THERMODYNAMIC MODELING OF WATER-ROCK REACTIONS IN THE PARENT BODY OF RYUGU. T. Shibuya[1], Y. Sekine[2], S. Kikuchi[1], K. Fukushi[3], T. Nakamura[4] and S. Watanabe[5], [1]JAMSTEC, [2]ELSI, Tokyo Tech, [3]Kanazawa Univ., [4]Tohoku Univ., [5]Nagoya Univ.

Introduction: The recent remote-sensing observation by Hayabusa2 is providing a large amount of data to unravel the origin of Ryugu. The Near Infrared Spectrometer (NIRS3) onboard Haybusa2 revealed that the IR reflectance of the global surface of Ryugu is extremely low (~0.02) and the spectra include small but clear absorption at 2.72 µm. These findings indicate the great abundance of dark materials and hydrous minerals in the surface rocks, respectively. Furthermore, the presence of absorption at 3.05 µm derived from NH_4-bearing minerals is still uncertain but its possibility cannot be excluded.

These materials on Ryugu are important clues to constrain the conditions of aqueous alteration such as the temperature experienced by the parent body and the original volatile compositions during accretion stage. In this work, we conducted thermodynamic modeling of chondrite-water reactions under various conditions to establish a model explaining the aqueous alteration of the parent body.

Modeling Methods: In the thermodynamic calculations, a mean composition of CV chondrites was assumed for the initial bulk rock (minor amount of carbon, nitrogen and chlorine are also included) [1, 2]. For the initial fluid, four cases were assumed; CO_2 concentration is 0, 1, 3 and 10 mol% (Cases 1–4, respectively) relative to water while the latter three cases also include NH_3 (0.5%) and H_2S (0.5%) additionally [3]. The equilibrium temperature and pressure were assumed to be 0, 100, 200, 300 and 350 °C, and vapor pressure of water. In the calculations, pyrene was considered as a representative of polycyclic aromatic hydrocarbon while C1 compounds except CH_4 were included as soluble species [4].

The thermodynamic modeling of water-chondrite reactions were conducted with EQ3/6 computer code [5]. The thermodynamic database required for the calculations was generated by SUPCRT92 [6], with thermodynamic data for mineral, aqueous species and complexes [7–13]. Thermodynamic parameters for a series of smectites were estimated by using the procedure of Wilson et al [14]. During the simulated seawater-chondrite reactions, incorporation of water into hydrated minerals substantially condenses dissolved species in reacted fluids under conditions of low water to rock mass ratio (W/R), which elevate salinity and ionic strength beyond the appropriate values of modeling (2–3 molal). Therefore, the initial W/R was assumed to be 0.2–10 in the modeling.

Results: The calculations showed that stabilities of hydrous minerals, carbonate, pyrene and NH_4-bearing minerals change with temperature and W/R value, as detailed below.

Stability of hydrous minerals. In Case 1 (CO_2-free), the altered chondrite consists of serpentine, troilite and subordinate amount of hydrous/unhydrous minerals (e.g., magnetite, Na-saponite, gibbsite and chlorite) at 0–300 °C. However, with increasing temperature above 300 °C, olivine and clinopyroxene become major phases as the amounts of serpentine, chlorite and magnetite decrease. At 350 °C, olivine becomes the most abundant minerals in conjunction with disappearance of serpentine. Similar temperature dependencies of hydrous mineral stabilities were also shown at low W/R in Cases 2–4 (CO_2=1–10%) whereas carbonate is predominant at high W/R (Fig. 1).

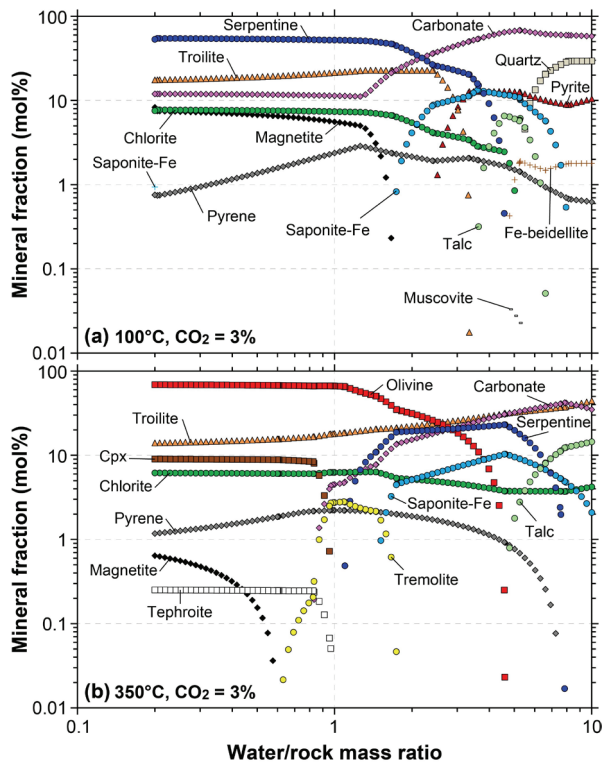

Fig. 1. Abundance of alteration minerals in chondrite at (a) 100 °C and (b) 350 °C in Case 3.

