

THE COMPOSITION OF THE EARTH

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ABSTRACT --- Integrating the diverse chemical components that exist from core to atmosphere establishes the Earth's composition. The silicate Earth, or Primitive Mantle, encompasses the crust and mantle. Mostly the systematics seen in the chemical and isotopic compositions of peridotites and primitive, mantle-derived magmas establishes the bulk composition of the Primitive Mantle. The core's composition is derived by using a volatility curve for the Earth, based on the Primitive Mantle's lithophile element abundances, and the chemical systematics seen in chondrites and Fe-meteorites. In all cases the Earth is assumed to have chondritic proportions of the refractory elements, although the absolute concentrations of elements in the Earth is established by data from the Primitive Mantle. Overall, the Earth has a volatile depletion pattern similar to that of the chondrites and a value of Fe/Al at $\sim 20 \pm 2$, which preclude some chondrite types from being the analog composition for the Earth. In our existing inventory of meteorites it appears that there is no identifiable archetype that distinguishes itself as being a perfect likeness of the Earth

The composition of the Earth, integrated from core to atmosphere, is comparable to that of undifferentiated meteorites (chondrites). But this simple statement offers little insight into the kind of chondrite the Earth most resembles or if even there is a good analogue to the Earth in our present spectrum of chondritic meteorites. It also tells us little of how the Earth got to its present configuration (Figure 1) (i.e., a 3 layered, metal-rock-water, system). The geophysical, geochemical and geological characteristics

of the Earth reveal much about the planet's overall system. However, when we seek to describe the whole body, such information requires considerable integration and interpretation to see through the last 4.6 Ga of geological history. Improving our understanding of the Earth's composition yields insights into how our planet formed and evolved, as well as providing insights into our planetary neighbors.

Estimating the composition of the Earth requires derivation of the core and silicate Earth (crust plus mantle) composition. A number of papers provide an estimate of the composition of the Primitive Mantle (or silicate Earth), which are based on samples of the mantle and meteorites and these show good agreement (Allegre et al., 1995b; Jagoutz et al., 1979; McDonough and Sun, 1995; O'Neill and Palme, 1997). Estimates of the core's composition are less certain, given uncertainties in the nature of the light element in the outer core. Iron meteorites give insights into elements that might be in the core, but these meteorites are products of low-pressure differentiation, whereas the Earth's core likely formed under markedly different conditions.

Meteorites and observable extra-solar processes tell us much about the nature, composition and evolution of our solar system. Current models suggest that our solar system formed from the gravitational collapse of a rotating interstellar cloud, which may have been triggered by a nearby supernova (Cameron, 1988; Wetherill, 1990). The evolution from a rotating cloud of gas and dust to a highly structured solar system is modeled as a series of collisional processes having some degree of hierarchical evolution. Dust grains accrete to form small particles and these combine to form planetesimals and protoplanets (asteroid like bodies). Following this, and perhaps at a slower accretion rate (due to decreased probabilities of collisions for they are fewer in number), the protoplanets coalesce to form larger bodies. Such large collisions may explain the origin of our Moon, the high Fe/silicate ratio of Mercury, and the retrograde orbit of Venus, among other things.

The time scale for these processes is not well known, but insight is provided from meteoritical studies. The oldest materials of our solar system are the Ca-Al inclusions in chondrites. They have radiometric ages (i.e., time of mineral closure for specific isotopic systems) that are within a few million years of T_0 (i.e., where T_0 is considered as the initiation of formation of our solar system and is on the order of 4.60 Ga) (see Russell et al. (1996) and references therein). In addition, extinct radio-nuclide systems

lend additional constraints on early solar system processes (e.g., timing of metal-silicate differentiation on planets and asteroids). Some of the oldest lunar and Martian materials are on the order of 0.1Ga after T_0 , leading one to conclude that bodies the size of the Earth were formed and differentiating within the first 100 Ma of solar system history.

Material that contributed to the growing Earth came from the same interstellar cloud that gave rise to the other planets and the sun, the later of which contains >99% of the solar system's mass. In its initial state, the interstellar cloud was likely to have been compositionally homogeneous to a first order, but became chemically heterogeneous during the formation and evolution of the planets (Cameron, 1988). The Sun and the outer planets have a substantially greater complement of gases and other volatiles than the inner, rocky planets. Most of the gaseous component in the inner solar system is believed to have been removed during the violent T-tauri stage of the early sun. Outstanding questions include: How did compositional heterogeneity in the solar system developed during planetary accretion? What degree of mixing of components between the "radial feeding zones" in the accreting solar disk is likely to have occurred during planetary coalescence? These questions remain in the realm of speculation until we can get a better handle on the composition of the bulk Earth, Moon, Mars and other inner planetary bodies.

Structure of the Earth

The Earth is made up of 3 major and distinctly different units: the core, the mantle-crust system and the atmosphere-hydrosphere system (Figure 1). These units are the products of planetary differentiation and are distinctive in composition. The mass of the core is about 1/3 of the Earth's mass, its volume is about 1/8 of the Earth's and its radius is about 1/2 of the Earth's. The silicate part of the Earth (crust and mantle) makes up the remaining 2/3 of its mass, and the rest of volume, aside from that of the atmosphere/hydrosphere. The Earth, thus, has 2 distinct boundary layers, the core-mantle boundary and the Earth's surface, with grossly contrasting physical properties above and below these regions. The core is an Fe-Ni alloy, with lesser amount of other siderophile elements and ~10% by mass of a light element. The crust-mantle system is a mixture of silicates containing primarily magnesium, iron, aluminum and calcium. The atmosphere-hydrosphere system is dominated by the mass of the oceans, but the atmosphere is unique within the solar system in that it is an 80/20 mixture of N_2 and O_2 .

A broad range of observations provide us with this first order picture of the Earth. Studies that directly measure physical properties of the Earth's interior include the Earth's seismological profile, its magnetic field, and its orbital behavior, the latter of which provides us with a coefficient of the moment of inertia for the Earth. Less direct information on the make-up of the Earth are provided by studies of meteorites and samples of various parts of the silicate Earth. It is from these investigations that we develop models for the composition of the bulk Earth and Primitive Mantle (i.e., the silicate Earth) and from these deduce the composition of the core.

The seismological profile of the Earth (Figure 1) images density with depth (Dziewonski and Anderson, 1981). Together this and laboratory studies constrain the mineralogical and chemical constituents of the core and mantle. The time it takes a seismic wave to pass through the Earth is a function of the temperature and elastic properties of its internal layers. The bulk sound velocity of a material is directly correlated to its average density and this in turn relates to its mean atomic number (Birch, 1952). The average density for the mantle immediately below the Moho, the seismic discontinuity between the crust and mantle, is 3.3 Mg/m^3 consistent with an olivine dominated mineralogical assemblage that also contains pyroxene and an aluminous phase (plagioclase, spinel or garnet, depending on pressure) (Ringwood, 1975). At deeper levels olivine converts to a β -spinel phase, giving rise to the 410 km depth seismic discontinuity (see review in Agee (1998)). At still deeper levels this olivine component breaks down into Mg-perovskite and magnesiowustite, giving rise to the 660 seismic discontinuity. The latter assemblage appears to continue to the core-mantle boundary (see review in Bina (1998)). At this depth there is a dramatic response change in the seismic profile for both P (compressional) and S (shear) waves, recording a fundamental change in the Earth's physical properties. The average density increases from about 6 Mg/m^3 in the mantle to over 10 Mg/m^3 in the core, reflecting its Fe-rich composition. A final seismic discontinuity is recorded at 5120 km depth and reveals the transition from a fluid outer core to a solid inner core. S waves do not propagate through the outer core, demonstrating that it is liquid.

