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The influence of suboxic diagenesis on Mn-Fe nodules from the CCFZ in the Pacific Ocean: new answers to old questions

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Polymetallic nodules occuring between the Clarion and Clipperton Fracture Zone (CCFZ) in the equatorial Pacific are of high economic interest due to high content of metals such as Ni, Cu, Co, Mo, Li, Te and high field strength elements (REY, Ti, Hf, Nb, Ta, Zr). These Mn-Fe oxy-hydroxide precipitations consist of a complex texture of irregular, concentrically banded zones of nm to μm thick layers of different genesis. We carried out chemical and mineralogical analyses of individual layers and distribution of their metals (e.g., Ni and Cu) in order to decipher the environmental conditions of nodule formation.

X-ray Photoelectron Spectroscopy (XPS) measurements of the youngest outermost layers (1-3nm) which precipitated around the nodules (surface, which was in contact with near-bottom water; bottom side, which was in contact with sediment pore water; rim which show the interface between sediment and water) represent low Mn/Fe ratios (1.4-2.8), low Ni+Cu contents (0.3 to 1.9 wt%) but higher Co content (0.3-1.4 wt%) on all sides of the nodules. These results are typical for hydrogenetic grow processes under oxic conditions. Oxygen concentration measurements of ocean bottom water and pore water (within the sediments) proved that the nodules are currently growing completely under oxic conditions. Individual layers within the nodules reveal a high chemical heterogeneity. These layers are characterized by highly variable Mn/Fe ratios (3-300) with high variations of Ni+Cu content (1-5.5 wt%) and low Co contents (< 0.2 wt%). Mineralogically, these layers consist of 10Å manganates such as the tectomanganate todorokite and the turbostatic phyllomanganate buserite and a 7Å phyllomanganate birnessite. These Mn-minerals were precipitated from pore water either under oxic (Mn/Fe 3-10) or suboxic (Mn/Fe $\geq$ 10; Ni+Cu 2-5 wt%; Co $\sim$ 0.1 wt%) conditions. These layers alternate with layers of low Mn/Fe ratios ($\leq$ 3) and low Ni+Cu concentrations ($\sim$1 wt%) but elevated Co content (0.2-0.5 wt%), similar to outermost layers. Mineralogically, these layers consist of Fe-vernadite (δ-MnO_2) which is epitaxial intergrown with FeOOH nanoparticles. Layers with high Mn/Fe ratios cannot grow under oxic conditions. The high fractionation of Mn and Fe is only possible under suboxic conditions as they are currently predominating in the Peru Basin (PB). Similar growth structures and Mn/Fe ratios of individual layers from CCFZ and PB nodules indicate suboxic conditions during the growth of these layers in the CCFZ. In contrast to the PB a suboxic front (down to 2.5 mbsf) could not be detected in the sediments. Therefore, we suggest periods of reduced ventilation or even suboxic bottom waters and/or increasing bioproductivity in surface waters during glacial periods in the central Pacific Ocean initiating diagenetic growth of nodules with high Mn-Fe fractionation.