Hydrogen and Other Light Elements in the Earth's Core

The Earth's metallic core, located at depths of 2890 to 6370 km from the surface, is not pure iron nor iron-nickel alloy but includes substantial amounts of low-atomic-number "light" elements that explain the seismologically observed ~8% density deficit and ~5% sound velocity excess with respect to pure Fe [1]. Although the presence of light elements in the core has been known since 1952, the core light element composition still remains under hot debate 70 years later. Five light elements (S, Si, O, C, and H) are considered primary candidates. Identifying the core light elements has profound implications in wide areas of earth and planetary sciences. To constrain the core composition, it is of great importance to determine the density and sound velocity of iron and iron alloys at core pressures and temperatures (>136 GPa, >~3500 K) by a combination of X-ray diffraction (XRD) and inelastic X-ray scattering (IXS) measurements at SPring-8 [2].

Recent planet formation theories [3-5] suggest that a large amount of water, ten to one hundred times as much as sea water, may have been delivered to our planet during its accretion phase. Such an extensive amount of water could have been sequestrated in the core as hydrogen with some oxygen. Indeed, *ab initio* simulations indicated that hydrogen-bearing liquid and solid alloys [6,7] can explain the observed density and velocity of the liquid outer and solid inner cores, respectively, suggesting that hydrogen is likely to be a major light element in the core.

Metal-silicate partitioning of hydrogen

The Earth was once covered with a "magma ocean", which incorporated most of the water transported to the Earth by that time. The partitioning of hydrogen between liquid metal and molten silicate (magma) is the key to understanding the fate of this water. However, its experimental determination has been challenging. Indeed, the examination of hydrogen-containing iron alloys is difficult because hydrogen is least soluble in iron under ambient conditions (it is thus difficult to determine the hydrogen content in alloys). In addition, the metal-silicate (core-mantle) partitioning occurred under high pressure and temperature (P–T) conditions, typically 50 GPa and 3500 K, in a deep magma ocean that extended to a depth of ~1200 km. There were no experimental reports on the metal-silicate partitioning of hydrogen under such high P–T conditions.

Recently, we have determined the partitioning of hydrogen between iron and silicate at 30–60 GPa and 3100–4600 K, corresponding to conditions at the bottom of a magma ocean [8]. High P–T experiments were performed in a laser-heated diamond-anvil cell (DAC) at SPring-8 BL10XU. We melted an iron foil + hydrous mid-oceanic ridge basalt (MORB) glass sample
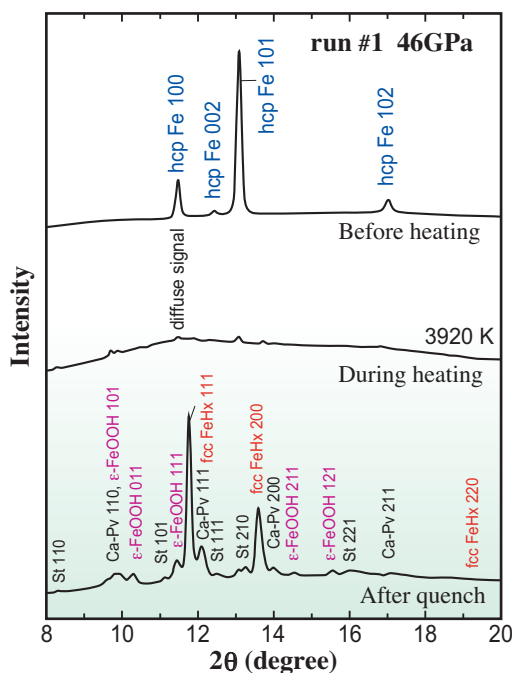

Fig. 1. XRD patterns collected at BL10XU before/during/after heating the Fe metal + hydrous MORB glass sample to 3920 K at 46 GPa [7]. Both iron and silicate were molten during heating. The hydrogen content in liquid metal was obtained from that in fcc FeH$_x$ on the basis of its lattice volume and the proportions of FeH$_x$ and ε-FeOOH estimated from microprobe analyses.

