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Carbon in the Core: Its Influence on the Properties of Core and Mantle

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INTRODUCTION

Earth's core is known to be metallic, with a density of about 9.90 Mg·m^{-3} at the core-mantle boundary and as such is substantially denser than the surrounding mantle (5.56 Mg·m^{-3} at the core-mantle boundary; Dziewonski and Anderson 1981). Comparison with cosmic abundances suggests that the core is predominantly Fe with around 5% Ni (Allègre et al. 1995; McDonough 2003) and 8-12% of one or more light elements (Birch 1952). The latter conclusion comes from the observation that the core is appreciably less dense than pure Fe or Fe-Ni alloys under any plausible core temperature conditions (Stevenson 1981). The nature of the light element (or elements) has been the subject of considerable speculation, because of its bearing on Earth's overall bulk composition, the conditions under which the core formed, the temperature regime in the core, and possible ongoing interactions between core and mantle. Any element with substantially lower atomic number than iron ($z = 26$) would have the required effect on core density, but it must also be of high cosmic abundance and it must be soluble in liquid Fe under both the conditions of core formation and those of the outer core. A review of the likely contributors to the core density deficit (Wood 1993) concluded that S and C were the most likely candidate elements and acknowledged that Si, which is extensively soluble in Fe at low pressures, could also conceivably be present. More recently, arguments have been put forward in favor of H (Okuchi 1997) and O (Rubie et al. 2004) as major "light" elements in the core. Although the presence of any of these other elements would not exclude C from the core, dissolution of most of them in liquid Fe require specific compositions of accreting planetesimals and specific conditions of core formation. In order to place constraints on core composition, therefore, it is necessary to consider the cosmochemical abundances of the elements and the process of core formation in the early solar system.

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Earth's earliest history was marked by accretion from protoplanetary materials and segregation of the core within about 35 m.y. (Kleine et al. 2002; Yin et al. 2002) and formation of the Moon by giant impact approximately 100 m.y. after the origin of the solar system. During this primary differentiation, all elements were distributed between the Fe-rich metallic phase and the silicate mantle according to their partition coefficients D_i ($D_i = [i]_{metal}/[i]_{silicate}$). The net result is that the mantle is relatively depleted in those (siderophile) elements with high D_i, which partitioned strongly into the core and enriched in lithophile elements with low D values. These qualitative observations are placed in context by the observation that Earth's mantle has strong compositional affinities with chondritic meteorites (Allègre et al 1995; McDonough and Sun 1995). Figure 1 shows the abundances of a large number of elements in silicate Earth compared to those in CI chondrites plotted against the temperature at which 50% of the element would condense from a gas of solar composition. Refractory lithophile elements (those which condense at highest temperature) are present in the mantle in approximately chondritic proportions, which implies that all refractory elements are present in bulk Earth (core plus mantle) in approximately chondritic proportions. In contrast, silicate Earth is depleted in volatile elements relative to CI chondrites with a decreasing relative abundance with decreasing condensation temperature. Siderophile elements are partitioned into the core and, in the case of refractory elements, their concentrations in the metal phase may be estimated by mass balance by assuming overall chondritic abundance in bulk Earth (McDonough 2003). In contrast, the abundances of volatile elements such as S, C, and Si in the core are more difficult to estimate because of the non-chondritic bulk Earth ratios of these elements. Nevertheless, plausible bounds may be placed on their concentrations, as discussed below.

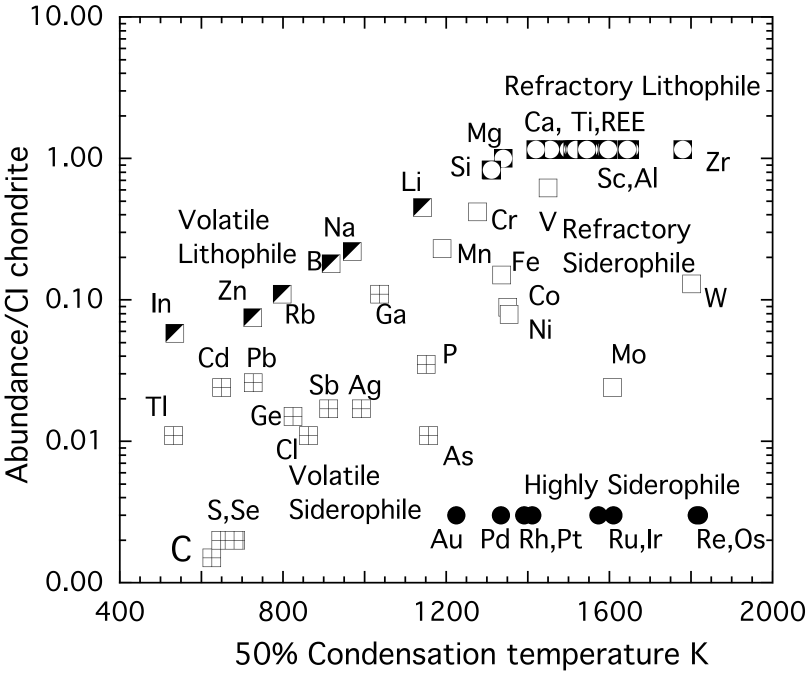

Figure 1. The concentrations of elements in bulk silicate Earth plotted as a function of the temperature at which 50% of the element would be condensed from a gas of solar composition (Lodders 2003). The elemental concentrations expressed as a ratio of abundance in Earth to CI chondrites have been normalized to Mg = 1.0.

The Si content of the core was estimated by Allègre et al. (1995) by assuming that Si, which is slightly depleted in silicate Earth, is in chondritic ratio to the bulk Earth contents of refractory lithophile elements. This plausible upper bound yields 7.3% Si in the core. In order to make an estimate of the S content of the core, it was assumed (Dreibus and Palme 1996) that the overall concentration of S in bulk Earth is in the same ratio to that in CI chondrites as elements of similar condensation temperature such as Zn. Then, by assuming that Zn is completely lithophile, Dreibus and Palme (1996) estimated that virtually all of Earth's S must be in the core and that, to give the whole Earth the same fraction of CI abundance as that of Zn, the core must contain about 1.7 wt% sulfur. The situation for carbon is more complex because it is much more difficult to estimate the bulk Earth concentration of this element than it is to estimate S abundance. The reason is that the condensation temperature of C is difficult to define and carbon behavior during accretion is also likely to have been quite complex. In Figure 1, we show a condensation temperature for carbon of 626 K, which is the estimate of Lodders (2003) based on an assumed equilibrium condensation of carbon to graphite but with kinetic inhibition of hydrocarbon formation. If complete equilibrium is assumed, with hydrocarbon species such as CH_4 forming, then the condensation temperature of carbon should correspond to that of methane ices at 41 K. Thus, there, is a wide range of potential condensation temperatures for carbon, which depend on the extent of kinetic inhibition of hydrocarbon formation, known to be significant, in the solar nebula. The result is that attempting to correlate carbon abundance with that of a lithophile element of "similar volatility" is impossible. Other cosmochemical arguments must be employed.

