

# **THE COMPOSITION OF THE EARTH'S CORE**

(for the Encyclopedia of Geomagnetism and Paleomagnetism, D. Gubbins, ed.),

William F. McDonough  
Department of Geology  
University of Maryland  
College Park, Maryland, 20742, USA

*Text: 2200 words, 15 references, 1 figure and 2 table*

Primary planetary differentiation produced a metallic core and silicate shell surrounded by a thin hydrous and gaseous envelope. Emil Wiechert proposed this simple first order picture of the Earth at the end of the 19<sup>th</sup> century, while in 1914 Beno Gutenberg, Wiechert's former PhD student, determined that the depth to the core-mantle boundary at 2900 km (c.f., the present day value is  $2895 \pm 5$  km depth, Masters and Shearer, 1995). Establishing a more detailed picture of the Earth's core has been a considerable intellectual and technological challenge, given the core's remote setting. The composition of the Earth's core is determined by integrating observations and constraints from geophysics, cosmochemistry and mantle geochemistry; a unilateral approach from any of these perspectives cannot produce a significant compositional model.

Geophysical methods provide the only direct measurements of the properties of the Earth's core. The presence and size of the core and its material properties are revealed by such studies. Foremost among these observations include 1) its seismic wave velocity and the free oscillation frequencies, 2) the moment of inertia (both of these observations plus the Earth's mass collectively define a density profile for the core and mantle that is mutually and internally consistent (Dziewonski and Anderson, 1981)), 3) the distribution and secular variation in magnetic field and 4) laboratory data on mineral physics (e.g., equation of state (EOS) for materials at core appropriate conditions). When combined with the element abundance curve for the solar system and compositional models for the Earth's mantle (McDonough and Sun, 1995) these observations give us constraints on the mineralogical and chemical constituents of the core and mantle. Washington (1925), Birch (1952) and more recent studies (see McDonough (2004) for a recent update and literature review) have used these constraints to develop compositional models for the

Earth and the core. These models consistently converge on the result that the core contains approximately 85% Fe, 5% Ni and  $\leq 10\%$  of minor lighter components (in weight %, or about 77% Fe, 4% Ni and 19% other in atomic proportions).

The minor component in the core is an alloy of lower atomic mass that accounts for the core's lower density when compared with that of liquid Fe at core conditions. Washington (1925), drawing upon analogies with phases in iron meteorites, recognized that the core contained a minor amount of an atomically light component (e.g., sulfide, carbide, phosphide). Birch (1964) suggested that this light component represented some 10% of the core's mass and offered a suite of candidate elements (e.g., H, C, O, Si, or S). Anderson and Isaak (2002) more recently reviewed the relevant literature and concluded that only  $\sim 5\%$  of this light component is needed. More recently, however, Masters and Gubbins (2003) show that the density increase for the liquid outer core to the solid inner core is much greater than previously considered and Lin et al (2005) found that Birch's law (a linear relationship between sound velocity and density) does not hold at core pressures. Both findings have implications for the bulk core composition and imply potentially greater amounts of a light component in the outer core. The nature and proportion of the elements that make up this alloy are controlled by 3 main factors: (1) the behavior of elements during metal-silicate segregation, (2) the integrated pressures and temperatures experienced during core formation, and (3) whether or not there is (or has been) mass transfer across the core-mantle boundary since core formation. Studies of meteorites identify the behavior of the elements in the early solar nebula and during planetesimal formation, thus identifying elements that are likely concentrated in the core. Analyses of mantle samples constrain the composition of the Earth's primitive mantle (the combined crust plus mantle) and from this one ascertains the volatile element inventory for the planet. Studies of the secular variation of the mantle composition define the extent of core-mantle mass exchange. However, there is the proviso that we must sample this change; chemical changes occurring at the core-mantle boundary that remain isolated at the base of the mantle can only be speculated upon, but not demonstrated. Collectively, these data establish a bulk planetary composition;

subtracting the primitive silicate mantle composition from this reveals the core composition.

