the bottom row provide descriptions of the state conditions for the core and its formation.

and seismic wave speed velocity (i.e., $V_p = ((K + 4/3\mu)/\rho)^{0.5}$, $V_s = (\mu/\rho)^{0.5}$, $d\rho/dr = -GM_r\rho(r)/r^2\Phi$ (the latter being the Adams-Williamson equation), where V_p is the P -wave velocity, V_s is the S -wave velocity, K is the bulk modulus, μ is the shear modulus, ρ is the density, $\rho(r)$ is the density of the shell within radius r , G is gravitational constant, M_r is the mass of the Earth within radius r , and $\Phi = V_p^2 - (4/3)V_s^2$ provides a density profile for the core that, in turn, is perturbed to be consistent with free oscillation frequencies (Dziewonski and Anderson, 1981). Combining seismological data with mineral physics data (e.g., equation of state (EOS) data for materials at core appropriate conditions) from laboratory studies gives us the necessary constraints for identifying the mineralogical and chemical constituents of the core and mantle.

Birch (1952) compared seismically determined density estimates for the mantle and core with the available EOS data for candidate materials. He argued that the inner core was “a crystalline phase, mainly iron” and the liquid outer core is perhaps some 10–20% less dense than that expected for iron or iron–nickel at core conditions. Later, Birch (1964) showed that the Earth’s outer core is $\sim 10\%$ less dense than that expected for iron at the appropriate pressures and temperatures and proposed that it contained (in addition to liquid iron and nickel) a lighter alloying element or elements such as carbon, or hydrogen (Birch, 1952) or sulfur, silicon, or oxygen (Birch, 1964).

Uncertainties in estimates of the composition of the Earth’s core derive from uncertainties in the core density (or bulk modulus, or bulk sound velocity) and in that of candidate materials (including pure liquid iron) when calculated for the temperatures and pressures of the outer core. Although there is an excellent agreement between the static compression data for ϵ -Fe (and Fe–Ni mixtures) at core pressures (Mao et al., 1990) and isothermal-based Hugoniot data for ϵ -Fe (Brown and McQueen, 1986), extrapolation of these data to core conditions requires knowledge of the thermal contribution to their EOS (see Chapter 3.15). Boehler (2000) calculated an outer core density

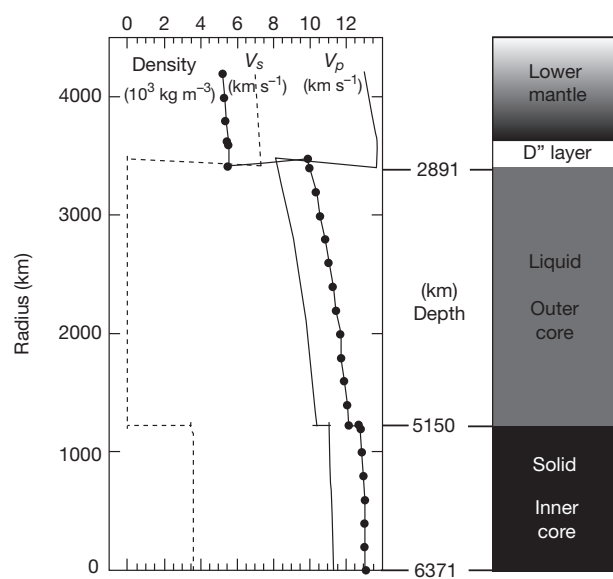


Figure 2 Depth versus P - and S -wave velocity and density for the PREM model (after Dziewonski and Anderson, 1981 and Masters and Shearer, 1995).

deficit of $\sim 9\%$ using these data coupled with an assumed value for the pressure dependence of α (thermal expansion coefficient) and outer core temperatures of 4000–4900 K. In a review of these and other data, Anderson and Isaak (2002) concluded that the core density deficit is $\sim 5\%$ (with a range from 3% to 7%, given uncertainties) and argued that the density deficit is not as high as the often-cited $\sim 10\%$. Their revised estimate is derived from a re-examination of EOS calculations with revised pressure and temperature derivatives for core materials at inner–outer core boundary conditions over a range of temperatures (4800–7500 K). This is a topic of much debate and a conservative estimate of the core density deficit is ~ 5 – 10% .

The solid inner core, which has a radius of 1220 ± 10 km (Masters and Shearer, 1995), represents 5% of the core’s mass and $<5\%$ of its volume. It is estimated to have a slightly lower density than solid iron and, thus, it too would have a small amount of a light element component (Jephcoat and Olson, 1987). Birch (1952) may have recognized this when he said that it is “a crystalline phase, mainly iron.” Like the outer core, uncertainties in the amount of this light element component is a function of seismically derived density models for the inner core and identifying the appropriate temperature and pressure derivatives for the EOS of candidate materials. Hemley and Mao (2001) have provided an estimate of the density deficit of the inner core of 4–5%.

The presence of an iron core in the Earth is also reflected in the Earth’s shape. The shape of the Earth is a function of its spin, mass distribution, and rotational flattening such that there is an equatorial bulge and flattening at the poles. The coefficient of the moment of inertia for the Earth is an expression that describes the distribution of mass within the planet with respect to its rotational axis. If the Earth was a compositionally homogenous planet having no density stratification, its coefficient of the moment of inertia would be $0.4 Ma^2$, with M as the mass of the Earth and a as the equatorial radius. The equatorial bulge, combined with the precession of the equinoxes, fixes the coefficient of the moment of inertia for the Earth at $0.330 Ma^2$ (Yoder, 1995) reflecting a marked concentration of mass at its center (see also Table 1).

Finally, studies of planets and their satellites show that internally generated magnetic fields do not require the existence of a metallic core, particularly given the diverse nature of planetary magnetic fields in the solar system (Stevenson, 2003). Alternatively, the 500+ years of global mapping of the Earth’s magnetic field in time and space demonstrates the existence of the Earth’s central magnetic core (Bloxham, 1995; Merrill et al., 1996). The generation of this field in the core also requires the convection of a significant volume of iron (or similar electrically conducting material) as it creates a self-exciting dynamo (Buffett, 2000). In the Earth, as with the other terrestrial planets, iron is the most abundant element, by mass (Wänke and Dreibus, 1988). Its high solar abundance is the result of a highly stable nuclear configuration and processes of nucleosynthesis in stars.

3.16.3 Constraining the Composition of the Earth’s Core

The major ‘core’ issues in geochemistry include: (1) its composition (both inner and outer core), (2) the nature and

distribution of the light element, (3) whether there are radioactive elements in the core, (4) timing of core formation, and (5) what evidence exists for core–mantle exchange. The answers to some or all of these questions provide constraints on the conditions (e.g., P , T , f_{O_2}) under which the core formed.

3.16.3.1 Observations from Meteorites and Cosmochemistry

That the core is not solely an Fe–Ni alloy, but contains ~5–10% of a light mass element alloy, is about the extent of the compositional guidance that comes from geophysics. Less direct information on the makeup of the Earth is provided by studies of meteorites and samples of the silicate Earth. It is from these investigations that we develop models for the composition of the bulk Earth and primitive mantle (or the silicate Earth) and from these deduce the composition of the core.

The compositions of the planets in the solar system and those of chondritic meteorites provide a guide to the bulk Earth composition (see [Chapter 3.1](#)). However, the rich compositional diversity of these bodies presents a problem insofar as there is no single meteorite composition that can be used to characterize the Earth. The solar system is compositionally zoned; planets with lesser concentrations of volatile elements are closer to the Sun. Thus, as compared to Mercury and Jupiter, the Earth has an intermediate uncompressed density (roughly a proportional measure of metal to rock) and volatile element inventory, and is more depleted in volatile elements than CI-chondrites, the most primitive of all of the meteorites.

There is a wide range of meteorite types, which are readily divided into three main groups: the irons, the stony irons and the stones (see also Volume 1 of the Treatise). With this simple classification, we obtain our first insights into planetary differentiation. All stony irons and irons are differentiated meteorites. Most stony meteorites are chondrites, undifferentiated meteorites, although lesser amounts are achondrites, differentiated stony meteorites. The achondrites make up ~4% of all meteorites, and <5% of the stony meteorites. A planetary bulk composition is analogous to that of a chondrite, and the differentiated portions of a planet – the core, mantle, and crust – have compositional analogues in the irons, stony irons (for core – mantle boundary regions), and achondrites (for mantle and crust).

Among the chondrites there are three main classes: the carbonaceous, enstatite, and ordinary chondrites. One simple way of thinking about these three classes is in terms of their relative redox characteristics. First, the carbonaceous chondrites, some of which are rich in organic carbon, have more matrix and Ca–Al inclusions and are the most oxidized of the chondrites, with iron existing as an FeO component in silicates. Second, the enstatite chondrites are the most reduced, with most varieties containing native metals, especially iron. Finally, the ordinary chondrites, the most abundant meteorite type, have an intermediate oxidation state (see review chapters in Volumes 1 and 2 and [Palme \(2001\)](#)). Due to chemical and isotopic similarities, some researchers have argued that the bulk Earth is analogous to enstatite chondrites ([Javoy, 1995](#)). In contrast, others believe that the formation of the Earth initially began from materials such as the enstatite chondrites with the later 20–40% of the planet's mass

forming from more oxidized accreting materials like the carbonaceous chondrites ([Wänke, 1987](#); [Wänke and Dreibus, 1988](#)). As of early 2000s, we do not have sufficient data to resolve this issue and at best we should treat the chondrites and all meteoritic materials as only a guide to understanding the Earth's composition.

A subclass of the carbonaceous chondrites that uniquely stands out among all others is the CI (or C1) carbonaceous chondrite. These chondrites possess the highest proportional abundances of the highly volatile and moderately volatile elements, are chondrule free, and they possess compositions that match that of the solar photosphere when compared on a silicon-based scale (see also [Chapter 3.1](#)). The photosphere is the top of the Sun's outer convection zone, which can be thought of as an analogue to the Sun's surface. The Sun's photospheric layer emits visible light and hence its composition can be measured spectroscopically. This, plus the fact that the Sun contains >99.9% of the solar system's mass, makes the compositional match with CI carbonaceous chondrites seem all that more significant.

