Possibility of S, O, Si and K in the Earth's Core Composition and its Problems

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Abstract: The light element candidates such as S, O, Si, and K are discussed for the reasonable compositions in the earth's core since the available data show density difference from pure iron core. These candidates are favored by the some evidences such as depletion in the crust and mantle, and lower eutectic temperature of Fe-FeS melt for sulfur. FeO phase for oxygen, lighter mass than sulfur and solubility in metallic phases for silicon, and partitioning in Fe-FeS melt for potassium. However, other problems such as short experimental data, initial compositions of these elements, and oxidation state during the formation of the earth should be solved simultaneously to confirm these light elements.

Keywords: light elements, earth's core, pure iron core

Introduction

The abundance of iron in the universe, as indicated by studies of meteorites and stars, coupled with iron deficiency in the earth's crust and mantle leads one to consider a possible concentration of iron in the earth's core. Iron has, roughly, the properties needed to fit both density and seismic data of core and this tends to confirm its presence. But the density of pure iron under core pressure-temperature conditions is slightly greater than that of the core as derived from the available data. To reduce the overall density of a pure iron core requires the introduction of some other elements, mixed or alloyed with iron. Nickel is initially thought to be a good candidate for mixture with iron in the core because of its deficiency in the earth's crust relative to its solar abundance and its presence with iron in meteorites. However, high pressure experiments showed nickel to compress almost identically to iron, thus proving that an iron nickel alloy would have virtually the same density as a pure iron core (Birch, 1964). Nickel can therefore be a major core component but would do little to lower the overall

density. What is needed was a light element, or elements to reduce the overall density of core.

The inner core is only about 5 wt% of the core. If the outer core also contains nickel then the amount of the light element must be increased accordingly. Also, depletion of siderophile elements in the crust and mantle can indicate that these elements are incorporated into the formation of the earth's core.

During the last two decades, various kinds of light elements have been suggested for the accounting of the less density, but the remaining favorite candidates are as follows: sulfur, oxygen, silicon, and potassium. Detailed discussion of each is a main goal of this paper and described as follows. Review of siderophile elements is out of the scope since data for these are not enough.

Light Elements

Possibility of light elements such as sulfur, oxygen, silicon and potassium in the earth's core compositions in described as follows.

Sulfur

Murthy and Hall (1972) suggested that the sulfur segregated with Fe to form a liquid core of Fe-FeS, as S is more anomalously depleted than other vola-

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tiles in the crust and mantle with respect to chondritic meteorites. Brett and Bell (1969) and Usselman (1972) showed the eutectic temperature of Fe-FeS at 1 bar (988°C and 998°C respectively). Usselman extrapolated it to the pressure of coremantle boundary and found that the temperature interval between melting of pure iron and eutectic increased with depth. Therefore, if the core formation occurred by sinking and coalescence of molten metal, eutectic melt (Fe-FeS) could have taken place and sunk more effectively through the mantle than pure iron, requiring a lower temperature gradient across the mantle to stay molten. But the melting point of pure iron is only a little less than that of most silicates and there would be a tendency for a descending iron melt to freeze, unless the early temperature caused almost the entire earth to be molten. So the descent of FeS melt provides a good mechanism for protocore formation following accretion. King and Ahrens (1973) suggested 10~12 wt% S based on shock wave experiments and Usselman provided 9~13 wt% S based on calculations of the densities at high pressure of Fe-FeS liquids. Wendlandt and Huebner (1979) conducted experiments on the Fe-S-O system at 30 Kbar. Their result showed that the Fe-S-O eutectic at 30 Kbar resembled the Fe-FeS composition, containing less than 1% oxvgen. The experimental data of Fe-FeS and shock wave strongly favored sulfur as a light element in the core.

Furthermore, Fe-meteorites often contained considerable proportions of iron-sulfide inclusions (troilite). If the outer core would not have much sulfur. earth might have lost large amounts of sulfur during accretion which would cause the earth's density to be significantly less than observed now. Also the electronic configuration of sulfur indicates that iron has a strong affinity to dissolve it.

Problem of Sulfur:

i) The above experimental data of Fe-FeS were derived from a certain limit pressure laboratory.

Therefore, the extrapolations to the deep core were unwarranted since the pressure effect on the system was unknown. This is especially true of the density change of FeS with increasing pressure (polymorph of FeS).

- ii) If S present in the mantle source rock formed a dense immiscible Fe-S-O liquid which had a higher density than that of the silicate melt, then S could not be transported to the surface in appreciable quantities. In this respect crustal depletion of sulfur, as indicated by surface rocks, could not be used as evidence that S is present in the core.
- iii) Finally, Ahrens (1979) suggested that an initial depletion of S at the time of the earth's formation would account for the low S content of the earth's crust. A sulfur component in the crust would therefore be difficult to account for.

