GEOSCIENCE

Hydrogen: An Important **Constituent of the Core?**

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Earth's core constitutes 32% of the planetary mass, yet we know little about how it was formed. We do know some of its properties: Seismological data show that the density of the core increases with depth from 10,000 kg m^{-3} at the mantle-core boundary (pressure = 136 GPa) to 13,000 kg m⁻³ at the center of the core (pressure = 364 GPa). Comparison of the composition of the outer, silicate part of Earth with cosmic abundances of the elements and comparison of the measured density with densities of metals at high pressure constrain the core to be dominantly liquid iron with a few percent nickel. The outer, liquid core appears to be crystallizing slowly from the bottom up, with the solid central part currently representing 4% of its volume. The results reported by Okuchi on page 1781 of this issue (1) indicate that the core may contain substantial amounts of hydrogen, which would have important implications for its formation and evolution.

Core formation was a dramatic event in the early history of Earth. It extracted the "siderophile" elements, which dissolve readily in Fe (for example, S, C, Ni, Co, and the Pt group), and stored them out of contact with the silicate material of the exterior. The patterns of depletion of siderophile elements in rocks, relative to abundances in undifferentiated meteorites, provide the material for ongoing vigorous debate on how the core formed. There are two end-member models: (i) the core formed in a single event at the end of the accretion of Earth, and (ii) core formation occurred progressively during accretion and ceased before Earth stopped growing. Recent isotopic dating with extinct 182 Hf (half-life = 9 million years) and its siderophile daughter ¹⁸²W (2) shows that the system was disturbed about 4.5 billion years ago (about 70 million years after the formation of the oldest objects in the solar system), giving 4.5 billion years as the approximate age of core separation.

One of the most important clues to the origin and evolution of the core is its density. It has been known for 50 years that core density, although close to that of Fe, is actually about 10% too low for it to be pure Fe or Fe-Ni alloy. There must also be about 10% of a low-atomic number element, such as H, C, O, S, or Si. This "light" element is obviously one that is abundant in the solar system, soluble in Fe at very high pressure, and probably soluble in Fe at the modest pressures at which core segregation is believed to have commenced. Oxygen can probably be excluded because of its low solubility in Fe under all conditions. Geochemists and cosmochemists have built most of their models around S and Si (3), two moderately abundant elements whose plan-



Core elements. Cutaway diagram showing schematically how hydrogen atoms (red) fill gaps left by iron atoms (blue), as proposed by Okuchi (1).

etary concentrations can be constrained reasonably well. Hydrogen and carbon are generally ignored because they are thought to have been so volatile during Earth's accretion that they were almost completely lost. In the case of atmospheric H, this loss, because of low atomic mass, has continued throughout geologic time. In contrast to the conventional wisdom, however, the findings of Okuchi (1) show that, far from reaching the atmosphere and escaping, most of the H in the primitive Earth should have dissolved into the segregating core and been stored in the deep interior (see figure). This observation is based on a set of carefully designed high-pressure experiments and has important implications for the core formation process.

It has been known for some time that intermetallic compounds of general formula FeH, are stable at pressures above 3 GPa and that they decompose to Fe plus hydrogen gas

upon decompression. Because such iron hydrides cannot be quenched and investigated at room pressure, it is not known whether they have been produced during earlier studies of silicate-metal partitioning at high pressures and temperatures. What Okuchi has done, however, is to react metal and silicate in the presence of H_2O at 7.5 GPa and to quench the sample so rapidly (1.5 GPa s^{-1}) that hydrogen cannot escape diffusively but is forced to generate bubbles. By counting the bubble density, he found that at 7.5 GPa, solid FeH_{0.33} is produced, and this solid melts between 1100° and 1200°C (700° below the melting point of Fe) to a liquid of approximate composition FeH_{0.4}. Furthermore, this takes place under conditions that are not implausibly reducing for core formation.

Using these data, Okuchi calculated the equilibrium constant for the reaction producing H and ferrous Fe from H₂O and metallic Fe, and then extrapolated to a reasonable bulk Earth composition with initial H₂O content of 2%. He found that 95% of the initial H would, in this case, dissolve into the core and not escape from Earth. Okuchi proposes, therefore, that the "light" element in the core is dominantly H with lesser amounts of S and C, with the further implication that almost all of Earth's H is in the core rather than in the hydrosphere.

The alternative "geochemical" model, in which the light component is a mixture of Si and S, requires that core formation was initiated under extremely reducing conditions (so as to dissolve Si in the metal) and became progressively more oxidizing as S was added to the core and oxidized iron to the silicate. This is a multistage model. The core composition proposed by Okuchi is, however, consistent with single-stage core formation, because it would segregate under relatively oxidizing conditions. What needs to be done now is to determine the densities and phase relations of these Fe-H mixtures at more realistic core pressures and to test whether their properties are consistent with those that have been determined for the core itself. The patterns of siderophile element depletion that would be generated in the silicate Earth by FeH_x separation need also to be determined and compared with the composition of the present-day silicate mantle.

References

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