It is not surprising that the Earth has so much Fe, given Fe is the most abundant element, by mass, in the terrestrial planets (due to the stability of the ^{56}Fe nucleus during nucleosynthesis). The presence of an Fe core in the Earth is also demonstrated by the Earth's shape and magnetic field. The shape of the Earth is a function of its spin and mass distribution. The Earth possesses an equatorial circular bulge and

has flattening at the poles, due to rotational flattening. The coefficient of the moment of inertia for the Earth is an expression for 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 (i.e., the Fe core). Moreover, the presence of the Earth's magnetic field requires the convection of a significant volume of Fe (or a similarly electrically conducting material) to create a self-exciting dynamo.

Chemical Constraints

Combined studies of meteorites and mantle samples place important constraints on compositional models for the silicate Earth. The silicate fraction of the Earth has a composition that is dissimilar to stony meteorites, or achondrites. These meteorites come from the silicate shells of differentiated planets that have also had a metallic core extracted. Bulk planetary compositional models based on meteorites compare the elemental abundance pattern for the planet with that of various chondrites, which are primitive, undifferentiated meteorites (Wasson and Kallemeyn, 1988). In particular, the CI carbonaceous chondrites, the most primitive of the chondritic meteorites, are often considered as the reference group of chondrites by which to compare planetary compositions (Anders and Ebihara, 1982).

Elements can be classified as refractory, moderately volatile or volatile, depending on their sequence of condensation into mineral phases (metals, oxides and silicates) from a cooling gas of solar composition (Larimer, 1988). Refractory elements (i.e., Ca, Al, Ti, Sc, REE) have the highest condensation temperatures and occur in all chondrites at similar relative abundance ratios (e.g., Ca/Al, Al/Ti, REE/Ti). The moderately volatile (e.g., Na, K, Rb, Fe, Ni P) and volatile elements (e.g., F, Cl, Tl, Bi, Pb) have lower condensation temperatures and their relative abundance ratios vary considerably between the different types of chondritic meteorites. The CI carbonaceous chondrites are free of chondrules and Ca-Al rich inclusions, possess the highest abundances of the volatile and moderately volatile elements relative to the refractory elements and have a composition that matches that of the solar photosphere when compared on a Si-based scale.

Another element classification scheme uses the chemical behavior of elements to group them as lithophile, siderophile, chalcophile or atmophile (Larimer, 1988). The lithophile elements are concentrated in the silicate shell of the Earth and are elements that bond readily with oxygen (i.e., the silicates). The siderophile elements are those that readily bond with Fe and are most concentrated in the Earth's core. The chalcophile elements bond readily with S and are distributed between the core and mantle, with a greater percentage of them in the core. Finally the atmophile elements are gaseous and concentrated in the thin layer of atmosphere that surrounds the planet. By combining these 2 different classification schemes we can better understand the relative behavior of elements, particularly during accretion and large-scale planetary differentiation.

Establishing the composition of Earth and its major compositional reservoirs can be done in a 4-step process. First, establish an estimate for the composition of the silicate Earth. Second, define a volatility curve for the planet, based on the abundances of the moderately volatile and volatile lithophile elements in the silicate Earth, assuming that none of these elements have been sequestered into the core (i.e., they are truly lithophile). Third, estimate the abundances of the siderophile and chalcophile elements in the core based on the volatility curve established in step 2, meteorite analogues and the small amount of these elements in silicate Earth. Fourth and finally, sum the core and mantle composition with that of the atmosphere to obtain a bulk Earth composition. The resulting model can be compared to geophysical data to test for consistency.

THE COMPOSITION OF THE SILICATE EARTH

Most models for the composition of the silicate Earth agree to within ~10% at the major element level (Allegre et al., 1995b; Anderson, 1989b; Jagoutz et al., 1979; McDonough and Sun, 1995). These models assume that the refractory elements are in chondritic proportion in the bulk Earth and that those that are lithophile are excluded from the core. The silicate Earth's composition is derived by comparing the compositions of peridotites (samples of the upper mantle) with that of primitive, mantle-derived magmas, the chemical complement to peridotites (Sun, 1982). Model compositions derived in this fashion are then compared with data from chondrites.

Compositional models for the silicate Earth usually fall in one of two categories based on major elements. One class of models assumes that the silicate Earth has a complement of Mg and Si that is equal to that in CI carbonaceous chondrites. Given this, the remaining elements are grouped into either more refractory (i.e., with higher condensation temperatures during solar system formation and equal to that in CI chondrites), or volatile groups. For those that are volatile, the rock record establishes their abundances in the silicate Earth. The second model depends on mantle samples to establish the Mg and Si abundance in the silicate Earth and shows that it does not have CI chondritic relative abundances of these elements when compared to the refractory lithophile elements. Of the 5 major element oxides in the silicate Earth (i.e., SiO₂, MgO, FeO, Al₂O₃, and CaO), only Al₂O₃, and CaO are truly refractory and are constrained by observations made on chondrites; the others are volatile and their abundances not fixed between different varieties of chondrites. Fe is siderophile and is partitioned between the core and mantle. In contrast, Mg and Si are lithophile and concentrated in the mantle, although under very reduced conditions Si will form metals and would be partitioned into the core.

In models thus derived relevant questions include 1) how representative are peridotites of the entire silicate Earth, and 2) do upper mantle samples faithfully record the composition of the lower mantle? Although there are other lithologies in our samples of the upper mantle, in principle, the upper mantle can be considered to be a peridotite, with volumetrically minor amounts of other components. In addition, because the continental crust is only 0.6% by mass of the silicate Earth, the addition of the continents to the mantle will have negligible effect on the major element composition of the mantle. However, the crust is a significant reservoir for the highly incompatible trace elements (e.g, K, Th, U) and thus it plays an important role in establishing the abundance of abundances of these elements in the silicate Earth (Rudnick and Fountain, 1995; Taylor and McLennan, 1985). The combined mineral physics and seismological data are consistent with compositional homogeneity between the upper and lower mantle (Bina, 1998; McDonough and Rudnick, 1998), although these data can also be considered as indicating differing compositions between the upper and lower mantle (Anderson, 1989a; Anderson, 1989b). On the other hand, the ample tomographic evidence for deep penetration of subducting slabs of oceanic lithosphere into the lower mantle (Van der Hilst et al., 1997) demonstrates that there is considerable transfer of material between these two regions. Likewise, the geological record of modern style plate tectonics for the last 3.8

Ga (e.g., Komiya et al. (1999) and references therein) and its presumed deep cycling argues for considerable whole mantle stirring for the last few billion years. Thus, we assume that the whole of the mantle has a relatively uniform major element composition.

