

## Origin of manganese oxide in cold spring, Saga Prefecture.

TAKASHIMA, Chizuru<sup>1\*</sup>, HIGASHI, Yuka<sup>1</sup>, MORI, Taiki<sup>1</sup>, OKUMURA, Tomoyo<sup>2</sup>

<sup>1</sup>Faculty of Culture and Education, Saga Univ., <sup>2</sup>Graduate School of Social and Cultural Studies, Kyushu Univ.

Manganese oxide plays an important role in material cycling and has been reported from fresh water, hot springs and deep-sea hydrothermal vents (e.g., Mita et al., 1994; Fitzgerald and Gillis, 2006). In this study, we focused on manganese oxide in cold spring and discussed about the origin and the water chemistries.

Study site is Hiramatsu cold spring in Saga City, Ssga Prefecture, and is used for bathing at Hiramatsu welfare center located ~60 m from the spring. The water emit from a well naturally and is first stored in a tank close to the spring (tank 1). Then, the water in tank 1 is transported by pomp to another tank next to the welfare center (tank 2) and used in bathtub after heating. Manganese-rich precipitate was prominent at the tank 2, but also seen in the spring, tank 1, and the bathtub,

We collected water samples from the spring, tank 1 and tank 2. They were used for analysis of water chemistries with XRF and oxygen and carbon isotopic ratio with a mass-spectrometer. For the manganese precipitate collected from the tank 2, we observed textures and microbes with optical and fluorescence microscope and SEM. Moreover, identification of mineralogy was performed by XRD.

The water at the spring was about 18 degrees and shows neutral or faintly alkaline pH. The springwater was microaerophilic, containing dissolved oxygen (DO) of about 0.6 mg/L. It is rich in Mg (about 50 mg/L), Ca (about 35 mg/L), Na (about 30 mg/L), Cl (about 17 mg/L). Mn concentration was about 2 mg/L, and Fe was hardly detected (below 0.1 mg/L). Concentration of Mn decreased from the vent to tank 2. Oxygen isotopic values were -6.9 to -6.0 permill and consistent with a value of meteoric water in north Kyushu area (-7.0 to -6.0 permill; Mizota and Kusakabe, 1994). Low carbon isotopic value (-17.6 permill) of the dissolved inorganic carbon indicates contribution of organic carbon in soil.

Manganese oxide of black to dark brown in color was very soft and unconsolidated. Mineralogy analysis conformed that it was manganese oxide, but shows a broad peak indicating the amorphous MnO<sub>2</sub>. The precipitate contained numerous brown colored filaments of 3-4 micrometers in width, which were covered with mineral precipitates. This showed that bacteria induced precipitation of MnO<sub>2</sub>. Inorganic oxidation reaction of manganese under neutral pH is slow even in an O<sub>2</sub> saturated setting, but is largely enhanced by bacterial activity (Zhang et al., 2002). It is known *Psuedomonas* sp. and *Leptothrix discophora* as manganese oxide bacteria, but at present, type of bacteria in this manganese oxide are not specified. Further examination is needed to identify the bacteria with detailed observation and phylotype analysis.

### [References]

Fitzgerald, C.E. and Gillis, K.M. (2006) Hydrothermal manganese oxide deposits from Baby Bare seamount in the Northeast Pacific Ocean. *Marine Geology*, 225, p. 145-156.

Mita, N., Maruyama, A., Usui, A., Higashihara, T and Hariya, Y. (1994) A growing deposit of hydrous manganese oxide produced by microbial mediation at a hot spring, Japan. *Geochemical Journal*, 28, p. 71-80.

Mizota, C. and Kusakabe, M. (1994) Spatial distribution of dD-d<sup>18</sup>O values of surface and shallow groundwaters from Japan, south Korea and east China. *Geochemical Journal*, 28, p.387-410.

Zhang, J., Lion, L.W., Nelson, Y.M., Shuler, M.L., and Ghiorse, W.C. (2002) Kinetics of Mn(II) oxidation by *Leptothrix discophora* SS1. *Geochimica et Cosmochimica Acta*, 65, p.773-781.

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