Formation of SiH₄ and H₂O by the dissolution of quartz in H₂ fluid under high pressure and temperature

A亚男 稲沢 1,2,*，北条 堅 3,4,†，野村 信子 2,5,†，藤本 博樹 2
国立科学研究機構 地球科学研究所，東京大学，東京都東京市文京区文京町113-0033，日本
2地球科学研究所，東京大学，千葉県船橋市千葉町790-8577，日本
3固体物理学研究所，東京大学，千葉県松戸市松戸町277-8581，日本
4国立新エネルギー技術研究所，茨城県つくば市茨城町305-0044，日本
5早川 祐一

ABSTRACT

Species dissolved in H₂ fluid were investigated in a SiO₂–H₂ system. Raman and infrared (IR) spectra were measured at high pressure and room temperature after heating experiments were conducted at two pressure and temperature conditions: 2.0 GPa, 1700 K and 3.0 GPa, 1500 K. With the dissolution of quartz, a SiH vibration mode assignable to SiH₄ was detected from Raman spectra of the fluid phase. Furthermore, an OH vibration mode was observed at 3260 cm⁻¹ from the IR spectra at 3.0 GPa. With decreasing pressure, the OH vibration frequencies observed between 3.0 and 2.1 GPa correspond to that of ice VII, and those observed at 1.4 and 1.1 GPa correspond to that of ice VI. These results indicate that the chemical reaction between dissolved SiO₂ components and H₂ fluid caused the formation of H₂O and SiH₄, which was contrastive to that observed in SiO₂–H₂O fluid. Results imply that a part of H₂ is oxidized to form H₂O when SiO₂ components of mantle minerals dissolve in H₂ fluid, even in an iron-free system.

Keywords: H₂–H₂O fluid; dissolution; Raman; IR; laser-heated diamond-anvil cell

INTRODUCTION

Fluids in the Earth’s mantle influence phase relations, melting temperatures, chemical compositions, and physical properties of coexisting silicate minerals. Consequently, fluids in the mantle play an important role in elemental transportation, melt formation, and mantle dynamics. Stability and phase relations of silicate minerals depend on the Mg/Si ratio of silicate component in the coexisting fluid. For example, the silicate composition dissolving in H₂O fluid changes sharply from SiO₂-rich to MgO-rich around 3 GPa, providing a change of the thermodynamically stable phase in MgSiO₃–H₂O system from enstatite+forsterite+fluid to enstatite+fluid (e.g., Zhang and Frantz 2000; Stalder et al. 2001; Mibe et al. 2002; Kawamoto et al. 2004). Such a change of Mg/Si ratio is regarded as induced by a change of the dissolution species of silicate components in H₂O fluid. The dissolution of silica in H₂O fluids has been extensively studied over a wide range of pressures and temperatures; the silica species observed in H₂O fluids are SiOH groups such as H₂SiO₄ and H₃SiO₄. Between 3 GPa (e.g., Anderson and Burnham 1965; Manning 1994; Shen and Keppler 1995; Zotov and Keppler 2000, 2002; Newton and Manning 2003, 2008; Mysen 2009, 2010). At pressures higher than 3 GPa, the existence of MgOH groups was reported from an investigation of the hydrous silicate melt structure (Yamada et al. 2011).

Fluids in the Earth’s mantle contain considerable amounts of H₂ in addition to H₂O. The ratio of H₂/H₂O is likely to depend on the surrounding oxidation state. In general, the crust and the shallow mantle are in an oxidizing condition (close to FMQ buffer) (Frost and McCammon 2008). Consequently, fluids in the shallow depth contain little H₂. The mantle is reduced progressively with depth. Then the oxidation state becomes close to the iron–wustite buffer at depths greater than >200 km (e.g., Woodland and Koch 2003; McCammon and Kopylova 2004; Rohrbach et al. 2007; Frost and McCammon 2008; Goncharov et al. 2012). Thermodynamical calculations demonstrated that a molar fraction of H₂ is expected to increase concomitantly with increasing depth and approached about 10–20% in such reduced mantle (e.g., Ballhaus 1995; Frost and McCammon 2008; Goncharov et al. 2012). Moreover, Sokol et al. (2009) demonstrated experimentally that the molar fraction of H₂ becomes >50% at 6.3 GPa, 1873 K, in the iron–wustite buffer. Results of these studies show that H₂ is a major component of fluids in the reduced mantle.

The existence of H₂ is predicted even in the shallow mantle because the oxygen fugacity does not vary with depth only, but also with local settings (Wood et al. 1990). For example, a certain amount of H₂ is producible by serpentinization in the shallow mantle (Sleep et al. 2004). In addition, H₂ is estimated as a major component in the atmosphere of the early Earth (e.g., Hashimoto et al. 2007; Schaefer and Fegley 2007). A considerable amount of H₂ can be dissolved in the magma ocean (Hirschmann et al. 2012). In the pressure and temperature conditions of the shallow part of the early mantle, immiscibility between H₂O and H₂ fluid