The spectrum of mantle derived samples used to model the Silicate Earth include peridotite xenoliths (mantle rock fragments brought by kimberlites and basalts), massif peridotites (large mountain-sized bodies of the mantle that have been thrust upon the Earth's crust) and primitive, high temperature magmas (e.g., basalts and komatiites). To a lesser extent crustal rocks are used to constrain the abundances of some elements (e.g., K and other highly incompatible elements) in the Silicate Earth. Peridotite studies provide direct information on the nature and composition of the upper mantle. Archean to modern, primitive lavas provide additional, although less direct, data about the initial composition of their source regions back to about 3.8 Ga. Thus, these rocks are useful in constructing a time-integrated evolutionary model of the mantle. The same is true for peridotites, to a certain extent, if their formation ages (or melt extraction ages) can be established.

Figure 2 shows the abundances of some elements in peridotites that exhibit limited compositional variation (McDonough, 1994). This then constrains the range of compositional models of the silicate Earth for these elements, assuming similar compositions for the upper and lower mantle. There is only a couple of percent variation in the SiO₂ content of peridotites and only about 10% variation in the Mg/Ni, Co and FeO values. A primitive mantle composition of ~38 wt% MgO can be derived from melt-residue relationships and compositional trends seen in MgO versus incompatible elements (i.e., elements that readily partition into magmas during mantle melting) plots. With this MgO content a number of other element concentrations (including CaO, Al₂O₃, TiO₂, refractory lithophile elements) can be estimated from these and similar graphs.

A model composition for the Silicate Earth is presented in Table 1. A detail description of how this and other similar models have been derived is given in McDonough and Sun (1995) and O'Neill and Palme (1997). This model is consistent with existing petrologic and isotopic data, as well as with seismologic, mineral physics, geodynamic and heat flow data.

Figure 3 shows the lithophile element composition for the silicate Earth model as compared to CI carbonaceous chondrites. It has long been established that the silicate Earth is depleted in volatile lithophile elements (e.g., K and Rb) relative to primitive chondritic meteorites. When compared to CI carbonaceous chondrites the Silicate Earth is depleted in Mg and Si relative to the refractory lithophile elements. The Earth shows a uniform decrease in the abundances of the moderately volatile and volatile lithophile elements with decreasing condensation temperature (FIGURE 3). Assuming that the elements that make up this volatility trend are excluded from the core, then this feature reflects the nature of the nebular material in the planetary feeding zone of the proto-Earth at ~1AU (i.e., the zone in which the Earth coalesced). Comparing this trend to that of siderophile and chalcophile elements allows one to establish the composition of the core (see next section).

The chemical signatures of peridotites and primitive lavas can also be used to constrain the amount of material exchange between the core and mantle through time. In terms of a secular variation at the major element level, there is little evidence for a gross compositional change in the mantle. For example, there is limited variation in Mg/Ni values (Figure 2) for peridotites from a variety of tectonic locations and ages, including samples that are >3.0 Ga old from the Kaapvaal craton, South Africa (McDonough, 1994). Given that >90% of the Earth's Ni is in the core, this suggests that significant mass transfer across the core-mantle boundary has not occurred throughout the geologic record. Likewise, there is ~20% variation in the P/Nd values of primitive lavas, from Archean to Recent (McDonough and Sun, 1995), including those from markedly different tectonic settings (e.g., mid-ocean-ridge, arc, ocean islands). Because ~95% of the Earth's P budget is in the core, this suggests that significant amounts of core material have not been added to the source regions of basalts.

THE COMPOSITION OF THE CORE

The Earth's core is metallic and is composed of an Fe-Ni mixture. This is based on 3 lines of evidence. First, the mean atomic number for core of the Earth derived from seismic studies (i.e., ~56), is matched by that of Fe or an Fe-Ni mixture. Second, the Earth has a magnetic field generated by a dynamo that is driven by convection of a conducting fluid such as molten Fe alloy. Third, if the Earth is assumed to have a chondritic composition, an Fe- and Ni-rich reservoir is required to balance the silicate Earth. In

addition, aside from the principal gaseous elements (e.g., H, He, C, N, O), Fe is one of the most abundant elements in the solar system and so it is reasonable that the core is the Earth's Fe-rich reservoir.

Several lines of evidence suggest that the core contains more than just Fe and Ni. Based on the relationship between seismic wave speed and mean atomic number of various materials Birch (1952) demonstrated that the core has properties comparable to that of Fe, with the outer, liquid core having ~10% on average of another, less dense component. Laboratory studies on the compression of Fe-Ni alloy at core pressures (Brown et al., 1984; Brown and McQueen, 1986; Mao et al., 1990) indicate that the outer core possess a significant proportion ($\sim 10\% \pm 4$) of a light element. Also, the large density increase between the inner and outer core, which is determined from the jump in P wave velocities at the inner-outer core boundary (Shearer and Masters, 1990), is inconsistent with an isochemical liquid-solid phase transition.

The nature of the light element component in the outer core has received considerable attention but consensus is yet to be had (e.g., see Birch (1952) and Poirier (1994) references therein). A host of elements that have been suggested for the light element: H, C, N, O, Mg, Si, S (and others). Alternatively, mixtures of 2 or more of these components have been considered. Poirier (1994) reviews this topic from both a petrological-cosmochemical perspective and from a seismological-mineral physics perspective. Since his review there have been other studies on this topic, but with little resolution. It is this author's opinion that we cannot conclude what the light component in the outer core is, although it is likely that a mixed component is needed (see discussion below).

Insight into the nature of the light component can be gained from determining the physical conditions of core formation in the early Earth. One class of models suggests that the Earth's core formed from an accumulation of core components from small planetismals, which differentiated at relatively low pressures. Upon accretion to the proto-Earth these high-density metals sank to the gravitational center experiencing little interaction with the surrounding silicate mantle. An alternative model envisages core separation at relatively high-pressure, which was initiated after much of the growing Earth was accreted. Under these conditions one expects quite different chemical consequences due to differences in partition coefficients between silicate and metal at low- versus high-pressure conditions. A third class of models

incorporates aspects of both scenarios in support of a hybrid model. It is possible that new isotope studies (see later discussions) will help to distinguish between these competing models.

A model composition of the core is presented in Table 2 (McDonough, 1999). The limits of our understanding of the core's composition (including the light element component) depend on models of core formation and the class of chondritic meteorites chosen for constructing models of the bulk Earth's composition. The core is the dominant repository of the siderophile elements in the Earth and there is limited variation in chondritic ratios of siderophile elements having similar volatility (FIGURE 4). This observation, together with the Earth's volatility curve (FIGURE 3), established using the lithophile elements in the silicate Earth, can be used to estimate the planetary budget for the volatile siderophile and chalcophile elements. By setting a limit of ~10% for the light element content of the core, the major and minor siderophile element content of the core is established. This yields a core with ~85% Fe, ~5% Ni, ~0.9% Cr and 0.4-0.2% P, Mn, Co, and C, along with trace quantities of other siderophile and chalcophile elements (Table 2). Mn, Cr and V appear to have been lithophile, siderophile, and chalcophile during core segregation, based on their abundances in the silicate Earth and core. The Mg/V value for the silicate Earth is 0.28 and this is greater than that seen in all chondritic meteorites (Wasson and Kallemeyn, 1988); as such this will reflect the bulk Earth's ratio if no V is in the core. Alternatively, using the core composition in Table 2 and assuming no Mg in the core, the bulk Earth has a Mg/V value (0.16) that is within the range of chondritic meteorites (0.15-0.24). The presence of Mn, V, and Cr in the core helps us to constrain the P-T- f_{O_2} - f_{S_2} of its formation.

