

Mineralogy and crystal chemistry of Mn, Fe, Co, Ni, and Cu in a deep-sea Pacific polymetallic nodule

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ABSTRACT

Minor-element concentrations in marine ferromanganese nodules are primarily controlled by the mineralogy, which itself depends on redox conditions at the sediment-water interface. Results are presented for the first in-depth X-ray microstructural and microspectroscopic investigation of a mixed hydrogenetic-diagenetic nodule, which is representative of ferromanganese deposits on abyssal plains. The measurements were conducted by micro-X-ray diffraction and X-ray absorption spectroscopy (both XANES and EXAFS) on homogeneous and diagenetic regions of the nodule. The hydrogenetic-diagenetic interface was imaged by X-ray microfluorescence, after which regions of interest were chosen to represent mineralogical and chemical transformations that occurred at the early stage of suboxic diagenesis. In the hydrogenetic nodule (oxic environment), Mn is speciated as Fe-vernadite, a nanocomposite material composed of intergrown ferroxhyte (δ -FeOOH) and monodispersed phyllo-manganate layers having no interlayer Mn (vernadite). In the diagenetic nodule (suboxic environment), Mn is speciated dominantly as Mg-rich 10 Å vernadite, which consists of a random intergrowth of vernadite and its transformation product todorokite. The authigenic 10 Å vernadite precipitated from the components of vernadite in Fe-vernadite that were dissolved in suboxic microenvironments of the sediment. Direct evidence supporting a redox-driven dissolution reaction is provided by the valence composition of Mn, as measured by micro-XANES, which is $0.69\text{Mn}^{4+} + 0.24\text{Mn}^{3+} + 0.07\text{Mn}^{2+}$ (average = 3.62 ± 0.04 v.u.) for Fe-vernadite and $0.61\text{Mn}^{4+} + 0.23\text{Mn}^{3+} + 0.16\text{Mn}^{2+}$ (average 3.28 ± 0.04 v.u.) for 10 Å vernadite. Ni and Cu, derived mainly from dissolved vernadite and oxidized organic matter, replace structural $\text{Mn}^{3+/4+}$ in both the MnO_2 layer and todorokite domains of 10 Å vernadite. Pure todorokite in highly diagenetic regions of the nodule has an average formula of $\text{Mg}_{0.167}^{2+}(\text{Mn}_{0.783}^{4+}\text{Mn}_{0.099}^{3+}\text{Co}_{0.002}^{3+}\text{Ni}_{0.076}^{2+}\text{Cu}_{0.040}^{2+})\text{O}_2 \cdot n\text{H}_2\text{O}$, with an atomic ratio of $(\text{Cu}+\text{Ni}+\text{Co})/\text{Mn} = 0.13$, which is slightly lower than 0.167 (1/6), the maximum metal uptake capacity reported for marine nodules. By analogy with synthetic todorokites we infer that Mg^{2+} , which has a hydrated diameter close to that of the $[3 \times 3]$ tunnel size of todorokite, and Mn^{3+} and Cu^{2+} , which prefer Jahn-Teller distorted octahedra, play a crucial role in templating the topotactic transformation of 10 Å vernadite to todorokite and stabilizing todorokite in suboxic marine sediments.

Keywords: Mineralogy, XRD, SXRF, XANES, EXAFS, nickel, copper, vernadite, todorokite, birnessite, phyllo-manganate, tectomanganate, ferromanganese nodule, polymetallic nodule, redox reaction