Element Partitioning and Earth's Core Composition

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Determining the composition of the Earth's Core is essential for understanding the internal structure, evolution, and present dynamics of the Earth. This area of research has extremely important consequences for much of the current research in the fields of mantle geochemistry, geodynamics, mineral physics, geomagnetism, and seismic tomography. Yet many researchers in these fields remain unaware of the implications the knowledge of the composition of the Earth's core has on our understanding of the solid Earth as a whole. Studying how and to what degree elements are partitioned into either metal (siderophile elements) or silicate (lithophile elements) is essential for understanding the processes in which the Earth differentiated and what the composition of the core might be. Better constraints on core formation and composition have the potential to either validate or discredit current models for formation, differentiation, and early evolution of the Earth, and may have a crucial role in reconciling current geochemical and seismological data.

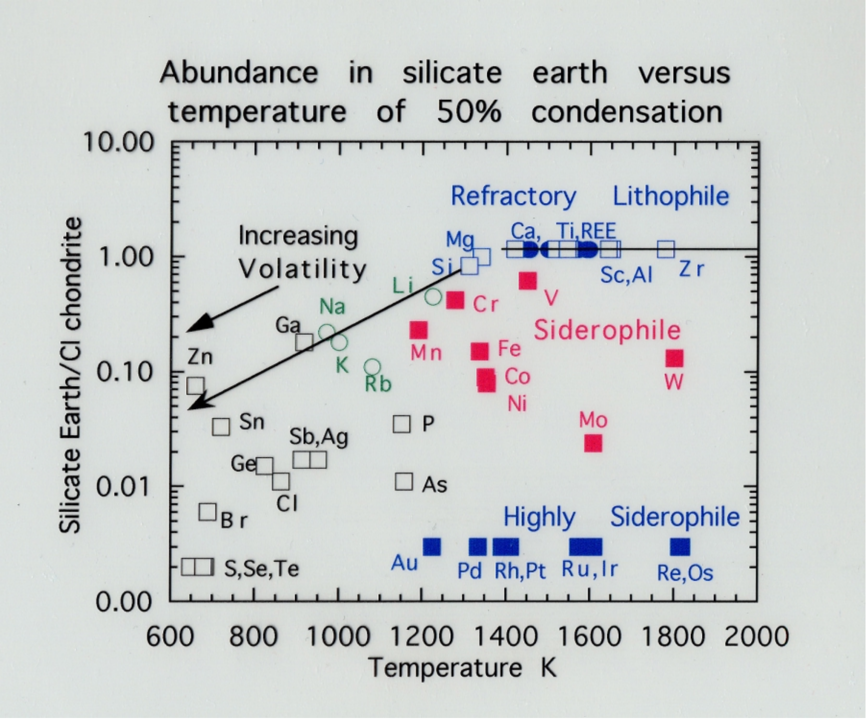

Figure 1. Abundance of elements in the silcate Earth relative to a CI chondrite plotted in order of increasing condensation temperature. This is used to estimate depletions in the silicate Earth, either due to having not been accreted to the Earth or by being dissolved in the Core. There is an observed trend with decreasing temperature of condensation that is there is increasing depletion of those elements.

In approaching the problem of composition of the core, the first thing one might think to do is examine the abundance of siderophile elements in the silicate portion of the Earth (Figure 1) relative to a CI chondrite, and indeed, this is what has been done. The silicate Earth is defined as the undifferentiated mantle, presumed to be a combination of continental crust and present day upper mantle composition. The CI chondrite is the type of meteorite which has a composition that most closely matches that of present solar values, and is therefore presumed to be the most primitive of all meteorites. The degree to which certain elements are siderophile is roughly known from experiments that have been done at low pressure and the appropriate oxidation state of the mantle to study the equilibrium partitioning. .

