

# Speciation of various elements using scanning transmission/fluorescence X-ray microscopy (STXM/SFXM) and bulk XANES analysis related to aqueous environment in the Ryugu parent body

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The parent body of the C-type asteroid Ryugu is thought to have been rich in volatile elements and abundant in liquid water, making it an important research target for the origin of water and organic matter on Earth. The water caused various alteration in the surrounding minerals, resulting in layered silicates such as smectite (saponite) and serpentinite being the main constituent minerals of the Ryugu (Nakamura et al., 2023). In this process, the organic matter of the Ryugu parent body also underwent chemical reactions and a wide variety of organic matter was synthesised (Naraoka et al., 2023). It is particularly important to obtain information on the water environment during the aqueous alteration, as the products of chemical reactions of organic matter in water depend on the pH and redox potential (Eh) of the water. In this study, speciation of various elements including iron (Fe), magnesium (Mg), calcium (Ca), and carbon (C) was investigated using scanning transmission X-ray microscopy (STXM) and bulk X-ray absorption near-edge structure (XANES) analysis in the soft X-ray region related to the aqueous environment in the Ryugu parent body. For the elements with concentrations below the detection limit of STXM, scanning fluorescence X-ray microscopy (SFXM), newly developed in SPring-8 and Photon Factory was applied such as nitrogen (N) and sodium (Na). The speciation of these elements in saponite is particularly important, since the Fe oxidation state and chemical composition within the interlayer of the saponite can indicate Eh-pH condition of the Ryugu water.

The Fe(II)/Fe(III) ratio in the octahedral structure of saponite was conducted by STXM. Based on our laboratory experiments, dithionite reduction of natural Fe-bearing saponite corresponding to Eh range from -0.47 to -0.66 (V) at pH = 7 shows the Fe(II)/Fe<sub>total</sub> ratio around 0.55. The incomplete reduction by dithionite reveals that Fe(II)-bearing saponite is a strong reductant. Assuming that the relationship between the Fe(II)/Fe<sub>total</sub> ratio and Eh of nontronite in Gorski et al. (2013) is similar to that of saponite, the Fe(II)/Fe<sub>total</sub> ratio greater than 0.68 measured by STXM indicates that the Eh was less than -0.45 (V).

On the other hand, because saponite has a negative charge in its layered structure, cations from the aqueous phase are adsorbed between the saponite layers during aqueous alteration. In this case, as shown by Fukushi et al. (2019), which cations are retained in the interlayer depends on the concentration of various cations in the coexisting aqueous phase and the selectivity coefficient K. Therefore, the cation composition in the water layer at the time of aqueous alteration can be estimated from the interlayer cation ratio determined by various analytical methods. In this processes, speciation of Na, K, and Ca were conducted to obtain their fractions retained in the interlayer. The comparison of the Al content in saponite enables us to estimate the Mg content in the interlayer. Contents of these cations with assumptions of dissolved silica etc. were used to construct an Eh-pH diagram of Mg. We have estimated pH range that can explain the presence of both saponite and dolomite, which are widely distributed in the altered crust in the Ryugu particles. The pH range estimated by the method was pH from 7.8 to 10. Although the range is somewhat wide, the range is consistent with the results suggested in Nakamura et al. (2022).

The combination of Eh around -0.45 (V) and the alkaline pH range estimated above showed that the water was highly reducing, which reveals that H<sub>2</sub> and CH<sub>4</sub> were present in the Ryugu water if we assume the equilibrium condition. Such an alkaline condition is suitable for the polymerisation of amino acids (Kitadai and Maruyama, 2018).

References: Fukushi K. et al. (2019) Semiarid climate and hyposaline lake on early Mars inferred from reconstructed water chemistry at Gale. *Nat. Commun.* **10**, 1–11.; Gorski C. A. et al. (2013) Redox properties of structural Fe in clay minerals: 3. Relationships between smectite redox and structural properties. *Environ. Sci. Technol.* **47**, 13477–13485.; Kitadai N. and Maruyama S. (2018) Origins of building blocks of life: A review. *Geosci. Front.* **9**, 1117–1153.; Nakamura T. et al. (2023) Formation and evolution of carbonaceous asteroid Ryugu: Direct evidence from returned samples. *Science* **379**, eabn8671.; Naraoka H. et al. (2023) Soluble organic molecules in samples of the carbonaceous asteroid (162173) Ryugu. *Science* **379**, eabn9033.