For this review the Earth's composition will be considered to be more similar to carbonaceous chondrites and somewhat less like the high-iron end-members of the ordinary or enstatite chondrites, especially with regard to the most abundant elements (iron, oxygen, silicon, and magnesium) and their ratios. However, before reaching any firm conclusions about this assumption, we need to develop a compositional model for the Earth that can be compared with different chondritic compositions. To do this we need to: (1) classify the elements in terms of their properties in the nebula and the Earth and (2) establish the absolute abundances of the refractory and volatile elements in the mantle and bulk Earth.

3.16.3.2 Classification of the Elements

Elements can be classified according to their volatility in the solar nebular at a specific partial pressure ([Larimer, 1988](#)). This classification scheme identifies the major components (e.g., magnesium, iron, silicon, and nickel), which are intermediate between refractory and volatile, and then assigns the other, less abundant elements to groups based on volatility distinguishing refractory (condensation temperatures >1250 K), moderately volatile (condensation temperatures <1250 K and >600 K), and highly volatile (condensation temperatures <600 K) elements, depending on their sequence of condensation into mineral phases (metals, oxides, and silicates) from a cooling gas of solar composition ([Larimer, 1988](#)). In terms of accretionary models for chondrites and planetary bodies, it is often observed that a model assuming a 10^{-4} atm partial pressure best fits the available data ([Larimer, 1988](#)). Those with the highest condensation temperatures (>1400 K) are the refractory elements (e.g., calcium, aluminum, titanium, zirconium, REE, molybdenum, and tungsten), which occur in all chondrites with similar relative abundances (i.e., chondritic ratios of Ca/Al, Al/Ti, Ti/Zr). Major component elements (aside from oxygen and the gases) are the most abundant elements in the solar system, including silicon, magnesium, and iron (as well as cobalt and nickel); these elements have condensation temperatures of ~1250 K. Moderately volatile elements (e.g., chromium, lithium, sodium, potassium, rubidium, manganese, phosphorus,

iron, tin, and zinc) have condensation temperatures of $\sim 1250\text{--}600\text{ K}$ (Palme et al., 1988), whereas highly volatile elements (e.g., thallium, cadmium, bismuth, and lead) have condensation temperatures $\sim 600\text{--}400\text{ K}$. Below this temperature the gas-phase elements (carbon, hydrogen, and nitrogen) condense. The relative abundance ratios of the major components, moderately volatile and highly volatile elements all vary considerably between the different types of chondritic meteorites. Figure 3 illustrates the differing proportions of the major component elements in chondrite groups and the Earth, which together with oxygen make up some 90% of the material in the Earth and other terrestrial planets.

Elements can also be classified according to their chemical behavior based on empirical observations from meteorites and systems in the Earth; this leads to the following groups: lithophile, siderophile, chalcophile, or atmophile. The lithophile elements are ones that bond readily with oxygen and are concentrated in the silicate shell (crust and mantle) of the Earth. The siderophile elements readily bond with iron and are concentrated in the core. The chalcophile elements bond readily with sulfur and are distributed between the core and mantle, with a greater percentage of them likely to be in the core. Finally, the atmophile elements (e.g., hydrogen, carbon, nitrogen, oxygen, and noble gases) are gaseous and are concentrated in the atmosphere–hydrosphere system surrounding the planet. A combination of these two different classification

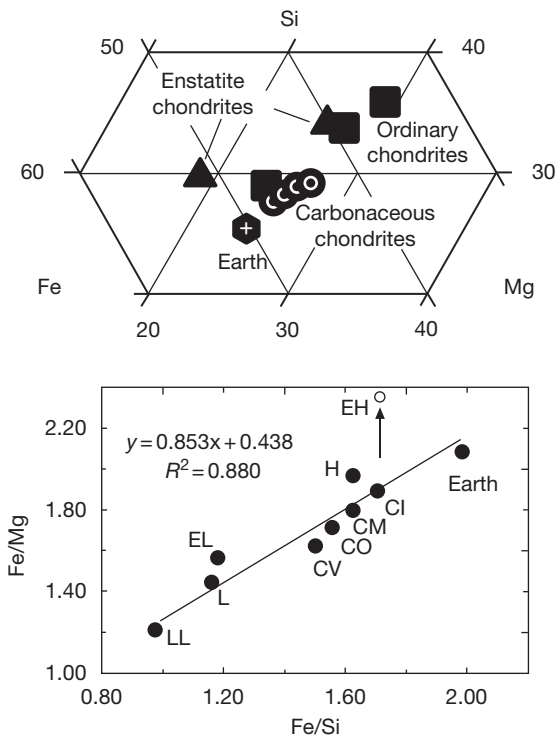


Figure 3 A ternary plot (upper) and binary ratio plot (lower) of the differing proportions (in wt%) of Si, Fe, and Mg (three out of the four major elements) in chondrites and the Earth. These elements, together with oxygen, constitute $>90\%$ by mass of chondrites, the Earth, and other terrestrial planets. Data for the chondrites are from Wasson and Kellemeyn (1988) and for the Earth are from Table 2. The regression line is derived using only chondrites and does not include the EH data.

schemes provides a better understanding of the relative behavior of the elements, particularly during accretion and large-scale planetary differentiation.

Developing a model for the composition of the Earth and its major reservoirs can be established in a four-step process. The first involves estimating the composition of the silicate Earth (or primitive mantle, which includes the crust plus mantle after core formation). The second step involves defining a volatility curve for the planet, based on the abundances of the moderately volatile and highly volatile lithophile elements in the silicate Earth, assuming that none have been sequestered into the core (i.e., they are truly lithophile). The third step entails calculating a bulk Earth composition using the planetary volatility curve established in step two, chemical data for chondrites, and the first-order features of the planets in the solar system. Finally, a core composition is extracted by subtracting the mantle composition from the bulk planetary composition, revealing the abundances of the siderophile and chalcophile elements in the core. Steps three and four are transposable with different assumptions, with the base-level constraints being the compositions of meteorites and the silicate Earth and the solar system's overall trend in the volatile element abundances of planets outward from the Sun.

3.16.3.3 Compositional Model of the Primitive Mantle and the Bulk Earth

The silicate Earth describes the solid Earth minus the core. There is considerable agreement about the major, minor, and trace element abundances in the primitive mantle (Allegre et al., 1995; McDonough and Sun, 1995; see Chapter 3.1). The relative abundances of the lithophile elements (e.g., calcium, aluminum, titanium, REE, lithium, sodium, rubidium, boron, fluorine, zinc, etc.) in the primitive mantle establish both the absolute abundances of refractory elements in the Earth and the planetary signature of the volatile element depletion pattern (Figure 4). The details of how these compositional models are developed can be found in Allegre et al. (1995); McDonough and Sun (1995), and Palme and O'Neill (Chapter 3.1). A model composition for the silicate Earth is given in Table 2, which is adapted from McDonough (2001); Palme and O'Neill (Chapter 3.1) present a similar model.

A first-order assumption is that lithophile elements, inclusive of the refractory, moderately volatile, and highly volatile ones, are excluded from the core. The moderately volatile and highly volatile lithophiles are depleted relative to those in CI-chondrites. Together, the lithophiles describe a coherent depletion or volatility pattern. This negative correlation (Figure 4) thus establishes the planetary volatile curve at $\sim 1\text{ AU}$, which is an integrated signature of accreted nebular material in the coalescing region of the proto-Earth. By comparison, Mars has a less depleted abundance pattern (Wänke, 1981), whereas Mercury has a more depleted abundance pattern (BVSP, 1981). The most significant feature of this pattern is that potassium follows all of the other moderately volatile and highly volatile lithophiles. This observation demonstrates that the potassium budget of the silicate Earth is sufficient to describe that in the planet and argue against any sequestration of potassium into the core.

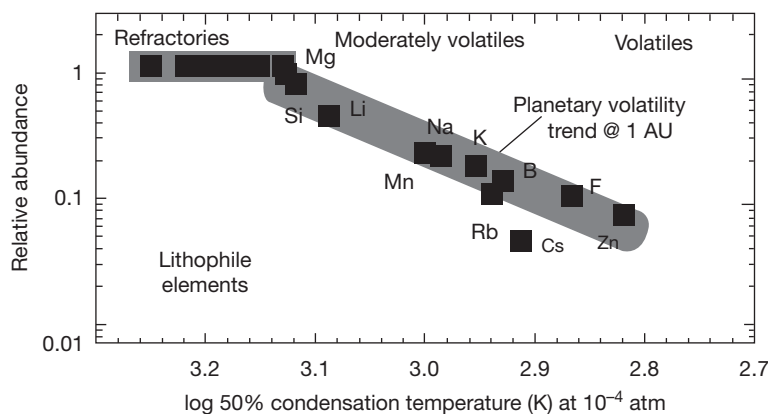


Figure 4 The relative abundances of the lithophile elements in the primitive mantle (or silicate Earth) plotted versus the log of the 50% condensation temperature (K) at 10^{-4} atm pressure. The relative abundances of the lithophile elements are reported as normalized to CI carbonaceous chondrite on an equal basis of Mg content. The planetary volatility trend (negative sloping shaded region enclosing the lower temperature elements) establishes integrated flux of volatile elements at 1 AU. Data for condensation temperatures are from Wasson (1985); chemical data for the chondrites are from Wasson and Kallemeyn (1988) and for the Earth are from Table 2.

