Thick Black Manganese-Rich Crusts Formed on the Wall of Canals in the Aso Caldera, Japan

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Black manganese-rich crusts were observed on the wall of canals flowing from the Kurokawa river located in the Aso caldera, Southwest Japan. Manganese coating on the surface of pebbles in the Kurokawa river were also observed from the midstream to the downstream. Manganese concentration in the middle reach of the Kurokawa river is elevated, as groundwater with high manganese concentration was flowing into the river through the tributary. This result suggests that manganese forming the crusts originates from dissolved manganese in the ground water mixed with the river water.

While typical occurrence of these crusts is hard coating with 1 to 2 mm thick in the river and open canals, thickness of crust reaches up to 2 cm in waterway tunnels and it is composed of thick soft deposit covering the coating. Even in the same waterway tunnel but flowing from adjacent river with low manganese concentration, only thin crusts were found on the walls. The result indicates that the water quality of the in Kurokawa river also affects thick crust formation.

Bulk XRF analysis shows that thick crusts contain about 25 to 50 wt% of manganese as MnO and XRD analysis indicates that main component is todorokite. Furthermore, Co, Mo, Tl, W, Zn, As, Ba, Cd and Ni in thick crusts are contained about 5 to 10 times more than those in the surrounding soil. FESEM-EDS analysis revealed that thick crusts are mainly composed of porous aggregates with flake-like texture on the surface with high Mn values, which are typical morphologies of biogenic Mn oxide [1,2]. Sequencing analysis of microbial community in thick crusts indicated the presence of previously known Mn oxidizing bacteria such as *Nitrospira*, *Sphingomonas*, *Bacillus*, *Pseudomonas* and *Hypomicrobium* at high ratio. These results suggest that the thick crust mainly composed of manganese was possibly formed biogenically.

[1] Miller *et al.* (2012) *Chem. Geol.* **322-323**, 181-191. [2] Bargar *et al.* (2009) *Geochim.Cosmochim.Acta* **73**, 889-910.