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A geochemical constraint on the formation process of a manganese carbonate nodule in the siliceous mudstone of the Juras

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Manganese (Mn) carbonate nodules, which are different from seafloor Mn nodules mainly composed of MnO2, are occasionally embedded as a lens shape in the Jurassic accretionary complexes such as the Tamba-Mino-Ashio Belt in Japan. The interpretation of the formation process of Mn carbonate is still controversial, namely whether the Mn carbonate was formed primarily or secondarily. The optical observation of thin sections shows that Mn carbonate nodules are comprised with abraded grains of rhodochrosite spherule with radiolarians and are sedimentarily embedded in siliceous mudstone. Microfossil radiolarians from the Mn carbonate nodules and the host red siliceous mudstone are dated as the Bajocian (170.3 ? 168. 3 million years ago), but radiolarians in the nodules are somewhat older than those in the host red siliceous mudstone. In this study, geochemical analyses focusing on the rare earth element (REE) were performed to unlock the formation process of Mn carbonate nodules in the Tamba-Mino-Ashio Belt.

Our analysis using the X-ray absorption near-edge structure on Ce shows dominance of trivalent Ce at present, despite of a positive Ce anomaly in the PAAS-normalized REE pattern of Mn carbonate. The REE adsorption experiment on synthesized MnCO3 does not show any distinctive positive Ce anomaly and a thermodynamic calculation suggests the possible coexistence of authigenic rhodochrosite and spontaneous oxidation of Ce. The leaching experiment that can selectively decompose carbonate phase demonstrated no Ce anomaly in the carbonate phase of Mn carbonate and poor contribution to the bulk REE concentration. The most plausible account of all the observational and experimental results is that rhodochrosite grains were primarily formed on the depositional site and subsequently transferred to the different site where siliceous mudstone was deposited.

Keywords: manganese carbonate, rare earth element, radiolarian, XAFS