Table 2 The composition of the silicate Earth

H	100	Zn	55	Pr	0.25
Li	1.6	Ga	4	Nd	1.25
Be	0.07	Ge	1.1	Sm	0.41
B	0.3	As	0.05	Eu	0.15
C	120	Se	0.075	Gd	0.54
N	2	Br	0.05	Tb	0.10
O (%)	44	Rb	0.6	Dy	0.67
F	15	Sr	20	Ho	0.15
Na (%)	0.27	Y	4.3	Er	0.44
Mg (%)	22.8	Zr	10.5	Tm	0.068
Al (%)	2.35	Nb	0.66	Yb	0.44
Si (%)	21	Mo	0.05	Lu	0.068
P	90	Ru	0.005	Hf	0.28
S	250	Rh	0.001	Ta	0.037
Cl	17	Pd	0.004	W	0.029
K	240	Ag	0.008	Re	0.0003
Ca (%)	2.53	Cd	0.04	Os	0.003
Sc	16	In	0.01	Ir	0.003
Ti	1200	Sn	0.13	Pt	0.007
V	82	Sb	0.006	Au	0.001
Cr	2625	Te	0.012	Hg	0.01
Mn	1045	I	0.01	Tl	0.004
Fe (%)	6.26	Cs	0.021	Pb	0.15
Co	105	Ba	6.6	Bi	0.003
Ni	1960	La	0.65	Th	0.08
Cu	30	Ce	1.68	U	0.02

Concentrations are given in $\mu\text{g g}^{-1}$ (ppm), unless stated as '%,' which are given in wt%.

Data for the content of lithophile elements in the Earth plus knowledge of the iron content of the mantle and core together establish a bulk Earth compositional model (McDonough, 2001). This model assumes chondritic proportions of Fe/Ni in the Earth, given limited Fe/Ni variation in chondritic meteorites (see below). This approach yields an Fe/Al of 20 ± 2 for the Earth. Aluminum, a refractory lithophile element, is considered the least likely of the lithophile elements (e.g., silicon, magnesium, and calcium) to be incorporated in the core. Thus, an aluminum content for the mantle translates directly into the aluminum content for the bulk Earth. This tightly constrained

Fe/Al value also provides a first-order compositional estimate of the planet that requires no knowledge of light elements in the core.

Chondritic meteorites display a range of Fe/Al ratios, with many having a value close to 20 (Allegre et al., 1995), although high Fe/Al values (35) are found in the iron-rich (EH) enstatite chondrites (Wasson and Kallemeyn, 1988). Combining these data and extending the depletion pattern for the abundances of nonrefractory, nonlithophile elements provides a model composition for the bulk Earth (Figure 5). A model composition for the bulk Earth is given in Table 3, which is adapted from McDonough (2001); Palme and O'Neill (Chapter 3.1) present a similar model. In terms of major elements this Earth model is iron and magnesium rich and coincident with the Fe/Mg–Fe/Si compositional trend established by chondrites (Figure 3). The Earth's volatility trend is comparable, albeit more depleted, than that of other carbonaceous chondrites (data in gray field in Figure 5).

3.16.4 A Compositional Model for the Core

As stated earlier, the Earth's core is dominantly composed of a metallic Fe–Ni mixture. This fact is well established by seismic data (P -wave velocity, bulk modulus, and density), geodynamo observations (the need for it to be reasonably good electrical conductor), and cosmochemical constraints. This then requires that the core, an iron- and nickel-rich reservoir, chemically balances the silicate Earth to make up a primitive, chondritic planet. Many iron meteorites, which are mixtures of iron and nickel in various proportions, are pieces of former asteroidal cores. These meteorites provide insights into the compositions of smaller body cores, given they are products of low-pressure differentiation, whereas the Earth's core likely formed under markedly different conditions (see Chapter 3.12). Thus, the Earth's core superficially resembles an iron meteorite; however, such comparisons are only first-order matches and in detail we should anticipate significant differences given contrasting processes involved in their formation.

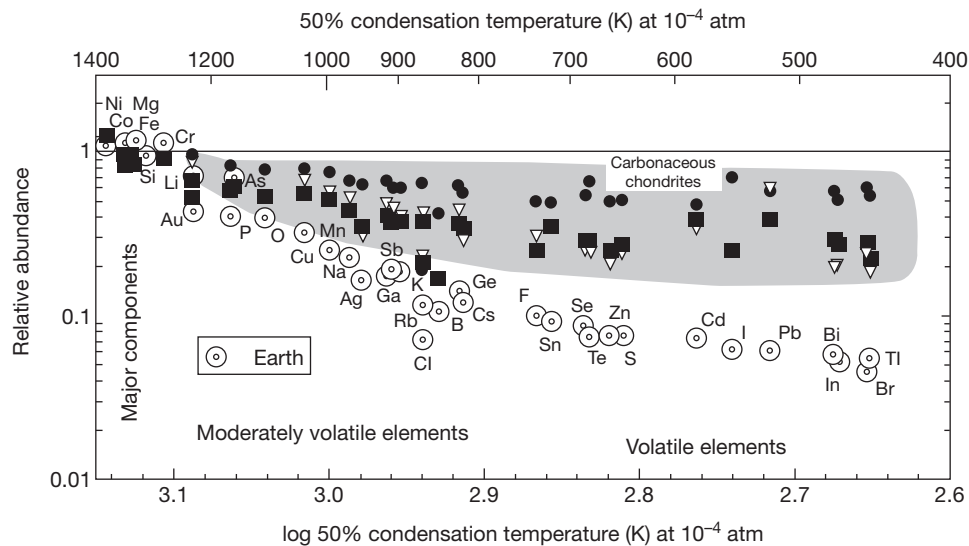


Figure 5 The relative abundances of the elements in the Earth and various carbonaceous chondrites plotted versus the log of the 50% condensation temperature (K) at 10^{-4} atm pressure. Data are normalized to CI carbonaceous chondrite on an equal basis of Mg content. The overall volatility trend for the Earth is comparable to that seen in these chondrites. The carbonaceous chondrites include CM (filled circles), CV (filled squares), and CO (open triangles) and define the shaded region. Data for condensation temperatures are from Wasson (1985); chemical data for the chondrites are from Wasson and Klemmeyn (1988) and for the Earth are from Table 3.

Table 3 The composition of the bulk Earth

H	260	Zn	40	Pr	0.17
Li	1.1	Ga	3	Nd	0.84
Be	0.05	Ge	7	Sm	0.27
B	0.2	As	1.7	Eu	0.10
C	730	Se	2.7	Gd	0.37
N	25	Br	0.3	Tb	0.067
O (%)	29.7	Rb	0.4	Dy	0.46
F	10	Sr	13	Ho	0.10
Na (%)	0.18	Y	2.9	Er	0.30
Mg (%)	15.4	Zr	7.1	Tm	0.046
Al (%)	1.59	Nb	0.44	Yb	0.30
Si (%)	16.1	Mo	1.7	Lu	0.046
P	715	Ru	1.3	Hf	0.19
S	6350	Rh	0.24	Ta	0.025
Cl	76	Pd	1	W	0.17
K	160	Ag	0.05	Re	0.075
Ca (%)	1.71	Cd	0.08	Os	0.9
Sc	10.9	In	0.007	Ir	0.9
Ti	810	Sn	0.25	Pt	1.9
V	105	Sb	0.05	Au	0.16
Cr	4700	Te	0.3	Hg	0.02
Mn	800	I	0.05	Tl	0.012
Fe (%)	32.0	Cs	0.035	Pb	0.23
Co	880	Ba	4.5	Bi	0.01
Ni	18200	La	0.44	Th	0.055
Cu	60	Ce	1.13	U	0.015

Concentrations are given in $\mu\text{g g}^{-1}$ (ppm), unless stated as '%', which are given in wt%.

3.16.4.1 Major and Minor Elements

A compositional model for the primitive mantle and bulk Earth is described above, which indirectly prescribes a core composition, although it does not identify the proportion of siderophile and chalcophile elements in the core and mantle. The mantle abundance pattern for the lithophile elements

shown in Figure 4 provides a reference state for reviewing the abundances of the siderophile and chalcophile elements in the silicate Earth, which are shown in Figure 6. All of the siderophile (except gallium) and chalcophile elements plot below the shaded band that defines the abundance pattern for the lithophile elements. That these nonlithophile elements fall below this band (i.e., the planetary volatility trend) indicates that they are depleted in the mantle, and therefore the remaining planetary complement of these elements are in the core. The relative effects of core subtraction are illustrated in both panels with light-gray arrows, extending downward from the planetary volatility trend. The displacement length below the volatility trend (or length of the downward-pointing arrow) reflects the element's bulk distribution coefficient between core and mantle (e.g., bulk $D^{\text{metal/silicate}}$ for $\text{Mo} > \text{P} \approx \text{Sb}$).

By combining the information derived from Figures 4–6, one can construct a compositional model for the Earth's core (Table 4), which is adapted from McDonough (1999). A first-order comparison of the composition of the bulk Earth, silicate Earth, and core in terms of weight percent and atomic proportion is presented in Table 5. The compositional model for the core has a light element composition that seeks to fit the density requirements for the outer core and is consistent with cosmochemical constraints. Significantly, along with iron and nickel the core contains most of the planet's sulfur, phosphorus, and carbon budget. Finally, this model composition is notable in that it is devoid of radioactive elements. The discussion that follows reviews the issues associated with compositional models for the core.