Then for those elements that have a high temperature of condensation, or are highly refractory, we observe several things. First, very siderophile elements are not depleted enough in the silicate portion. For example Nickel should be .002 x CI but is 0.068 x CI, Cobalt should be .02 x CI but is 0.077 x CI, and Platinum Group Elements (PGE) such as Re, Os, Ir, Ru, Pt, Rh, Pd, and Au should be 10E-5 x CI, but instead are .003 x CI. On the other hand, elements that are seen at low pressure to be only weakly siderophile are too depleted. For example, Vanadium, Chromium, and Manganese should be ~0.95 - 0.99 x CI, but instead are 0.53, 0.36, and 0.2 (x CI), respectively. This is the first clue that there are some very interesting things going on during core formation.

Another interesting observation is that the core's density can't be explained with a pure Iron composition. Iron meteorites are suspected to be fragments of the cores of asteroids or small planetisimals which have since collided and broken into smaller pieces. The composition of the Iron meteorites is nearly pure Iron, and if the Earth's core were made of pure Iron, it's density, after accounting for high pressure phases of Iron, would be much larger than the observed density. Instead, the density of the core is observed to be much less than that of a pure Iron core. This is another clue that Earth's core has a different composition than that of smaller planetisimals, and indeed may have had different processes involved in its core formation. The processes involved may be unique to the Earth with respect to it's size, which implies that the effects of high pressures may have a role in determining the composition. Adding elements such a Nickel, Cobalt, and other metals to the composition of the core does not gain much towards the goal of decreasing the core's densityThis arises from the fact that they are all approximately as dense as Iron, and they are not observed in large enough quantities in chondrites to account for being a large component of the core's composition. Therefore, there must be a sufficient amount (about 10 weight percent) of some light element or combination of light elements in the core that can account for the lower density. However, many of the candidate light elements also have low temperatures of condensation, and are therefore quite volatile. Since the silicate Earth is depleted in volatile elements, it is difficult to reconcile how some volatile elements made it into the core. So any scenario of core formation needs to be able to explain both the abundances of siderophile elements in thesilicate Earth as well as the presence of a light element in the core.

Figure 1 shows that any element with abundances in the silicate Earth lower than the chondritic value, are referred to as being depleted. In general, there are two ways to make something depleted: not accrete it in the first place (due to the Earth being primarily composed of high temperature involatile materials), or to dissolve the elements in the core. Either of these will deplete a given element in the silicate Earth relative to the chondrites. By only studying the highly refractory elements at first, the issue of volatility is avoided and the degree to which these elements partitioned into the core can be isolated. The information required to provide constraints on core composition of highly refractory, siderophile elements is the composition of the Bulk Earth (BE) and composition of the Bulk Silicate Earth (BSE), the difference of which gives the composition of the Core. The composition of the Bulk Silicate Earth is derived from the compositions of the most primitive peridotites available and it is assumed there are no hidden reservoirs in the lower mantle. The composition of the Bulk Earth is derived from the observation that chondritic meteorites and primitive peridotites have essentially constant ratios of the refractory lithophile elements such as Ca, Al, Sc, Ti, and the Rare Earth Elements. It is assumed then that the relative abundances of elements in the bulk Earth are similar to the relative abundances of elements in chondrites, and therefore it is appropriate to assume that the depletions of elements in Figure 1 are actual depletions. In other words, it's probably a good assumption to use chondritic ratios of elements to determine the degree to which elements are depleted in the silicate Earth.

There have been a number of efforts (Hart and Zindler, 1986; Allegre et al., 1995; McDonough and Sun, 1995; and Allegre et al., 2001) to build a BSE model, and since these models all make similar assumptions concerning the relation of mantle peridotites to chondrites, all the models are in fairly good agreement with each other. These models are a starting place to estimate the composition of the core, which are again mostly in agreement with one another. Together these models propose about 80-85% Iron, about 5% Nickel, and another few percent being made up of various amounts of the other siderophile elements (Mn, Co, Cr, P). All these models leave about 10 weight percent to be composed of a light element or combination of light elements: Hart and Zindler, 1986 propose about 9% Oxygen, McDonough And Sun, 1995 are unspecific, Allegre et al. 1995 suggest 7.35% Silicon, 2.30% Sulfur, and 4.10% Oxygen. Also considering that Carbon and Hydrogen may also be in the core and we now have a list of all the light element candidates that have been suggested to be in the core.

