SHOCK WAVE DATA AND THE COMPOSITION OF THE EARTH'S CORE

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Abstract

The pressures existing in the outer liquid core of the earth are 130 to 320 GPa. Seismic data demonstrate that the density of the liquid core is some 8 to 10% less than pure iron. Portions of statics of Fe-60, Fe-56, C, Fe-54, Pa, Kr-85, and Fe-57, over the appropriate pressure interval, and a range of possible core temperatures (3000 to 5000 K), can be used to place constraints on the cosmochemically plausible light element constituents of the core (Si, C, S, K, and U). The internally derived density profile allows from 14 to 20 wt. % Si in the outer core. The inclusion of Si or, possibly C (up to 11 wt. %), in the core is possible if the earth accreted inhomogeneously within a region of the solar nebula in which a C/O (atomic) ratio of 0.1 existed, as compared in C/O ≈ 0.4 for the present solar photosphere. In contrast, a homogeneous accretion permits Si but not C, to enter the core via reduction of silicates to metallic Fe-Si core material during the late stages of the accumulation of the earth. The evolution of state data for the iron sulfides allow up to 6 to 12% S in the core. This composition would provide the entire earth, with a S/Si ratio in the range 0.2 to 0.3 comparable to extraterrestrial and cosmic abundances. Shock-wave data for Kr-85 give little evidence for an electronic phase change from α to β in orbitals which has been suggested to occur in K and allow the earth to store a cosmic abundance of K in the metallic core.

Introduction

Knowledge of the composition of the earth’s core is inextricably interwoven with theories of the origin, differentiation, and thermal evolution of the earth, as well as coupled to theories of the onset and regeneration of mantle-deep hydrodynamic flows in the liquid outer core. Most of our present knowledge of the earth is derived from seismic data which specifies both the longitudinal elastic velocity and the density versus depth in the outer (liquid) and inner (solid) core of the earth (1). As demonstrated in Fig. 1, the entire range of pressures existing within the earth’s interior, including those present in the outer and inner core are accessible to the laboratory using the shock wave generating technique of hypervelocity impact. This method relies on the launching of metal-bearing projectiles (flyer plates) (e.g., composed of tungsten or tantalum) using, for example, a 1.5-MJ-stage light gas gun (2) which upon impact at speeds of up to 6 km/sec will induce pressures of ~ 5 Mbar or 400 GPa in core materials, e.g., Fe. The pertinent shock wave data for the light element core constituents are summarized and discussed in terms of their cosmochemical abundances and the relation of their possible occurrence in the earth to theories of the formation of the earth’s core.

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Comparison of the seismic and (raw) shock wave (Rugnolot) data demonstrate (Fig. 2) that the density of the outer (solid) core of the earth is some 8 to 10% less dense than pure iron or iron-nickel (solid) composition similar to that found in metallic meteorites. The core density deficit has been generally attributed to the inclusion of about 10 to 15% by mass of various geochronologically plausible, and chemically abundant elements such as S, O, and C and possibly some minor amounts of N, H, and B.

After the discovery of the core density deficit in the early 1950's, the hypothesis that silicon was the light element within the core was widely accepted on the basis of geochemical arguments preferred by Ringwood (8). Data for iron-silicon alloys (9) demonstrated that from 10 to 20% by weight of metallic silicon is required to lighten the core. From a cosmic abundance point of view, a silicon-bearing core yields a total earth iron to silicon atomic ratio, Fe/Si, of < 0.9, in close agreement with the same value observed in carbonaceous chondrites (10) and in the sun (Fe/Si = 0.73 ± 0.2) (10), whereas if the light constituent of the core is not silicon the earth appears to be decidedly enriched in Fe, with a Fe/Si value of about 1.2. Moreover it appears that there are at least two different types of processes which could result in the earth accreting a Si-bearing core. Larimer (10) calculated that if the earth accreted inhomogeneously in a carbon-rich environment such that C/Fe > 2, instead of C/Fe > 0.4, as is the case for present solar photosphere, the initial condensates would be FeS, FeO, FeS, TiO, and-more moderate amounts of C, Fe3C, and SiC. This silicate containing assemblage is found in enstatite chondrites; these meteorites apparently formed in such a reducing environment. If the earth's core formed in this way it would be composed of FeS and contain the high temperature condensates, including silicon, and have an appreciable carbon content. Maximum carbon contents of the earth's core, may be inferred from laboratory measurements at a range of temperatures which may be representative of the core-mantle interface using Rugnolot data for Fe3C (Fig. 2) (5) and diamond (11). Densities comparable to that of the outer liquid core of the earth are compatible with a calculated mixture of iron and 1% carbon by mass. This value for a maximum carbon content is almost independent of temperature from 1000 to 5000 K and 120 to 1200 GPa (the latter represents the pressure range of the outer core). When this (maximum) C abundance for the earth is used in the form of a total earth ratio, C/FeS, and compared to solar abundance, the earth is, at best, depleted in C by at least a factor of 10 (Table 1). Moreover the favorable comparison with carbonaceous chondrites is somewhat misleading as the carbon in these objects is in a highly volatile form of hydrogen-carbonates. Although carbon because of its volatility is precipitated from entering the core of the earth, if the earth accreted from homogeneous material similar to carbonaceous chondrites, Ringwood has shown (8) how in the latter stages of such a process, large quantities of silicates and iron might be reduced by the carbonaceous material in chondrites and form the hypothetical Fe-Si core material. This is the second mode via which Si, but not C, could enter the core. In both cases, the resulting hypothetical earth cores are grossly in chemical disequilibrium with the overlying mantle. In the first case a silicate- refractory (more volatile) and oxidized silicate mantle, containing H2O and CO2, accreted later, and covered over, a reduced, and refractory, core containing Fe, Si and C. In the second, homogeneous accretion case, the oxidized and volatile

