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 hydrogeneous and diagenetic regions of the nodule. The hydrogeneous-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 hydrogeneous nodule (oxic environment), Mn is speciated as Fe-vernadite, a nocomposite material composed of intergrown feroxhyite (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 0.69Mn3+ + 0.24Mn4+ + 0.07Mn2+ (average = 3.62 ± 0.04 v.u.) for Fe-vernadite and 0.61Mn3+ + 0.23Mn4+ + 0.16Mn2+ (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 Mn3+/4+ in both the MnO6 layer and todorokite domains of 10 Å vernadite. Pure todorokite in highly diagenetic regions of the nodule has an average formula of Mg16.15(Mn3.783

INTRODUCTION

Sediments from oxygenated deep-sea plains often are covered with ferromanganese nodules that are characteristic in Ni, Cu, and Li (Goldberg 1954; Usui 1979; Jiang et al. 2007). Mean concentrations of Ni, Cu, and Li in abyssal areas of greatest economic interest are about 1.1–1.3, 0.6–1.1, and 0.01–0.03 wt%, respectively (Hein et al. 2013). Deep-sea nodules acquire their major (Fe, Mn), minor (Ni, Cu), and trace (Co, Pb, Ce) metals from two sources, seawater (hydrogenetic) and pore fluids (diagenetic) (Price and Calvert 1970; Piper and Williamson 1981). Diagenetic nodules are characterized by a high-Mn/Fe ratio (typically >2.5), Ni and Cu enrichment, and a mineralogy dominated by 10 Å manganates (Halbach et al. 1981; Lei and Boström 1995). In contrast, hydrogenetic nodules are lower in Mn, Ni, and Cu, but higher in Fe and trace metals, and their mineralogy is dominated by Fe-vernadite, an intergrowth of feroxhyite (δ-FeOOH) with monodispersed phyllo-manganate layers (Burns and Burns 1975, 1979; Golden et al. 1986; Manceau and Combes 1988; Varentsov et al. 1991; Manceau et al. 1992).Although nodules occur that are solely hydrogenetic (e.g., on seamounts and sediment-free ridges) or diagenetic (e.g., in the southeastern Pacific) (Price and Calvert 1970), most show alternating micrometer laminae of the two genetic types (Margolis and Glasby 1973; Halbach et al. 1982). The rhythmic sequences of microlayers with different chemical and mineralogical characteristics are explained by variations of metal supply in the microenvironment of the accreting nodule surface. The