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Distribution of zirconium, hafnium, niobium and tantalum in marine ferromanganese crusts

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Hydrogenetic ferromanganese crusts precipitate from seawater. Very slow growth rates and the high adsorption capacity for dissolved elements lead to the accumulation of large quantities of metals from seawater and make them generally suitable for the investigation of environmental and paleooceanographic conditions in the past. The crusts are used as archives of paleo-seawater isotopic and elemental compositionand the record of radiogenic isotope ratios (e.g., Hf) is widely applied. From an economic point of view, ferromanganese crusts are considered as potential source of rare metals for high-technology and green industries.

Here, we present new concentration data for the high field strength elements Zr, Hf, Nb, and Ta from crust surfaces, bulk samples, and individual layers of hydrogenetic ferromanganese crusts from the NE Atlantic and the Central Pacific obtained wit ICP-MS. Concentrations of Zr, Hf, Nb in these crusts are strongly enriched (Zr: 300-1000 ppm, Hf: 5-20 ppm, Nb: 25-100 ppm) relative to bulk continental crust concentrations, while Ta (0.3-2.7 ppm) is moderately enriched. Detrital contribution is only minor and the hydrogenetic enrichment from seawater via adsorption is proven. In deep seawater, Zr-Hf is strongly fractionated and distinctive for individual water masses, while Nb/Ta is rather uniform and close to the chondritic ratio (Firdaus et al., 2011). Neither the crust surfaces nor the bulk samples of Fe-Mn crusts display the total dissolved Zr/Hf or Nb/Ta ratios of modern deep seawater. This implies that the geochemical twin elements are fractionated during incorporation into oxide deposits, which makes them unsuitable as proxy tracer for changes in paleocirculation as previously suggested by Frank et al (2011). Further, concentration and fractionation of both element pairs depend on accumulation time: Highest concentrations were found in crusts with relatively high Fe concentrations but slow accumulation rates. Ferromanganese crusts recovered in the NE Atlantic and Central Pacific Ocean are characterized by systematic differences in their HFSE distribution: bulk crusts from the Atlantic Ocean are relatively more enriched in Hf and Ta relative to Zr and Nb, respectively, which is likely related to the respective seawater signatures. Comparing absolute concentrations, Nb and Ta are generally more enriched in Atlantic crusts, while the highest Hf and Zr concentrations were observed in individual layers of Pacific crusts.

Firdaus et al, 2011: Nature Geoscience 4, 227–230
Frank, M., 2011: Nature Geoscience4,220–221