Experimental investigations on hydrothermal reactions within large icy satellites and Martian crustal rocks using a 130-MPa hydrothermal autoclave

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Geochemical cycles of carbon (C) and sulfur (S) within interior oceans on icy satellites are key to understand the chemical evolution of the oceans and potential habitability (Gaido et al., 1999). Knowledge on geochemical cycles of C and S on early Mars is also critical for its chemical and climate evolution of the surface environment (Halevy et al., 2007). In the geochemical cycles on these bodies, oxidizing C- and S-bearing species, CO_2 and SO_2 , could have been reduced to CH_4 and H_2S , respectively, by reactions with H_2 under hydrothermal conditions at water-rock interfaces. For instance, CH_4 in Titan's atmosphere could have been generated through high-temperature water-rock interactions in its interior during the formation and early evolution (Atreya et al., 2006). On Europa, H_2SO_4 and CO_2 on the surface might have been transported into the subsurface ocean and could have reduced in the interface between the ocean and rock components, which, in turn, may control redox state of the oceans and availability of metabolic energy for microbial life (e.g. Zolotov and Shock, 2004; Vance et al., 2016). On Mars, CH_4 could have been produced through hydrothermal reactions within deep crustal rocks, which may explain the detection of a trace amount of CH_4 on Mars (Webster et al., 2015).

Despite the importance of hydrothermal reactions of CO_2 and SO_2 , kinetics of these reactions under the conditions corresponding to the interiors of icy satellites and Mars' crustal rocks are poorly constrained. This is because the previous experimental studies have mainly focused on the reactions in hydrothermal systems on Earth, where pressure typically reaches at ~30–50 MPa (e.g. McCollom et al., 2001). On the other hand, hydrothermal reactions within icy satellites and Mars' crustal rocks are proposed to occur at higher pressures (e.g., > 100 MPa) (Vance et al., 2016). In fact, recent experimental studies suggested the presence of pressure dependence on reaction products of the hydrothermal reactions (Lazar et al., 2015). However, both kinetics and reaction mechanisms remains unclear because they have used closed-system hydrothermal autoclaves, which is incapable of tracing time variations of dissolved species during the experiments.

In the present study, we have developed a 130-MPa hydrothermal apparatus that allows to perform on-line sampling using a flexible gold reaction cell, based on the experimental apparatus for investigations of Earth's hydrothermal systems (e.g., McCollom and Seewald, 2003, Shibuya et al., 2013). During the experiments on hydrothermal reactions of CO_2 and SO_2 , we measure time variations of dissolved gas species. Based on the results, we discuss the reaction mechanisms and implications for the aqueous environments on icy satellites and early Mars.

Keywords: hydrothermal reaction, geochemical cycle, icy satellite, mars