

THERMODYNAMIC ANALYSIS OF WATER-ROCK REACTIONS IN THE PARENT BODY OF RYUGU.

T. Shibuya¹, Y. Sekine², S. Kikuchi¹, H. Kurokawa², K. Fukushi³, T. Nakamura⁴ and S. Watanabe⁵,
¹JAMSTEC (takazos@jamstec.go.jp), ²ELSI, Tokyo Tech., ³Kanazawa Univ., ⁴Tohoku Univ., ⁵Nagoya Univ.

Introduction: The recent remote-sensing observation by Hayabusa2 provided a large amount of data to unravel the origin of Ryugu [1–3]. The Near Infrared Spectrometer (NIRS3) onboard Hayabusa2 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 $2.72\text{ }\mu\text{m}$. The findings indicate the great abundance of dark materials and the subordinate amount of hydrous minerals in the surface, respectively [3]. These materials 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) [4, 5]. 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 [6]. The equilibrium temperature and pressure were assumed to be 0, 100, 200, 300 and $350\text{ }^\circ\text{C}$, 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 [7].

In the water-chondrite reactions, molecular hydrogen is generated through reduction of water by metal iron and FeO in chondrite, which elevate $f\text{H}_2$ of fluid to H_2 saturation level in some cases. Therefore, it was assumed that $f\text{H}_2$ of fluid does not exceed water pressure ($P_{\text{H}_2\text{O}}$). Considering that the ice melting and subsequent water-chondrite reactions of the parent body starts from its center, the water-chondrite reactions that $f\text{H}_2$ reaches $P_{\text{H}_2\text{O}}$ potentially supply excess H_2 to outer part of the parent body as ice melting proceeds outward. Therefore, water-chondrite reactions likely start under H_2 -rich conditions in the outer part of the parent body. Thus, two initial $f\text{H}_2$ conditions were assumed; $f\text{H}_2$ (initial) = 0 and $f\text{H}_2$ (initial) = $P_{\text{H}_2\text{O}}$. These two $f\text{H}_2$ (initial) conditions qualitatively reflect the inner and outer parts of the parent body, respectively.

The thermodynamic calculations of water-chondrite reactions were conducted with EQ3/6 com-

puter code [8]. The thermodynamic database required for the calculations was generated by SUPCRT92 [9] with thermodynamic data for mineral, aqueous species and complexes [10–16]. Thermodynamic parameters for a series of smectites were estimated by using the procedure of Wilson et al. [17].

Results and discussion: The calculations showed that stabilities of hydrous/anhydrous minerals, carbonate, pyrene change with temperature and water/rock mass ratio (W/R). In Case 1 (CO_2 -free), the altered chondrite consists of serpentine, troilite and subordinate amount of hydrous/anhydrous minerals (e.g., magnetite, saponite, gibbsite and chlorite) at $0\text{--}300\text{ }^\circ\text{C}$. However, with increasing temperature above $300\text{ }^\circ\text{C}$, olivine and clinopyroxene become major phases as the amounts of serpentine, chlorite and magnetite decrease. At $350\text{ }^\circ\text{C}$, olivine becomes the most abundant minerals in conjunction with decrease in the amount of serpentine.

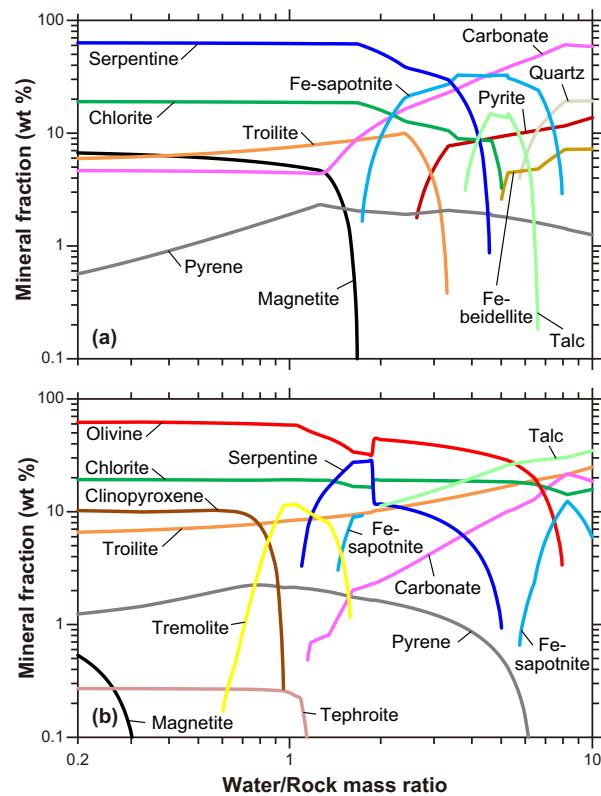


Fig. 1. Abundance of alteration minerals under the condition of $f\text{H}_2$ (initial) = 0 at (a) $100\text{ }^\circ\text{C}$ and (b) $350\text{ }^\circ\text{C}$ in Case 3 (CO_2 = 3%).

Similar temperature dependencies of hydrous mineral stabilities were also shown at low W/R in Cases 2–4 ($\text{CO}_2=1\text{--}10\%$) whereas carbonate is predominant at high W/R (Fig. 1). Although the abundance of hydrous minerals in the surface of Ryugu 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. In contrast, if the amount of hydrous minerals is relatively small, higher temperatures (>350 °C) may account for the observed IR spectra, which is consistent with the model that the parent body underwent instantaneous high-temperature events such as impacts after the aqueous alteration [2].