One of the short-lived radionuclides that was present at the beginning of the solar system, ^{107}Pd, decays to stable ^{107}Ag with a half-life of 6.5 m.y. Figure 1 shows that relatively volatile Ag is more abundant in silicate Earth, relative to CI chondrites, than is refractory Pd; that is, Pd/Ag of silicate Earth is subchondritic. This observation means that the ^{107}Ag/^{109}Ag ratio of silicate Earth would also be expected to be subchondritic since much of the current ^{107}Ag was produced from ^{107}Pd. In fact, despite the strong depletion of silicate Earth in Pd due to its highly siderophile nature, silicate Earth has a ^{107}Ag/^{109}Ag ratio the same as that of CI chondrites (Schönbächler et al. 2010). This similarity must mean that the Ag present in silicate Earth had its ^{107}Ag/^{109}Ag ratio established in a body (not silicate Earth) with chondritic Pd/Ag ratio (Schönbächler et al. 2010). In order to retain its chondritic ^{107}Ag/^{109}Ag ratio this silver must have mainly been added to Earth after ^{107}Pd was extinct so that no more ^{107}Ag was being produced. At this point, ~30 m.y. after the beginning of the solar system, Earth was already ~90% accreted. The implication is that Ag (and elements of similar volatility) was accreted to Earth late in accretionary history. Schönbächler et al. (2010) model the timing of this event as the first ~87% of accretion occurring from volatile-poor (Ag-poor) material and with the last 13% corresponding to volatile-rich (Ag-bearing) material perhaps related to the Moon-forming giant impact. This model explains the Ag isotopic composition of silicate Earth and would require that Ag and other volatile elements such as S and C were accreted from a volatile-rich (CI-like) impactor late in accretionary history. If this idea is correct, then we can estimate the C content of Earth by assuming that Earth has the C/S ratio of volatile-rich chondrites. This value would place an upper bound on the C content of the core of 1.1 wt% if we assume that the core contains 1.7 wt% sulfur and Earth has a C/S ratio the same as that of CI chondrites.

CARBON ISOTOPES AND CARBON CONTENT OF THE CORE

An additional constraint on the carbon content of the core can be gained by considering carbon isotope ratios in Earth and comparing them with other solar system bodies. Carbon has two stable isotopes ^{12}C (98.9%) and ^{13}C (1.1%). The ^{13}C/^{12}C ratio is a convenient way to express the separation of the two isotopes relative to an internationally accepted standard, Pee

Dee Belemnite (PDB). Deviations in this ratio are expressed in delta notation, where $\delta^{13}C = [(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{PDB} - 1] \times 1000$.

Traditionally, carbon isotopes have been used to trace the movement and cycling of carbon between the atmosphere, oceans, and shallow subsurface environments. Experimental and theoretical work on isotope fractionation at high pressures and temperatures in the mantle has focused principally on the fractionation between graphite and diamond and a gas (such as CO_2; Bottinga 1969; Javoy et al. 1978). Since high temperatures cause decreases in equilibrium stable isotope fractionations, it was assumed for decades that carbon isotope fractionation under deep Earth conditions would be negligible. However, Peter Deines in an elegant paper (Deines 2002) summarized all the carbon isotope data to date and hypothesized that there might be "as yet unknown high-temperature fractionation" processes characterized by large fractionations.

The carbon isotopic signature of all whole rock mantle xenoliths and separated minerals is bimodal with sharp peaks at $\delta^{13}C = -5$ and -25‰ (Fig. 2). It has become accepted (see Deines 2002 for a review) that the peak at −5‰ represents the primitive mantle signature (that is, the signature that silicate Earth has had since its formation), and that the peak at −25‰ represents the incorporation of subducted organic material from the surface. Organic material on the surface is depleted in ^{13}C and through plate tectonic processes makes its way to the upper mantle, mixing with the carbon present, hence creating reservoirs with a −25‰ signature. Thus, it is generally accepted that bulk silicate Earth has a carbon isotope signature of about $\delta^{13}C = -5$‰ (Fig. 3). Figure 3 shows a comparison of silicate Earth carbon isotopic composition with those of other planetary and asteroidal bodies. As can be seen, all of the other solar system bodies for which we have data have more negative $\delta^{13}C$ than Earth. In Figure 3 Mars is represented by measurements of magmatic phases in the SNC meteorites (Grady et al. 2004), while Vesta is represented by measurements of HED meteorites (Grady et al. 1997). A large range in $\delta^{13}C$ is exhibited by chondrites, as shown in Figure 3 with values obtained from CO, CV, CI, and CM chondrites. We have excluded enstatite chondrites because of bulk compositional and Si isotopic evidence that they can only have provided a small fraction of the material present in bulk Earth (Fitoussi and Bourdon 2012). We also neglected the values for soluble organic matter and carbonates from the CI and CM chondrites, as they are a small percentage of the

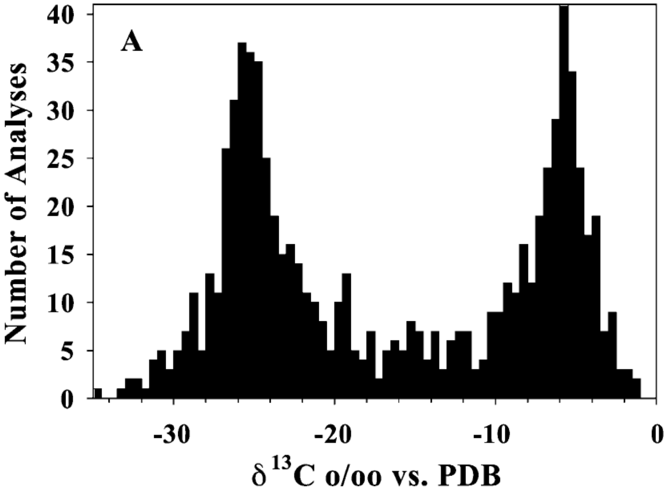

Figure 2. Figure from Deines (2002) illustrating the carbon isotopic fractionation of all whole rock mantle xenoliths and separated minerals from these xenoliths.

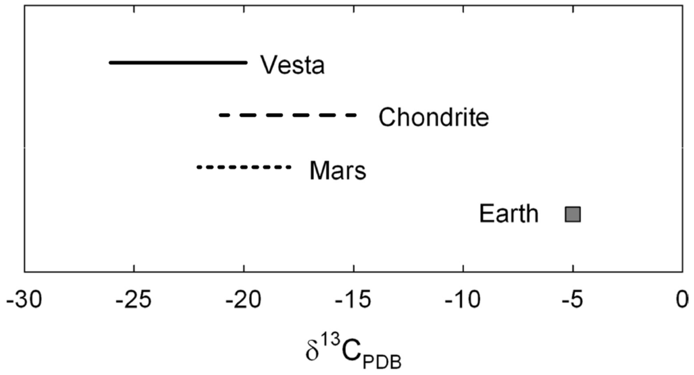

Figure 3. A summary of the carbon isotopic compositions of the silicate parts of planetary bodies as determined from HED meteorites (Vesta), SNC meteorites (Mars), and Earth compared to CI, CM, CO, and CV chondrites (Chondrite). See text for more detail.

carbon in meteorites and are not believed to be representative of the carbon-bearing material accreted to the Earth (Grady and Wright 2003).

It can readily be seen in Figure 3 that silicate Earth is an outlier, that is, that the supposed primitive Earth signature is in fact quite different from those of meteorites, and therefore of other planetary and asteroidal bodies. Current models of planet formation suggest that as they began to grow, Earth and the other terrestrial planets swept up volatile-poor material in fairly narrow feeding zones (Chambers 2005). Later in accretion, larger asteroidal and protoplanetary bodies from further out in the solar system were scattered into the inner solar system, causing violent impacts and delivering the more volatile elements to Earth and Mars (Chambers 2005). In support of these models, silver isotopic evidence, discussed above, suggests addition of CI-chondrite-like material to Earth late-on in its accretionary history (Schönbächler et al. 2010). A corollary of this accretionary scenario is that Earth, Mars, and the asteroids all received their volatiles, including carbon, from a similar source. This conclusion is in agreement with the suggestion that similarities between the isotopic compositions of H and N in Earth, Mars and chondritic meteorites indicate that these bodies all received their isotopic signatures from a common reservoir, which was isotopically well mixed (Marty 2012; Marty et al. 2013). We will therefore assume that the carbon isotopic compositions of Earth, Mars, Vesta, and chondrites were initially the same and that observed differences arose from differences in the accretionary processes on the different bodies.

