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Role(s) of microorganisms on the formation of manganese deposits in hot springs

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The natural manganese distributed widely during environment. The +II, +III, and +IV are the most prevalent oxidation states of Mn in nature, in particular, +III and +IV manganese exist as oxides mainly. It is considered that the manganese oxide (MnO_2) formation is attained by 1) inorganic process including autocatalysis and 2) organic process by microbial oxidation. The latter is further classified into two groups, the direct process and indirect process. In general, it seems the organic process is more important than the inorganic process. The organic direct process with the Mn-oxidizing bacteria attracts attention particularly recently. On the other hand, it has been published the experiment with isolated and cultured photosynthesis microorganisms indicates the Mn-oxidation reaction promoted by photosynthesis. However, those most were speculated by culture experiments and simulations, therefore, the relative importance of above these processes and mechanisms in the natural Mn-oxidation reaction does not yet become clear. In this study, it is intended to clarify an elementary process of the Mn oxides formation based on an in situ evaluation in the environment. The subject of this study is Sanbe hot spring (in Shimane, Japan) and Onneto yuno-taki (in Hokkaido, Japan), the representative example of the terrestrial large-scale Mn oxides deposit.

At the Sanbe hot spring, Mn oxides layer form at thickness up to approximately 1 cm in the lower area by 150 m from the spring site. According to thin section observation, many photosynthetic organisms inhabit in the surface, and it is confirmed most of them are buried in the oxides. In addition, *Hyphomicrobium* sp. was detected by 16S rDNA Analysis. In this study, through four kinds in total of microelectrode-measurement (pH, Eh, dissolved oxygen DO, Mn^{2+}), the chemical profiles in the vicinity of the oxide surface were evaluated. Under the light condition, DO, Eh, pH rose in the oxides surface, and Mn^{2+} showed decrease. Under the dark condition, DO decreased, and the tendency to increase or decrease of Eh, pH, Mn^{2+} profiles were remain unchanged in comparison with them under the light condition, but each flux was all smaller than it under the light condition. From the result, it was found the oxygen generated by photosynthesis may promote the Mn-oxidation reaction (organic indirect process) under the light condition, and MnO_2 change into the dissolved chemical species (Mn^{3+}), by the oxidation-reduction reaction in Mn^{2+} and MnO_2 under the dark condition. This is supported by the observation with the Mn oxides layer being thin for the decrement amount of Mn^{2+} in the surface. Furthermore, regardless of difference of light or dark condition, the contribution to manganese oxidation by Mn-oxidizing bacteria was likely small so that cannot be detected by microelectrode-measurement.

At the Onneto yuno-taki, the manganese deposit layer distribute respectively about 100 m from two spring site and is thick relatively (about 10 cm). Onneto yuno-taki has also many photosynthetic organisms inhabiting in the surface, and it is confirmed by thin section, most of them are buried in the oxides by thin section observation. According to the result of microelectrode-measurement, DO, Eh, pH rose in the oxides surface, and Mn^{2+} showed decrease under the light condition. Under the dark condition, all profile has tendency to decrease. Mn^{2+} flux was especially smaller than its under the light condition. Therefore, it was suggested that the oxygen generated by photosynthesis may promote the Mn-oxidation reaction (organic indirect process) under the light condition, on the other hand, it may occur the Mn-oxidation reaction by Mn-oxidizing bacteria (organic direct process) It was also thought that the effect of dissolution of MnO_2 was respectively small. In fact, the manganese deposit of Onneto yuno-taki is very thick.