The compositional diversity of the planets in the solar system and that of chondritic meteorites (primitive, undifferentiated meteorites) provide a guide to the bulk Earth composition. However, this diversity of samples presents a problem in that there is no unique meteorite composition that characterizes the Earth. The solar system is compositionally zoned from volatile-poor planets closer to the sun to volatile-rich gas giants further out. Relative to the other planets, the Earth has a relatively intermediate size-density relationship and volatile element inventory and is more depleted in volatile components than CI chondrites, the most primitive of all of the meteorites. The bulk Earth's composition is more similar to that of some carbonaceous chondrites and less so the ordinary or enstatite chondrites (Figure 1), especially in regard to the 4 most abundant elements (Fe, O, Si, and Mg; in terms of atomic proportions these elements represent 95% of the inventory of elements in chondrites and the Earth) and their ratios. Thus, we need to establish the absolute abundances of the refractory elements in the Earth and the signature of the volatile element depletion pattern.

The silicate Earth, or primitive mantle, encompasses the solid Earth minus the core. There is considerable agreement at the major and minor element level for the composition of the primitive mantle. The relative abundances of the lithophile elements (e.g., Ca, Al, Ti, REE (rare earth elements), Li, Na, Rb, B, F, Zn, etc) in the primitive mantle establish both the absolute abundances of the refractory elements in the Earth and the planetary signature of the volatile element depletion pattern. The volatile lithophile elements, those with half-mass condensation temperatures  $<1200$  K (i.e., a reference temperature at which half the mass of a specific element condenses into a mineral from a cooling solar nebular under a given oxygen partial pressure) and excluded from the core, have CI chondrite relative abundances that systematically decrease with condensation temperature.

A compositional model for the Earth, the core and mantle is presented in Table 1. The model core composition is derived from the above constraints and has a light element

component that is consistent with existing geophysical requirements. Significantly, along with Fe and Ni the core contains most of the planet's sulfur, phosphorous, and carbon, it contains little or no gallium, an element widely found in iron meteorites, and is devoid of radioactive elements.

#### LIGHT ELEMENTS IN THE CORE

Given an outer core density deficit of 5% to 10%, a host of elements (e.g., H, C, O, Si, P, S) can potentially be present. Commonly, metallurgical or cosmochemical arguments, coupled with meteoritical analogies (e.g., reduced metals, such as silicides in enstatite chondrites) are used to argue for one's preferred candidate element. There is sufficient evidence to suggest that some, but not all, of this density deficient is due to the presence of sulfur (McDonough, 2004). However, beyond this we are still working to place further constraints on this issue and a number of elements in the mix (particularly H, C, O, Si) are considered viable for explaining the core's density deficit.

The Earth's volatility curve can be established from the relative abundances of the lithophile elements, which are elements that 1) are excluded from the core and concentrated in the mantle, 2) have different condensation temperatures and 3) widely vary in their chemical characteristics (McDonough, 2004). A comparison of the Earth's volatility curve with that of chondritic meteorites shows that the sulfur content of the core is restricted to 1.5-2 wt% due to its volatility. In addition, the planetary volatility curve reveals that the proportions of Si and O in the Earth, both of which have half-mass condensation temperatures <1200 K, cannot be readily established from chondritic observations.

There are a number of issues that need to be evaluated when considering a mixed alloying element to account for the core's density deficit. In calculating the density deficit one needs to know the thermal gradient in the deep Earth and the EOS for appropriate alloys at core conditions. Such data are still lacking for many of these alloys at core conditions. Likewise, the mutual compatibility of different alloying element pairs has yet to be established for many of these elements. There appears to be good evidence

showing that alloys of Si-O and Si-S are not compatible because of contrasting solubility (see recent review of Li and Fei, 2004). Thus, based on a model of heterogeneous accretion for the Earth (i.e., a secular variation in the composition of material that contributed to the growing Earth), the ~2% (by mass) sulfur in the core is mixed with either silicon or oxygen as the other dominant alloying element in the outer core. From this perspective 2 competing models for the composition of the core are offered in Table 2, which contain either Si or O, but not both. Other light elements contribute to the density deficit in the core, including H, C, and P (see Table 1), but these elements are in significantly lower proportions due to their partitioning into other parts of the Earth and the markedly lower condensation temperatures for H and C. Such a diverse array of light elements may well be mutually compatible in iron liquids, particularly if liquid segregation occurs at high pressure (circa 10-25 GPa).