at high pressures and then quenched the temperature to 300 K. Since hydrogen escapes from solid iron during decompression when the iron transforms into the bcc phase, the hydrogen concentration in quenched liquid metal must be determined at high pressures. XRD measurements *in situ* under high *P–T* conditions revealed that molten iron crystallized into FeH_x and a minor amount of FeOOH upon quenching (Fig. 1). The lattice volume of FeH_x was larger than that of pure Fe under equivalent conditions because the incorporation of hydrogen in the interstitial sites of the Fe lattice causes volume expansion. We obtained hydrogen concentrations in liquid Fe based on the lattice volume of FeH_x and the proportions of FeH_x and FeOOH in quenched liquid. Earlier experiments [9] demonstrated that the thermal annealing of such FeH_x quenched crystals only slightly changed their unit-cell volume, indicating the validity of such determinations of the hydrogen content in liquid. On the other hand, hydrogen was present as water in silicate melt that coexisted with hydrogen-bearing Fe liquid in these experiments. After recovering a sample from the DAC under ambient conditions, its cross section at the center of a laser-heated portion was prepared parallel to the compression/laser-heating axis, using a focused ion beam (FIB). Subsequently, the hydrogen content in a quenched silicate melt was determined with an isotope microscope system at Hokkaido University. This system yields quantitative maps of secondary ions emitted from the sample surface (Fig. 2).

These XRD and SIMS analyses detected 5300 to 26000 ppm H (by weight) in metal at high pressures (before decompression) and 90 to 470 ppm H (present as water) in quenched silicate melts, respectively. The calculated metal-silicate partition coefficient of hydrogen, $D_H^{metal-silicate}$ (weight fraction basis), ranged from 29 to 57 (Fig. 3), indicating that
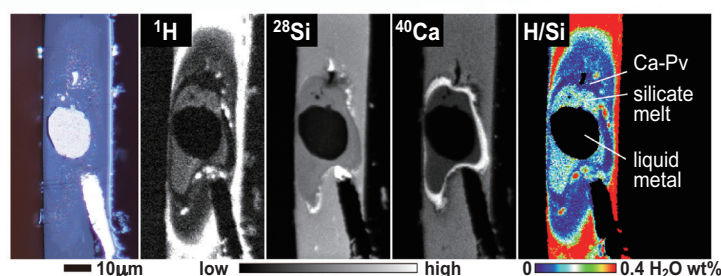

Fig. 2. Micrograph (left), secondary ion images for $^1H^+$, $^{28}Si^+$, and $^{40}Ca^+$ (middle), and a distribution map of water (right) in cross section of the sample recovered from the same metal + silicate melting experiment as in the case of Fig. 1 [7]. Hydrogen is absent in metal, because it escaped from iron upon the release of pressure. The hydrogen (water) content in the quenched silicate melt was obtained with ±2–7% uncertainty.

hydrogen is a strong siderophile (iron-loving) at high pressures. The metal-silicate partitioning of hydrogen occurs as an oxidation-reduction reaction:

$$HO_{0.5}^{silicate\ melt} + \frac{1}{2}Fe^{metal}$$
$$= H^{metal} + \frac{1}{2}FeO^{silicate\ melt} \quad (1)$$
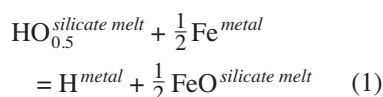
$D_H^{metal-silicate}$, therefore, changes with oxygen fugacity as well as *P* and *T*.

Hydrogen in the core

The metal-silicate partition coefficient of hydrogen is useful for estimating the concentration of hydrogen in the core based on the amount of water present in the mantle + crust + oceans, which has been estimated to be a total of 687 ppm H_2O corresponding to two times the mass of oceanic water [8]. Conceptually simple "single-stage" core formation models [10-12] reconcile the known mantle abundances of moderately siderophilic elements with core-mantle chemical equilibration at around 50 GPa and 3500 K and oxygen fugacity relevant to the FeO content in the mantle (2.3 log unit below the iron-wüstite buffer). If this is the case, $D_H^{metal-silicate} = 46.2$ for 50 GPa and 3500 K gives 0.40 wt% H in the core (Fig. 4). When considering the minimal average mantle H_2O abundance to be as much as that found in the

upper mantle (although the upper mantle is generally considered to be depleted in melt components and water), the lower bound for the core hydrogen concentration is 0.24 wt%. Furthermore, taking the estimated range of *P–T* conditions for core-mantle equilibration, the core may include 0.24–0.60 wt% H.

Previous *ab initio* calculations revealed that both the density and P-wave velocity of the liquid outer core are explained with liquid Fe containing 1.0 wt% H [6]. The 0.24–0.60 wt% H accounts for ~20–60% of the density deficit and velocity excess of the liquid core with respect to pure iron, indicating that hydrogen is an important light element in the core. It is equivalent to the amount of hydrogen included in 30–74 times the total amount of seawater on the Earth. This suggests that an extensive amount of water was transported to the growing Earth, which is consistent with recent planet formation theories [3-5].

