

Possible Immiscibility of Iron Hydride and Iron Sulfide in the Martian Core

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Abstract

Although many proposals have been made to explain the sudden cessation of dynamo in early Mars, many of these models require rapid cooling in early Mars, which is not in line with magmatic activities continued to later period. Our new experiments found that hydrogen destabilizes iron sulfide, forming separate iron hydride and iron sulfide at the pressure and temperature conditions of the Martian core. In the early Martian mantle, compositional and/or phase stratification could have suppressed the partitioning of H from the mantle to the core, allowing for the early dynamo. Once mantle convection was initiated, hydrogenation of the core could result in H-rich outer core and S-rich inner core. Such chemical stratification would have profound impact on the dynamics and therefore the dynamo generation in the Martian core.

1. Introduction

Although the Mars does not currently have a global magnetic field, the Mars Global Surveyor mission discovered strongly magnetized ancient basins [1]. The Martian dynamo was likely stopped between 4.0 and 4.1 billion years ago and never restarted afterward [2, 3]. A range of models have been proposed to explain the cessation of the Martian dynamo [4–10]. Many of these models require a rapid decrease in heat flow to a sufficiently low value at the core-mantle boundary (CMB) to shut down the dynamo. However, magmatic activities in Mars continued to a much later period, requiring substantial heat flow at the Martian CMB even after the dynamo cessation.

2. Internal Structure of Mars

At the Earth's core-mantle boundary (CMB), bridgmanite (or post-perovskite for cold areas) and ferropericlase are in contact with liquid iron metal of the outer core. Because of the lower pressure expected at the

Martian CMB, ringwoodite is likely in direct contact with the metallic iron core [11] (Fig. 1). Unlike bridgmanite and ferropericlase, which are known to have little storage capacity for H₂O, ringwoodite can store up to a few wt% H₂O [12, 13]. Experiments have shown that H strongly partitions into metallic iron over silicates at elevated pressures [14].

In the early Mars, the H₂O stored in the lower mantle may have been isolated from the Martian core, or at least hydrogen exchange between the mantle and the core may have been limited because of compositional stratification in the solidified mantle [15]. Also, a dry bridgmanite layer might have existed at the CMB because of the high temperature of the early Martian mantle and the negative Clapeyron slope of the post-spinel boundary. Once the early stratification disappeared through overturn and the mantle convection starts, ringwoodite in the mantle would have lost hydrogen to the core [14]. However, little is known about the effects of hydrogen on Fe-S alloy at high P – T , mainly because of experimental challenges associated with hydrogen.

3. Experimental Method

Pulsed laser heating and high-pressure hydrogen gas loading in diamond-anvil cell (DAC) enabled us to study the effects of hydrogen on Fe-S alloys directly at the P – T conditions expected for the Martian core. We conducted experiments on FeS₂ starting material immersed in a hydrogen medium. The samples were heated to 1200–2200 K at 25–50 GPa while we measured in situ X-ray diffraction patterns for phase identification. The experiments were conducted at the GSECARS sector of the Advanced Photon Source. After the synchrotron experiments, we analyzed the recovered samples using a Scanning Electron Microscope (SEM) at Arizona State University.

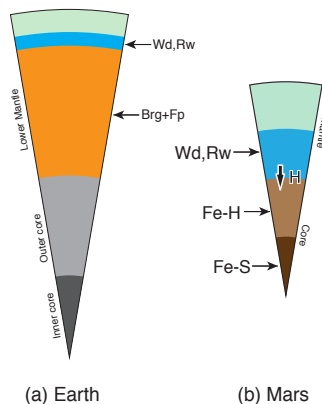


Figure 1: Comparison of the internal structures between Earth and Mars. Wadsleyite (Wd) and ringwoodite (Rw) have large H_2O storage capacities, while bridgmanite (Brg) and ferropericlase (Fp) have very little.

4. Result

At 27 GPa, we found that FeS appears at temperatures over 2000 K, indicating that the FeS_2 starting material breaks down to FeS and a S-rich phase. Because H-free experiments have shown the stability of FeS_2 at this P - T condition, such breakdown in our experiments can be attributed to the effect of hydrogen. When we quenched to room temperature at high pressure, diffraction lines of FeH_2 and Fe_3S appeared. The measured unit-cell volumes indicate that FeH_2 and Fe_3S do not contain any significant amounts of S and H, respectively.

Our heating temperature (2000 K) is higher than the expected solidus of Fe-S-H (1800 K) and Fe-H (1600 K) [16, 17]. Therefore, observation of FeH_2 and Fe_3S only after temperature quench suggests that these were separate liquids during heating. The analysis of the recovered sample also supports the interpretation. Our experimental observations can be summarized as: $4FeS_2 + H_2 \rightarrow FeH_2 + Fe_3S + 8S$ or $4FeS_2 + 8H_2 \rightarrow FeH_2 + Fe_3S + 7H_2S$.

5. Implications

Our experiments suggest: S and H may not be compatible with each other in liquid iron metal and therefore form separate metallic alloys with iron. If hydrogen can be partitioned into the Martian core as suggested

above, hydrogen would result in separation of iron hydride and iron sulfide. Because of their density differences, these two phases could segregate into: a H-rich outer liquid core and a S-rich inner core (Fig. 1). Such chemical stratification may have profound implications for the dynamics and the dynamo generation in the Martian core. Also, the Martian mantle is believed to contain much more sulfur than Earth. If sulfur is released from the Martian core, as suggested by our experiments, it could raise the S fugacity of the Martian mantle, altering the mineralogy and redox conditions of the region.

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