#### RADIOACTIVE ELEMENTS IN THE CORE

The existence of radioactive elements in the Earth's core is usually invoked to offer an explanation for the power needed to run the geodynamo (Labrosse et al, 2001) and/or as a way to increase the volatile element content of the Earth. An alternative model for the core's power budget was offered by Christensen and Tilgner (2004) who showed that ohmic losses by the core's geodynamo are sufficiently large enough to remove the need for radioactive heating in the core. Arguments for potassium in the core are based on three lines of evidence: (1) cosmochemical – potassium sulfide is found in some meteorites, (2) high pressure s-d electronic transition, and (3) solubility of K in Fe-S (and Fe-S-O) liquids at high pressure.

The cosmochemical argument for K in the core is based on the observation that a potassium-bearing sulfide (djerfisherite) is found in trace quantities in enstatite chondrites (Lodders, 1995). However, this *ad hoc* hypothesis overlooks the fact that enstatite chondrites also contain a myriad of other sulfides that are more abundant than djerfisherite, including oldhamite (CaS), ferroan alabandite ((Mn,Fe)S), and niningerite ((Mg,Fe)S), and that alkali sulfides like djerfisherite are typically found in trace quantities as replacement or alteration phases (Brearley and Jones, 1998). Incorporating

the more common, higher temperature sulfide phases, which contain REE and other refractory lithophile elements in non-chondritic proportions, would grossly and adversely change both the elemental and isotopic abundances of the Sm/Nd, Lu/Hf and Th/U isotopic systems. Given an absence of fractionation of these isotopic and elemental systems, one can also conclude that there are negligible quantities of K sulfide in the core. At high pressure s-orbital electrons in alkali metal can be compressed into d-orbital electronic states. For K this electronic transition is theoretically possible, but this effect is likely to be even greater for Rb and Cs. Whereas an argument can be made for Cs in the core, it cannot be so for Rb (McDonough, 2004). Moreover, the coherent depletion pattern of the volatile lithophile elements is not restricted to just the alkali metals and thus the pattern cannot be dismissed as “being stored in the core” based on pressure induced s-d electronic transitions. Finally, Gessmann and Wood (EPSL, 2002) demonstrate that K is soluble in Fe-S and Fe-S-O liquids at high pressure and suggested that K can therefore be sequestered into the core. However, Ca is also incorporated into the metallic liquid and having Ca in the core creates problems given that the mantle’s Ca content is in chondritic proportions. Other recent models (Rama Murthy et al., 2003; Lee and Jeanloz, 2003) proposing K in the Earth’s core, however, also are accompanied by geochemical consequences that limit their acceptability (see McDonough, 2003 for a further review). Overall, it is unlikely there is any K in the core, although much debate continues.

## TIMING OF CORE FORMATION

Defining the age and duration of core formation depends on having an isotope system in which the parent - daughter isotope pair are fractionated by core sequestration over a time interval within the functional period of the system’s half-life. Fortunately, recent analytical advances in the W-Hf isotope system provide us with a tool to gauge the timing of core formation. Both Hf and W are refractory elements (lithophile and siderophile, respectively) having chondritic relative concentrations in the Earth, with ~90% of the Earth’s budget of W being hosted in the core and the entire planet’s Hf budget in the silicate Earth. Recent studies (Yin et al. 2002; Kleine et al. 2002; Schoenberg et al. 2002) found that the Earth’s W-isotopic composition is higher than that

of chondrites, indicating that core separation had to have been completed by  $\sim 30$  Ma after  $t_0$  (4.56 Ga ago).