3.16.4.2 The Light Element in the Core

Given constraints of an outer core density deficit of 5–10% and a host of candidate elements (e.g., hydrogen, carbon, oxygen,

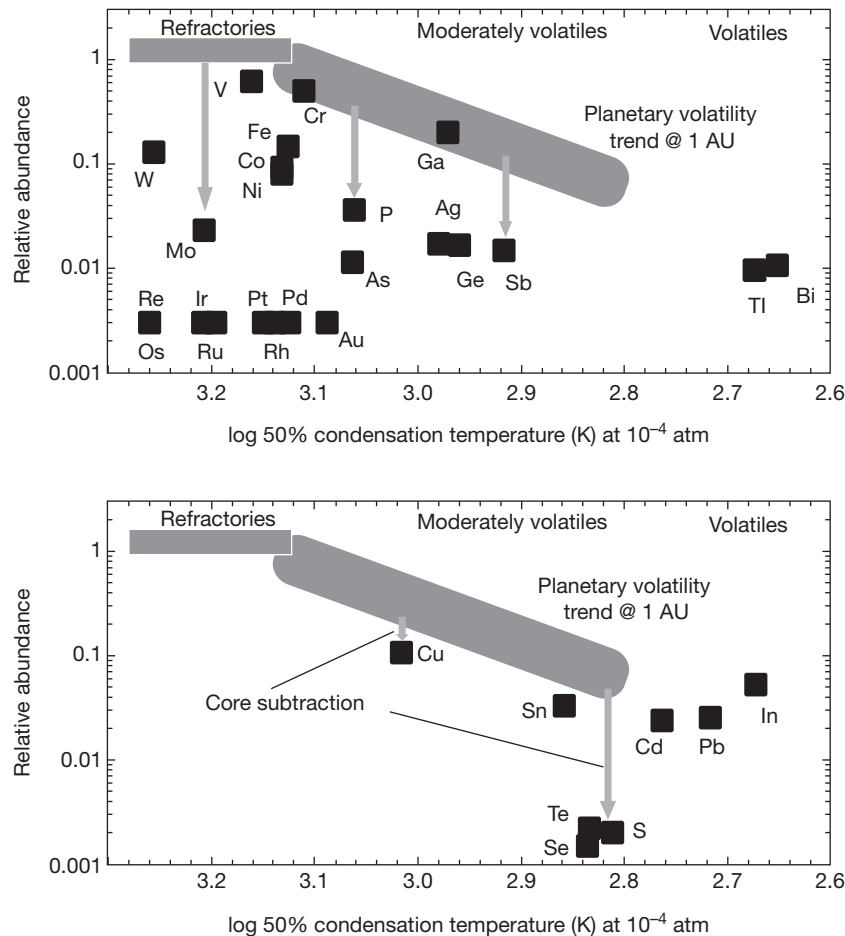


Figure 6 The relative abundances of the siderophile elements (upper panel) and chalcophile elements (lower panel) in the primitive mantle (or silicate Earth) plotted versus the log of the 50% condensation temperature (K) at 10^{-4} atm pressure. Data are normalized to CI carbonaceous chondrite on an equal basis of Mg content. The gray shaded region illustrates the relative abundances of the lithophile elements as reported in Figure 4. The light gray, downward pointing arrows reflect the element's bulk distribution coefficient between core and mantle during core formation; the longer the length of the arrow, the greater the bulk D (data sources are as in Figure 4).

silicon, and sulfur), we need to evaluate the relative potential of these elements to explain core density deficit. Uniformly, the bolstering of one's view for these components in the core involve metallurgical or cosmochemical arguments, coupled with the identification of candidate minerals found in meteorites, particularly iron meteorites and reduced chondrites (the classic example being the high-iron (EH) enstatite chondrite).

Washington (1925), of the Carnegie Institution of Washington, developed a model for the chemical composition of the Earth based on the Wiechert structural model, the Oldham–Gutenberg revised core radius, and the newly derived Adams–Williamson relationship (Williamson and Adams, 1923) for determining the density profile of the planet. Washington's model for the core assumed an average density for the core of $\sim 10 \text{ g cm}^{-3}$ (cf. $\sim 11.5 \text{ g cm}^{-3}$ for today's models), and a "considerable amount, up to $\sim 5\%$ or so, of phosphides (schreibersite, $(\text{Fe,Ni})_3\text{P}$), carbides (cohenite, Fe_3C), sulfides (troilite, FeS) and carbon (diamond and graphite)." This amazing and insightful model, which is now ~ 90 yr old, provides us with a good point from which to consider the light element component in the core.

There are good reasons to assume that the core contains some amount of carbon, phosphorus, and sulfur. These three elements are among the 12 most common in the Earth that account for $>99\%$ of the total mass (Table 5), as based on geochemical, cosmochemical, and meteoritical evidence. Seven out of 12 of these elements (not including carbon, phosphorus, and sulfur) are either refractory or major component elements, and so their abundances in the Earth are relatively fixed for all planetary models (see also Figure 2). The remaining five elements are sodium, chromium, carbon, phosphorus, and sulfur (Table 5); all of these are highly volatile to moderately volatile and estimates of their abundances in the bulk Earth and core are established from cosmochemical constraints. A significant question concerning the abundance of carbon, phosphorus, and sulfur in the core, however, is whether their incorporation into the core can account for the density discrepancy?

The planetary volatility trend illustrated in Figures 4 and 5 does not extend out to the lowest temperature components, including the ices and gases (e.g., hydrogen, carbon, nitrogen,

oxygen, and the noble gases). Estimates for the Earth's content of these components (Figure 7) are from McDonough and Sun (1995) and McDonough (1999, 2001) and are based on data for the Earth's mantle and a comparison of carbonaceous chondrite data. Figure 7 provides a comparison of the Earth's estimate of these elements relative to the data for chondrites; the estimate for the Earth comes from an extrapolation of the trend shown in Figure 5. Although these extrapolations can only provide an approximate estimate, the abundance of carbon in the Earth is suggested to be of the order <0.1 wt%. This estimate translates to a core having only ~0.2 wt% carbon (Tables 3 and 4). By comparison Wood (1993) estimated a

factor of 10–20 times more carbon in the core. Wood's estimate seems most unlikely insofar as it is inconsistent with data for meteorites, which are not markedly enriched in highly volatile elements (Figure 7). This view is untenable when compared with data trends in Figure 5 for the Earth and the carbonaceous chondrites. It is also noted that the Earth's budget for hydrogen and nitrogen are such that the core would likely contain a minor amount of these elements. The consequences of having hydrogen in the core are significant and have been reviewed by Williams and Hemley (2001).

There is ~90 ppm of phosphorus in the silicate Earth (McDonough et al., 1985), and the bulk Earth is estimated to have ~0.1 wt% phosphorus. Using the relationships in Figure 6 the core is thus estimated to have ~0.20 wt% phosphorus (Table 4). Thus, 90% of the planet's inventory of phosphorus is in the core (Table 6) and the core's metal/silicate phosphorus enrichment factor is ~22. Similarly, the core hosts, ~90% of the planet's carbon budget, and has a metal/silicate enrichment factor only slightly lower at ~17.

The sulfur content of the core is said to be ~1.5–2 wt% (McDonough and Sun, 1995; Dreibus and Palme, 1996). This number is based on calculating the degree of sulfur depletion in the silicate Earth relative to the volatility trend (Figure 6). Figure 8 illustrates the problem with suggesting that the core contains 10% sulfur, which is commonly invoked as the light element required to compensate for the density deficit in the outer core. Accordingly, the total sulfur, carbon, and phosphorus content of the core constitute only a minor fraction (~2.5 wt%) and this mixture of light elements cannot account for the core's density discrepancy. Thus, it is likely that there is another, more abundant, light element in the core in addition to these other components.

A model core composition has been constructed using silicon as the other light element in the outer core, which is also consistent with evidence for core formation at high pressures (e.g., 20–30 GPa; see Chapter 3.15). This model is at best tentative, although comparisons of Mg/Si and Fe/Si in the Earth and chondrites (Figure 2) show that it is permissible. Silicon is known to have siderophilic behavior under highly reducing conditions and is found as a metal in some enstatite chondrites. A number of earlier models have suggested silicon

Table 4 The composition of the Earth's core

H	600	Zn	0	Pr	0
Li	0	Ga	0	Nd	0
Be	0	Ge	20	Sm	0
B	0	As	5	Eu	0
C (%)	0.20	Se	8	Gd	0
N	75	Br	0.7	Tb	0
O (%)	0	Rb	0	Dy	0
F	0	Sr	0	Ho	0
Na (%)	0	Y	0	Er	0
Mg (%)	0	Zr	0	Tm	0
Al (%)	0	Nb	0	Yb	0
Si (%)	6.0	Mo	5	Lu	0
P (%)	0.20	Ru	4	Hf	0
S (%)	1.90	Rh	0.74	Ta	0
Cl	200	Pd	3.1	W	0.47
K	0	Ag	0.15	Re	0.23
Ca (%)	0	Cd	0.15	Os	2.8
Sc	0	In	0	Ir	2.6
Ti	0	Sn	0.5	Pt	5.7
V	150	Sb	0.13	Au	0.5
Cr (%)	0.90	Te	0.85	Hg	0.05
Mn	300	I	0.13	Tl	0.03
Fe (%)	85.5	Cs	0.065	Pb	0.4
Co	0.25	Ba	0	Bi	0.03
Ni (%)	5.20	La	0	Th	0
Cu	125	Ce	0	U	0

Concentrations are given in $\mu\text{g g}^{-1}$ (ppm), unless stated as '%', which are given in wt%.

Table 5 The composition of the bulk Earth, mantle, and core and atomic proportions for abundant elements

wt%	Earth	Mantle	Core	Atomic prop.	Earth	Mantle	Core
Fe	32.0	6.26	85.5	Fe	0.149	0.024	0.768
O	29.7	44	0	O	0.483	0.581	0.000
Si	16.1	21	6	Si	0.149	0.158	0.107
Mg	15.4	22.8	0	Mg	0.165	0.198	0.000
Ni	1.82	0.20	5.2	Ni	0.008	0.001	0.044
Ca	1.71	2.53	0	Ca	0.011	0.013	0.000
Al	1.59	2.35	0	Al	0.015	0.018	0.000
S	0.64	0.03	1.9	S	0.005	0.000	0.030
Cr	0.47	0.26	0.9	Cr	0.002	0.001	0.009
Na	0.18	0.27	0	Na	0.002	0.002	0.000
P	0.07	0.009	0.20	P	0.001	0.000	0.003
Mn	0.08	0.10	0.30	Mn	0.000	0.000	0.000
C	0.07	0.01	0.20	C	0.002	0.000	0.008
H	0.03	0.01	0.06	H	0.007	0.002	0.030
Total	99.88	99.83	99.97	Total	1.000	1.000	1.000

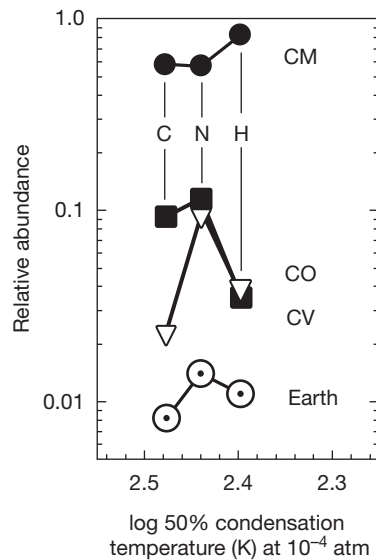


Figure 7 The relative abundances of C, N, and H in the Earth plotted versus the log of the 50% condensation temperature (K) at 10^{-4} atm pressure. The Earth's estimate is based on compositional estimates of these gases in the mantle and the Earth's surface, as well as by comparison with data for carbonaceous chondrites (data sources are as in [Figure 5](#)).