Oxygen

Oxygen has been favored especially by Ringwood and his groups. According to their idea, earth accreted mainly from two components such as (a) reduced condensate separating from the solar nebular, and (b) volatile rich components. Most of the earth accreted homogeneously from a mixture of 85 ~90% of (a) and 10~15% of (b). After partial oxidation of metallic iron by water from (b), a substantial excess of metallic iron relative to FeO remained. The metallic iron and FeO segregated to form a core. At a later stage, the water from outer solar system (Jupiter) sufficed to oxidize all metallic iron from (a) to FeO and Fe₂O₃. This late condensate also contained a significant amount of FeS with the excess FeO. About 2~5 percent of a dense FeO-FeS melt was generated during this stage, segregating to sink rapidly into the core. So rapid segregation of the FeS-FeO melt would leave the upper mantle with a higher FeO content than it now possessed. This dense upper layer would sink into the lower mantle, accompanied by exsolution of the high pressure phase of FeO (MaCammon et al.: 1983). This FeO then entered the core.

Problem of Oxygen:

This candidate is supported by sufficient oxidation, rapid segregation, and exsolution of FeO. However, oxygen has very strong lithophilic tendencies, so it is very difficult to explain the segregation process of FeO from mantle. Furthermore, Macammon's suggestion (exsolution of high-pressure phase of FeO) is merely based on the calculation data of FeO-MgO system, so exsolution of FeO was unwarranted.

Silicon

Silicon is a lighter element than sulfur, so less silicon is needed to provide a density match. Shock compression studies at outer core pressures (Birch, 1964) showed that 90% Fe, 10% Si alloy yields a good match with the observed density, whereas about 15% sulfur is needed for the same match. Furthermore, a small amount of silicon dissolved in metallic phases (Sinoite Si3N4) was found in the enstatite chondrite meteorites. These points favor silicon as candidate for the light element in the outer core.

Problem of Silicon:

To make a Fe-Si alloy, Fe-oxides and some silica should be reduced. Also, the rate of sinking of metal during the protocore formation had to be very fast compared to the rate of chemical reequilibration by diffusion. These processes suggested that upper mantle had a lower f_{02} in its early history and that the mantle and core might be in disequilibrium. However, it was unlikely that extreme disequilibrium could be maintained during core formation because silicon had strong lithophilic tendency and iron oxides occured in the crust and mantle. Also redox characteristics of upper mantle was not yet clearly known.

Potassium

The earth's magnetic field may be generated by the thermal convection due to the decay of radioactive elements (such as ⁴⁰K) or by the gravitational

convection due to growth of the inner core (large density contrast between FeS liquid and newly crystallized solid grains). Like sulfur, potassium seems depleted in the crust relative to meteoritic material. So potassium is thought to be a major heat source in the core. Some unpublished experimental data (Goettel, 1975) showed the significant potassium partitioning in Fe-FeS melts in equilibrium with potassium feldspar and potassium solubility increased with temperature and pressure. Also, Goettle suggested that potassium would behave more like iron or nickel (possible metallic form of K) at the pressure of the core-mantle boundary.

Problem of Potassium:

Potassium partitioning experiments were limited to relatively low pressures, so it is hard to extrapolate to the deeper core. Also, until now, there was insufficient experimental data to confirm the possibility of potassium in the core. So potassium looks like a potential candidate, but it had to be as a heat source. Furthermore, potassium might not alone be present in sufficient amount to bring the density of the predominately iron core to the known value.

Discussion and Conclusions

Until now, several of the light element candidates were favored among scientists, but no theory has been conclusively verified. It can be assumed that elements other than S, O, Si, and K must be present in the core in trace or minor elements. If there were sulfur in the core, some chalcophile elements should be present also. Siderophile elements (Ir, Os, Re, An) could be present in the core from the depletion in the mantle. Carbon also might be present in the core since FeS melt was a good solvent for carbon and could carry toward the center of the earth.

For further understanding of the compositions of the earth's core, the following intensive research works are required:

i) Exact determination of partitioning of trace ele-

ments and element (chalcophile, siderophile ...) between Fe-FeS or Fe-S-O liquid and various kinds of melts (basaltic liquid, FeO-SiO2 liquid), and solid silicates over a range of P, T, and f₀₂ because these elemental abundances can be related to the abundances of elements in the core.

- ii) The properties of Fe and its alloys (or mixture) must be determined at the pressures and temperatures of the core since if we know these properties (melt properties, density, viscosities, ...). then we can derive some reactions between the solid silicate mantle and molten outer core, composition of the inner core, and whether the inner core is growing.
- iii) All theories pertaining to the formation of the earth's core must be consistent with theories of the initial development of the earth. Did the earth form rapidly through direct condensation or more slowly by the accumulation of smaller planetesimals? These questions must be thoroughly integrated into any theory concerning the evolution of the earth's core.

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