The simplest way to explain the differences among Earth, Mars, Vesta, and chondrites is that Earth's primitive signature is not $\delta^{13}C = -5‰$ but similar to the other bodies at ~ −20‰ (Grady et al. 2004; Mikhail et al. 2010). The single largest event in Earth's history that changed its composition significantly is core formation (Fig. 1) and carbon is a strongly siderophile element. While Earth, Mars, and Vesta have all undergone core formation, and therefore might be expected to show similar carbon isotopic fractionations, there are important differences in the conditions attending their differentiation that could cause differences in the compositions of their cores. We will discuss these differences after we have addressed the potential for carbon isotopic fractionation due to core formation on Earth. Previous work on silicon (Georg et al. 2007; Shahar et al. 2011) has shown that core formation can impart a stable isotope signature to the planet, even at the very high temperatures necessary for segregation of liquid metal from liquid silicate. So would it be plausible that core formation could change the carbon isotopic signature of the entire silicate part of the planet by 15‰? And if so, what would that mean for the composition of the core?

In order to estimate the effect core formation could have on Earth's carbon isotope budget, it is necessary to know the isotopic fractionation factor for carbon partitioning between liquid metal and liquid silicate. In most cases of interest the fractionation factor has been measured experimentally, or can be estimated from natural samples or from theoretical calculations. However, for carbon none of these avenues is currently available: high-temperature experiments have only been done in the Fe-C system (Satish-Kumar et al. 2011); theoretical calculations have only been published for graphite, diamond, and carbon dioxide (Bottinga 1969; Polyakov and Kharlashina 1995); and iron meteorites show only a high-temperature carbon isotope fractionation in the Fe-C system. Therefore, due to the absence of data, we will estimate the potential for isotopic fractionation by using the Fe-C system as an analog for core formation.

Satish-Kumar et al. (2011) determined the carbon isotope fractionation between molten iron-carbon alloy and graphite as a function of temperature—the first study to address experimentally high-temperature (>1300 °C) carbon isotope fractionation. In this study, the authors find that ^{12}C preferentially incorporates into the metallic phase, leaving a ^{13}C-enriched signature in the graphite or diamond (depending on the pressure of the experiment). The fractionation factor Δ^{13}C follows the normal temperature dependence:

$$\Delta^{13}\mathrm{C}(_{gr/dia\text{-}\mathrm{FeC}}) = 8.85\left\{\frac{10^6}{T^2}\right\} + 0.99 \tag{1}$$

where

$$\Delta^{13}\mathrm{C}(_{gr/dia-\mathrm{FeC}}) = \delta^{13}C_{gr/dia} - \delta^{13}C_{metal} \tag{2}$$

Iron meteorite data on a similar system reflect the same fractionation direction (Deines and Wickman 1975), where graphite is more enriched in ^{13}C than coexisting cohenite [$(\mathrm{Fe,Ni})_3\mathrm{C}$]. These studies imply that if Earth has carbon in its core, it is enriched in ^{12}C, and has created a higher ^{13}C/^{12}C ratio in the mantle during core formation (Grady et al. 2004; Mikhail et al. 2010). This fractionation is in the right direction to explain an Earth that began with a δ^{13}C similar to other planetary bodies (−20‰) and evolved to −5‰ after core formation. There are two possible end-member models for core formation and carbon segregation to the metal: (1) A single stage of mantle-core equilibrium with initial δ^{13}C of the system of −20‰, and (2) Continuous core formation from the same system with Rayleigh isotopic fractionation.

The single stage model (1) leads to the following mass balance:

$$\delta^{13}\mathrm{C}_{BSE}X_\mathrm{C} + \delta^{13}\mathrm{C}_{core}\left(1 - X_\mathrm{C}\right) = \delta^{13}\mathrm{C}_{bulk\ earth} \tag{3}$$

where $\delta^{13}\mathrm{C}_{BSE}$ is the carbon isotopic composition of bulk silicate Earth, X_C is the fraction of Earth's carbon that is in the silicate portion of the planet, $\delta^{13}\mathrm{C}_{core}$ is the isotopic composition of the core, and $\delta^{13}\mathrm{C}_{bulk\ earth}$ is the isotopic composition of chondrites (−20‰). It is easily shown that ($\delta^{13}\mathrm{C}_{BSE} - \delta^{13}\mathrm{C}_{core}$) must be greater than 15‰ in order for this mass balance to work with a BSE value of −5‰ and an initial bulk Earth value of −20‰. According to the measured fractionations of Equation (1), an isotopic fractionation factor greater than 15‰ could only apply at temperatures below 800 K, which are implausibly low for liquid metal coexisting with liquid silicate. Therefore, a single stage of segregation can be excluded unless it is found that metal-silicate carbon isotope fractionations are much larger than those in the Fe-C system.

For model (2), continuous core extraction with Rayleigh fractionation, the relevant equation is:

$$\delta^{13}\mathrm{C}_{BSE} - \delta^{13}\mathrm{C}_{bulk} = \Delta^{13}\mathrm{C}(_{core\text{-}BSE})\ln F \tag{4}$$

where F is the fraction of the original carbon remaining in the mantle. We obtain an F of 0.05 if the fractionation factor on the right hand side is −5‰ and an F of 0.014 if the fractionation factor is −3.5‰. Equation (1) (note the change of sign in $\delta^{13}C$) indicates that this would correspond to temperatures of 1500-1900 K, which are plausible if rather low given the high temperatures (~2500-3500 K) inferred by many authors to have attended terrestrial core formation (Wood et al. 2006; Rudge et al. 2010; Rubie et al. 2011). The result in terms of C content of the core varies widely because of the range of estimates of C content of bulk silicate Earth. The value of 120 ppm given by McDonough and Sun (1995), for example, leads to a core carbon content of 0.5-2.0 wt%, which is in reasonable accord with the cosmochemically derived value. However, a more recent estimate of carbon content of bulk silicate Earth of 765±300 ppm (Marty 2012; see also Dasgupta 2013) leads, assuming Rayleigh fractionation, to implausibly large C contents of the core (up to 15%). In the latter case a hybrid Rayleigh-equilibrium model would be required to yield lower, more plausible, carbon contents of the core. We conclude that the carbon isotopic composition of silicate Earth is consistent with core formation having fractionated carbon isotopes but that it is not currently possible to constrain the processes involved.