## THE INNER CORE AND CORE - MANTLE EXCHANGE

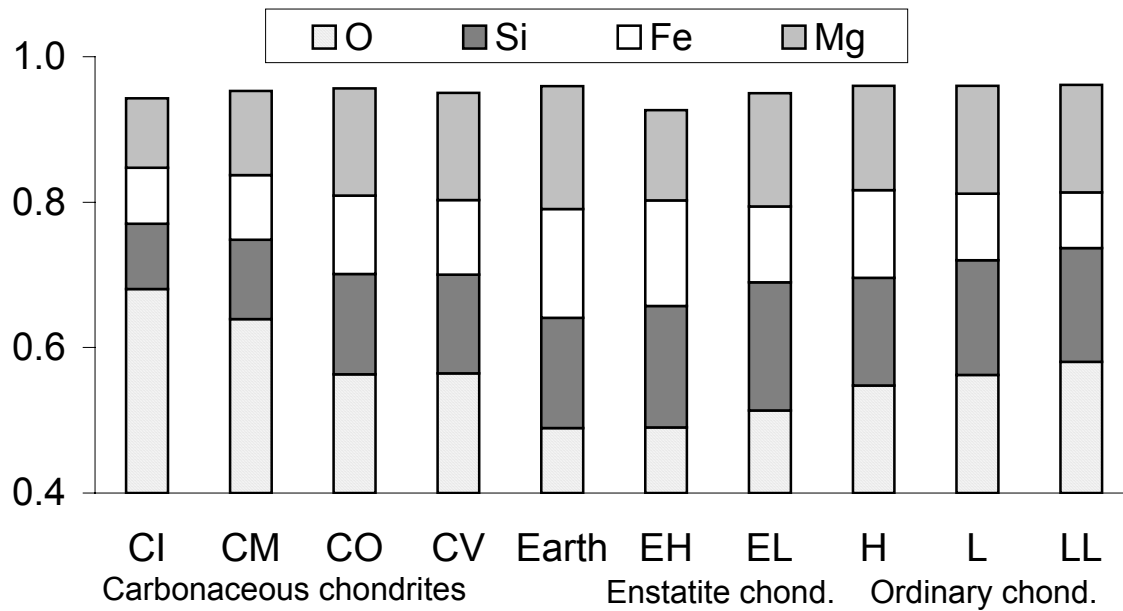
Based on geophysical data the inner core comprises  $\sim 5\%$  of the core's mass. Its existence is not disputed, although there is much speculation about when the inner core began to crystallize, the extent of element fractionation between the inner and outer core and the role it plays in models of core-mantle exchange. Recently, Labrosse et al. (2001), examining the power budget for the core, suggested that inner core crystallization began in the latter half of Earth's history (circa 1-2 Ga) and that some amount of radioactive heating is necessary. In contrast, however, support for early inner core crystallization comes from the Os isotopic compositions of some Hawaiian basalts, which has been explained by parent-daughter isotope fractionation due to core differentiation followed by core contributions to the Hawaiian magma source region. The origin of this Os isotopic signature in these basalts is interpreted to be due to exchange across the core-mantle boundary (with the base of the mantle being the putative source of these basalts) of a radiogenic Os isotopic component that was generated by inner core crystallization, which incorporated Os and to a lesser extent, Re and Pt (Brandon et al. 2002). The extent of core-mantle exchange can be monitored, albeit on a less sensitive scale, from studies of peridotites and basalts. Ratios of Mg/Ni and Fe/Mn in the mantle have been fixed (i.e.,  $\leq \pm 15\%$ ) for the last 3.8 Ga (McDonough and Sun 1995), which is inconsistent with significant core-mantle exchange, given the proportions of these elements in the core and mantle. Likewise, other sensitive element ratios (e.g., Re/Yb, P/Nd, Mo/Ce, W/Ba) involving siderophile elements (e.g., Re, P, Mo, W) and similarly incompatible (i.e., elements readily entering a melt relative to the solid) lithophile elements (e.g., Yb, Ce, Nd, Ba) show that  $< 0.5\%$  of a core contribution can be incorporated into the source regions of mid-ocean ridge basalts or intra-plate (plume-derived) basalts. In general, however, models invoking early growth of the inner core are at odds with findings from power budget calculations.

