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# Crystal-chemistry of Ni in marine ferromanganese crusts and nodules

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## Abstract

Marine ferromanganese crusts and nodules are highly enriched in transition metals such as Ni and Co, yet the crystal chemistry and mode of incorporation of these metals is poorly known. We characterized the crystal chemistry of Ni in two hydrogenetic Pacific ocean ferromanganese crust samples and a hydrogenetic nodule from the Madeira abyssal plain. Energy dispersive spectrometry shows that Ni is associated with the manganese oxide phases, in agreement with previous work. X-ray diffraction patterns show that the dominant $Mn^{3+/4+}$ oxide is a phyllomanganate similar to hexagonal birnessite or $\delta$-$MnO_2$. Extended X-ray absorption fine-structure spectroscopy shows that the coordination environment of Ni results from structural incorporation into the phyllomanganate phase by replacement of $Mn^{3+/4+}$. In contrast, Ni initially sorbs to freshly prepared synthetic birnessite by surface complexation over vacancy sites in the $MnO_2$ layer. We propose that the transformation of Ni sorption from surface complexation to structural incorporation provides a potentially irreversible sink for Ni in seawater.

**Keywords:** Nickel, ferromanganese, hexagonal birnessite, goethite, adsorption, solid solution, scanning electron microscopy, EXAFS spectroscopy