Recently, Li and Agee (1996) presented compelling experimental evidence for high T-P conditions of core formation. They found that the partitioning of Ni and Co between metal and silicate at high P-T (in the region of the lower Transition Zone and upper Lower Mantle) is similar and would thus produce the observed chondritic value for Ni/Co in the mantle. This result contrasts with low P-T studies that show these elements fractionating from one another, with Ni being strongly partitioned into the metal (Jones and Drake, 1986). Thus, Li and Agee (1996) concluded that the Earth experienced high-pressure equilibration of metal and silicate during core formation.

Among the elements that are classified as siderophile, Ga is an anomaly (Figure 3). Gallium is found in the metal phases of Fe meteorites and shows somewhat depleted abundances in stony meteorites, which is why it is considered siderophile. During crust-mantle differentiation, Ga follows Al (as predicted from their relative positions on the periodic table) and thus the abundance of Ga in the silicate Earth is well established (McDonough, 1990a). Ga plots within the field defined by the volatile lithophile elements (Figure 3) suggesting that either the assumed temperature at 50% condensation is incorrect, or that Ga behaved solely as a lithophile element during core formation. If the latter is true, then determining under what conditions Ga becomes wholly lithophile provides an important constraint on core formation.

Based on the Earth's volatility curve (FIGURE 3), it appears that the bulk of the planetary budget for sulfur (and selenium and tellurium, other strongly chalcophile elements) is held within the core and not the mantle, given its marked depletion in the latter (Table 1). This partitioning of sulfur into the core accounts for only <2% (not 10%) of the light element component in the outer core (McDonough and Sun, 1995), suggesting that this component is a mixture of elements, including sulfur. Given this, and evidence for core formation at high-pressure (e.g., 20-30 GPa), a model using Si as the other light element in the outer core is presented in Table 2. The estimate for Si in the core (c.f., O'Neill (1991) and O'Neill and Palme (1997)) is based on the volatility curve for lithophile elements in the Earth (FIGURE 5), and this is not well constrained, particularly given the marked variations in Si contents of chondritic meteorites. Silicon is known to behave as a siderophile element under very reducing conditions and is found as a metal in some enstatite chondrites. This model for the light element component in the outer core is at best tentative. Presently, considerable efforts are being invested to gain further insights into the nature of the light element in the Earth's core. Until this is established with better certainty we must entertain multiple hypotheses on its nature.

The timing of core formation is not well constrained. From high pressure experimental studies and chemical and isotopic observations it seems that the core formed after most of the planet accreted. Also, core separation appears to have been completed within the first few hundred million years (or less) of the Earth's history. Recent studies of an extinct, short-lived radioactive isotope of hafnium (^{182}Hf , a lithophile element decays to ^{182}W , a siderophile element, with a 9 Ma half-life) demonstrate that core formation may have been short, circa 20-50 million years (Halliday et al., 1996; Jacobsen and Harper, 1996; Lee and

Halliday, 1995). The isotopic composition of W in the Earth's mantle is similar to that in chondritic meteorites and is unlike that in iron meteorites, indicating that core separation in the Earth must post-date the decay of most of the short-lived ^{182}Hf . In contrast, depletion of ^{182}W in the W isotopic spectrum of iron meteorites is firm evidence for the early separation of a W-bearing iron core from a Hf-bearing mantle in these planetesimals.

The Moon may also provide constraints on the timing of the Earth's core formation. If the Moon formed from a giant impact event (see review in Melosh (1990)) its composition is likely to be a mixture of the impactor and the Earth. The Moon's bulk density and composition is similar to that of the Earth's mantle (Ringwood, 1979). This, plus the high Fe contents of lunar rocks suggests that the Moon has a small (2-4% by mass) core (Hood, 1986), implying that much of the core components of both the impactor and the Earth were excluded from the Moon during its accretion. Lee et al. (1997) found that lunar rocks have a significant variation in $^{182}\text{W}/^{184}\text{W}$, indicating that the Moon formed, experienced core segregation, and developed various silicate reservoirs early (i.e., circa <4.50 Ga) in its history. Thus, a better understanding of lunar origins is likely to provide important insights into aspects of core formation and evolution on the Earth.

The U-Pb isotope system is also considered useful for constraining the timing of core formation (Allegre et al., 1995a). This is because Pb, often considered to be chalcophile, was believed to have been sequestered into the core during its formation, while U, a lithophile element, was concentrated in the mantle. However, as noted above, there is abundant evidence for depletion of moderately volatile and volatile lithophile elements in the Earth. Pb is a volatile element and it, along with the other volatile chalcophile elements (e.g., In, Cd, Hg), displays depletions comparable to those observed in lithophile elements of similar volatility. Thus, it difficult to establish the Earth's initial ratio of U/Pb, which is essential for dating core formation, assuming Pb was extracted into the core. Moreover, based on the Earth's volatility trend (Figures 3 and 5) it appears that the bulk of the Earth's Pb budget has remained in the mantle, with little or no Pb partitioned into the core. If true, the U/Pb isotope system is not particularly suitable for dating core formation.

A final question is the extent of core separation that may have continued throughout geologic time and the extent of core-mantle exchange that may still be taking place. The composition of the Earth's earliest rocks (circa 4.0 Ga) suggests that core separation was completed after about the first half billion years of earth history or earlier. Komatiites, ancient high magnesium lavas generated by large degrees of melting, and basalts carry with them a compositional signal of the Earth's mantle at their time of their eruption. The limited variation in ratios of siderophile to lithophile elements (e.g., Fe/Mg, Fe/Mn, and P/Nd) in these lavas throughout time demonstrate that there has been limited core-mantle exchange (McDonough and Sun, 1995). Likewise, the compositions of peridotites stored beneath the continents (continental roots) for billions of years are a secular record of the mantle. These rocks also possess constant values of key lithophile/siderophile ratios (e.g., Mg/Ni as seen in Figure 2), further indicating that negligible amounts of exchange has occurred between the core and mantle, since early core formation. We cannot constrain these observations further without specific knowledge of the volumes of mantle represented by these samples. If collectively the lava and peridotite samples are faithfully recording the composition of the whole mantle to a first order, then we can argue that these samples restrict core-mantle exchange to less than a fraction of a percent, based on mass proportions and compositions in Tables 1 and 2. Recent models invoking the addition of core components to explain the Os isotopic compositions of Hawaiian basalts (Brandon et al., 1998; Walker et al., 1995) are permissible, as long as the mass contribution is at the fraction of a percent level or less. Larger amounts of a core contribution would shift key lithophile/siderophile ratios to values outside those observed in basalts (McDonough and Sun, 1995).