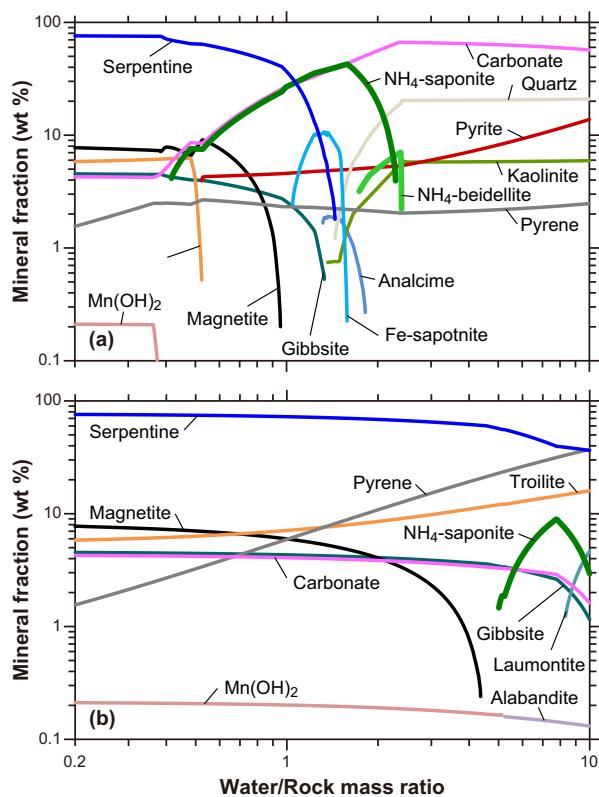


Fig. 2. Abundance of alteration minerals under (a) $f\text{H}_2(\text{initial}) = 0$ and (b) $f\text{H}_2(\text{initial}) = \text{P}_{\text{H}_2\text{O}}$ conditions at 0 °C in Case 4 ($\text{CO}_2 = 10\%$).

Among the predicted alteration minerals, abundance of pyrene and/or magnetite should be much higher than other minerals to account for the darkness of Ryugu (pyrene is not dark by itself but can be altered to dark organic matter through thermal maturation). Especially, pyrene can be consolidated through reduction of CO_2 in Cases 2–4 even under the condition of $f\text{H}_2(\text{initial}) = 0$. 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 because water-chondrite reactions at low W/R generate abundant hydrogen. Therefore, the results indicate that the altered chondrites broadly become darker with decreasing W/R. However, if the water-chondrite reactions start under H_2 -rich condition (e.g., $f\text{H}_2 \text{ initial} = \text{P}_{\text{H}_2\text{O}}$), the CO_2 in the fluid would be effectively reduced to form organic materials (Cases 2–4) even at high W/R (Fig. 2), which also potentially contribute the low reflectance of Ryugu.

Although it is still uncertain if NH_4 -bearing minerals are present on the surface of Ryugu, the results of calculations showed that NH_4 -bearing smectites (NH_4 -saponite and NH_4 -beidellite) appear at 0 °C under both $f\text{H}_2$ conditions in Cases 2–4 but are unstable at 100–350 °C. The calculations of temperature dependence of the stability of NH_4 -bearing minerals indicate that NH_4 -saponite change to Fe-saponite at around 70–80 °C due to decrease in pH and increase in Fe concentration of fluid with increasing temperature. If NH_4 -bearing minerals are included in the samples collected by Hayabusa2, the temperature of water-chondrite reactions should be lower than 100 °C.

A series of our thermodynamic calculations revealed that large redox gradient could occur due to transportation and condensation of H_2 generated by water-chondrite reactions within the parent body. As a result, secondary mineral assemblages and organic contents could greatly change depending on not only temperature and initial volatile composition but also redox gradient. The direct analysis of collected samples will provide constraints on the alteration temperature, redox state, initial volatile composition and the original distance from the sun of the parent body.

- References:** [1] Watanabe S. et al. (2019) *Science*, 364, 268–272. [2] Sugita S. et al. (2019) *Science*, 364, eaaw0422. [3] Kitazato K. et al. (1996) *Science*, 364, 272–275. [4] Pearson V. K. et al. (2006) *Meteoritics & Planet. Sci.* 41, 1899 – 1918. [5] Clay P. L. et al. (2017) *Nature*, 551, 614–618. [6] Mumma M. J. and Charnley S. B. (2011) *Annu. Rev. Astron. Astrophys.*, 49, 471–524. [7] Zolotov M. Y. *Icarus*, 220, 713–729. [8] Wolery, T.W. and Larek, R.L., (2003) *Sandia National Lab.* [9] Johnson, J. W. et al. (1992) *Comput. Geosci.*, 18, 899–947. [10] Helgeson H. C. et al. (1978) *Am. J. Sci.* 278-A, 1–229. [11] Shock, E. L. and Helgeson, H. C. (1988) *GCA*, 52, 2009–2036. [12] Shock, E. L. and Koretsky, C. M. (1995) *GCA*, 59, 1497–1532. [13] Shock, E. L. et al. (1989) *GCA*, 53, 2157–2183. [14] Shock, E. L. et al. (1997) *GCA*, 61, 907–950. [15] Sverjensky, D. A. et al. (1997) *GCA*, 61, 1359–1412. [16] McCollom, T. M. and Bach, W. (2009) *GCA*, 73, 856–875. [17] Wilson, J. et al. (2006) *GCA*, 70, 306–322.