X-Ray Photoelectron Emission Microscopy as a Probe for Understanding the Chemistry of Ferromanganese Crusts from North-West Pacific Ocean

Ting Xue[1, 2], Mike Abrecht[3], Huifang Xu[1], Xiaoming Sun[2]

1 Department of Geology and Geophysics, University of Wisconsin, Madison, WI 53706, USA
2 Department of Earth Sciences, Sun Yat-sen University, Guangzhou 510275, China
3 Synchrotron Radiation Center, 3731 Schneider Dr. Stoughton WI, 53589

Ferromanganese crusts (FMCs) that formed on seamounts are major sinks for transition metals and rare earth elements that could be our future mineral resources in marine environment. In FMCs, Ti, Co, Ni and other trace metals are predominantly associated with microporous birnessite-like manganese oxide nano-plates. The nano-plates of the Mn-oxide contains significant amount of Fe with Mn/Fe ratios ranging from 2 to 5. TEM observations indicate there are very limited amount of ferric iron in the form of independent mineral of goethite (α-FeOOH). The concentrations of Ni and Co the FMCs are directly related to Mn concentration. Crystal chemistry and microstructure of the Mn-minerals can provide important information that relating to the formation of the FMCs and mechanism for enriching / scavenging the trace elements.

XPEEM is a powerful technique for characterizing the chemistry of complex materials. We use the state-of-the-art SPHINX spectromicroscope on the new high flux Varied Line Space Plane Grating Monochromator (VLS-PGM) beamline at the UW Synchrotron Radiation Center to identify the oxidation states and local chemical environments of Mn, Fe, Co, and Ca in the FMCs. The spectra of Fe L-edges reveal ferric iron in the FMCs. The spectra with broad peaks indicate the iron is in poorly crystalline birnesite-like nano-sheets, instead of independent phases of well crystalline Fe-oxides like hematite or goethite. The FMCs contains about 4% of Calcium. X-ray powder diffraction patterns do not show any calcite and aragonite phases. The obtained spectra are different from the Ca L-edges from apatite and calcite. The spectra of Ca L-edges are very similar to those from aragonite, which indicate that Ca is not in 6-coordinated environment, rather than in a large coordination number environment. The spectra without pre-edge peaks indicate very weak crystal filed (or loose coordination environment) for the Ca^{2+}. It is proposed that Ca may be incorporated into interlayer sites and surface sites through sorption of the birnessite-like phase. Similar mechanism may be also responsible for the enrichment of rare earth elements in the FMCs.

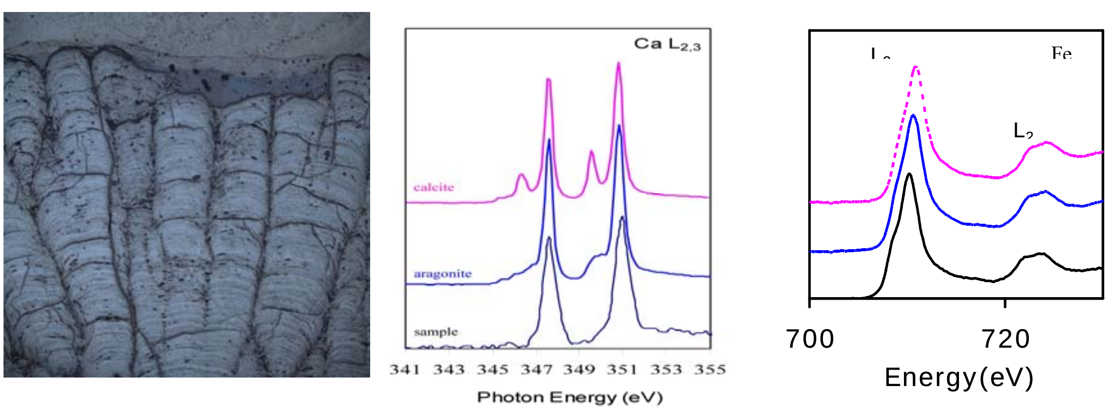

Figure1: Optical microscopic image (reflection mode) of the FMC (left), and X-PEEM spectra of Fe ($L_{2,3}$) (right) and Ca ($L_{2,3}$) (center) edges from the ferromanganese crust.