THE COMPOSITION OF THE EARTH

The Earth, with all the terrestrial planets, is assumed to have chondritic proportions of the refractory elements and is modeled at ~2.75 times their abundance levels in CI carbonaceous chondrites. This enrichment factor is due to two factors. First, these chondrites are rich in water and CO₂, whereas the Earth is not. Second, core subtraction results in the silicate Earth being enriched by a factor of 1.5, based on mass proportions. Likewise, the planet is assumed to possess chondritic proportions of Fe and Ni, given the limited variation in Fe/Ni in chondritic meteorites (Figure 4).

Aluminum, a refractory lithophile element, is considered least likely of the major lithophile elements (e.g., Si, Mg, Ca) to be incorporated in the core. Therefore, the combined Fe content of core and silicate Earth and the Al content of the silicate Earth establishes the Earth's value of Fe/Al at $\sim 20 \pm 2$, given a core with 85% Fe (Table 3) (Allegre et al., 1995b; McDonough and Sun, 1995). Thus, this Fe/Al value for the Earth is an important result; it provides an estimate of the composition of the planet that does not require knowledge of the nature of the light element in the core.

The Fe/Al constraint for the Earth provides a measure of evaluating which of the different groups of chondritic meteorites are the best candidates as analogs to the bulk Earth's composition. Chondritic meteorites, including carbonaceous, enstatite and ordinary varieties, display a range of Fe/Al ratios, with many having a value close to 20 (Allegre et al., 1995b). However, the EH enstatite chondrites have high Fe/Al values (35) and the CV and CK carbonaceous chondrites have low Fe/Al values (13-15) (Wasson and Kallemeyn, 1988). Thus, none of these chondrite groups possess the major element characteristics that make them suitable analogs for the bulk Earth. This result is at odds with the oft-cited observation that the Earth has a Mg/Si ratio like that of CV and CK chondrites and that these meteorites may be good analogs for the Silicate Earth (O'Neill and Palme, 1997). Overall, the Earth has a volatile depletion pattern similar to that of the chondrites (FIGURE 5). However, in our existing inventory of meteorites it appears that there is no identifiable archetype that distinguishes itself as being a spitting image of the Earth.

Early evolution of the Earth

The Formation of the Earth's core and mantle at about 4.6-4.5 Ga via planetary accretion and core separation suggests a very hot early Earth that continues to convect vigorously in order to remove heat from the planet's interior. This thermal evolution has had a marked influence on the chemical evolution of the planet (Davies, 1990). The mantle and its properties regulate the removal of heat from the Earth's core. Likewise, the atmosphere controls the Earth's capacity to radiate heat to outer space.

The accretion of the inner planets was likely to have occurred in a relatively high temperature environment. The collapse of the proto-solar cloud to form the sun produced a hot central region in the solar system and a considerable temperature gradient across it (Boss, 1998; Lewis, 1974). The inner solar system (e.g., perhaps out to 3 AU or more) experienced high temperature processing (Boss, 1998),

including the melting of grains, inclusions, and chondrules (high temperature components of meteorites). The earliest formed materials have crystallization ages on the order of <3 Ma (or less) after T_0 (Allegre et al., 1995a). It is these high-temperature condensates, along with lesser amount of lower-temperature condensates that coalesced to form grains and larger sized fragments, which further accreted to form larger bodies including planetismals and ultimately planets. A considerable amount of thermal energy is evolved in this process resulting in substantial internal heat in the latter stages of planet building that must be dissipated from the planet's interior. In addition, the giant impact event hypothesized to form the Moon would have significantly heat the Earth (Melosh, 1990).

If the Earth accreted from a mixture of silicates and metal particles followed by metal-silicate differentiation, separation of the Earth's core would heat the mantle (Birch, 1965; Elsasser, 1963; Flasar and Birch, 1973). It was calculated that the gravitational energy released by core formation would be converted into thermal energy, which would be enough to heat the mantle by about $1000-2000^\circ\text{C}$ - thus driving mantle convection (Davies, 1990).

How fast this heat was dissipated to space depends on the nature of the early atmosphere. If the Earth had a significant gaseous envelope surrounding it throughout most of its accretion, it would have enhanced the chances of the upper portion of the mantle being wholly molten through thermal blanketing and greenhouse heating of the surface. Alternatively, if there was no atmosphere, the planet's heat is rapidly lost to space by radiation and little to no extensive melting of the mantle would have occurred.

The above considerations lead to the suggestion that the Earth's mantle experienced large scale melting during accretion and core formation. Collectively these processes start the convective engine for the mantle. Given the likely event of the outer portion of the mantle experiencing significant global melting, one would expect that the mantle would have also experienced some degree of differentiation (crystal-liquid separation). However, there is no geochemical and/or isotopic evidence, based on a wide spectrum of crustal and mantle rocks (including peridotites and komatiites), in support of this global differentiation process (see the recent review by Carlson (1994)). Thus, if differentiation of the mantle occurred in the Hadean, its effects have been completely erased by the processes of rapid and vigorous convection.

FIGURE CAPTIONS

FIGURE 1. Schematic diagram of the basic structure of the Earth identifying its 3 distinct layers: metallic core, rocky silicate shell and its hydrous gaseous exosphere. The density and seismic wave structure (PREM) is shown for comparison (Dziewonski and Anderson, 1981).

FIGURE 2. Element variation diagrams illustrating the extent of chemical variation in peridotites (mantle samples) worldwide. The MgO content of peridotites is given in weight percent and is a measure of the peridotite's refractory character. Peridotites with low MgO contents (e.g., ~37 wt%) are fertile and have had little melt extracted, whereas those with high MgO contents (e.g., ~48 wt%) are refractory and have experienced extensive melt depletion. The MgO versus Mg/Ni plot shows the variation in a lithophile/siderophile ratio for these mantle samples and demonstrates that this ratio has remained constant throughout the mantle and geologic time (see text for further details). This together with the plots for Co and FeO demonstrate that there is limited chemical exchange between the core and mantle since core extraction in earliest Earth history. The MgO versus SiO₂ plot shows the limited variation in SiO₂ contents in peridotites, regardless of the degree of melt extraction. The numbers and the +/- values are the average and 1st standard deviation values; n = 1240 refers to the number of samples used in the diagrams. The different symbols identified in the legend are for peridotites from different geological and tectonic settings and ages; further details on these differences are given in McDonough (1990b; 1994) and McDonough and Sun (1995). The data are from the literature; an updated compilation is available at the GERM (Geochemical Earth Reference Model) website.

FIGURE 3. The abundance of elements in the silicate Earth normalized to their abundances in CI carbonaceous chondrites (for an equal abundance of Mg) versus their 50% condensation temperature from a model solar system gas condition. Elements are grouped according to their dominant chemical behavior, with the lithophile elements being rock-forming elements that are partitioned into the silicate Earth. The gray bar in the plots of siderophile and chalcophile elements (those that follow Fe and S, respectively) illustrates the Earth's volatility trend, assuming that the volatile lithophile elements that establish this trend are excluded from the core. The markedly lower concentrations of S, Se and Te (as compared to the other chalcophile elements) in the silicate Earth reflects their partitioning into the core. Not identified are the

refractory lithophile elements, whose abundances are at 1.16 times the CI and Mg normalized reference value. The condensation temperature scale is taken from Wasson (1985). The data for the element abundances are from Table 1.