- Solid material condenses from the gas and is directly accreted into planets. Thus some planets accrete, less refractory minerals. The intermediate stage of planetaryesimal formation is thus bypassed.
rich material initially accreted in the protoplanet center is displaced by the liquid, Fe-Si, but not the core material which is formed at the surface during the final stages of accretion of chondritic material (8).

Fig. 1 Shock pressure versus particle velocity for a range of candidate mantle and core materials. Shock states achievable with tungsten projectiles impacting at speeds from 4 to 8 km/sec are indicated.

Fig. 2 Shock pressure versus density relations for candidate materials of the earth's core, Fe_{90}S (3), Fe_{90}Ge_{10} (4), Fe_{75}C (5), Fe (6), and Fe_{75}Ge_{25} (7) as compared to properties of the earth's outer (liquid) and inner (solid) core (1).

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Candidate Light Elements of the Earth's Core, Earth and Cosmochemical Abundances</th>
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<tbody>
<tr>
<td>Light Element (X%)</td>
<td>Mixture in the Core</td>
</tr>
<tr>
<td>Fe_{90}C(hcp)+C</td>
<td>11</td>
</tr>
<tr>
<td>Fe_{90}G(hcp)+Fe(hcp)+C</td>
<td>0.24-0.52</td>
</tr>
<tr>
<td>Fe_{90}O(hcp)+Fe(hcp)</td>
<td>7-9</td>
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</table>

Sulfur, potassium, and sodium are the major volatile elements which appear to be depleted in the earth's mantle and crust, relative to chondritic and solar abundances. As is demonstrated in Table 1, and Fig. 3, if the outer core is composed of a mixture of iron and the shock-induced high pressure phases of either Fe_{90}C or Fe_{75}C, Ge/Si ratios close to meteoritical or solar abundances are inferred. In addition to being present in a gaseous form, the major elements of a model earth containing sulfur as the major light element in the iron core is the lowering of the melting point, of Fe or FeS which at ~100 GPa is expected to be
\( \text{Shock Wave Data} \)

\( \text{A} \) 600 K, versus \( \text{B} \) 2100 K for the asthenic in the Fe-Mg system (11). Thus considerably lower temperatures are realized early in the earth's history in not only permit the earth to retain a moderate inventory of volatiles but also permit generation of a magnetic field via core fluid motion, of comparable strength to the present field, some 10^3 years after earth formation. The apparent insensitiveness of the earth to accrete nearly its cosmic abundance complement of such volatiles such as \( \text{Fe}, \text{Cl}, \text{Kr}, \text{Ne}, \text{Ar}, \text{Br} \) and \( \text{Xe} \) in addition to \( \text{S} \) in contrast to a depletion of \( \text{X} \) and \( \text{S} \) presents a problem. It has been suggested that the earth might contain substantial quantity of \( \text{X} \) because under high pressure this element might undergo an electronic transition from 1-s to 3-d type orbitals. Thus it might take on an electronic structure similar to a transition metal, and thus possibly be soluble in a Fe or Fe-X-rich core. Recent shock wave experiments on \( \text{KFe}_{3} \) (initial density \( 2.4 \text{ g/cm}^3 \)) do not however support this hypothesis (6). In Fig. 4 the volume of \( \text{X} \) in the high pressure phase of \( \text{KFe}_{3} \) (zero-pressure density \( 4.4 \text{ g/cm}^3 \)) as inferred from shock wave experiments is seen to be comparable to metallic \( \text{X} \), which is known to be insoluble in \( \text{Fe} \). However detailed thermochemical calculations do not indicate that \( \text{X} \) will partition from a silicate into a metallic phase at core pressures (13).