Table 6 The metal/silicate enrichment factor and the proportion of element in the core relative to the planet

Elements	Metal/silicate enrichment factor	% of planetary inventory in the core
Re, PGE	>800	98
Au	~500	98
S, Se, Te, Mo, As	~100	96
N	~40	97
Ni, Co, Sb, P	~25	93
Ag, Ge, C, W	~17	91
Fe (%)	~14	87
Cl, Br, and I	10–15	85
Bi and Tl	~10	80
H and Hg	~6	70
Cu, Sn, Cd, Cr	3–4	60–65
Cs and Pb	~3	55–60
V	~2	50
Si and Mn	0.3	~10

as the dominant light element in core ([Macdonald and Knopoff, 1958](#); [Ringwood, 1959](#); [Wänke, 1987](#); [O'Neill, 1991b](#); [Allegre et al., 1995](#); [O'Neill and Palme, 1997](#)). The estimate for silicon in the core is based on the volatility curve for lithophile elements in the Earth ([Figure 4](#)).

An alternative case can be made for oxygen as the predominant light element in the core. On the grounds of availability, oxygen is a good candidate; it is the second most abundant element in the Earth and only a few percent might be needed to account for the core's density discrepancy. However, [O'Neill et al. \(1998\)](#) point out that oxygen solubility in iron liquids increases with temperature but decreases with pressure and thus showed that only ~2% or less oxygen could be dissolved

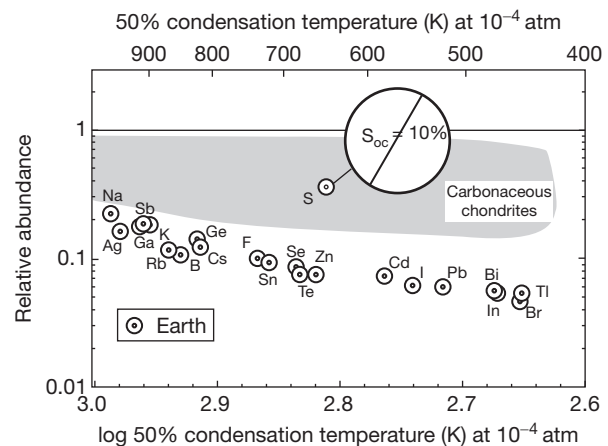


Figure 8 An illustration showing where S would plot if the core contained 10 wt% sulfur so to account for the core's density discrepancy (see text for further discussion). The relative abundances of the elements in the Earth are plotted versus the log of the 50% condensation temperature (K) at 10^{-4} atm pressure. Data are normalized to CI carbonaceous chondrite on an equal basis of Mg content. The overall volatility trend for the Earth is comparable to that seen in these chondrites. The shaded region for the carbonaceous chondrites is the same as in [Figure 5](#) (data sources are as in [Figure 5](#)).

into a core forming melt. The planetary volatility trend provides no guidance to the core's oxygen abundance. A plot of the log 50% condensation temperature versus element abundance (i.e., [Figure 5](#)) does not consider oxygen, because its 50% condensation temperature is not considered in systems where it is the dominant element in rocks and water ice. The core and Earth model composition, assuming oxygen as the light element in the core, is presented in [Table 7](#), along with that for the silicon-based model. Both model compositions attempt to fit the density requirements for the outer core by assuming a mean atomic number of ~23, following [Birch \(1966\)](#). In terms of the light-element-alloy component in the core, this results in ~9% (by weight) for the silicon-based model and ~6% (by weight) for the oxygen-based model ([Table 7](#)).

Less attractive models that consider complex mixtures (e.g., Si–O mixture) are unlikely, given the conditions required for core formation. [O'Neill et al. \(1998\)](#), [Hillgren et al. \(2000\)](#), and [Li and Fei \(Chapter 3.15\)](#) have reviewed the literature on the topic concluding that silicon and oxygen are mutually exclusive in metallic iron liquids over a range of pressures and temperatures. Until there is a clear resolution as to which compositional model is superior, we must entertain multiple hypotheses on the core's composition. The two compositional models for the core presented here (a silicon-bearing core versus an oxygen-bearing core) are offered as competing hypotheses.

3.16.4.3 Trace Elements in the Core

The abundance of trace siderophile elements in the bulk Earth (and that for the core) may be constrained by examining their abundance ratios in chondrites. [Figure 9](#) presents data for various groups of chondrites, which show limited variation for Fe/Ni (17.5) and Ni/Co (20), and slightly more variation

for Fe/Cr (67) and Cr/V (45). Using the iron content for the core and the silicate Earth abundances for iron, nickel, cobalt, chromium, and vanadium, the Earth's core composition is established by assuming chondritic ratios of the elements for the planet. Following similar lines of reasoning for siderophile and chalcophile elements, the trace element composition of the core is also determined (Tables 4 and 6).

Based on these results, the core appears to be rich in chromium and vanadium (i.e., 50–60% of the planet's budget for these elements, Table 6), with a minor amount of manganese in the core (~10% of the planet's budget). Discussions relating to incorporation of chromium into the core usually also involve that for manganese and vanadium, because the partitioning behavior of these three elements during core formation may have been

similar (Ringwood, 1966; Dreibus and Wänke, 1979; Drake et al., 1989; Ringwood et al., 1990; O'Neill, 1991a; Gessmann and Rubie, 2000). However the model presented here does not take into account element partitioning behavior during core formation, it is solely based on the planetary volatility trend and a model composition for the silicate Earth.

The minor amount of manganese in the core reflects the volatility model assumed for this element. O'Neill and Palme (1997) argue that manganese and sodium have similar volatilities based on the limited variation in Mn/Na ratios in chondrites (see also Chapter 3.1). However, a plot of Na/Ti versus Mn/Na in chondrites (Figure 10) shows that indeed Mn/Na varies as a function of volatility; this illustration monitors volatility by comparing titanium, a refractory lithophile element, with sodium, a moderately lithophile element. Therefore, given the planetary volatility trend (Figure 4) and a reasonably well-constrained value for Na/Ti in the silicate Earth (McDonough and Sun, 1995), one estimates a planetary Mn/Na value of 0.45 for the Earth, implying that the core hosts ~10% of the planet's manganese budget.

The behavior of gallium, a widely recognized siderophile element, during core formation appears to be the most anomalous; this is most clearly illustrated by noting that gallium plots directly on the planetary volatility trend (Figure 6, top panel), indicating its undepleted character in the mantle. This result implies that there is little to no gallium in the Earth's core, which is a most unexpected result. The silicate Earth's gallium content of 4 ppm is well established and there is little uncertainty to this number (McDonough, 1990). In the silicate Earth gallium follows aluminum (these elements are above one another on the periodic table) during magma generation, as well as during the weathering of rocks, with overall limited and systematic variations in Al/Ga values in rocks. That gallium plots within the field defined by the moderately volatile and highly volatile lithophile elements (Figure 6) suggests that either the assumed temperature at 50% condensation is incorrect (unlikely given a wide spectrum of supporting meteorite data), or gallium behaves solely as a lithophile element during core formation. If the latter is true, then determining under what conditions gallium becomes wholly lithophile provides an important constraint on core formation.

Table 7 Compositional comparison of two models for the Earth and core

wt%	Si-bearing		O-bearing	
	Earth	Core	Earth	Core
Fe	32.0	85.5	32.9	88.3
O	29.7	0	30.7	3
Si	16.1	6	14.2	0
Ni	1.82	5.2	1.87	5.4
S	0.64	1.9	0.64	1.9
Cr	0.47	0.9	0.47	0.9
P	0.07	0.20	0.07	0.20
C	0.07	0.20	0.07	0.20
H	0.03	0.06	0.03	0.06
Mean atomic #		23.5		23.2
Atomic proportions				
Fe		0.768		0.783
O		0.000		0.093
Si		0.107		0.000
Ni		0.044		0.045
S		0.030		0.029
Cr		0.009		0.009
P		0.003		0.003
C		0.008		0.008
H		0.030		0.029
Total		1.000		1.000

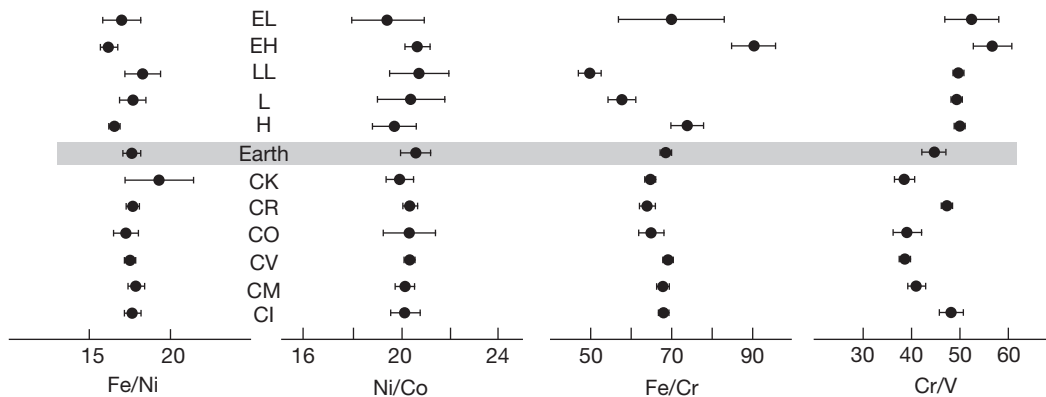


Figure 9 A plot of the variation in Fe/Ni, Ni/Co, Fe/Cr, and Cr/V values in various chondrites and the Earth. The different groups of carbonaceous chondrites include CI, CM, CV, CO, CR, and CK; the ordinary chondrites include H-, L-, and LL-types, and the enstatite chondrites include EH- and EL-types. The error bars represent the 1 SD of the data population. The Earth's composition is shown in the shaded bar and data are from Table 3 (including data are from various papers of Wasson and Kellemeyn cited in Wasson and Kellemeyn (1988)).