Earth's core composition

Hydrogen accounts for ~20–60% of the density deficit and velocity excess of the outer core, indicating that the remaining 40–80% is attributed to other light elements such as sulfur, silicon, oxygen, and carbon [1]. Traditionally, sulfur has been considered to be one of the major core light elements because it is commonly included in iron
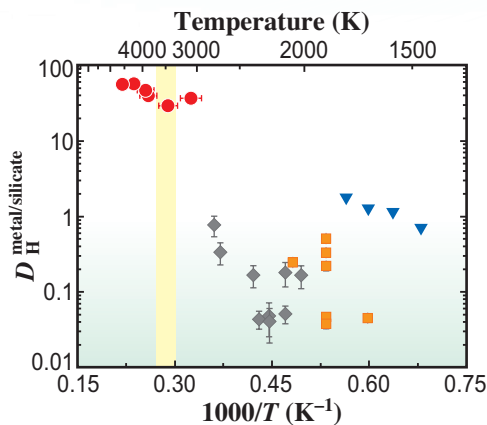
Fig. 3. Metal-silicate partition coefficient *D* for hydrogen as a function of reciprocal temperature. Tagawa *et al.* [7] (red circles) showed that hydrogen is highly siderophilic under the formation conditions of the Earth's core. Reported *D* values (gray diamonds [13], orange squares [14]) were lower by one to three orders of magnitude than the present results because hydrogen was lost from metals during decompression in those experiments. Pioneer experimental results (blue inverse triangles [15]) are also plotted.

by the crystallization of SiO_2 upon secular cooling. With the present-day temperature at the core side of the core-mantle boundary (CMB) being 3500 K, the remaining silicon and oxygen account for ~40–80% of the outer core density deficit and velocity excess [13]. Finally, 0 to 1.3 wt% C may be present in the outer core, contributing to 0–20% of the outer core density deficit and velocity excess, in addition to hydrogen (~20–60%), sulfur (20%), and silicon + oxygen (~40–80%).

The above arguments are based on the seismologically observed density and P-wave velocity of the outer core, along with metal-silicate (core-mantle) partitioning and simultaneous solubility limits of Si+O. In addition, the outer core liquid is in chemical equilibrium with the solid inner core at the inner core boundary (ICB) located at a depth of about 5200 km. Therefore, its light element composition can be calculated from the inner core solid composition constrained by the observations of its density and P-wave and S-wave velocities using the solid-metal/liquid-metal partition coefficient of each light element [1].

meteorites that represent the metallic cores of small rocky bodies. The bulk Earth sulfur content can be calculated on the basis of that of chondrites (primitive meteorites); the depletion of sulfur on the Earth relative to chondrites is estimated using elements that are present only in the silicate part (mantle + crust) and exhibit volatility similar to that of sulfur. The sulfur concentration in the Earth's core is then obtained to be about 2.0 wt% by subtracting the known amount of sulfur in the silicate from the bulk Earth quantity. The 2.0 wt% S accounts for about 20% of the density deficit and velocity excess of the liquid core.

Silicon and oxygen are major elements in the silicate mantle. It is known that higher amounts of silicon and oxygen are incorporated into molten iron at high temperatures [12,13]. Recent models suggest that core-forming metals equilibrate with silicate at relatively high temperatures, typically 3500 K, and thus the core is enriched in both silicon and oxygen. However, the literature on steel making shows that simultaneous solubilities of silicon and oxygen in liquid iron are limited at 1 bar (Fig. 5(a)). Furthermore, our

recent experiments also demonstrated the limited simultaneous solubilities of silicon and oxygen in molten iron at core pressures [13], indicating that the Earth's liquid core may have included large amounts of both silicon and oxygen in its early history and is now saturated with SiO_2 (Fig. 5(b)). The silicon and oxygen concentrations in the core should have decreased
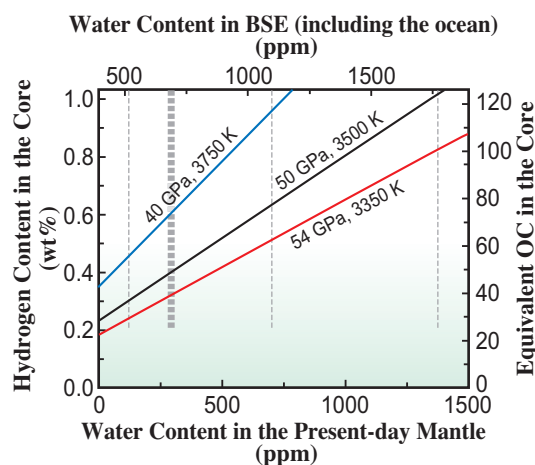

Fig. 4. Estimates of hydrogen concentration in the Earth's core. Three lines show the hydrogen content in the core relative to the water abundance in the present-day mantle + crust + ocean ("BSE", vertical lines). Hydrogen content reached chemical equilibrium with silicate under high P–T conditions (blue [9], gray [10], red [11]). Even a modest amount of water in the present-day mantle (two vertical lines showing relatively low H_2O contents in the mantle) suggests 0.24–0.60 wt% H in the core, corresponding to 30–74 times hydrogen that exists in the oceans (right vertical axis). This accounts for ~20–60% of the density deficit and velocity excess of the Earth's outer core relative to pure iron.