## REFERENCES

- Anderson O. L. and Isaak D. G. (2002) Another look at the core density deficit of Earth's outer core. *Physics of the Earth and Planetary Interiors* **131**(1), 19-27.
- Birch F. (1952) Elasticity and Constitution of the Earth's Interior. *Journal of Geophysical Research* **57**(2), 227-286.
- Birch F. (1964) Density and Composition of Mantle and Core. *Journal of Geophysical Research* **69**(20), 4377-4388.
- Brandon A. D., Walker R. J., Puchtel I. S., Becker H., Humayun M., and Revillon S. (2003)  $^{186}\text{Os}/^{187}\text{Os}$  systematics of Gorgona Island komatiites: implications for early growth of the inner core. *Earth Planetary Science Letters* **206**, 411-426.
- Brearley A. J. and Jones R. H. (1998) Chondritic meteorites. In *Planetary Materials* (ed. J. J. Papike). Mineralogical Soc. Amer., Washington, DC, vol. **36**, pp. 3-01–3-398.
- Christensen U. R. and Tilgner A. (2004) Power requirement of the geodynamo from ohmic losses in numerical and laboratory dynamos. *Nature* **429**, 169-171.
- Dziewonski A. and Anderson D. L. (1981) Preliminary reference Earth model. *Physics Earth Planetary Interiors* **25**, 297-356.
- Labrosse S., Poirier J. P., and LeMouel J. L. (2001) The age of the inner core. *Earth Planet. Sci. Lett.* **190**, 111–123.
- Lodders K. (1995) Alkali elements in the Earth's core—evidence from enstatite meteorites. *Meteoritics* **30**(1), 93–101.
- Gessmann C. K. and Wood B. J. (2002) Potassium in the Earth's core? *Earth and Planetary Science Letters* **200**(1-2), 63-78.
- Kleine T., Münker C., Mezger K., and Palme H. (2002) Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf-W chronometry. *Nature* **418**, 952-955.
- Lee K.K.M. and Jeanloz R. (2003) High-pressure alloying of potassium and iron: Radioactivity in the Earth's core? *Geophys. Res. Lett.*, **30**, No. 23, 2212, doi:10.1029/2003GL018515.



- Li J. and Fei Y. (2003) Experimental constraints on Core Composition, pp 521-546. In The Mantle and Core (ed. R. W. Carlson.) Vol. 2 Treatise on Geochemistry (eds. H.D. Holland and K.K. Turekian), Elsevier-Pergamon, Oxford.
- Lin J.-F., Strarhahn W., Zhao J., Shen G., Mao H.-k., and Hemley R.J. (2005) Sound velocities of hot dense iron: Birch's Law revisited. *Science* **308**, 1892-1895.
- Masters G. and Gubbins D. (2003) On the resolution of density within the Earth. *Physics Earth Planetary Interiors* **140**, 159-167.
- Masters T. G. and Shearer P. M. (1995) Seismic models of the Earth: Elastic and Anelastic. In *Global Earth Physics: a handbook of physical constants*, Vol. AGU Reference Shelf (ed. T. J. Ahrens), pp. 88-103. American Geophysical Union.
- McDonough W. F. and Sun S.-s. (1995) The composition of the Earth. *Chemical Geology* **120**, 223-253.
- McDonough W.F. (2003) Compositional Model for The Earth's Core, pp 547-568. In The Mantle and Core (ed. R. W. Carlson.) Vol. 2 Treatise on Geochemistry (eds. H.D. Holland and K.K. Turekian), Elsevier-Pergamon, Oxford.
- Rama Murthy, V., van Westrenen, W. and Fei, Y. (2003) Experimental evidence that potassium is a substantial radioactive heat source in planetary cores. *Nature* **423**, 163– 165.
- Schoenberg R., Kamber B. S., Collerson K. D., and Eugster O. (2002) New W-isotope evidence for rapid terrestrial accretion and very early core formation. *Geochimica et Cosmochimica Acta* **66**, 3151-3160.
- Washington H. S. (1925) The chemical composition of the Earth. *Am. J. Sci.* **9**, 351-378.
- Yin Q., Jacobsen S. B., Yamashita K., Blichert-Toft J., Télouk P., and Albarede F. (2002) A short timescale for terrestrial planet formation from Hf-W chronometry of meteorites. *Nature* **418**, 949-952.