The composition of the Earth's core, which was likely established at relatively high pressures (~20 GPa; see Chapters 3.12 and 3.15), can be compared with that of iron meteorites, which are low-pressure (<1 GPa) differentiates. Wasson's (1985) chemical classification of iron meteorites uses nickel, gallium, germanium, and iridium to divide them into 13 different groups. He shows that gallium is clearly a siderophile element found in abundance in the metal phases of iron meteorites. Also, gallium is highly depleted in achondrites. A comparison of the composition of the Earth's core with that of different iron meteorites is given in Figure 11. The Earth's core and some iron meteorites have comparable nickel, germanium, and iridium contents, albeit on the low end of the nickel spectrum. In contrast, the

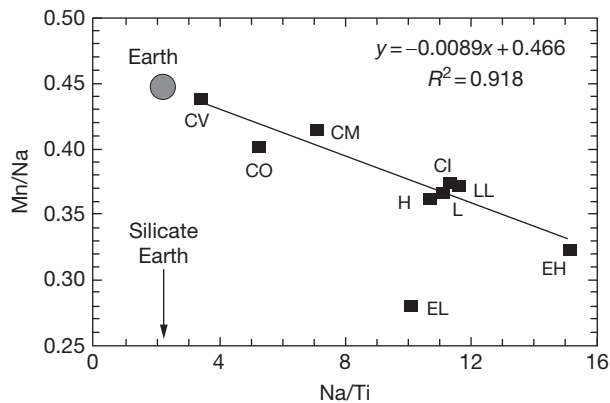


Figure 10 A plot of the variation in Na/Ti versus Mn/Na ratios in chondritic meteorites and the Earth. Data for chondrites are from Wasson and Kellemeyn (1988). The value for the Na/Ti ratio of the silicate Earth is indicated with an arrow (data from McDonough and Sun, 1995). The regression line, R^2 value, and the coefficients for the line equation are derived from the data for chondrites, not including the low-Fe enstatite chondrite. This regression and the Na/Ti ratio of the silicate Earth together provide a method to estimate the Mn/Na ratio for the Earth and indicate that the core is likely to contain a small fraction of the Earth's Mn budget.

gallium content of the Earth's core (Figure 11) is substantially lower than that found in all iron meteorites, which may reflect the markedly different conditions under which core separation occurred in the Earth.

It has been suggested that there is niobium in the core (Wade and Wood, 2001). This suggestion is based on the observation that niobium is siderophile under reducing conditions (it is not uncommon to find niobium in steels) and if core extraction were sufficiently reducing, then some niobium would have been sequestered into the core. In addition, Wade and Wood (2001) observed that the partitioning data for niobium mimicked that for chromium and vanadium. Given the distribution of chromium and vanadium between the core and mantle, it is expected that a considerable portion of the Earth's niobium budget is hosted in the core. The Wade and Wood model was, in part, developed in response to the observations of McDonough (1991) and Rudnick et al. (2000), who reported that niobium and tantalum are depleted in the upper mantle and crust and that both reservoirs have low Nb/Ta values relative to chondrites. These observations lead to the suggestion that refractory components of subducting oceanic crust would contain the complementary niobium- and tantalum-enriched reservoir of the silicate Earth (McDonough, 1991; Rudnick et al., 2000). However, Wade and Wood (2001) proposed an alternative model in which niobium, but not tantalum, is extracted into the core. To address this issue it is useful to examine the relative abundances of Nb-Ta-La in the crust-mantle system, because this triplet may characterize silicate Earth processes and reservoirs.

The range of Nb/Ta and La/Ta values in the continental crust and depleted mantle (MORB source) are given in Figure 12. This illustration shows that both of these major silicate reservoirs are clearly depleted in Nb/Ta relative to chondrites. In addition, both the continental crust and the depleted source regions of MORBs plot in the field that characterizes depletions of both niobium and tantalum relative to lanthanum, and tantalum relative to niobium. Niu and Batiza (1997) showed that during melting $D_{\text{Nb}} < D_{\text{Ta}} < D_{\text{La}}$ such that increasing melt extraction depletes the MORB source regions respectively and progressively in these elements so that they

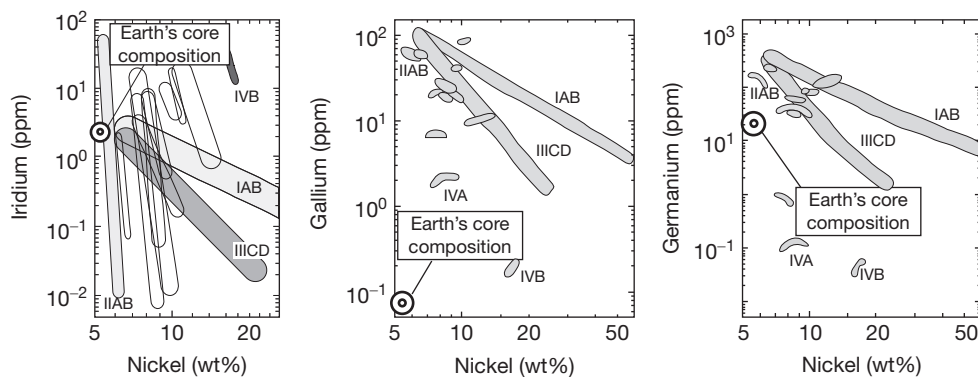


Figure 11 A plot of the variation in Ni versus Ir, Ni versus Ga, and Ni versus Ge in iron meteorites and the Earth. Data for the iron meteorites are adapted from the work of Wasson (1985). Data for the Earth's core are from Table 4. The plot of Ni-Ir shows that the composition of the Earth's core is comparable to that of various iron meteorites, whereas the Earth's core appears to have a slightly lower Ge content and a markedly lower Ga; the latter being unlike anything seen in iron meteorites. These four elements are the ones that are used to define the chemical classification of iron meteorites (reproduced by permission of W. H. Freeman from *Meteorites, Their Record of Early Solar-system History*, 1985, p. 41, 42).

would plot in the same field as continental crust (Figure 12). This demonstrates that both the production of continental and oceanic crusts result in the production of a crustal component that, when processed through a subduction zone filter, generates residues with high Nb/Ta and low La/Ta that remain in the mantle. Is the core another niobium-enriched reservoir in the Earth? As of early 2000s, this is an unresolved issue, but crucial tests of this hypothesis will be gained by further examination of silicate Earth samples, iron meteorites, and further tests from experimental petrology.

Finally, Table 4 lists the halides – chlorine, bromium, and iodine – in the core. McDonough and Sun (1995) noted the marked depletion of these elements in the silicate Earth and suggested that this effect is due possibly to their incorporation into the Earth's core, or that the region of the nebula at 1 AU was anomalously depleted in the halides. There are iron halides, some of which are found in chondrites. However, such halides in chondrites are believed to be decompositional products created during terrestrial weathering (Rubin, 1997).

3.16.5 Radioactive Elements in the Core

Those that have suggested the presence of radioactive elements in the Earth's core have usually done so in order to offer an alternative explanation for the energy needed to run the geodynamo, and/or as a way to explain Earth's volatile elements inventory. Potassium is commonly invoked as being sequestered into the Earth's core due to: (1) potassium sulfide found in some meteorites; (2) effects of high-pressure s-d electronic transitions; and/or (3) solubility of potassium in Fe-S (and Fe-S-O) liquids at high pressure. Each of these is considered below and rejected.

The cosmochemical argument for potassium in the core is based on the presence of a potassium iron sulfide (djferfisherite) and sodium chromium sulfide (carswellsilverite) in enstatite chondrites, and the plausibility of these phases in coreforming liquids (Lodders, 1995). However, this hypothesis does not

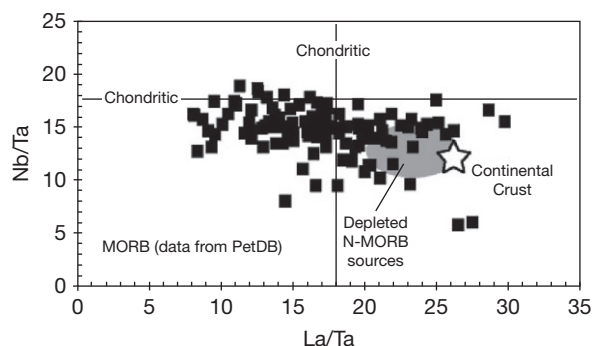


Figure 12 A plot of the Nb/Ta and La/Ta variation in MORB and the continental crust. The continental crust, MORBs, and their source regions all plot below the chondritic Nb/Ta value. Likewise, the continental crust plots and depleted MORB source regions are strongly depleted in Ta relative to La. See text for further details (data for MORB are from the PetDB resource on the web (<http://petdb.ideo.columbia.edu/petdb/>); the estimate of the continental crust from Rudnick and Gao (Chapter 4.1).

consider that enstatite chondrites also contain a myriad of other (and more abundant) sulfides, including niningerite ((Mg,Fe)S), titanium-bearing troilite (FeS), ferroan alabandite ((Mn,Fe)S), and oldhamite (CaS). These common, higher-temperature sulfide phases contain substantial concentrations of REE and other refractory lithophile elements (see review in Brearley and Jones (1998)). If these were incorporated into the Earth's core, the composition of the silicate Earth would be grossly changed on both an elemental and isotopic level. However, there is no evidence, even at the isotopic level (e.g., Sm/Nd and Lu/Hf systems), for REE depletion in the silicate Earth and, thus, it is unlikely that such sulfides were incorporated into the core. The mere identification of a potassium bearing sulfide does not demonstrate the existence of potassium in the core; it simply allows for the possibility. Plausibility arguments need to be coupled with corroborating paragenetic evidence that is also free of negating geochemical consequences.

