

## **Enrichment processes of rare metals in marine ferromanganese nodules and crusts**

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Ferromanganese deposits form by precipitation of Mn oxides and Fe oxyhydroxides from seawater (hydrogenetic), pore water (diagenetic) or hydrothermal fluids (hydrothermal), thereby acquiring variable amounts of trace metals like Co and Ni from solution. For some elements, the seawater distribution is even controlled by their incorporation into these deposits (e.g., Ce). The relative enrichment depends on the mode of adsorption, the Fe/Mn ratio, the growth rate and the composition of the source water.

This study compares the relative enrichment of Pt, Te, Zr, Hf, Nb, Ta, Mo, and W in ferromanganese crusts and nodules formed in different marine environments (hydrogenetic, mixed hydrogenetic-diagenetic, hydrothermal) and discusses possible mechanisms of incorporation.

Results of adsorption experiments indicate, that Te, and possibly Pt, are surface-oxidized by Mn oxides (as known for Co and Ce) and form surface precipitates; the enrichment is directly related to the growth rate. The high-field strength elements Zr, Hf, Nb, and Ta are probably adsorbed by non-oxidative scavenging, a process controlled by the relative stabilities of solution and surface complexes. Of the investigated elements, these strongly particle-reactive elements show the strongest enrichment compared to their seawater concentrations in hydrogenetic crusts.

Ferromanganese deposits may also play a dominant role in the fractionation of geochemical twins in the marine environment, as has been discussed for the pair Y-Ho (Bau et al., 1996) and as is shown for Te and Se (see contribution of Schirmer et al., this meeting). Geochemical twins behave very similar during magmatic processes controlled by ionic charge and radii. In aqueous systems, however, chemical speciation and particle reactivity control the element mobility. Depth profiles of Zr-Hf and Nb-Ta measured in hydrogenetic crusts show decreasing elemental ratios with increasing concentrations, which indicates the preferential adsorption of Hf and Ta relative to their twin elements Zr and Nb, respectively. This fractionation may explain superchondritic Zr-Hf and Nb-Ta ratios measured in seawater and is most likely controlled by differences in the stability constants of solution and surface complexes between these elements. Non-oxidative scavenging is also suggested for Mo and W. We observe a 200 times stronger enrichment of W with respect to its seawater concentration compared to Mo. The decoupling of these elements is also obvious in the preferential enrichment of Mo in pure Mn crusts formed in hydrothermal environments compared to hydrogenetic crusts, which has not been observed for W.

### References

Bau, M., Koschinsky, A., Dulski, P., and Hein, J.R. (1996) Comparison of the partitioning behaviours of yttrium, rare-earth elements, and titanium between hydrogenetic marine ferromanganese crusts and seawater. *Geochim Cosmochim Acta* 60: 1709-1725

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