Chemical reactions in the Fe$_2$SiO$_4$-D$_2$ system with a variable deuterium content at 7.5 GPa

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ABSTRACT

Hydrogen-induced decomposition of fayalite (Fe$_2$SiO$_4$) at high pressure is of considerable interest for a better understanding of the chemical processes occurring in the cores and mantles of icy satellites. At pressures up to 10 GPa and temperatures 250–300 °C (typical of the cores and mantles of Jupiter’s and Saturn’s satellites), a variable amount of hydrogen can react with fayalite contained in their rocks. Volatile compounds that can form via these reactions are usually identified by mass spectroscopy. In our experiments, we used compressed deuterium gas instead of hydrogen to ensure that the volatiles analyzed by mass spectroscopy could only result from the decomposition of fayalite. To study the effect of the amount of deuterium present in the system, the fayalite (Fa) samples were deuterated at $P = 7.5$ GPa and $T = 280$ °C with the preset molar ratios D$_2$/Fa = 1, 1.5, 2.2, and 5 in the reaction cell. The deuterated samples were further quenched to the liquid N$_2$ temperature and, after releasing the pressure, removed from the reaction cell and studied by quadrupole mass-spectroscopy, X-ray diffraction, and Raman spectroscopy. Our results showed that the high-pressure deuteration invariably led to the chemical decomposition of fayalite. The solid products of the reaction varied from a mixture of ferrosilite (FeSiO$_4$) and iron at D$_2$/Fa = 1 to a mixture of silica and iron at D$_2$/Fa = 2.2. The decomposition occurred via breaking the Fe-O bonds and was always accompanied by the formation of water. Applying the observed reactions to the natural conditions of, e.g., the center of Titan or Ganymede, one may infer that fayalite can be dissolved in the hydrogen fluid or replaced by iron, ferrosilite, or silica depending on the molar ratio H$_2$/Fa.

Keywords: Fayalite, hydrogen, ferrosilite, high pressure, decomposition reaction, silica, iron

INTRODUCTION

The recent discovery of considerable amounts of molecular hydrogen in the Enceladus plumes (Waite et al. 2017) suggests its presence in the interiors of other icy moons of Saturn and those of Jupiter. Most hydrogen on Enceladus is assumed to be produced by the reaction of the waters of its mantle ocean with a silicate core (Waite et al. 2017), and mantle oceans and silicate cores are typical of many icy moons. Under natural conditions, the hydrogen thus produced can form a pure fluid (Bali et al. 2013), which will react with the silicates, too. It is expected that the silicate cores of such icy moons as Enceladus and, for example, Titan are largely composed of olivines, solid solutions Mg$_{2-x}$Fe$_x$SiO$_4$, and water ice (Fortes 2012). Consequently, our understanding of the processes occurring in the inner parts of icy satellites will be incomplete in the absence of physico-chemical data on the interaction of olivines with hydrogen at high pressures. Previous X-ray diffraction and Raman spectroscopy studies revealed a partial decomposition of the magnesium end-member of olivines, forsterite (Mg$_2$SiO$_4$), to MgO and SiO$_2$ at hydrogen pressures 2–10 GPa and $T > 1000$ °C (Shinozaki et al. 2012, 2013). Recently (Efimchenko et al. 2019) we observed the hydrogen-induced decomposition of another end-member olivine compound, fayalite (Fe$_2$SiO$_4$), at much lower temperatures ranging from ~375 °C at $P = 1.4$ GPa to ~175 °C at $P = 7.5$ GPa. Fayalite was shown to completely decompose to a mixture of silica, water, and metallic Fe or FeH, when it was surrounded with a large amount of molecular hydrogen (H$_2$/Fa ≥ 5).

However, fayalite can be in contact with a smaller amount of hydrogen (H$_2$/Fa < 5) in the natural conditions. As is known, a deficiency of one component can lead to an interruption in the chemical reaction or to a change in the composition of the reaction products. The standard reaction of hydrogen-induced fayalite decomposition at $P = 7.5$ GPa:

$$\text{Fe}_2\text{SiO}_4 + 3\text{H}_2 \rightarrow 2\text{FeH} + \text{SiO}_2 + 2\text{H}_2\text{O}, \tag{1}$$

requires H$_2$/Fa = 3 (Efimchenko et al. 2019). If the amount of hydrogen is less than H$_2$/Fa = 3, two different reaction paths are possible. First, fayalite may simply not decompose on contact with less hydrogen (H$_2$/Fa < 3). The second way is the decomposition of fayalite into a mixture of compounds different from that observed at H$_2$/Fa ≥ 5. In particular, hydrogen can form only one hydrogen-rich compound, iron hydride or water. The formation of iron hydride can occur by the following reaction:

$$\text{Fe}_2\text{SiO}_4 + \text{H}_2 \rightarrow 2\text{FeH} + \text{SiO}_2 + \text{O}_2. \tag{2}$$

Water can be formed by the reaction:

$$\text{Fe}_2\text{SiO}_4 + 2\text{H}_2 \rightarrow 2\text{Fe} + \text{SiO}_2 + 2\text{H}_2\text{O}. \tag{3}$$

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