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## High-tech metals in marine ferromanganese nodules and crusts: contents and possibilities of selective extraction

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Recent technological breakthroughs in the fields of ceramics, medicine, aerospace engineering and electronics (semi- and superconductors) are constantly creating new uses and an ongoing increasing demand for a variety of rare valuable trace metals. These so-called high-tech elements such as hafnium (Hf), titanium (Ti,) niobium (Nb), tantalum (Ta), zirconium (Zr), molybdenum (Mo), vanadium (V) and the rare earth elements (REE), many of them of strategic importance, occur inter alia at elevated and potentially economic concentrations in marine ferromanganese nodules and ferromanganese crusts, making those deep sea deposits potential future resources of these metals.

Apart from the challenges of mining these deposits, processing and selective separation of individual target elements or element groups will require specially adapted procedures. As these metals are mostly present in the lattice of the manganese and iron phases, which are strongly intergrown, rather than in separate mineral phases within the nodules and crusts, reductive dissolution of the host phases is a prerequisite to release and dissolve the valuable metals. To evaluate the association of these rare valuable metals with their mineral carrier phases, sequential leaching experiments were carried out on selected samples in a first step in our project. Subsequently, selective leaching experiments with organic ligands like siderophores and humic acid on marine ferromanganese nodule and crust samples were done, with a special focus on the selective extraction of rare valuable or strategic trace metals.

Sequential leaching results of ferromanganese mixed-type nodules as well as a pure diagenetic nodule and a hydrogenetic crust clearly indicate a preferential bonding of the rare valuable metals Ti, Zr, Hf, Nb, Ta, and rare earth elements to the iron oxyhydroxide phase, except for V and Mo which partly show associations to the manganese oxide phase.

Preliminary experiments to selectively release metals out of their carrier phases demonstrated the potential of siderophores as organic complexing agents. Besides Fe, also Li, Zr and Mo were leached in the presence of siderophores. The experiments with humic acid as leaching reagent revealed a weaker leaching effect for these elements. However, Cu was better mobilisable with humic acid than with siderophores. These results show the potential of selective chemical leaching for the recovery of rare valuable metals from mined ferromanganese nodules and crusts in the future. Further steps include application to other valuable metals such as platinum (Pt), optimization of the effectiveness of the procedure and the test of other varieties of organic leaching agents.