FIGURE 4. Plots showing the variations in elements ratio for different classes of chondritic meteorites and the bulk Earth composition. The elements selected are those that were strongly partitioned into the core. There is clearly limited variation in relative abundances of Fe, Ni and Co in different classes of chondrites. This restricts the potential variation in the amount of Ni and Co in the core for a given Fe content. There is greater variation seen in Cr, V and P contents, but these, along with other observations, provide for a relatively narrow range of plausible core contents for these elements. Ratio values are expressed in relative weight fractions. The carbonaceous chondrites are CI, CM, CO, and CV. The ordinary chondrites are H, L and LL (representing high, low and very low Fe contents, respectively). The enstatite chondrites are EH and EL (representing high and low Fe contents, respectively). Data for chondrites from Wasson and Kellemeyn (1988) and for Earth is from Table 3.

FIGURE 5. The abundance of elements in the Earth and various carbonaceous chondrites normalized to their abundances in CI carbonaceous chondrites (for an equal abundance of Mg) versus their 50% condensation temperature from a model solar system gas condition. Only shown here are the volatile elements. The grey field illustrates the trend for the less primitive, carbonaceous chondrites, including the types CM (open boxes), CO (white circles with dots) and CV (white diamonds). Data for chondrites from Wasson and Kellemeyn (1988) and for Earth is from Table 3.

Table 1. 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	0.1
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 $\mu\text{g/g}$ (ppm), unless stated as “%”, which are given in weight %.

Table 2. The composition of the 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	2000	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	3500	Ru	4	Hf	0
S	19000	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	9000	Te	0.85	Hg	0.05
Mn	3000	I	0.13	Tl	0.03
Fe %	85	Cs	0.065	Pb	0.4
Co	2500	Ba	0	Bi	0.03
Ni	52000	La	0	Th	0
Cu	125	Ce	0	U	0

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

Table 3. The composition of the 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	0.1
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	0.1
Na %	0.18	Y	2.9	Er	0.3
Mg %	15.4	Zr	7.1	Tm	0.046
Al %	1.59	Nb	0.44	Yb	0.3
Si %	16.1	Mo	1.7	Lu	0.046
P	1210	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	1700	I	0.05	Tl	0.012
Fe %	31.9	Cs	0.035	Pb	0.23
Co	880	Ba	4.5	Bi	0.01
Ni	18220	La	0.44	Th	0.055
Cu	60	Ce	1.13	U	0.015

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

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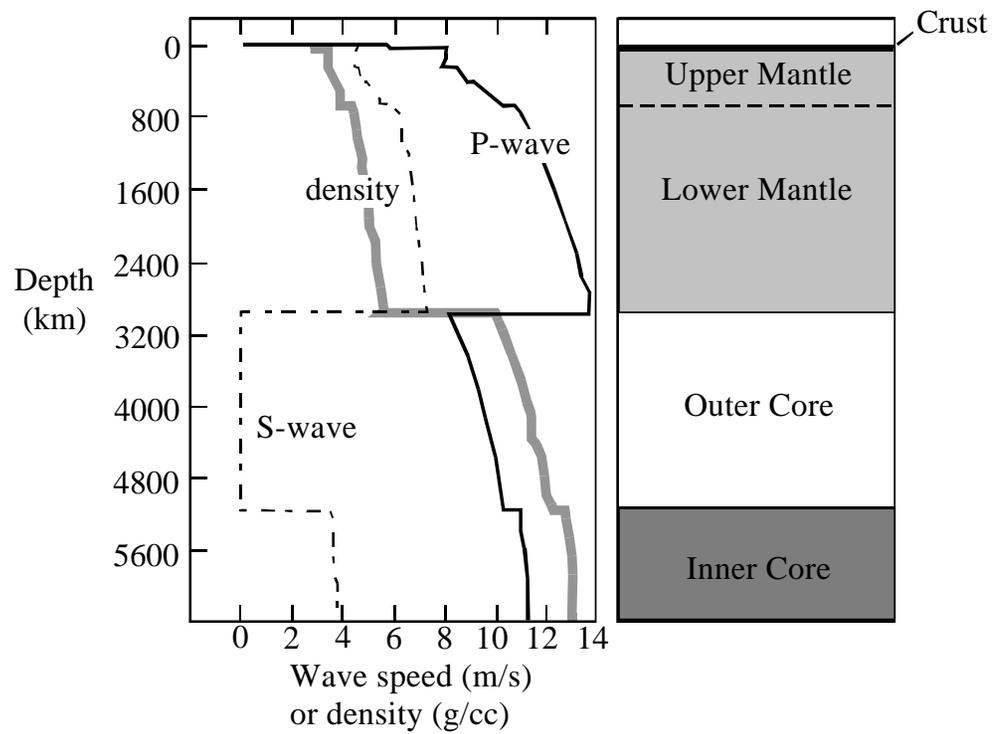


