Mineralogical transformations in polymetallic Mn-nodules upon burial in sediments and the changes in the crystal-chemistry of Ni, Cu, Co

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Polymetallic nodules from the Clarion and Clipperton Zone, of the equatorial Pacific Ocean were studied for their chemistry and mineralogy with regard to their formation and metal enrichment processes. In our study, nodules from the sediment surface, shallow (14 - 16cm), and deep buried (5 - 10m) nodules within the sediment column were studied. The two former experience oxic conditions whereas the latter are found under suboxic conditions **[1]**. Surface nodules consist of turbostratic phyllomanganates (7/10 Å vernadite, δ-MnO_2) **[2]** whereas shallow buried nodules consist of phyllomanganates as well as todorokite, and deep buried nodules mainly of todorokite. This study indicates that, upon burial of the nodules, phyllomanganates transform to todorokite over time. If further, buried nodules enter suboxic conditions Mn-phases start to dissolve, beginning with δ-MnO_2 dissolution of hydrogenetic layer growth structures (LGS). During dissolution and mineral transformation, the chemical composition changes. Metals such as Ni, Zn, and Mo are released in solution and Co, W and Te are enriched in buried nodules compared to surface ones. Cu concentration remains constant in both types of nodules. X-ray absorption spectroscopy shows that the incorporation mechanism of Ni, Cu as well as Co change with buried depth: Ni and Cu are incorporated in octahedral sheets of phyllomanganates of surface nodules, whereas Cu is located at the crystal edges. In buried nodules Ni and Cu are rather adsorbed as outer-sphere complexes probably within the tunnels of todorokite. In general, in surface nodules Co is incorporated in δ-MnO_2 of hydrogenetic LGS whereas in buried nodules Co is incorporated within todorokite of suboxic-diagenetic LGS.

References: [1] Kuhn et al. (2017), Geol. 45, 799 – 802. **[2]** Wegorzewski et al. (2015) Am. Min. 100, 2497 – 2508.