

Mineralogical characterization of individual growth structures of Mn-nodules with different Ni+Cu content from the central Pacific Ocean

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ABSTRACT

The mineralogy of manganese nodules from the German license area in the eastern Clarion and Cliperton Zone (CCZ) of the central Pacific Ocean was studied using X-ray diffraction. Their individual nanometer to micrometer thick genetically different (hydrogenetic/diagenetic) layer growth structures were investigated using high-resolution transmission electron microscopy. Relationships between the mineral phases and metal content (e.g., Ni+Cu) were assessed with electron microprobe analyzer.

The main manganese phase detected in nodules of this study was vernadite, a nanocrystalline and turbostratic phylломanganate with hexagonal layer symmetry. In layer growth structures of hydrogenetic origin, Fe-vernadite dominates. Layer growth structures of suboxic-diagenetic origin contain three vernadite forms, which are the main Ni and Cu carriers. These Mn-phases were identified on the basis of their structural layer-to-layer distances (7 and 10 Å) and on their capacity to retain these distances when heated. The first form is 7 Å vernadite, which is minor component of the nodules. The second is a thermally unstable ~10 Å vernadite collapsing between room temperature and 100 °C, and the third is a thermally stable ~10 Å vernadite collapsing between 100 and 300 °C. Todorokite was neither detected in bulk nodules nor in any of the individual suboxic-diagenetic growth structures. Because the mineralogical composition of the nodule is quite homogeneous (only different vernadite-types), it is suggested that the content of Ni and Cu in the individual growth structures is controlled by their availability in the environment during individual growth phases.

A profile through a CCZ nodule revealed that the thermal stability of the vernadites change from younger (thermally unstable vernadites, collapsing <100 °C) to older growth structures (thermally stable 10 Å vernadites, collapsing >100 °C) of the nodule accompanied with changes in type and amount of interlayer cations (e.g., Mg, Na, Ca, K). The stability of the vernadites is probably due to re-organization and incorporation of metals within the interlayer of the crystal structure.

Keywords: Manganese nodules, phylломanganates, vernadite, todorokite, HRTEM analysis, cation exchange experiments