Figure 1 - McDonough

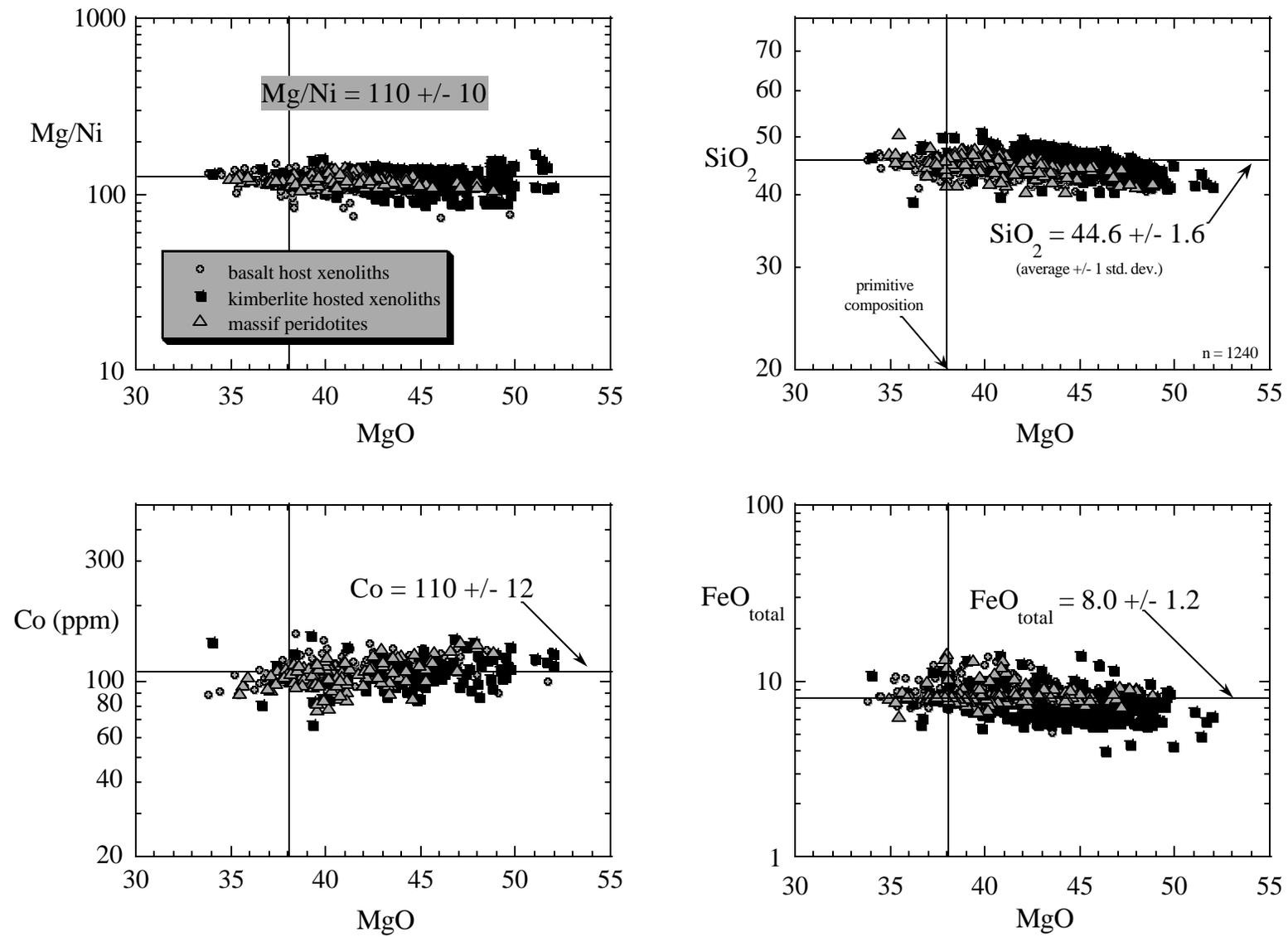
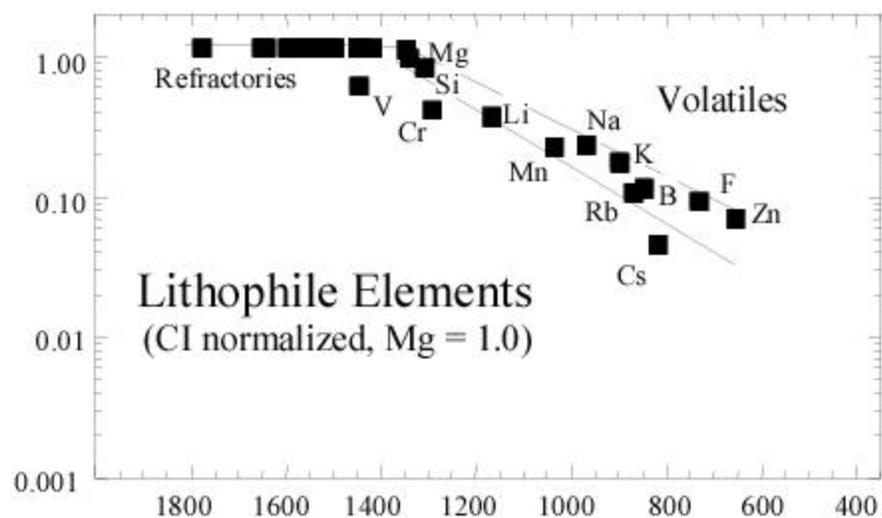


FIGURE 2



Refractory Lithophile Elements:

Al, Ca, Sc, Ti,
Sr, Y, Zr, Nb,
Ba, Ree, Hf, Ta
Th and U

(all are in chondritic relative abundances)

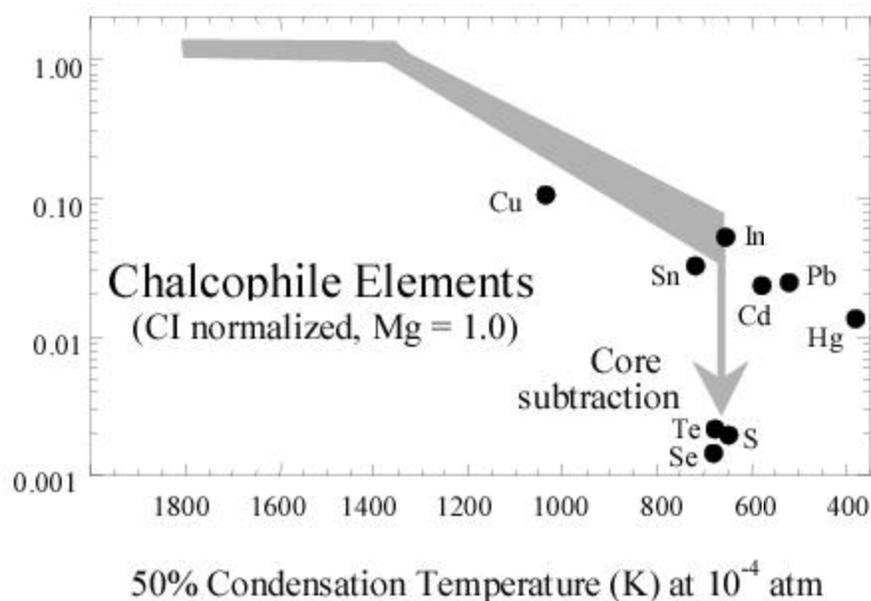
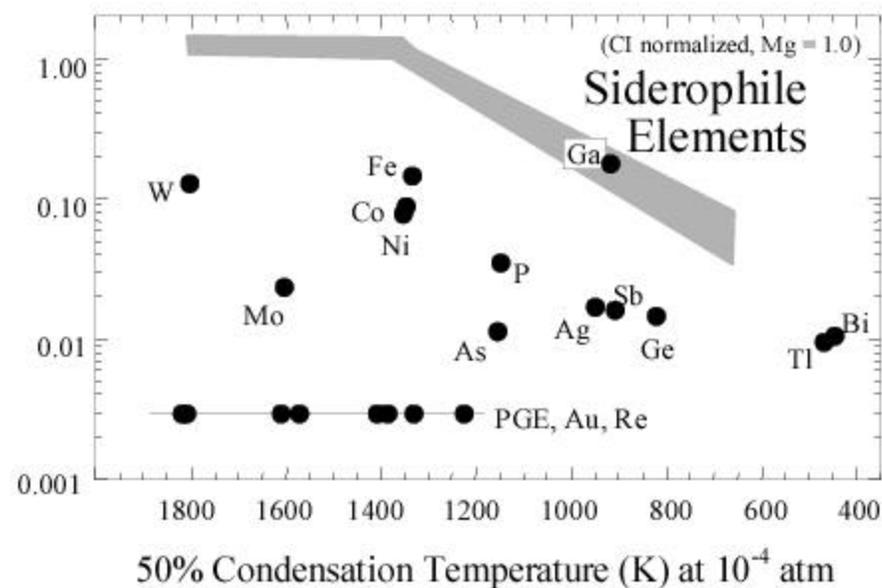