The s-d electronic transitions occur at higher pressures, particularly for larger alkali metal ions (e.g., caesium, rubidium, and potassium). Under high confining pressures the outer most s-orbital electron transforms to a d¹-orbital configuration, resulting in transition metal-like ions. This electronic transition changes the chemical characteristics of the ion making it more siderophilic and potentially allowing it to be sequestered into the core. It has been suggested that some amount of caesium (see Figure 4) may have been sequestered into the Earth's core via this mechanism (McDonough and Sun, 1995). However, data for rubidium and potassium show that this effect is unlikely to have taken place based on the depletion pattern for the moderately volatile lithophile elements.

The third argument for the presence of radioactivity in the core usually involves finding a condition ($P-T-X-f_{O_2}$) under which potassium is soluble (Hall and Rama Murthy, 1971; Lewis, 1971; Chabot and Drake, 1999). Gessmann and Wood (2002) demonstrated that potassium is soluble in Fe-S and Fe-S-O liquids at high pressure; these authors argued that potassium was sequestered into the core (see also Chapter 3.15). However, these experimental studies suffer from either examining only simple liquid systems (e.g., synthetic Fe-Ni-S), or overlooking the consequences of other minor and trace elements (e.g., Th, U, and REE). In the case of the Gessmann and Wood's (2002) study, calcium is also incorporated into the metallic liquid and the consequences of this are that it creates even more problems. For example, the silicate Earth has a calcium content that is in chondritic proportions to other refractory lithophile elements (e.g., Ca/Al, Ca/Sc, Ca/Yb), demonstrating that there was neither calcium nor potassium incorporated into the core. Similar arguments can also be made for uranium and thorium, which are also based on ratios with other refractory lithophile elements. No experimental evidence exists that shows similar solubility for uranium and thorium (i.e., two elements with significantly different siderophilic behavior) in Fe-S and Fe-S-O liquids at high pressure that does not incorporate other refractory lithophile elements.

An Earth's core containing a significant amount of radioactive elements has been proposed by Herndon (1996). This model envisages a highly reduced composition for the whole Earth and, in particular, for the core. Unfortunately, Herndon has developed a core compositional model that is inconsistent

with chemical and isotopic observations of the Earth's mantle and a chondritic planetary composition. Herndon's core contains significant quantities of calcium, magnesium, uranium, and other elements typically considered lithophile. Drawing upon analogies with enstatite chondrites (highly reduced meteorites), Herndon has suggested that these elements were extracted into a metal phase as sulfides (e.g., oldhamite and niningerite). However, these phases are known to grossly fractionate many lithophile elements from one another (Croaz and Lundberg, 1995), which would lead to a mantle with significantly nonchondritic ratios of Sm/Nd, Lu/Hf, and Th/U (element pairs constrained by isotopic evidence), as well Ca/Ti, Ca/Al, Ti/Sc, and others (element pairs whose bulk mantle properties are well constrained to be chondritic in the mantle), and this is not observed (McDonough and Sun, 1995).

Finally, there is a question of the need for radioactive heating of the core to support the necessary energy budget. Some geophysicists have speculated that there is either potassium or uranium in the core that supplies a portion of the core's power budget. These model calculations for the energy budget in the Earth's core are nontrivial and involve a number of parameters, with many assumptions and extrapolations of data to appropriate core conditions (Gubbins, 1977; Gubbins et al., 1979; Buffett and Bloxham, 2002). The competing models of the geodynamo require different amounts of energy to drive convection in the outer core, and the details of the various models are vastly different (Glatzmaier, 2002). Labrosse et al. (2001) proposed a model for the timing and rate of inner core solidification that requires radioactive heating. Likewise, Anderson (2002) examined the energy balance at the CMB and concluded that there is a need for some amount of radioactive heating in the core. In contrast, no radioactive heating is required in other models of the core's energy budget (Stacey, 1992), which is consistent with geochemical evidence for its general absence in the core.

3.16.6 Timing of Core Formation

Defining the age and duration of core formation depends on having an isotope system in which the parent–daughter isotope pairs are fractionated by core subtraction over a time interval within the functional period of the system's half-life. Fortunately, analytical advances in the W–Hf isotope system provide us with a tool to gauge the timing of core formation (Kleine et al., 2002; Yin et al., 2002).

The W–Hf isotope system involves the decay of ^{182}Hf to ^{182}W with a half-life of 9 Myr (thus the system became extinct within the first 100 Myr of Earth history). Both hafnium and tungsten are refractory elements (lithophile and siderophile, respectively) and thus their relative concentration in the Earth is set at chondritic. Some 90% of the Earth's budget of tungsten is hosted in the core (Table 6), whereas all of the planet's hafnium is hosted in the silicate Earth. Early studies found that iron meteorites have lower $^{182}\text{W}/^{184}\text{W}$ isotopic compositions (by about some $4\epsilon_{182\text{W}}$ units, where ϵ units express difference in parts per 10000) than the Earth (Lee and Halliday, 1995; Harper and Jacobsen, 1996; Horan et al. (1998)); the Lee and Halliday (1995) study found no difference between the Earth and chondrites for their tungsten

isotopic compositions. The findings of Lee and Halliday (1995), however, have been challenged by Yin et al. (2002), Kleine et al. (2002), and Schoenberg et al. (2002), who found that the Earth's tungsten isotopic composition is some $2\epsilon_{182\text{W}}$ units higher than that of chondrites. (These studies measured some of the same chondrites as reported in the Lee and Halliday (1995) study and were able to resolve the compositional differences between the Earth and chondrites.) This difference means that core separation was very early, and happened prior to the effective decay of the ^{182}Hf system such that the tungsten remaining in the silicate Earth became enriched in ^{182}W relative to that in the core. These studies demonstrate that much of the core's separation must have been completed by ~ 30 Ma after t_0 (4.56 Ga) in order to explain the Earth's higher $\epsilon_{182\text{W}}$ signature (Figure 13). There are possible scenarios in which one could argue for significantly shorter, but not longer time interval for core formation (Kleine et al., 2002; Yin et al., 2002). By implication the core must have an $\epsilon_{182\text{W}}$ of about -2.2 compared to the zero value for the silicate Earth.

The U–Pb, Tc–Ru (^{98}Tc has a half-life between 4 Ma and 10 Ma), and Pd–Ag (^{107}Pd has a half-life of 9.4 Ma) isotope systems have also been examined in terms of providing further insights into the timing of core separation. Overall, the results from these systems are definitive, but not very instructive. The extinct systems of Tc–Ru and Ag–Pd have parent and daughter isotopes that are siderophilic and so were strongly partitioned into the core during its formation. The absence of isotopic anomalies in these systems indicates that core separation left no signature on the silicate Earth. The extant U–Pb system (^{235}U with a half-life of 0.7 Ga) has also been examined with respect to the incorporation of lead into the core, with the result being that core separation must have happened within the first 100 Myr of the Earth's formation in order to reconcile the lead isotopic evolution of the silicate Earth (see review of Galer and Goldstein (1996)).

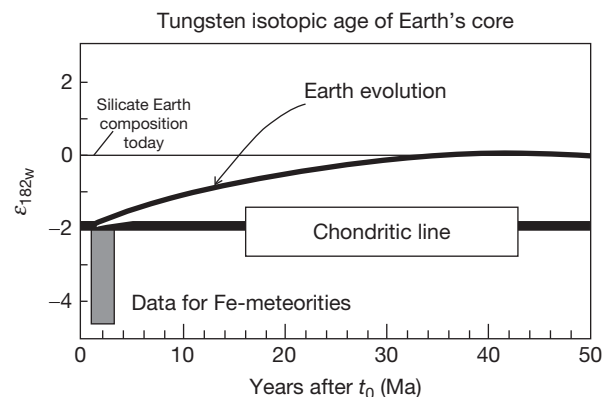


Figure 13 An evolutionary model of time versus the $\epsilon_{182\text{W}}$ composition of the silicate Earth for the first 50 of Earth's history. The higher $\epsilon_{182\text{W}}$ composition of the Earth relative to chondrites can only be balanced by a complementary lower than chondrites reservoir in the core. Extraction age models for the core are a function of the decay constant, the difference between the silicate Earth and chondrites, the proportion of W and Hf in the mantle and core and the rate of mass extraction to the core. Details of these models are given in the above citations, with the upper limit of the age curves shown here (sources Yin et al., 2002; Kleine et al., 2002; Schoenberg et al., 2002).

3.16.7 Nature of Core Formation

Core formation is not a well-understood process. Constraints for this process come from pinning down the timing of the event, characterizing its bulk chemical properties, and establishing a bulk Earth compositional model. The W–Hf isotope studies dictate that core formation happened early and was virtually completed within 30 Ma of solar system formation. The findings of Li and Agee (1996) and related studies (see Chapter 3.15) demonstrate that the integrated pressure and temperature of core formation was accomplished at mid- to upper-mantle conditions, not in predifferentiated planetismals. This finding, however, does not preclude the accretion of predifferentiated planetismals; it simply requires that these additions were rehomogenized back into the larger and still evolving Earth system. Finally, the nickel content of the silicate Earth places significant restrictions on oxidation potential of the mantle during core formation. These findings have led to the competing hypotheses of homogeneous and heterogeneous planetary accretion (Wänke, 1981; Jones and Drake, 1986). The former envisages the composition of accreting materials to remain constant throughout Earth's growth history, whereas heterogeneous accretion models postulate that there was a significant compositional shift during the latter stages of the Earth's growth history. These models were developed in order to account for the observed chemical features of the mantle.

The homogeneous accretion model requires a fairly restricted set of conditions to attain the silicate Earth composition observed today (Jones and Drake, 1986). Continued support for this model is waning given its failure to reconcile a number of rigorous chemical and isotopic constraints (see reviews of O'Neill, 1991b; O'Neill and Palme, 1997; and Palme and O'Neil (Chapter 3.1)). For example, it is well established from osmium isotope studies (Meisel et al., 1996; Walker et al., 1997, 2002) that the mantle abundances of rhenium, osmium, and platinum are in chondritic proportions (to within 3% and 10% uncertainty, respectively, for Re/Os and Pt/Os) and as of 2003 no model of homogeneous accretion has been successful in generating such a result. In order to address these and other issues (e.g., the high nickel, sulfur, and selenium content of the mantle) many have appealed to models of heterogeneous accretion (Morgan et al., 1981; Wänke, 1981; Wänke and Dreibus, 1982; Ringwood, 1984; O'Neill, 1991b; O'Neill and Palme, 1997).

