

Lead phase transfer during phosphatization of Fe-Mn crusts

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Ferromanganese (Fe-Mn) crusts form by precipitation of iron and manganese oxides from seawater onto a hard rock substrate and are therefore considered hydrogenetic in origin. Diagenetic influence is possible, however, through the process of phosphatization. During phosphatization, abundant dissolved phosphate in seawater replaces the carbonate in the detrital fraction as well as directly precipitates within the Fe-Mn matrix as carbonate fluorapatite (CFA), likely accompanied by the partial dissolution or replacement of the oxide phases [1]. As a result of these diagenetic processes, adsorbed trace elements are released and can either be depleted or enriched in the phosphatized crust layers. Pb, for example, is unique in that sequential leaching experiments reveal association with the iron oxyhydroxide (FeOOH) phase in purely hydrogenetic layers, while >95% of Pb in phosphatized crust layers is found in the CFA fraction [2, 3]. Thus, we hypothesize that Pb vacates the FeOOH phase during diagenesis, evidenced by the decrease of FeOOH in phosphatized crust layers in leaching experiments [2], and may then either replace Ca in the CFA structure or co-precipitate as stable lead phosphate phases, in accordance with CFA studies of Nathan 1984 [4]. Here we will present XANES and EXAFS data of Pb in hydrogenetic and phosphatized Fe-Mn crusts compared to a variety of standards, including Pb sorbed onto synthetic iron and manganese oxides and marine CFA as well as Pb-phosphate and Pb-phosphite compounds. We can then determine the form that Pb takes in both hydrogenetic and phosphatized Fe-Mn crusts and provide a possible model for the transfer of Pb from the oxide phases to the CFA phase.

[1] Koschinsky *et al.* (1997) *Geochim. Cosmochim. Acta* **61**, 4079-4094. [2] Koschinsky & Halbach (1995) *Geochim. Cosmochim. Acta* **59**, 5113-5132. [3] Koschinsky & Hein (2003) *Mar. Geol.* **198**, 331-351. [4] Nathan (1984) In: Nriagu, J.O., Moore, P.B. (Eds.), *Phosphate Minerals*. Springer, 275-288.