

Chemical and mineralogical investigations of the fine growth structures of Mn-nodules from the CCZ, Pacific Ocean

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Marine Mn-nodules are encrustations of nm- μ m thick layer growth structures (LGS), which incorporate high amounts of economically interesting metals such as Ni, Cu, Co, Zn, Li and high field strength elements [1]. Since 2006, BGR holds an exploration license area for Mn-nodules located within the Clarion and Clipperton Zone (CCZ) in the Pacific Ocean.

In this study, detailed chemical (electron microprobe, X-ray photoelectron spectroscopy) and mineralogical (X-ray diffraction, high resolution transmission electron microscopy) analyses of individual LGS of Mn-nodules were carried out to get a better understanding of their genesis. Further, the knowledge of the metal contents in context with the mineralogy is very important to tailor a specific metallurgical treatment in order to optimize the metal extraction procedure.

Recent analyses of Mn-nodules revealed that they consist of up to 60% of LGS with high Mn/Fe ratios (9-826) and high metal contents (e.g., Ni+Cu: 1-6.5 wt%), which were formed under suboxic conditions. Mineralogically, these LGS consist of turbostratic disordered 7 Å and 10 Å phyllo-manganates (vernadite) forming the major metal-bearing (e.g., Ni, Cu) Mn-phase. These LGS alternate with LGS of low Mn/Fe ratios (<3) and low Ni+Cu contents (<1.5 wt%), which originated from hydrogenetic growth under oxic conditions. Mineralogically, these LGS consist of Fe-vernadite [2]. XPS analyses of the outermost LGS around bulk nodules (surface, rim, bottom side) showed typical hydrogenetic growth indicating that the same metal enrichment processes has prevailed recently in the oxic pore water [3] as well as in the oxic seawater [2]. A high abundance of suboxic-diagenetic LGS indicate that the environmental conditions of nodules changed from oxic to suboxic in the past, which was probably caused by changes of the glacial and interglacial periods [4].

[1] Hein et al. (2013) *Ore Geology Reviews* **51**, 1-14. [2] Wegorzewski and Kuhn (2014) *Marine Geology* **357**, 123-138. [3] Mewes et al. (2014) *Deep Sea Research Part I: Oceanographic Research Papers* **91**, 125-141. [4] Bradmilller et al. (2010) *Earth and Planetary Science Letters* **299**, 417-425.