Enrichment mechanisms and phase associations of platinum in marine ferromanganese crusts and nodules

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Marine ferromanganese (FeMn) crusts and nodules host high concentrations of many economically interesting metals including platinum (Pt). We found a range of 44 to 3207 ppb Pt in 182 analysed crust and nodule samples collected from the global ocean, and applied a multi-method approach including bulk analyses, statistics (correlations and Q-mode factor analyses), sequential leaching, sorption experiments and XANES and EXAFS measurements to shed more light on the accumulation mechanism of Pt and its association with the mineral phases. Our data support the idea of a coupled sorption/oxidation mechanism to explain the high Pt enrichment in FeMn crusts, with Pt(II) oxidation to Pt(IV) only taking place on the Mn-oxide phase but not on the Fe-oxyhydroxide phase of crusts, where only sorption of $Pt^{2+}_{(aq)}$ was observed. Nodules show lower concentrations and a lesser association of Pt with the Mn phase as the latter is partly of diagenetic origin while Pt originates from seawater, and Pt(II) oxidation is not favored in (sub)oxic porewaters. Platinum concentrations are consistently highest in phosphatized Fe-Mn crusts where they appear to be related to the occurrence of a todorokite-like Mn-oxide phase; in this regard, phosphatized crusts are likely to be the best exploration target for Pt in FeMn crusts in the global ocean. However, further work is needed to understand the geochemical reactions responsible for the enrichment of Pt under suboxic conditions during phosphatization of crusts.

The complex Pt geochemistry in marine FeMn crusts and nodules due to the different phase associations and enrichment processes on the different carrier phases make a straightforward interpretation of Pt data difficult. A combination of methods with high spatial resolution and species-specificity, including synchrotron-based x-ray spectroscopy, will be needed to determine which of several proposed mechanisms are actually responsible for Pt enrichment in marine FeMn crusts and nodules.