

The distribution of Mo in Mn-Fe nodules and crusts and associations with the mineral phases

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Manganese nodules are well known scavengers of economically important metals such as Ni (1.4%), Cu (1.2%), Co (0.3%), Mo (200 – 900 ppm), and REE (500 ppm), from ocean water and sediment pore water.

Nodules consist of turbostratic phyllo-manganates (7/10 Å vernadite, Fe-vernadite), tectomanganates (todorokite), and amorphous δ -FeOOH. In general, the mineral phases influence the distribution of the elements. The behavior and incorporation mechanism of metals like Ni and Cu into the Mn and Fe phases of nodules is well known whereas that of other metals such as Mo is poorly understood. The surface charge of the Mn- and Fe-mineral phases is responsible for the association and adsorption of elements, which occur as hydrated cations (e.g. Ni^{2+} , Cu^{2+} , Co^{2+}) and anionic complexes (e.g., WO_4^{2-} , MoO_4^{2-}) within ocean water [1]. Under the pH conditions of the deep ocean (pH=8.0), the zero point of charge (pH_{zpc}) of phyllo-manganates is ~ 2.8 resulting in a strong negative surface charge, whereby Fe phases show a pH_{zpc} of $\sim 7.9-9$ resulting in a neutral or slightly positive charged surface [1]. Based on this electrochemical model, Mo should be associated with the Fe phase, but our data show it is not. Element (Mo, Mn, Fe) distribution maps show that Mo is associated with the Mn phase and the Mo-EXAFS data furthermore indicate that Mo is incorporated as an inner-sphere complex within those Mn phases. In contrast, leaching experiments of different genetic Mn and Fe precipitates (diagenetic/hydrogenetic) show that Mo is leached preferentially with the Fe phase if the Fe/Mo ratio is >0.009 . A decrease of the Fe/Mo ratio to ~ 0.003 shows a higher Mo leaching (20 – 40%) with the Mn Phase [2]. Mo-EXAFS data collected before and after the leaching step indicate that the crystal chemistry of Mo changed during the procedure. Mo released from the Mn phase will probably be re-adsorbed by the Fe phase, or occur as an insoluble Mo(IV) component in the reduced solution from the FeOOH leach. [1] Koschinsky and Halbach, 1995; GCA 59, 5113-5132. [2] C. Kleint, 2011, Masters thesis University of Bremen, 44 pp.