An important distinction to point out is that the list of suggested light elements are of variable volatility. Oxygen and Silicon condense at relativelty high temperatures while Sulfur, Carbon, and Hydrogen are more volatile. However, all of the BSE models hinge upon the assumption that the volatile elements did not condense into the material that formed the Earth in similar quantities to the other elements. If these elements are greatly depleted in the Bulk Earth to begin with, then they are unlikely to be available in sufficient enough quantities to account for the light element in the core. Therefore, in order for the BSE models to be internally consistent, the light element of the core should be one of the refractory elements, Oxygen or Silicon. If neither Oxygen nor Silicon is the light element in the core, then the assumptions which the BSE models are built upon are questionable at best, and subsequent BSE models would lead to very different pictures of the composition of the Earth. In other words, the abundances and relative proportions of all elements in the whole Earth rest upon the behavior of just two elements, Oxygen and Silicon, and whether either one is sufficiently siderophile to be the light element in the core.

By determining the equilibrium partitioning of these proposed light elements, these various hypotheses of core compositions can begin to be tested. The minimum criterion that must be met in order for a light element candidate to remain possible are that the element(s) must be soluble in Fe-rich metal under the conditions of core segregation and they must be abundant in chondritic meteorites. The list is immediately narrowed by observing that the solubility of Oxygen appears to be too low under any conditions. As for Hydrogen, due to its small size, it is not clear that large amounts of Hydrogen will decrease the density of the core, as it may very well fit in the open spaces between atoms of Iron and actually increase the core's density.

For the remaining volatile candidates, the amount of their content is simply estimated from Figure 1. Since Zinc and Sulfur have similar volatility, and Zinc is a lithophile element, the amount of Sulfur in the core is estimated by taking the difference in abundance between Zinc and Sulfur on Figure 1. This gives a Sulfur content in the core of 1.9%, however, it is important to note that this estimation hinges upon the assumption that there is no Zinc in the core. Carbon and Hydrogen contents are estimated in a similar fashion, and since Carbon and Hydrogen are even more volatile than Sulfur, there must be lower amounts of these elements in the core. Another way to estimate Carbon abundance in the Bulk Earth is to look at the correlation with Ar36, again, assuming that there is no Ar in the core, so the relative amounts of C/Ar in the Silicate Earth is that of the Bulk Earth. These simple estimations give about 0.2% Carbon in the core and an even smaller amount of Hydogen. When combining all these estimations together for Sulfur, Carbon, and Hydrogen, it accounts for less than 3% of the core. By making these assumptions about the volatility trend seen in Figure 1 and thereafter applying the process of elimination, this leaves Silicon as having to account for about 7% of the core, as hypothesized by Allegre.

The main problem with Silicon is that it is not very siderophile, so it doesn't naturally enter the core. However, in general, there are two ways to make an element more siderophile: make conditions reducing enough or consider