Given the hypothesis of a large shift in $\delta^{13}C$ of BSE from −20‰ to −5‰ due to core formation, we must now consider why Vesta and Mars, which both have cores, do not also exhibit shifts in their carbon isotopic signatures relative to the chondritic reference. The answer for Vesta may simply be a matter of the pressure of core formation. In order for significant amounts of C to dissolve in the liquid metal forming the core, oxygen fugacities must be close to (i.e., not too far above) those for equilibrium with graphite or diamond, otherwise all carbon will be present as oxidized species CO and CO_2. At atmospheric pressure equilibrium between graphite and C-O-H-S gas requires oxygen fugacities at least 6 $\log f_{O_2}$ units below the Fe-FeO (IW) buffer. Under these conditions, silicate melt coexisting with metal contains only a few hundred ppm of FeO (Wood BJ, unpublished data). The fact that Vesta was much more oxidized than this during differentiation is apparent from the FeO contents of eucrites, which are 2 orders of magnitude richer in FeO, corresponding to at least 4 log units higher in oxygen fugacity and hence far above graphite saturation. With increasing pressure graphite equilibrium moves to higher relative oxygen fugacities so that at 1.5 GPa it lies 3-4 log units above IW (Wood et al. 1990). However pressures within Vesta are only a few atmospheres so the low-pressure data are relevant and we can exclude conditions close to carbon saturation during core formation. Carbon should not, therefore, have been strongly partitioned into Vesta's core, an observation that also explains the low C contents of magmatic iron meteorites. Silicate Vesta then should not show any carbon isotopic difference from chondrites, as observed. The situation is much more complex for Mars because pressures within Mars during core formation must have been sufficiently high to stabilize graphite or diamond at oxygen fugacities above the IW buffer, which is the maximum conceivable during core segregation. If the explanation for silicate Earth's isotopic signature is correct then either Mars had core formation close to model (1), single-stage equilibrium, or most of the carbon in Mars' mantle was added to the planet after core formation had ceased—the so-called "late veneer." W isotopic data for Mars indicates that this planet grew very rapidly, being 50% accreted within 1.8 m.y. (Dauphas and Pourmand 2011), so single-stage core formation may approximate the differentiation process on Mars, but not on Earth, which grew 10 times more slowly (Kleine et al. 2002). In addition, recent data on the highly siderophile elements show that a "late veneer" of chondritic material after cessation of core formation occurred on Mars as well as Earth (Dale et al. 2012) so it is possible that this late veneer dominates carbon in silicate Mars, but not in the more slowly-accreting silicate Earth. In either case it is clear that the carbon present in silicate Mars has a very different history from that found in silicate Earth.

From the above discussion we can conclude that the carbon isotopic signature of silicate Earth is consistent with Earth's core containing ~1 wt% carbon, provided the silicate-metal fractionation factors for this element are close to those of graphite-liquid Fe carbide and that the core was extracted from the mantle under conditions approaching Rayleigh fractionation.

DENSITY AND PHASE DIAGRAM CONSTRAINTS ON THE CARBON CONTENT OF THE CORE

The preceding discussion, based on the estimated S content of the core and the isotopic composition of carbon in silicate Earth, leads us to the conclusion that the core may contain ~1% C. The question now is whether or not concentrations at this level are testable seismically. The presence of low atomic number elements in Earth's core was initially inferred from seismic observations and mineral physics measurements. These data showed that the core is less dense than pure iron under the corresponding pressure-temperature conditions by 5-8% in the outer liquid part and 2-5% in the inner solid part (Birch 1952; Stevenson 1981; Jeanloz 1990; Poirier 1994; Hillgren et al. 2000; Anderson and Isaak 2002; Li and Fei 2003; Komabayashi and Fei 2010).

Based on long extrapolations of the equation of state data available at the time, Wood (1993) proposed that Fe_3C was likely to be the first phase to crystallize out of an Fe-S-C liquid under core conditions, even for C contents <1% and hence could form the inner core. Recent experimental work on the Fe-C phase diagram, however, suggests that Fe_7C_3 would be a stronger candidate for the inner core than Fe_3C since it probably replaces Fe_3C to become the liquidus phase at core pressures (Lord et al. 2009; Nakajima et al. 2009; Oganov et al. 2013). An inner core dominated by iron carbide (either Fe_3C or Fe_7C_3) would be the largest reservoir of carbon in Earth, dwarfing the combined budget of known carbon in the atmosphere and crust by an order of magnitude. In order to test the hypothesis of a carbide-rich inner core we need, of course, to know the liquidus phase of the Fe-C, Fe-C-S-(Si) and related systems at core pressures.

The Fe-C phase diagram

Wood (1993) predicted that the eutectic composition in the system Fe-C becomes more iron-rich with increasing pressure to approach the iron end member at inner core pressures. As pressure increases, the stability field of Fe_3C was expected to expand relative to iron, with its melting point increasing more rapidly to substantially exceed that of iron at core pressures. Consequently, Fe_3C was predicted to be the first phase to crystallize from a liquid core containing sulfur and a small amount of carbon (< 1 wt%). This liquidus behavior is the basis of the prediction of carbide as the principal phase in the inner core.

The phase diagram of the Fe-C system at 1 atmosphere has been extensively studied because of its applications in the steel industry (Chipman 1972; Zhukov 2000). The binary system has a eutectic point between iron and Fe_3C at 4.1 wt% carbon (Fig. 4).

A number of experimental studies have aimed at measuring the effect of pressure on the eutectic composition in the Fe-C system using the large volume press apparatus. Some, but not all, of the data support Wood's (1993) prediction that the eutectic composition becomes poorer in carbon with increasing pressure (Hirayama et al. 1993; Nakajima et al. 2009). For example, the reported eutectic composition near 5 GPa is at 3.2 wt% (Strong and Chrenko 1971), 3.6 wt% (Nakajima et al. 2009), and 4.8 wt% carbon (Chabot et al. 2008), as opposed to 4.1% at atmospheric pressure. A much higher pressure study of Lord et al. (2009), however, supports the predicted shift in the eutectic composition with pressure. Lord et al. (2009) used a novel X-ray radiographic technique to measure the eutectic melting behavior of Fe-Fe_3C mixtures up to 70 GPa. They found a rapid drop in the carbon content of the eutectic composition at pressures above 20 GPa, based on which they predicted that the eutectic composition is nearly pure iron by ~50 GPa. Extrapolation of the eutectic data beyond 70 GPa can be inferred to indicate a shift back in the eutectic composition to higher carbon contents (Lord et al. 2009), but this estimate is speculative. What does appear to be established is that there is a trend to ~50 GPa of increasing stability of the carbide at a eutectic of decreasing carbon contents.

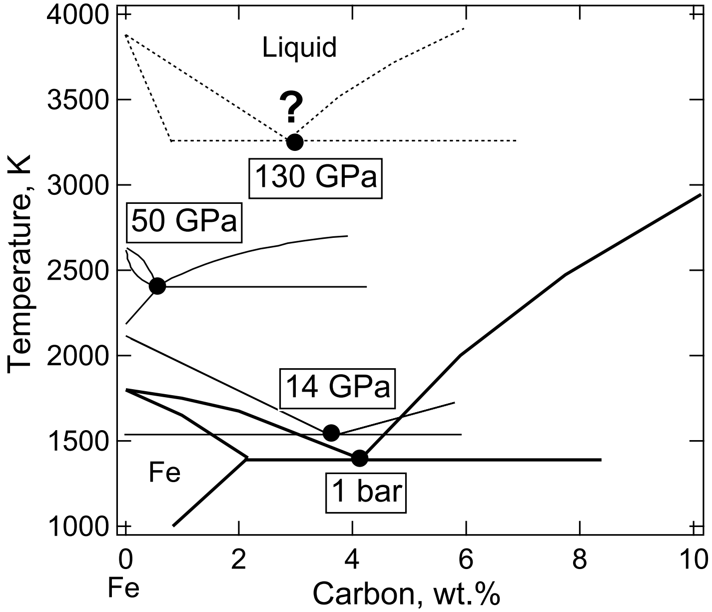

Figure 4. Phase diagram of the iron-carbon system showing the eutectic composition (solid circles) at different pressures. Note the decrease in observed carbon content at the eutectic to 50 GPa and that the 130 GPa diagram is an extrapolation.