**Figure 1.** Atomic proportions of oxygen, silicon, iron and magnesium in carbonaceous chondrites, the Earth, enstatite chondrites and ordinary chondrites.

**Table 1. The composition of the Earth, Core and Mantle (Silicate Earth)**

	Earth	Core	Mantle		Earth	Core	Mantle		Earth	Core	Mantle
H	260	600	100	Zn	40	0	55	Pr	0.17	0	0.25
Li	1.1	0	1.6	Ga	3	0	4	Nd	0.84	0	1.25
Be	0.05	0	0.07	Ge	7	20	1.1	Sm	0.27	0	0.41
B	0.2	0	0.3	As	1.7	5	0.05	Eu	0.10	0	0.15
C	730	0.20	120	Se	2.7	8	0.075	Gd	0.37	0	0.54
N	25	75	2	Br	0.3	0.7	0.05	Tb	0.067	0	0.10
O %	29.7	0	44	Rb	0.4	0	0.6	Dy	0.46	0	0.67
F	10	0	15	Sr	13	0	20	Ho	0.10	0	0.15
Na %	0.18	0	0.27	Y	2.9	0	4.3	Er	0.30	0	0.44
Mg %	15.4	0	22.8	Zr	7.1	0	10.5	Tm	0.046	0	0.068
Al %	1.59	0	2.35	Nb	0.44	0	0.66	Yb	0.30	0	0.44
Si %	16.1	6.0	21	Mo	1.7	5	0.05	Lu	0.046	0	0.068
P	715	0.20	90	Ru	1.3	4	0.005	Hf	0.19	0	0.28
S	6350	1.90	250	Rh	0.24	0.74	0.001	Ta	0.025	0	0.037
Cl	76	200	17	Pd	1	3.1	0.004	W	0.17	0.47	0.029
K	160	0	240	Ag	0.05	0.15	0.008	Re	0.075	0.23	0.0003
Ca %	1.71	0	2.53	Cd	0.08	0.15	0.04	Os	0.9	2.8	0.003
Sc	10.9	0	16	In	0.007	0	0.01	Ir	0.9	2.6	0.003
Ti	810	0	1200	Sn	0.25	0.5	0.13	Pt	1.9	5.7	0.007
V	105	150	82	Sb	0.05	0.13	0.006	Au	0.16	0.5	0.001
Cr	4700	0.90	2625	Te	0.3	0.85	0.012	Hg	0.02	0.05	0.01
Mn	800	300	1045	I	0.05	0.13	0.01	Tl	0.012	0.03	0.004
Fe %	32.0	85.5	6.26	Cs	0.035	0.065	0.021	Pb	0.23	0.4	0.15
Co	880	0.25	105	Ba	4.5	0	6.6	Bi	0.01	0.03	0.003
Ni	18200	5.20	1960	La	0.44	0	0.65	Th	0.055	0	0.08
Cu	60	125	30	Ce	1.13	0	1.68	U	0.015	0	0.02

Concentrations are given in  $\mu\text{g/g}$  (p.p.m.), unless stated as “%”, which are given in weight %.

**Table 2. Competing models for the composition of the Earth and Core**

	Si-bearing model		O-bearing model	
wt%	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	
S	0.030		0.029	
Cr	0.003		0.003	
P	0.009		0.009	
C	0.008		0.008	
H	0.030		0.029	
total	1.000		1.000	