Lead enrichment and speciation in the carbonate fluorapatite phase of phosphatized Fe-Mn crusts

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Ferromanganese (Fe-Mn) crusts are considered hydrogenetic in origin, forming by precipitation of iron and manganese oxides from seawater onto a rock substrate. Diagenesis, however, occurs during phosphatization when abundant dissolved phosphate in seawater replaces carbonates in the detrital fraction as well as directly precipitates within the Fe-Mn matrix pore space as carbonate fluorapatite (CFA). Phosphatization is widely observed in the older (>10 Ma) layers of FeMn crusts throughout the global ocean, yet its effects on trace metal distribution still need to be better constrained and enrichment processes identified. Sequential leaching studies have shown that Pb concentrations in Fe-Mn crusts, for example, are uniquely affected by phosphatization; Pb associates with the iron oxyhydroxide phase in purely hydrogenetic layers, while >95% of Pb in phosphatized crust layers is found in the residual fraction, which is largely CFA [1,2]. To confirm Pb enrichment in the CFA phase at finer resolution, 17 subsamples from througout the phosphatized portion of 3 FeMn crusts underwent reductive leaching to remove Fe and Mn oxides as well as purification to remove residual carbonate, producing the pure CFA phase from each sample. The chemical compositions of these CFA samples will be presented here and compared with those in the non-phosphatized layers of the same crusts to quantify the percent enrichment of Pb in CFA. We also measured age dates of the CFA using Sr isotopes to determine if the augmentation of Pb is variable amongst phosphatization events. When combined with Pb XANES and EXAFS that define the speciation of Pb in hydrogenetic and phosphatized crusts and CFA, these data will further refine a model for the transfer of Pb from the oxide phases to the CFA phase during phosphatization.

[1] Koschinsky & Halbach (1995) *Geochim. Cosmochim. Acta* **59**, 5113-5132. [2] Koschinsky & Hein (2003) *Mar. Geol.* **198**, 331-351.