There are strong interactions between carbon and sulfur dissolved in liquid Fe such that there is an extremely large miscibility gap in the Fe-S-C liquid system at 1 atm. Although this miscibility gap shrinks with increasing pressure up to 20 GPa (Wang et al. 1991; Corgne et al. 2008; Dasgupta et al. 2009), the net effect of adding sulfur is to increase the activity coefficient for C dissolved in Fe-rich liquids (Wood 1993). This change means that addition of S should decrease the carbon contents of liquids saturated in Fe_3C or Fe_7C_3. The implication is that, at core pressures, metallic liquids containing several % S may crystallize carbide first even if the carbon content of the liquid is very low (< 1%).

Densities of iron carbides

As discussed above, the presence of low atomic number ("light") elements in Earth's core was initially inferred from seismic observations and mineral physics measurements. Although a wide range of mixtures of Si, O, C, and S have been proposed as possible constituents of the "light" element in the outer core, the inner core is most likely to be an Fe-alloy or a compound of Fe with one of these low atomic number elements. The suggestion by Wood (1993) that Fe_3C would be the stable liquidus phase at very low C contents of the liquid outer core and that its density should be close to that observed, has stimulated a number of studies of the effects of compression on densities and elastic properties of iron carbides.

The natural form of Fe_3C, cohenite, occurs in iron meteorites (Ringwood 1960; Hazen et al. 2013). At 1 atm and 300 K, Fe_3C has an orthorhombic structure (space group *Pnma*, *Z* = 4). Its density (7.68 g/cc) is 2.5% smaller than that of iron in the bcc structure (7.88 g/cc), corresponding to ~ 0.4% density reduction for each 1 wt% carbon. Synchrotron-based X-ray diffraction (XRD) studies have shown that the crystal structure of Fe_3C remains stable to at least 187 GPa and 1500 K (Rouquette et al. 2008; Ono and Mibe 2010; Sata et al. 2010) and possibly to 356 GPa and 5520 K (Tateno et al. 2010).

On the basis of estimated equation of state (EOS) parameters, Wood (1993) suggested that Fe_3C approaches the observed density of the inner core under the appropriate high-pressure and high-temperature conditions. Compression measurements (Scogt et al. 2001; Li et al. 2002) support Wood's estimates, with best-fit isothermal EOS parameters of $K_0 = 174 \pm 6$ GPa, $K_0' = 4.8 \pm 0.8$ (using a neon pressure medium to 32 GPa), and $K_0 = 175 \pm 4$ GPa, $K_0' = 5.2 \pm 0.3$ (using a methanol-ethanol-water mixture combined with laser annealing). In contrast, based on first-principles calculations, Vočadlo et al. (2002) excluded Fe_3C as a major inner-core-forming phase. Their calculations suggest that Fe_3C transforms from ferromagnetic to non-magnetic at ~ 60 GPa and 0 K (Vočadlo et al. 2002; Mookherjee 2011; Oganov et al. 2013). A pressure-induced loss of magnetism at 300 K was also observed at ~ 25 GPa using X-ray emission spectroscopy (XES; Lin et al. 2004), at 9 GPa using X-ray magnetic circular dichroism (XMCD; Duman et al. 2005), and at 20-30 or 4.3-6.5 GPa using synchrotron Mössbauer spectroscopy (Prakapenka et al. 2004; Gao et al. 2008). The magnetic collapse was found to cause abrupt reduction in volume (Ono and Mibe 2010) and compressibility (Vočadlo et al. 2002; Lin et al. 2004; Sata et al. 2010), which may make it difficult to reconcile the density and elastic properties of Fe_3C with those of the inner core. It should be noted, however that the pressure of magnetic collapse in Fe_3C is highly uncertain, ranging from ~5 GPa to ~55 GPa (Lin et al. 2004; Duman et al. 2005; Gao et al. 2008; Ono and Mibe 2010). The discrepancies likely arise from the different methods used to detect the transition. Alternatively, it may reflect variable amounts of non-hydrostatic stress in samples compressed in neon, NaCl, or no pressure medium. Furthermore, as can be seen from Figure 5, the equation of state of Fe_3C has been determined to 200 GPa

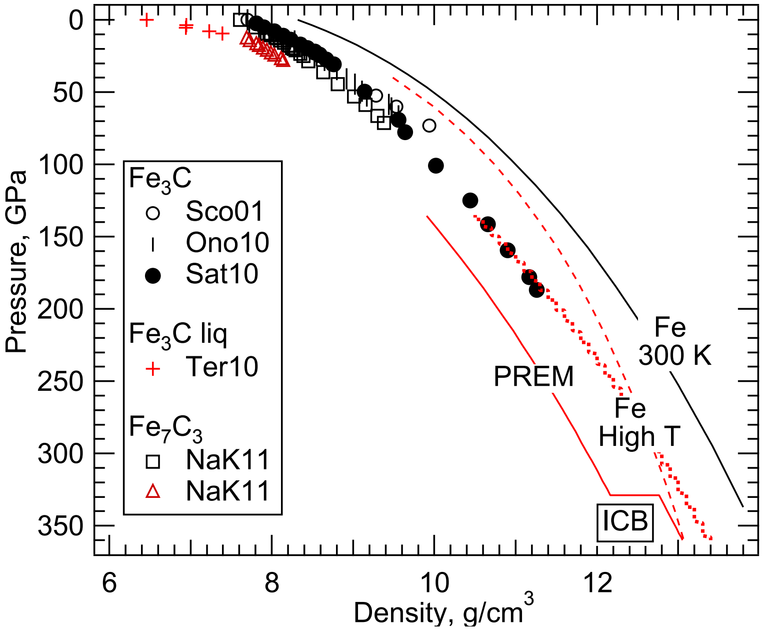

Figure 5. Densities of iron, iron carbides, and Earth's core as a function of pressure. Data sources: PREM (Dziewonski and Anderson 1981). Dashed line: Shocked Fe along a Hugoniot (Brown 2001). Solid line: statically compressed hcp Fe at 300 K (Mao et al. 1990). Note slightly higher densities in a more recent paper (Dewaele et al. 2006). Dotted line: Statically compressed hcp Fe at 5000 K (Dubrovinsky et al. 2000; Komabayashi and Fei 2010). Solid Fe_3C at 300 K (Ono and Mibe 2010; Sata et al. 2010; Scott et al. 2001) (vertical bars, solid circles and open circles respectively). Liquid Fe_3C (Terasaki et al. 2010). Solid Fe_7C_3 at 300 K (squares) and high temperature (triangles) (Nakajima et al. 2011).

at 300K (Sata et al. 2010) and the change in compressibility and volume associated with the suggested magnetic transition was found to be very small. Comparison of the density of Fe_3C with that of the inner core based on the EOS parameters of Sata et al. (2010) indicate that Fe_3C cannot be excluded as the principal inner core phase (Fig. 5).

Based on phase equilibrium measurements, it has recently been suggested that Fe_7C_3 is a more likely candidate for Earth's inner core than is Fe_3C (Lord et al. 2009; Nakajima et al. 2009). At 1 atm and 300 K, Fe_7C_3 adopts a hexagonal or orthorhombic structure (Fang et al. 2009; Oganov et al. 2013). In the more stable hexagonal structure (space group $P6_3mc$, $Z = 2$), the density of Fe_7C_3 (7.61 g/cc) is 3.4% smaller than bcc iron (7.88 g/cc), corresponding to ~0.4% density reduction for each 1 wt% carbon, which is nearly identical to that of Fe_3C. A synchrotron X-ray diffraction study found that the crystal structure of Fe_7C_3 remains stable up to 71.5 GPa and 1973 K, although anomalous compression behavior was observed at 18 GPa and 300 K, which is attributed to a ferromagnetic to paramagnetic transition (Nakajima et al. 2011). A theoretical study predicted magnetic collapse at ~67 GPa, causing a small increase in the bulk modulus (Mookherjee et al. 2011). A consideration of the measured densities of Fe_7C_3 (Fig. 5) show, however that, like Fe_3C, this phase could have the appropriate density for the inner core under inner core conditions.

