

# Speciation of Divalent Transition Metal Ions in Ryugu Samples: Implications for Elemental Solubility in Sulfide-Dominated Ancient Oceans

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## 【Background and Purpose】

Life relies on dissolved ions for sustenance, and trace metal elements are essential for life maintenance. The current ocean is an "oxide world," where adsorption to oxides such as ferrihydrite, manganese oxides, and clay minerals governs the dissolved concentrations of trace elements. Conversely, many researchers believe that ancient oceans were in a "sulfide world," characterized by a more reducing environment where interactions with sulfides controlled the water solubility of elements. In this case, it is thought that the chemical species of trace elements were different from those today. This environment is also presumed to be similar in the Ryugu parent body, which has preserved conditions during water alteration without the influence of Earth's atmosphere. Therefore, this study aims to investigate the factors governing the solubility of elements in primordial solar system materials from an astrobiological perspective, particularly identifying which elements are influenced by sulfides in the sulfide world through the speciation of elements in Ryugu. The goal of this study is to contribute to our understanding of the evolution of life, elemental behavior, and metal concentration processes. In this study, we focus on manganese (Mn), nickel (Ni), zinc (Zn), and iron (Fe), which are primarily stable as +2 oxidation states during water alteration of Ryugu and attempt to identify the host phases of these elements using X-ray absorption fine structure (XAFS) to determine the factors governing their water solubility.

## 【Experiments】

Samples from the C-type asteroid Ryugu (A0477, C0289) and resin-embedded samples of CI chondrite (Orgueil meteorite, CI chondrite) were prepared under an anaerobic condition. XAFS analyses of Mn, Ni, Zn, and Fe were conducted while maintaining anaerobic conditions at Photon Factory BL-9A and BL-12C (bulk analysis using a beam size of approximately 1 mm) and SPring-8 BL37XU (local analysis using a beam size of approximately 1  $\mu$ m).

## 【Results and Discussion】

In the Ryugu samples, minerals such as saponite, serpentine, pyrrhotite, magnetite, dolomite, and apatite were observed. In Orgueil, the K-edge XANES of Fe indicated that the primary minerals were mainly phyllosilicates, magnetite, and pyrrhotite. Additionally, approximately 70 % of Mn was found to exist as phosphates or carbonates, regardless of the redox environment. In contrast, the K-edge XANES of Ni and Zn in Ryugu could be fitted as a linear combination of two components: (i) Zn and Ni from terrestrial pyrrhotite ores and (ii) adsorption states on saponite prepared in the laboratory. The ratios of these two components were 92 % for Ni and 82 % for Zn, suggesting a larger proportion of sulfides for Ni. Saito et al. (2003), which reconstructed trace element concentrations in ancient oceans based on thermodynamic constants, indicated that Zn is more stably distributed to sulfides, suggesting the need for more rigorous experimental studies on sulfide partitioning. Based on these results, I conduct adsorption experiments under various conditions on sulfides (primarily pyrrhotite) for the elements Ni and Zn, which show significant differences between the sulfide and oxide worlds. This will involve determining distribution coefficients and identifying host phases using XAFS, further elucidating the systematics of elemental solubility in systems governed by solid-liquid partitioning with sulfides.