Furthermore, in the outer core liquid, Fe must crystallize instead of light-element-rich compounds such as FeO and FeH, otherwise the dense inner core does not form. Combining a total of eight independent constraints, the outer core composition, including five light impurity elements and ~5wt% Ni, should be tightly constrained in future studies. To do so, we plan to perform XRD measurements at SPring-8 BL10XU to obtain 1) melting phase diagrams including the solid-liquid partitioning of light elements, particularly in hydrogen-bearing Fe alloy systems and 2) the density of liquid Fe alloys, as well as IXS measurements at BL43LXU to obtain 3) sound velocities of liquid and solid Fe and Fe alloys.

Implications of core light element composition

The metallic core constitutes one-third of the Earth's mass and includes >30 atm% light elements. Since the light element composition is unknown, the chemical composition of the bulk Earth also remains unknown. It is highly possible that the core includes >90% of the Earth's carbon and hydrogen. Both are highly volatile and should have condensed outside the Earth's orbit and then somehow transported to our planet. Thus far, it is impossible to specify how, when, and how much of these elements arrived on the Earth.

Recent planet formation theories such as the "Grand Tack Model" or "Pebble Accretion Model" have attracted considerable attention. They suggest that more organic matter and water were delivered to the Earth than do traditional models. An understanding of the amounts of carbon and hydrogen in the bulk Earth is indispensable to confirm of such recent theories.

In addition, because the amount of silicon present in the core is unknown, the Mg/Si ratio, the principal element ratio of the bulk Earth, remains unknown. The Mg/Si molar ratio of the accessible Earth's upper mantle composition (=1.3) is significantly different from the solar composition (=1.0), which is another important unsolved problem. The presence of silicon in the core could fill this gap. Moreover, the Earth was likely made of reducing substances that were present at the inner solar system and oxidizing substances that were from the outer solar system. Since the amount of oxygen in the core is unknown, their proportions are not yet understood.

Furthermore, the current estimates of the Earth's core temperature include large variations. For example, the previously estimated temperature at the CMB ranges from 3400 to 4600 K [1]. The liquid core composition provides the temperature at the ICB, the boundary between the solid and

liquid cores, which corresponds to the liquidus (onset of crystallization) temperature of the outer core liquid at 330 GPa. The isentropic outer core temperature profile including the CMB temperature is calculated from the ICB temperature. The core temperature itself has profound implications for the present state of the core. In addition, the CMB temperature is a key to interpreting the complex seismic structures of the lowermost mantle and estimating heat flow from the core to the mantle, which is very important for the thermal histories (cooling speeds) of both the core and the mantle.

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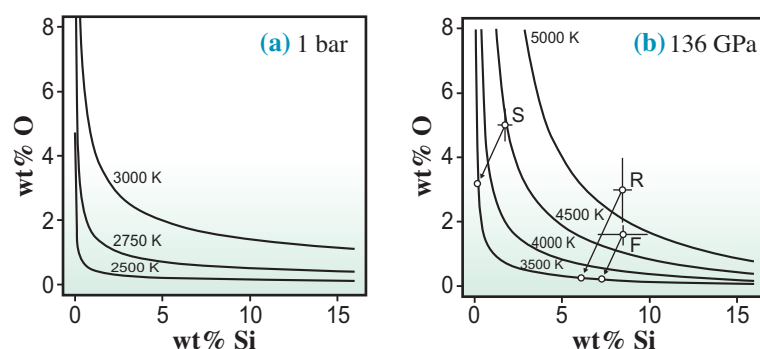[17] D.C. Rubie *et al*.: Icarus **248** (2015) 89.

Fig. 5. Simultaneous solubility limits of Si+O in liquid Fe at (a) 1 bar and (b) 136 GPa (pressure at the CMB). The silicon and oxygen contents in the initial core indicated by 'S' [16], 'R' [17], and 'F' [11] are beyond the solubility limit in the present-day outer core, which has caused the SiO$_2$ crystallization and the depletion of Si and O in the liquid core over the Earth's history (see arrows).