In summary, EOS data available to date indicate that either Fe_3C or Fe_7C_3 could have the observed density of the inner core under inner core conditions. In order to discriminate between these and other phases it will be necessary to obtain density data under pressure-temperature conditions closer to those of the inner core. It should be noted however, that, even if carbides are shown not to be present in the inner core, there could still be substantial amounts of carbon in the liquid outer core.

Sound velocities of Fe, Fe_3C and those of the inner core

Apart from the density of the inner core, the solid phase or phases present must have appropriate sound velocities and anisotropy. Compared to the Preliminary Earth Reference Model (PREM) the compressional wave velocity (v_P) of Fe is somewhat higher and has a greater dependence on density while the shear wave velocity (v_S) is much higher but has a similar dependence on density to Earth (Fig. 6). In addition, seismic studies have shown that compressional waves travel through the inner core at velocities that are faster by 3-4% in the polar direction than in the equatorial plane (Creager 1992; Tromp 1993). Recent observations suggest shear-wave velocity in the inner core is also anisotropic (Wookey and Helffrich 2008). A candidate inner core component must therefore match the depth-dependent sound velocities from Earth's center to the inner core radius and also account, in large measure, for the compressional- and shear-wave anisotropy in the inner core. At ambient conditions the v_S of Fe_3C is 3.0 km/s according to ultrasonic interferometry and nuclear inelastic X-ray scattering (NRIXS) measurements (Dodd et al. 2003; Gao et al. 2008). The results on v_P vary from 5.2 km/s (ultrasonic; Dodd et al. 2003), 5.89 km/s (NRIXS; Gao et al. 2008), to 6.10 km/s by inelastic X-ray scattering (IXS; Fiquet et al. 2009). For comparison, the v_P and v_S of bcc Fe are 5.8 and 3.1 km/s, respectively (Lübbers et al. 2000; Fiquet et al. 2001; Mao et al. 2001).

At high pressures and 300 K, NRIXS data up to 50 GPa on Fe_3C show that v_P and v_S increase linearly with density (Gao et al. 2008). Upon magnetic transition near 5 GPa, the slope for v_S becomes significantly shallower, however, leading to an extrapolated v_S that is considerably smaller than that of iron under inner core pressures and plausibly in better agreement with PREM (Fig. 6). Furthermore, one set of measurements on Fe_3C to 47 GPa and 1450 K shows that, at high temperature v_S deviates from the linear relationship at 300 K towards lower values, potentially matching the anomalously low v_S in the inner core under the relevant pressure and temperature conditions (Gao et al. 2011). The results provide further support for Fe_3C as a major component of the inner core. In addition, experimental and computational data on Fe_3C

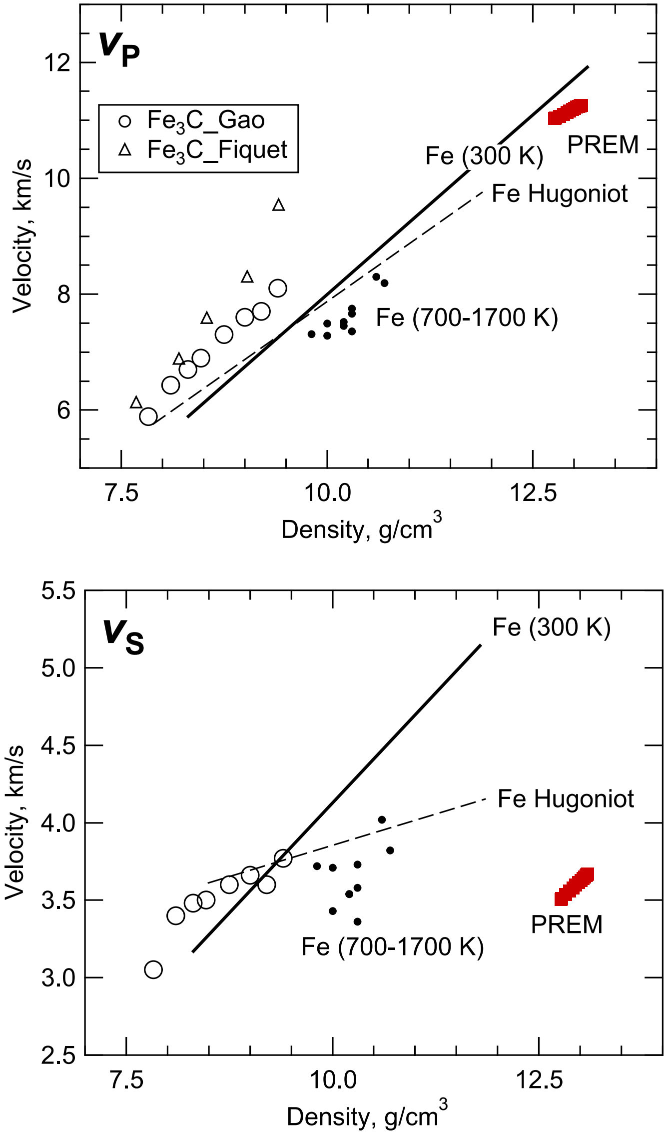

Figure 6. Aggregate compressional velocity (v_P) and shear velocity (v_S) versus density of Fe and Fe_3C in comparison with the PREM model. Data sources: Dashed line refers to shocked Fe along a Hugoniot (Duffy and Ahrens 1992). Statically compressed Fe at 300 K (solid line; Mao et al. 2001). Statically compressed Fe at high temperature (solid circles, Lin et al. 2005). NRIXS data on Fe_3C at 300 K (open circles, Gao et al. 2008, 2009). IXS data on Fe_3C at 300 K (triangles, Fiquet et al. 2009). PREM (Dziewonski and Anderson 1981).

indicate strong anisotropy in sound velocity under ambient conditions, providing yet another piece of supporting evidence for Fe_3C as a plausible candidate for the inner core (Nikolussi et al. 2008; Gao et al. 2009). In contrast to these results, however, the v_P derived from IXS data up to 68 GPa are considerably larger than the NRIXS results, suggesting that 1 wt% carbon in

Fe-Ni alloy (as opposed to 6.67% carbon in Fe_3C) could be sufficient to explain the difference in compressional wave velocity between PREM and experiments (Fiquet et al. 2009).

In summary, phase equilibrium experiments are consistent with crystallization of carbide (Fe_3C or Fe_7C_3) on the liquidus at very low C contents of a Fe-C liquid at pressures of 50 GPa and higher (Fig. 4). The stability of carbide or of C-bearing Fe alloy on the liquidus is enhanced by the addition of sulfur to the core because of the raised activity coefficient of C when S is added to the Fe-rich metallic liquid. Although density data to core pressures, available v_P and v_S data, and measured elastic anisotropy of Fe_3C are all broadly consistent with the inner core being dominantly Fe_3C or Fe_7C_3, some v_P data are more consistent with an Fe-Ni alloy containing a smaller amount of carbon. More high-temperature data at pressures approaching those of the inner core are required to refine these conclusions further.