![Fig. 3. Calculated maximum content of sulfur for the earth's outer core assuming a mixture of the high pressure phase of pure iron and \text{FeS} of \text{FeS}_{2} for temperatures of 3550 and 5000 K. The heavy curves are calculated from raw Vogelot data and indicate an enormous apparent decrease of sulfur content with depth (4).](image)

![Fig. 4. Volume per mole, variances, isostatic pressure for sulfur in \text{FeS} (top) and \text{FeS}_{2} (bottom) and potassium as \text{KFe}_{3} (bottom) after Sechelle and Almen (14)).](image)

Recently obtained shock wave data for \( \text{FeS}_{2} \) (initially in the 31, or \( \text{NH}_{3} \) structure, demonstrates (15) the occurrence of a pressure-induced transition to an unknown phase at \( \text{A} 70 \text{ GPa} \) (Fig. 5). If this transition as well as the previously discovered (16) shock-induced phase transitions in \( \text{FeS}_{2} \) and \( \text{FeS}_{3} \) represent the onset of either metallic phases or strongly covalent, crystal structures in which the 3-d electron in \( \text{Fe} \) are in a low spin state, it is possible that oxygen will demonstrate solubility in metallic iron at high pressure (17). Rigney has suggested (8) that if the earth accreted from a mixture of two components, a highly reduced, metallic rich refractory material and a volatile-rich material similar to carbonaceous chondrites, the \( \text{FeO} \) which dissolves in the core could have come from oxidized metallic iron. Because of the relatively low density of \( \text{FeS}_{2} \), only 7 to 8 \text{ wt.} \text{X oxygen dissolved in iron is required to yield core densities of outer core pressures for temperatures in the range 3500-5000 K.}

The solubility of oxygen in liquid iron is critical to assessing the oxygen-in-the-core hypothesis. Near the liquidus at ambient pressure the solubility of oxygen...
is low (0.62) although, its solubility increases substantially with temperature. Recent phase equilibria measurements at 3 GPa and high temperature, in the Fe-S-O system demonstrate a marked decrease in solubility of oxygen with pressure (18). As in the case of K the available evidence for the solubility of O in liquid iron at high temperatures and pressures do not support the suggestions that it is soluble in the earth's core.

Fig. 5 Shock wave data for FeO$_2$O (after Jamieson and Ahrens, (17) and Jackson and Ringwood, (17)). Curves a and b have slightly different equation of state and are based on assumed zero-pressure densities of 6.30 and 6.65 g/cm$^3$.

**CONCLUSIONS**

Shock wave data for iron silicides, Fe$_5$C, C, iron sulfides and FeO can be used to place constraints on the maximum abundances of the light elements, Si, C, S and O in the earth's core. These range from 1% to 20% (by mass) for Si down to 7% to 8% for O. Si can enter the core as the result of two very different processes. One mechanism is via heterogeneous accretion in an environment with a C/O ratio of 2.1, (as compared to C/O > 0.6 for the present solar photosphere). In this case a Fe-Si core will condense first. C will also be present in the form of refractory carbon in this environment. A second type of process would occur during the terminal stage of the homogeneous accretion of the earth from a chondritic-like composition. Liquid Fe-Si core material could form upon the hot and reducing earth's surface and sink to the core. The latter process would not yield appreciable C in the core. Another hypothesis is that involving the solubility of oxygen in the core. This suggestion is not inconsistent with the occurrence of major shock-induced transitions in oxides. These transitions which all occur below 100 GPa in FeO, Fe$_5$O$_4$ and Fe$_3$O$_4$ may reflect changes in iron's electronic configuration. However recent high pressure equilibrium data indicate a marked decrease in the solubility of oxygen in the Fe-O-S system with pressure which makes the solubility of oxygen in the core appear difficult. The hypothesis that S (8 to 12% by mass) is the light constituent of the earth's core is consistent with shock wave data for iron sulfides and implies that the earth accreted nearly
it's entire cosmic complement, of this volatily element. This is in accord with terrestrial abundance of other volatile specifically, the halogens and gases. Because of the low eutectic melting point in the Fe-Se metal system at 10 GPa of 710°K versus 4000°K for Fe, (at these pressure) the inclusion of S in the core provides a mechanism for producing a molten core early in each history and retaining the earth's volatile component. The earth's apparent depletion in other major volatiles such as K and Xe is not however explained.

Acknowledgments

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References