Figure 3

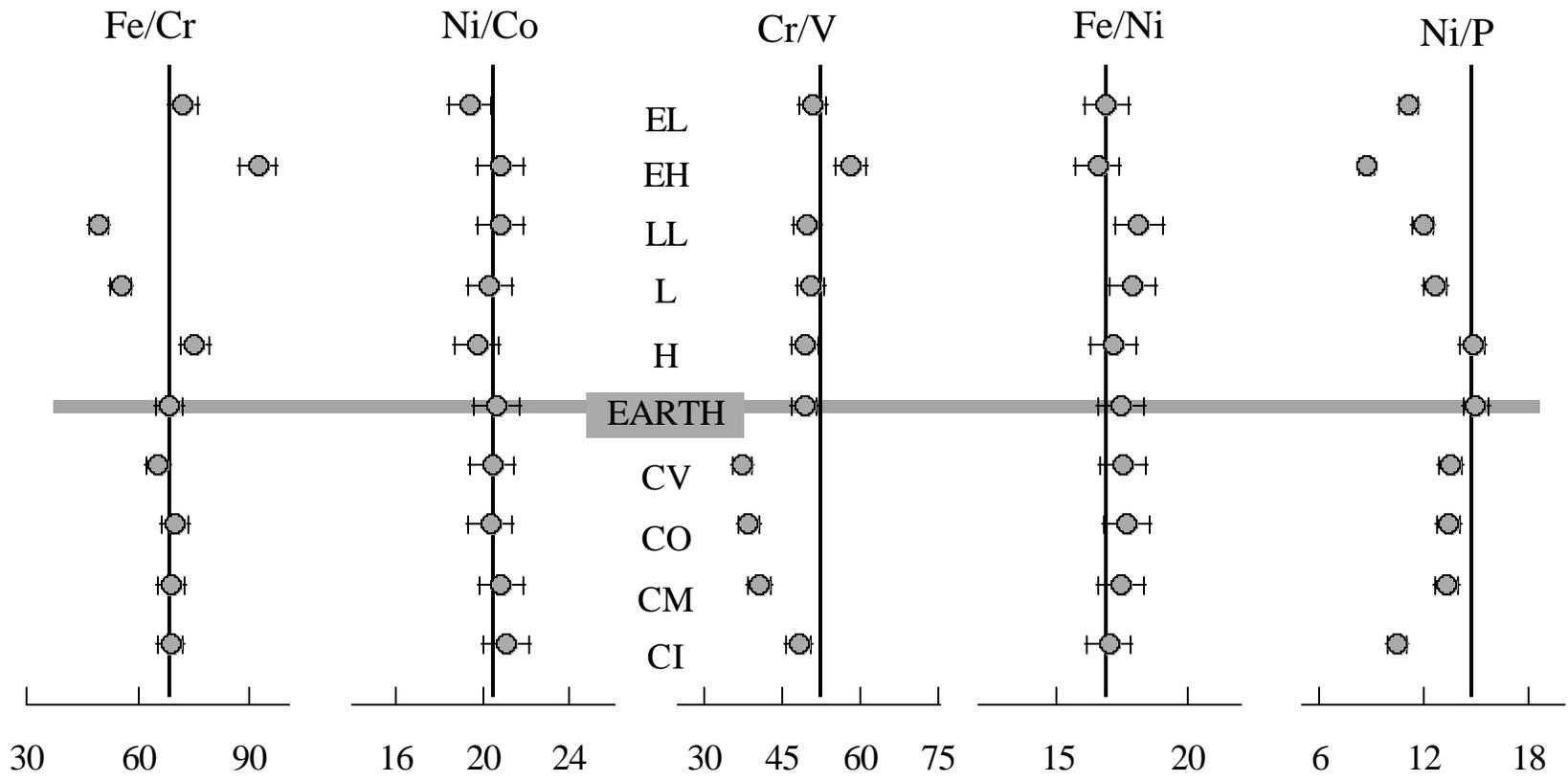


Figure 4

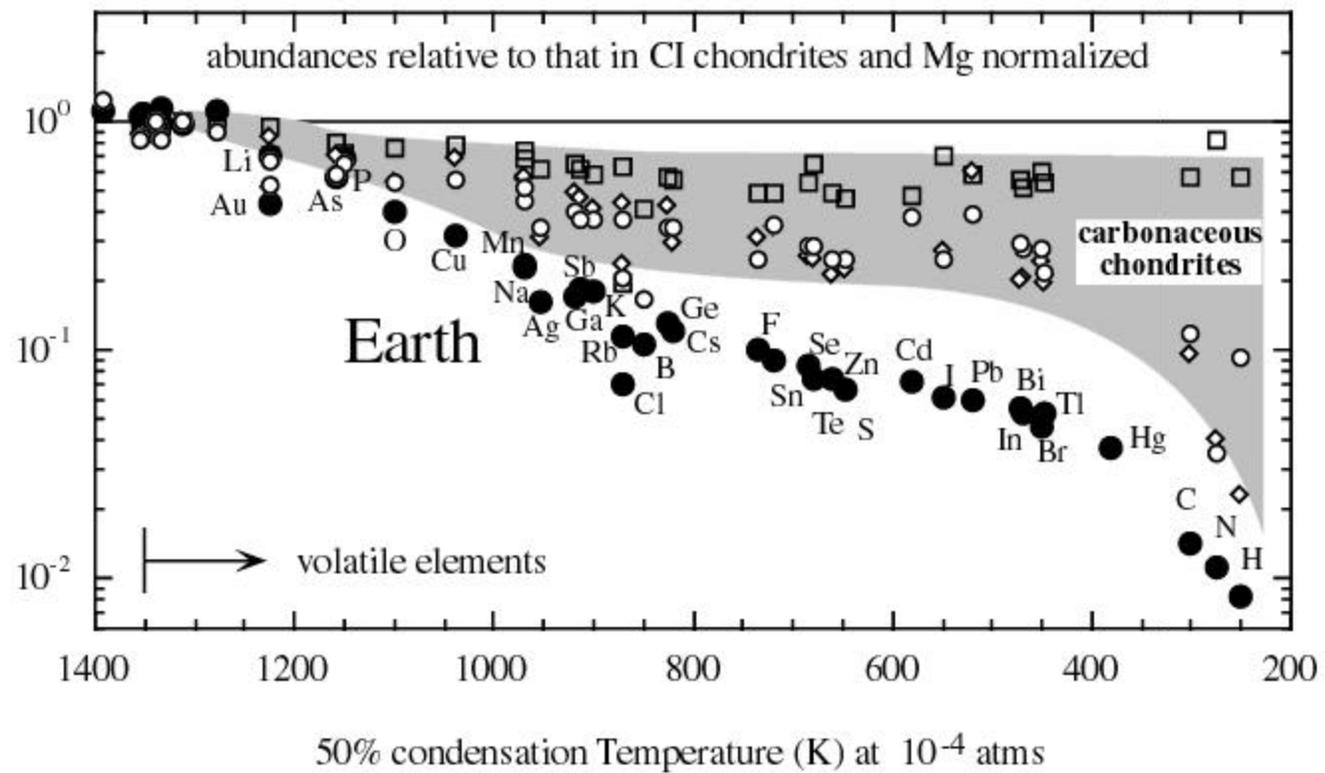


Figure 5 (McDonough)