CARBON IN THE CORE AND SIDEROPHILE ELEMENTS IN THE MANTLE

A final way of constraining the concentrations of "light" elements in the core is to return to the observation that, as the core was extracted from the mantle, siderophile elements were partitioned between metal and silicate according to their partition coefficients D_i ($D_i = [i]_{metal}/[i]_{silicate}$). Since alloys of iron metal with carbon, sulfur, silicon and other light elements are non-ideal solutions, the identities and concentrations of the light elements in the core will have, in some cases, marked effects on how strongly siderophile elements have partitioned into the core. It has been shown, for example, that addition of 4-5% carbon to liquid Fe changes the behavior of Pb from siderophile to lithophile because of strong Pb-C interactions in the metal (Wood and Halliday 2010). In contrast, W has a strong affinity for small amounts of C dissolved in the metal and becomes more siderophile as the C content of the metal increases (Wade et al. 2012). These effects have the potential to enable us to constrain the light element concentrations in the core from the concentrations of siderophile elements in the mantle. Wade et al. (2012) have shown, for example, that addition of sulfur to the metal has the potential to change the relative behavior of Mo and W from the prediction that W was more strongly partitioned into the core than Mo to the observed behavior, which implies that Mo was more siderophile during core formation than W. We consider now whether or not similar arguments can be used to constrain the C content of the core.

In order to consider the effects of S on the partitioning of Mo and W between the core and the mantle, we used a simple model of Earth accretion initially proposed several years ago (Wade and Wood 2005). Wade and Wood (2005) used a model of continuous accretion and core segregation in which every increment of metal added to the core equilibrated with a well-mixed mantle reservoir. They then showed that the experimental data on metal-silicate partitioning of Ni, Co, V, Mn, and Si would result in the observed concentrations of these elements in the mantle provided pressures of metal-silicate equilibration increased and Earth became progressively more oxidized as it grew. The model has been refined several times, most recently by addition of terms for the interactions between Si and the other elements dissolved in the metal (Tuff et al. 2011) and by the inclusion of a comprehensive database for Mo and W (Wade et al. 2012). As a basis we use the version of the accretionary model presented by Tuff et al. (2011), which makes explicit provision for Silicon-*i* interactions in the metal where *i* is any minor element of interest. This model generates the observed partitioning behavior of Co, Ni, W, Cr, V, Nb, and Si as the pressure of metal segregation increases from 0 to 36 GPa and Earth becomes more oxidized.

In order to expand the accretionary model to take account of the effects of S and C on the composition of the mantle and core, we have adopted Sulfur-*i* and Carbon-*i* interactions from the Steelmaking data sourcebook (Steelmaking 1988), which are used in conjunction with the epsilon model of activity coefficients in the metal:

$$\begin{aligned}\ln\gamma_{\mathrm{Fe}}^{met} = {} & \sum_{i=2}^{N}\varepsilon_i^i(x_i+\ln(1-x_i)) - \sum_{j=2}^{N-1}\sum_{k=j+1}^{N}\varepsilon_j^k x_j x_k\left(1+\frac{\ln(1-x_j)}{x_j}+\frac{\ln(1-x_k)}{x_k}\right) \\ & +\sum_{i=2}^{N}\sum_{\substack{k=2\\k\neq i}}^{N}\varepsilon_i^k x_i x_k\left(1+\frac{\ln(1-x_k)}{x_k}-\frac{1}{1-x_i}\right)+\frac{1}{2}\sum_{j=2}^{N-1}\sum_{k=j+1}^{N}\varepsilon_j^k x_j^2 x_k^2\left(\frac{1}{(1-x_j)}+\frac{1}{(1-x_k)}-1\right) \\ & -\sum_{i=2}^{N}\sum_{\substack{k=2\\k\neq i}}^{N}\varepsilon_i^k x_i^2 x_k^2\left(\frac{1}{1-x_i}+\frac{1}{1-x_k}+\frac{x_i}{2(1-x_i)^2}-1\right)\end{aligned} \tag{5}$$

and

$$\begin{aligned}\ln\gamma_i^{met} = {} & \ln\gamma_{\mathrm{Fe}}^{met}+\ln\gamma_i^{\mathrm{o}}-\varepsilon_i^i\ln(1-x_i) \\ & -\sum_{\substack{k=2\\k\neq i}}^{N}\varepsilon_i^k x_k\left(1+\frac{\ln(1-x_k)}{x_k}-\frac{1}{1-x_k}\right) \\ & +\sum_{\substack{k=2\\k\neq i}}^{N}\varepsilon_i^k x_k{}^2 x_i\left(\frac{1}{1-x_i}+\frac{1}{1-x_k}+\frac{x_i}{2(1-x_i)^2}-1\right)\end{aligned} \tag{6}$$

In Equations (5) and (6), x_i refers to the mole fraction of *i* in the metal, γ_i^{met} is the activity coefficient of *i*, γ_i^{o} is the activity coefficient of *i* infinitely dilute in liquid Fe, and ε_i^j is the interaction parameter between elements *i* and *j*. The interested reader may follow our activity calculations using the online calculator at *http://www.earth.ox.ac.uk/research/groups/experimental_petrology/tools*. All relevant ε_i^j terms are given by Wade et al. (2012) except for those involving carbon. The later, taken from the steelmaking data sourcebook are $\varepsilon_{\mathrm{C}}^{\mathrm{Mo}}$ of −6.15 and $\varepsilon_{\mathrm{C}}^{\mathrm{W}}$ of −6.64. We incorporated these values, together with those of the other elements of interest, in the model and found that the effects of adding carbon on core-mantle partitioning of Co, Ni, Cr, V, Nb, and Si are quite small but that carbon can have large effects on W and Mo. We therefore concentrated on these two elements and made versions of the model, all of which generated the correct mantle concentrations of Co, Ni, Cr, V, Nb, and Si.

For partitioning of W and Mo between a liquid peridotitic mantle and liquid Fe-rich metal we used the expressions given by Wade et al. (2012):

$$\log\left(K_D^{\mathrm{W}}\right)_{wt} = 1.85-\frac{6728}{T}-\frac{77P}{T} \quad \pm 0.24 \tag{7}$$

The uncertainty corresponds to one standard error of the fit to a large number of experiments. Core-mantle partitioning (D_{W}) for tungsten is defined relative to that for Fe (well-known for Earth as a whole) in the expression for K_D:

$$\left(K_D^{\mathrm{W}}\right)_{wt} = \frac{\left(D_{\mathrm{W}}^{wt}\gamma_{\mathrm{W}}^{met}\right)}{\left(D_{\mathrm{Fe}}^{wt}\gamma_{\mathrm{Fe}}^{met}\right)^3}$$

Note that, for pure Fe $\gamma_{\mathrm{Fe}}^{met}$ is 1.0 while $\gamma_{\mathrm{W}}^{met}$ is 3.0 (at 1873 K; *http://www.earth.ox.ac.uk/research/groups/experimental_petrology/tools*). The D_{Fe} term is cubed to take account of a +6 oxidation state for W in the silicate.

For Mo the corresponding equation is:

$$\log K_D^{\mathrm{Mo}} = 1.44 - \frac{143}{T}-\frac{167P}{T} \quad \pm 0.19 \tag{8}$$

Where in this case the D_{Fe} term in the denominator of K_D is squared to take account of a +4 oxidation state of Mo in the silicate and $\gamma_{\mathrm{Mo}}^{met}$ in pure Fe is 1. Note that the oxidation states account for the partitioning behavior of Mo and W as a function of oxygen fugacity at oxygen fugacities down to at least 3.3 logf_{O_2} units below the IW buffer.