Heterogeneous accretion models for the formation of the Earth advocate the initial accretion of refractory, less-oxidized components that make up the bulk of the planet (some 50–80%), followed by the accretion of a lower-temperature, more oxidized component (e.g., perhaps comparable to carbonaceous chondrites). The overall nature of the initially refractory material is not well characterized, but it could have affinities to ordinary or enstatite chondrites. These two component mixing models seek to reconcile the observational constraints from chemical and isotopic studies of the silicate Earth. As of early 2000s, we do not have sufficient data to identify in detail the nature of these two components of accretion if they existed.

Data for sulfur, selenium, and tellurium (the sulfonic elements, the latter two are also strongly chalcophile and sit

below sulfur on the periodic table) show that these elements were sequestered into the core in equal proportions (Figure 6). The upper and lower panels of Figure 6 also show that the mantle content of the highly siderophile elements (HSEs) – rhenium and gold – and the platinum group elements (PGEs) – ruthenium, rhodium, palladium, osmium, iridium, and platinum – are depleted to approximately the same level as that for the sulfonic elements. This is consistent with all of these elements being delivered to the mantle by either the entrainment of small amounts of a core material in plumes coming off of the early CMB (McDonough, 1995) or a model that invokes the addition of a late stage veneer component added to the Earth (Kimura et al., 1974; Chou, 1978; Morgan et al., 1981). Quantitatively, it has been demonstrated that either an endogenous delivery mechanism (former model) or an exogenous delivery model (the latter model) is consistent with the early (ca. pre-4.0 Ga) addition of a sulfonic-HSE component to the mantle (McDonough, 1995).

The endogenous delivery mechanism is inefficient in that it requires core entrainment by plumes that arise off of a newly formed CMB. Kellogg and King (1993) and Kellogg (1997) have shown that such plumes can incorporate $\sim <1\%$ of core material and that this material can be reentrained back into the mantle. However, such plumes would have been considerably more vigorous during the Hadean, assuming a significant temperature contrast across the core–mantle boundary (i.e., established some 10^5 – 10^8 yr following accretion and core formation) and a higher-temperature state of the planet resulting from accretion, Moon formation, and core separation. Therefore, it is likely that some degree of entrainment of core material into the mantle occurs in the aftermath of establishing a core–mantle boundary.

Walker et al. (2002) demonstrated that the primitive upper mantle has $^{187}\text{Os}/^{188}\text{Os}$ values similar to ordinary and enstatite chondrites, and that this mantle signature is distinct from that of carbonaceous chondrites. These observations translate to different Re/Os values in different chondrite classes (ordinary, enstatite, and carbonaceous), with the mantle having Re/Os a value unlike that of carbonaceous chondrites. This raises the importance of this late addition (i.e., the sulfonic-HSE signature material), given its distinctive composition. Therefore, the diagnostic sulfonic-HSE signature of the mantle reflects either the nature of the very earliest accreted material delivered to the forming Earth (the endogenous model) or that delivered at the final stages of accretion (the exogenous model).

If the sulfonic-HSE signature derives from material extracted from the core, we can use its HSE signature to characterize the nature of material delivered to the early accreting Earth. Standard heterogeneous accretion models argue that this early accreting material is reduced, with compositional characteristics comparable to ordinary chondrites. Thus, the observations of Walker et al. (2002) on Re/Os values of the silicate Earth are consistent with the early accretion of a reduced component. Alternatively, the exogenous delivery model (i.e., late veneer component) would contradict standard heterogeneous accretion models, which envisage accretion of an initial reduced component followed by the subsequent accretion of a more oxidized component. Thus, the exogenous model requires yet another, final shift in the oxidation state of the late accretion material.

In summary, core formation was early and fast and was accomplished at mid- to upper-mantle conditions in a hot energetic Earth. Given silicon as the dominant light element component in the core, then core–mantle equilibrium occurred under fairly reducing conditions. (If instead oxygen was the dominant light element component in the core, then core–mantle equilibrium occurred under fairly oxidizing conditions.)

3.16.8 The Inner Core, its Crystallization, and Core–Mantle Exchange

The solid inner core represents only ~5% of the core's mass and ~4% of its volume. Geophysical models of the inner core have identified its structure, elastic properties, and modeled its crystallization history. This, without question, is the most remote region of the planet and little is known of its properties and origins. There are no direct insights to be gained from either compositional studies of the mantle or those of meteorites. The high-pressure conditions of the inner core limit the applicability of any insights drawn from analogies with iron meteorites, which were formed at <1 GPa conditions.

Labrosse et al. (1997, 2001) examined the power budget for the core and its implications for inner core crystallization. These calculations generally find that inner core crystallization began in the latter half of Earth's history (ca. 1–2 Ga) and that some amount of radioactive heating is necessary to extend the age of crystallization back in time (Labrosse et al., 2001). Similarly, Brodholt and Nimmo (2002) concluded that models for inner core crystallization could perhaps be developed with long lifetimes (~2.5 Ga) for inner core crystallization with some potassium in the core producing radioactive heating. A long protracted history for inner core crystallization, however, would satisfy those who view the paleomagnetic record in 3.5 Ga old rocks as evidence for an inner core, which gave rise to the early Earth's geomagnetic field. The fundamental problem with developing an early inner core (i.e., older than 2.5 Ga) is with Earth's cooling rates, and the power needed to drive the geodynamo.

Isotopic studies have also considered ways in which to constrain the timing of inner core crystallization. Walker et al. (1995) argued that enrichment of $^{187}\text{Os}/^{188}\text{Os}$ in some plume-derived systems relative to the ambient mantle was a signature from the outer core delivered by CMB-originating plumes. The origin of this isotopic signature would be due to inner core crystallization, which produces an outer core relatively enriched in ^{187}Re (the parent isotope) but still overall depleted in rhenium and osmium. Following this, Brandon et al. (1998) found coupled enrichments in $^{187}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ similar to those predicted by Walker et al. (1995), which provided further support for Walker's model of inner core crystallization that left behind an outer core relatively enriched in ^{187}Re and ^{190}Pt (the parent isotopes) with respect to osmium. These constraints, however, argued for significant element fractionation due to inner core crystallization that was relatively early and rapid in the Earth's history (<1 Ga) in order to obtain the observed elevated isotopic compositions. Brandon et al. (2003) have extended these observations to include the Cretaceous komatiite suite from Gorgona Island and again re-enforced a model of early and rapid growth of the

inner core, conclusions that are not mutually exclusive with findings from Labrosse et al. (2001) but are more difficult to reconcile.

In summary, there are two models of inner core crystallization: one involving early and rapid growth (osmium isotopic model) and one involving later, slow growth (energy balance model). These models address very different problems and concerns, are mutually independent, and reach somewhat divergent conclusions. The inner core exists and began forming after core formation (i.e., after the first 30 Ma of Earth's history). In addition, the generation and maintenance of a planetary dynamo does not require inner core growth (Stevenson, 2003). Thus, as of 2003, we are unable to resolve the issue of when inner core crystallization began.

A final observation on the amount of core–mantle exchange, albeit on a less sensitive scale, can be gained from studies of peridotites. It is recognized that by ~3.8 Ga, when we begin to have a substantial suite of crust and mantle samples, the mantle's composition is relatively fixed as far as key ratios of lithophile-to-siderophile elements in mantle samples. McDonough and Sun (1995) showed that ratios of Mg/Ni and Fe/Mn in the mantle have been fixed (total of $\pm 15\%$ SD for both ratios) for mantle peridotites spanning the age range 3.8 Ga to present (their Figure 7), which is inconsistent with continued core–mantle exchange. At a finer scale, there is ~20% variation in P/Nd values of Archean to modern basalts and komatiites, which because of the core's high P/Nd value (virtually infinity) and mantle's low value ($\sim 70 \pm 15$) restricts mass exchange between the core and mantle to <1%. Collectively, these and other ratios of lithophile (mantle)-to-siderophile (core) elements bound the potential core–mantle exchange to <1% by mass since core formation. The suggested mass fraction of core–mantle exchange based on Re–Os and Pt–Os isotopic studies is at a much smaller scale by at least two orders of magnitude, the scaling is only relative to the mass of the upwelling plume.

3.16.9 Summary

An estimate of the density deficit in the core is ~5–10% (Boehler, 2000; Anderson and Isaak, 2002); the uncertainty in this estimate is dominantly a function of uncertainties in the pressure and temperature derivatives of EOS data for candidate core materials and knowledge of the temperatures conditions in the core. A tighter constraint on this number will greatly help to refine chemical and petrological models of the core. A density deficit estimate for the inner core is 4–5% (Hemley and Mao, 2001).

The Fe/Ni value of the core (16.5) is well constrained by the limited variation in chondritic meteorites (17.5 ± 0.5) and the mantle ratio (32), as well as the mass fraction of these elements in the two terrestrial reservoirs. The total content of sulfur, carbon, and phosphorus in the core represents only a minor fraction (~2.5 wt%) of the light element component and this mixture is insufficient to account for the core's density discrepancy. A model composition of the core using silicon as the additional light element in the outer core is preferred over an alternative composition using oxygen as the other light element. Within the limits of our resolving power, either model is tenable.

The trace element content of the core can be determined by using constraints derived from the composition of the mantle and that of chondritic meteorites. This approach demonstrates that there is no geochemical evidence for including any radioactive elements in the core. Relative to the bulk Earth, the core contains about half of the Earth's vanadium and chromium budget and it is equivocal as to whether the core hosts any niobium and tantalum. As compared to iron meteorites, the core is depleted in germanium and strongly depleted in (or void of) gallium. Collectively, the core's chemical signature provides a robust set of restrictions on core formation conditions (i.e., pressure, temperature, and gas fugacity).

The W–Hf isotope system constrains the age of core–mantle differentiation to within the first 30 Ma years of Earth's history (Kleine et al., 2002; Yin et al., 2002). However, the age of inner core crystallization is not resolved.

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