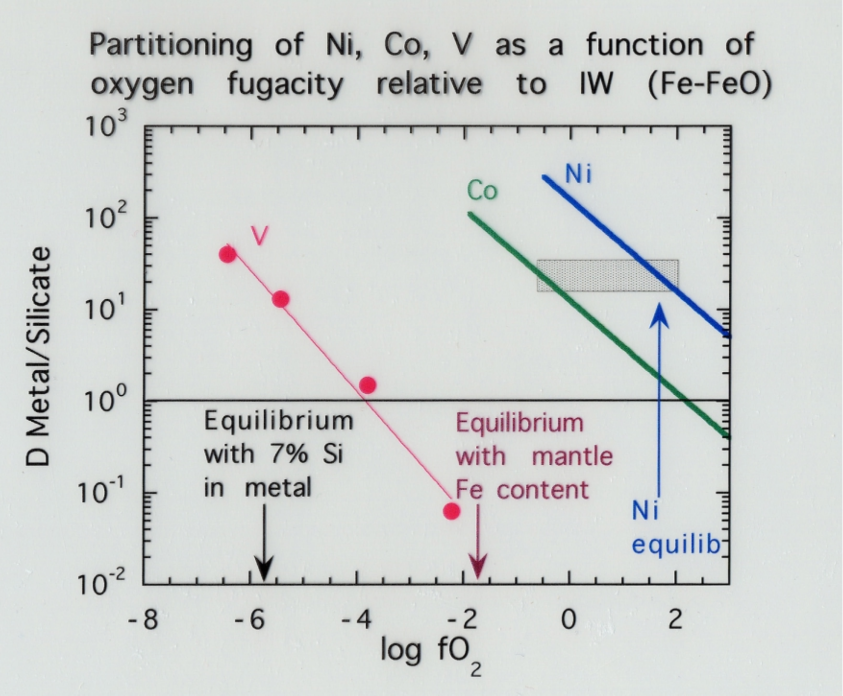

Figure 2. The degree to which Co, Ni, and V are siderophile or lithophile as determined by the partitioning into either metal of silicate as a function of oxygen fugacity. It appears that a single oxygen fugacity has difficulty explaining the correct depletions of V, Co, and Ni if the curent Fe content of the mantle is in equilibrium with the Fe in the core at 1.9 log units below Fe-FeO.

equilibration at higher pressures. For the moment we will only consider the former. The oxidation state is measured by the oxygen fugacity for a given reaction, namely, Fe-FeO. The curent Fe content of the mantle indicates that at 1.9 log units below Fe-FeO, the mantle would be in equilibrium with the Fe in the core (Figure 2). In order to change the oxidation state in the Earth to put ~7% Silicon in the core, conditions would have to become extremely reducing (the oxygen fugacity would need to be 6 log units below Fe-FeO). However, under these conditions it is likely that the chondritic ratios of some of the lithophile elements in the mantle would be disturbed. Furthermore, it can be seen that to get the right amount of Co and Ni in to the core, the core would have to have an oxygen fugacity of 0 or greater. While weakly siderophile elements such as Vanadium require a more reducing environment. Clearly, there seems to be a problem with all these elements requiring a different oxygen fugacity, so it appears to be not possible to make the present mantle with a single oxygen fugacity. This is when the idea of "heterogenous accretion" came into being, suggesting that as the Earth accreted, the oxidation state was changing.

We can now consider the effects of pressure on the metal-silicate partitioning of these elements. Figure 3 shows that when one takes effects of high pressure into account, it is possible to have a single oxygen fugacity and explain the amounts of Cobalt and Nickel. It is seen that over a given range of higher pressures, Nickel becomes much less siderophile relative to the amount that Cobalt becomes less siderophile. Extrapolating these trends just slightly beyond the data indicates that at a pressure of roughly 25-30 GPa, they will come to an equilibrium that can explain their abundances in the core for the oxidation conditions of the present mantle. Therefore, the pressure effect on the very siderophile elements Nickel and Cobalt is to make them less siderophile, which accounts for the observation stated earlier that these elements were apparently not depleted enough in the mantle. These elements are simply less siderophile at

