

Direct evidence for biogeochemical process in the formation of ferromanganese crust; Western Pacific Magellan Seamount

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Redox reaction is a ubiquitous process in the formation of ferromanganese crust that may reflect one of paleo-environments, particularly variations of Fe/Mn redox states and microbial diversity in the crust suggests the unique biogeochemical reactions when the ferromanganese crust layer forms. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Electron Energy Loss Spectroscopy (EELS), and Polymerase Chain Reaction (PCR) were utilized to determine the redox states of Fe/Mn and microbial diversity at each layer. A sample collected from Magellan Seamount (OSM11), western Pacific, was characterized in five well-defined crust layers, top to bottom (L1-5). Some microbial like structures of sheath-like with filaments (L1 -L3), capsule-shaped (L2), fossilized coccolith mounds with phosphatized globules (L4), and bean-shaped (L4) were detected in entire layers. The cross sectional observation of bean-shaped microbe like structures encrusted with Fe-vernadite (L3) by Scanning Transmission Electron Microscopy (STEM) and Focused Ion Beam (FIB) technique revealed $\sim 1\text{-}\mu\text{m}$ diameter cavity in the center and porous structures of encrusting Fe-vernadite in periphery. Moreover, strong EELS profiles of organic carbon around the hole in the FIB-sectioned sample for microbe-like structure indicates that the microorganism used to occupy in the crusts and may play a role in the formation of Fe-Mn crusts. Indeed, presence of Fe- (*coxC*) and Mn-oxidizing gene (*cumA*), particularly displaying a strong PCR band of *coxC* in L2-3 indicate the dominant oxidizing conditions compared with L4 where CFA formed. The cloning and sequencing of DNA PCR fragments revealed the appearance of geobacter species in L3 (*G. sulfurreducens* and *G. lovleyi*). The present study collectively suggests that biogeochemical processes in the formation of Fe-Mn crust reveal unique paleo-environments of formation.

Keywords: Ferromanganese crust, EELS, TEM