Figure 7 shows the results of the calculated effects of sulfur on the overall partitioning of W and Mo between mantle and core. As stated above we used the accretionary model described by Tuff et al. (2011) and Wade et al. (2012) with increasing oxidation state of silicate Earth as the planet grew. Sulfur was added to the core only during the last 13% of accretion in order to be consistent with the results of Schönbächler et al. (2010). As can be seen from Figure 7, addition of 2% S (rounded-up from the cosmochemical estimate of 1.7%) to the core (as 15% S in the last 13% of accreted metal) dramatically increases partitioning of Mo into the core and pushes calculated partitioning towards the range of probable partitioning behavior in Earth. Sulfur has little effect on W partitioning. Addition of carbon (Fig. 8) enhances partitioning of both Mo and W into the metal, such that ~0.6% carbon in the metal (as 5% C in the last 13% of segregated core) would enable the core-mantle partitioning of both Mo and W to reach the expected values, consistent with the observed concentrations of these elements in silicate Earth. Addition of 1% carbon would, however take both elements out of the expected range of core-mantle partitioning. Nevertheless, values > 0.5% carbon in the core are possible provided accretion of C was more protracted, over the last 25-30% of accretion for example.

CONCLUSIONS

We have used several distinct approaches to the problem of constraining the carbon content of Earth's core. The cosmochemical approach is firstly to consider the sulfur content of the core.

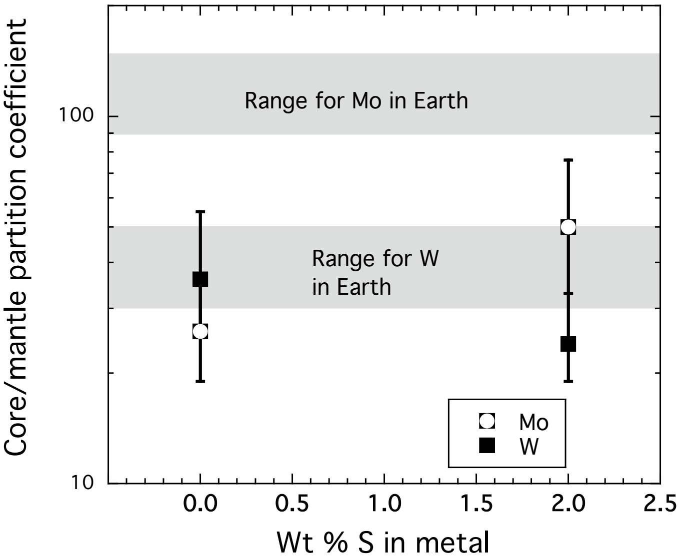

Figure 7. This figure illustrates the effect of adding 2% S in the metal on the core-mantle partitioning of W and Mo. The calculations are based on an accretionary model, which correctly reproduces the observed core-mantle partitioning of V, Cr, Nb, Co, Ni and Si (see text). S, which affects W and Mo much more than the other elements, was incorporated into the metal during the last 13% of accretion, consistent with Ag isotopic data on silicate Earth (Schönbächler et al. 2010).

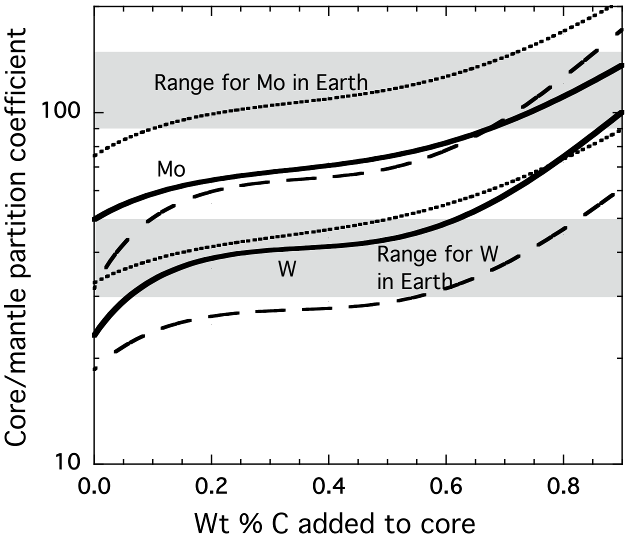

Figure 8. Same as Figure 7, but with addition of C together with S. Upper solid line is overall core/mantle partitioning of Mo and lower solid line equivalent partitioning of W. Short dashed and long dashed lines are uncertainty limits based on experimental uncertainties (Eqns. 7 and 8). In order to match observed core-mantle partitioning of Mo and W we need to add ~0.6% C to the core during the last 13% of accretion. The amount of C added can be increased if accretion of S and C is extended over the last 25-30% of accretion rather than the final 13% (see text).

Dreibus and Palme (1996) noted the decrease in abundance of lithophile elements in silicate Earth with decreasing condensation temperature (Fig. 1). They then correlated the observed silicate Earth abundance of S with that of Zn, a relatively lithophile element of virtually identical condensation temperature to S. Then, by assuming that S should, in the absence of a core, be present in the same ratio to Zn in the silicate Earth as in CI chondrites, they calculated the amount of sulfur "missing" from silicate Earth. This "missing" S was assumed to be present in the core, giving a concentration in the latter reservoir of 1.7 wt%. Our cosmochemical estimate of a maximum of 1.1% carbon in the core was obtained from this S concentration by noting that the Ag isotopic composition of silicate Earth is most readily reconciled with the observed value if volatile elements such as Ag, S, and C were added in approximately CI chondritic ratios to refractory elements late in Earth's accretion (Schönbächler et al. 2010). The CI chondritic ratio of C to S gives 1.1% C in the core.

Silicate Earth is profoundly different in C isotope ratios from other asteroidal and planetary bodies. Silicate Earth has a $\delta^{13}C$ of approximately −5‰, substantially higher than those of Mars, Vesta, and carbonaceous chondrite meteorites whose $\delta^{13}C$ values are all approximately −20‰. We show that, given plausible isotopic fractionations between liquid metal and liquid silicate, the difference between Earth and other bodies is explicable by strong partitioning of C into Earth's core. The major requirements would be that C was extracted to the core by a process approximating Rayleigh Fractionation and that the core contains ~1% C. The latter estimate can be greatly improved by better experimental data on metal-silicate fractionation of carbon isotopes and more precise estimates of the carbon content of bulk silicate Earth.

A third approach to constraining the core's carbon content is provided by available data on the densities, elastic properties, and phase equilibria of potential core materials under the pressure-temperature regime of the core. Phase equilibrium studies show that the eutectic composition in the Fe-C system shifts towards the Fe side with increasing pressure and that, at 50 GPa, compositions with <1% C can precipitate a carbide (Fe_3C) on their liquidus. This behavior likely continues to higher pressures, although Fe_3C may be replaced by Fe_7C_3 as the liquidus carbide phase. The densities and elastic properties of Fe_3C and Fe_7C_3 have not been measured at core conditions; however, it is conceivable, based on available data and the known properties of the core, that one of these phases is the predominant carbon-bearing component of the solid inner core. Demonstration that carbide is present in the inner core would enable us to constrain the carbon content of the core more precisely. Current data suggest, however, that a core carbon content of about 1% is feasible.

Our final method for constraining the carbon content of the core was to consider the effects of S and C on the partitioning of siderophile elements between core and mantle during Earth's accretion. We applied a simplified accretionary model in which Earth's growth was accompanied by oxidation of the mantle and extraction of the liquid core continuously at monotonically increasing pressure. This model generates the observed mantle concentrations of a number of weakly- and moderately-siderophile elements (V, Cr, Nb, Co, Ni, Si). The core-mantle partitioning of W and Mo were found to be very sensitive to the S and C contents of the metal. If we assume that ~2% S is present in the core and that this S was added during the last 13% of accretion (Schönbächler et al. 2010), then the current W and Mo contents of the mantle would be consistent with ~0.6% carbon in the core.

We conclude that all 4 approaches to carbon as a component of the "light" element in the core lead to an upper likely concentration of ~1% of this element in the core.

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