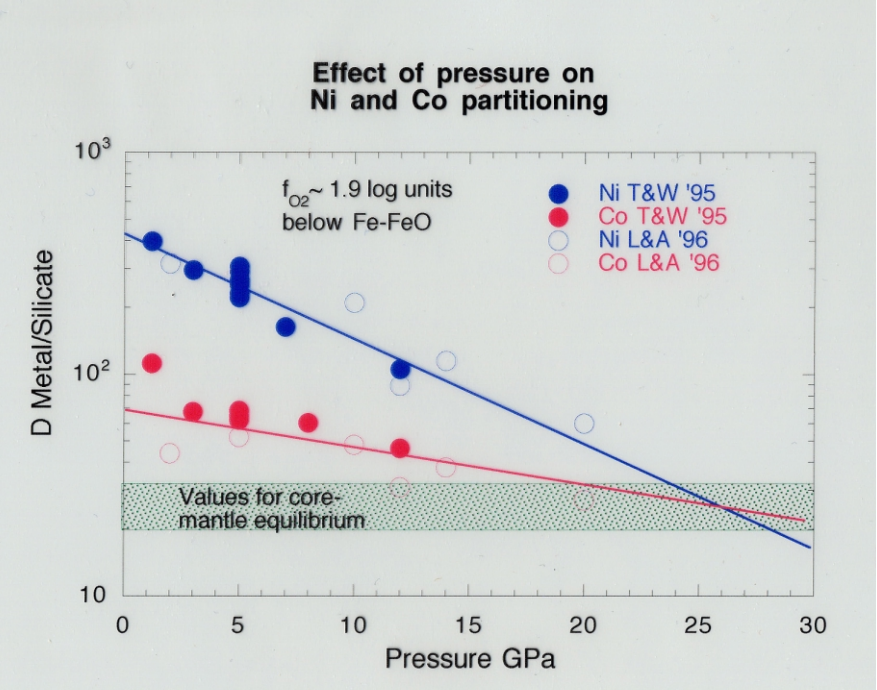

Figure 3. The effect of pressure on the partition coefficients for Ni and Co which shows that at high enough pressure (~25 - 30 GPa), Ni and Co will have the same amount of depletion in the silicate Earth at the observed oxygen fugacity of the mantle.

higher pressure, so there should be less of them in the core.

Interestingly, the opposite is true when considering the effects of pressure on the weakly siderophile elements, such as V, Cr, and Mn, since they all become more siderophile with greater pressure, not less siderophile. This increase in partitioning into the metal can account for the observation of their apparently being too depleted in the mantle, as was mentioned earlier. The fact that the PGE, which are very siderophile, are not depleted enough in the mantle may also be due to them behaving similarly to Nickel and Cobalt, by becoming less siderophile with greater pressure. Yet an entirely different explanation may be that of an addition of a late stage veneer of material deposited after the Earth had undergone core segregation, and of course these ideas are not mutually exclusive. One thing that stands out is the assumption that all these elements seem to be able to be explained by invoking equilibration at a single, high pressure of 25 GPa.

This brings up the idea of a magma ocean during the early accretion of the Earth in which some fraction of the mantle remains molten the entire time the Earth is growing. As the Earth accretes mass, its outer radius grows with time, core radius grows with time, and the profile of gravitational force with depth changes with time, yet the depth of the magma ocean can be defined throughout the entire accretional history by a depth equivalent to a single pressure of order 25 GPa. The base of this magma ocean corresponds to the stability of the perovskite phase of peridotite, below which the mantle would be a solid in the stable perovskite assemblage. With this model, it is possible for all of the mass of the accreting Earth to be processed through a magma ocean, with the metallic portion of it ponding at the base of the magma ocean, and coming to chemical equilibrium at a single pressure of 25 GPa. One further observation is that provided from the W-Hf isotopic system in which the timescale of core formation is constrained to be within 50 Million years after the formation of the Earth. This suggests that chemical equilibration happened relatively quickly and that the magma ocean was relatively short lived.

Now that there are hypothesized models to provide the conditions under which elements equilibrated under, namely, a single oxygen fugacity equal to the present equilibrium of the mantle of 1.9 log units below Fe-FeO and a single pressure of 25 GPa, experiments can be carried out to investigate the partition coefficients of the hypothesized light element, Silicon. Experiments show that indeed Silicon becomes less lithophile at higherpressure, yet for the present oxidation state of the mantle, even at high temperature (2200 C) and high pressure (18 GPa), Silicon is still a lithophile element. However, experiments done at even higher pressure (25 GPa) and higher temperatures (from 2500 C to 2800 C) show that Silicon does become siderophile and would result in a core content of less than 2%. If one were to extrapolate to even higher temperatures (3000 C), depending on the model used to make the extrapolation, one could dissolve about 5% Silicon into the core. When added to ~2% Sulfur and ~0.5% Carbon and Hydrogen, these values are approaching the amount of light element needed to explain the density of the core. However, the conditions required to dissolve roughly 7% Silicon in the core would suggest a magma ocean much hotter than 3000 C. In conclusion, it is possible to have Silicon be the light element in the core, but due to large differences in the models used for extrapolation, it is difficult to say how plausible. It seems that it is difficult to put as much as 7% Silicon in the core, but certainly a few percent is likely. In any case, if Silicon were the major component of the light elements, then as a refractory lithophile element, it would have to become more siderophile than all of the other refractory lithophile elements.