Dark materials. In the predicted alteration minerals, pyrene and/or magnetite are considered as the abundant dark materials in Ryugu (pyrene is not dark by itself but can be altered to dark organic matter through geologic time). Especially, pyrene can be consolidated

through reduction of CO_2 in Cases 2–4, These solid phases are minor or absent at high W/R where carbonate is predominant but the sum of them exceeds several % at low W/R (Fig. 1). Therefore, the results indicates that the altered chondrites broadly become darker with decreasing W/R.

NH4-bearing minerals. The results of calculations showed that NH_4-bearing minerals (saponite-NH_4 and beidellite-NH_4) appear at 0 °C but are unstable at 100–350 °C in Cases 2–4. Furthermore, the amount of NH_4-bearing minerals tend to reach a maximum at the W/R where carbonate is predominant. Thus, we calculated temperature dependence of mineral assemblage bearing saponite-NH_4 at W/R = 10 in Case 1 (Fig. 2). In this case, saponite-NH_4 change to saponite-Fe at around 73 °C with increasing temperature. The compositional change of coexisting fluid indicates that this mineralogical change closely relates to drastic decrease in pH and increase in Fe concentration at that temperature. This compositional change of fluid is also well correlated with increasing amount of serpentine and decomposition of carbonate as temperature increases.

Discussion: The thermodynamic calculations simulating water-chondrite reactions provided constraints on the stability of hydrous minerals, dark materials and NH_4-bearing minerals. The absorption at 2.7 µm of IR reflectance spectra observed by NIRS3 indicates the presence of hydrous minerals on the surface of Ryugu. Although the total amount of hydrous minerals in the rocks is still unconfirmed, the calculation results suggest that the temperature of hydrothermal reactions experienced by Ryugu is lower than approximately 300 °C if a certain amount of hydrous minerals are present in the surface rocks. Furthermore, if the absorption at 3.05 µm (NH_4-bearing minerals) is confirmed in the future, the temperature of reactions is likely lower than 100 °C. In contrast, if the amount of hydrous minerals is relatively small, higher temperatures (>350 °C) may account for the observed IR spectra. In this case, the parent body may have undergone high-temperature hydrothermal reactions that could occur in relatively large body. Otherwise, it is also possible that the parent body underwent instantaneous high-temperature events such as impact after the aqueous alteration.

The abundant dark materials inferred from the very low IR reflectance of Ryugu may be explained by the high content of magnetite and/or organic matter in the altered chondrite. The thermodynamic modeling revealed that this condition possibly requires relatively low W/R during the hydrothermal alteration of the parent body of Ryugu. In contrast, the rocks are dominated by carbonate at high W/R, which should result in higher IR reflectance. Therefore, the localized bright area on Ryugu may reflect the presence of carbonate formed by high-W/R hydrothermal alteration in the parent body. Further modeling of IR reflectance spectra based on this thermodynamic modeling will be presented [15].

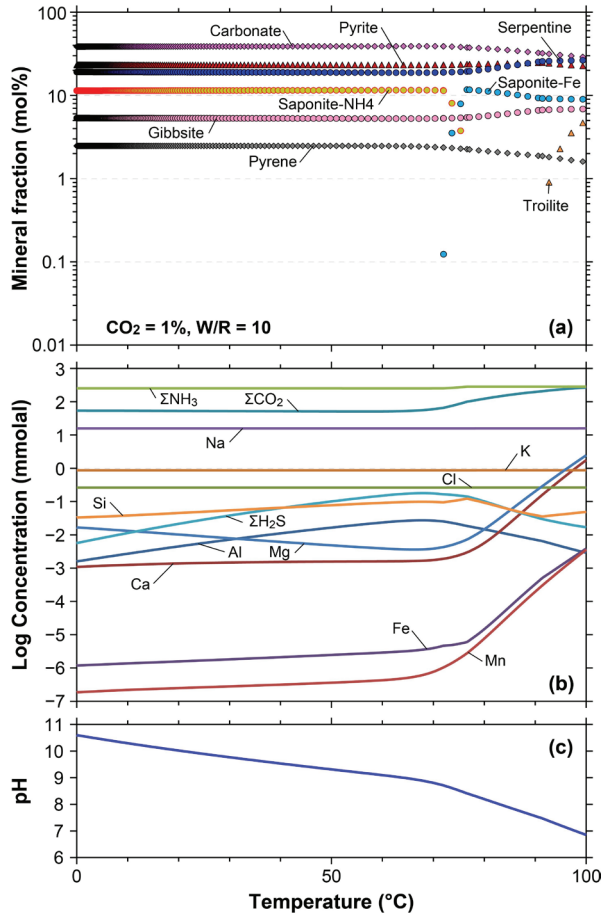

Fig. 2. Temperature dependency of (a) abundance of alteration minerals (b) concentrations of dissolved element/species in fluid and (c) in-situ pH of fluid.

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