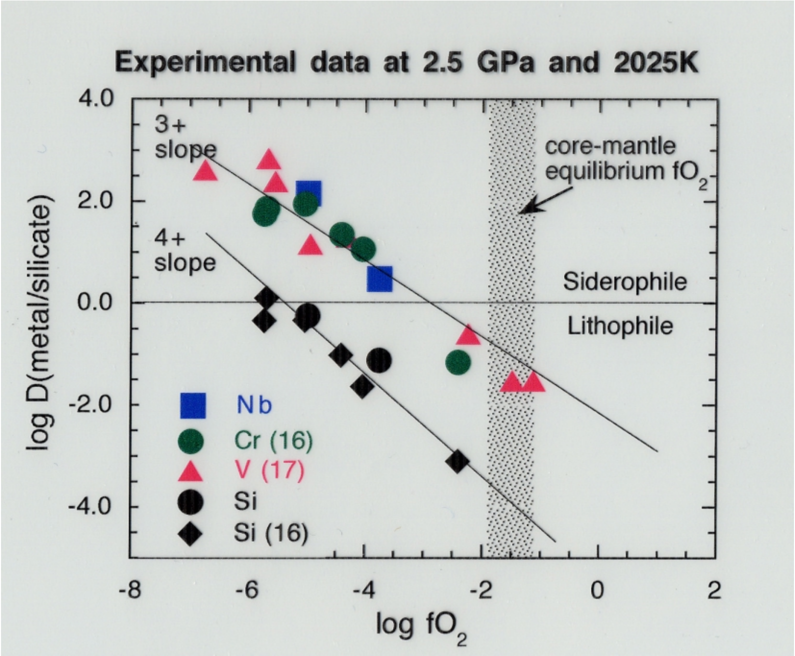

Figure 4. Experimental partition coefficient data for several elements at low pressure. Silicon, along the 4+ slope, is strongly lithophile at the oxygen fugacity of the present mantle. Niobium has roughly the same chemical behavior as Vanadium.

Since it appears to be difficult to constrain the temperature at which the base of the hypothesized magma ocean would have been, other ways of constraining the amount of Silicon in the core should be considered. There may be a way to constrain the amount of Silicon in the core if one considers Niobium. Figure 4 shows just how lithophile Silicon is at low pressures and in the range of Oxygen fugacity appropriate for core-mantle equilibrium. Niobium is another refractory lithophile element, but has virtually identical siderophile character to Vanadium. Also, Niobium is slightly depleted in the silicate Earth relative to other refractory lithophile elements. Thus, if the Vanadium depletion in the silicate Earth is due to dissolution in the metal, Vanadium must be accompanied by Niobium in the core. Therefore, the depletion of Niobium in the silicate part of the Earth should tell us roughly how much Silicon is in the core, so we need to find out how much Niobium is in the core. Another loose end is the depletion of Gallium in the silicate part of the Earth. Noting back on Figure 1, Gallium is a siderophile element which falls directly on the line of the volatility trend. The assumption inherent in the BSE models is that the depletion of Gallium in silicate Earth is due entirely to volatility. However, since Gallium is a moderately siderophile element, it makes it hard not to put some Gallium into the core. So there must be at least some Gallium in the core, meaning the depletion of at least one volatile element is not due entirely to volatility and therefore, the observed volatility trend should not be taken as a hard constraint to which there are no exceptions.