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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 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 feroxyhite (δ-FeOOH) and monodispersed phyllomanganate 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 $\text{Mg}^{2+}_{0.167}(\text{Mn}^{4+}_{0.783}\text{Mn}^{3+}_{0.099}\text{Co}^{3+}_{0.002}\text{Ni}^{2+}_{0.076}\text{Cu}^{2+}_{0.040})\text{O}_2\cdot n\text{H}_2\text{O}$, with an atomic ratio of (Cu+Ni+Co)/Mn = 0.13, which is slightly lower than 0.167 (⅙), 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 × 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, phyllomanganate, tectomanganate, ferromanganese nodule, polymetallic nodule, redox reaction

INTRODUCTION

Sediments from oxygenated deep-sea plains often are covered with ferromanganese nodules that are characteristically rich 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 feroxyhite (δ-FeOOH) with monodispersed phyllomanganate 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

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hydrogenous component results from direct precipitation or accumulation of suspended nanoparticles from the bottom waters, whereas the diagenetic component results from oxic or suboxic diagenesis (Dymond et al. 1984). Under suboxic diagenetic conditions, such as are typical during microbial decomposition of organic matter, the redox potentials of the Mn^{4+}/Mn^{2+} and the Fe^{3+}/Fe^{2+} redox pairs lead to delayed dissolution of Fe oxides (e.g., feroxyhite) compared to Mn oxides (e.g., vernadite) (Lynn and Bonatti 1965; Calvert and Price 1977; Marchig and Gundlach 1981; Davison 1993). Divalent metal ions released from dissolution of Mn oxides diffuse upward in interstitial waters and reprecipitate under oxic diagenetic conditions at the sediment surface as 10 Å manganates around the accreting nodules. Redox-driven separation of Fe and Mn in suboxic sediments is a common post-accretional early diagenetic process also observed in shallow marine and lacustrine environments (Moore 1981; Tazaki 2000; Hlawatsch et al. 2001, 2002).

The structure and chemical composition of the manganese oxide phases covered in the term "10 Å manganates," and the crystal chemistry of incorporated trace metals, are long-standing questions of fundamental importance in marine mineralogy and geochemistry. We know from early electron microscopy observations that todorokite, a tectomanganate with [3 × 3] tunnel structure (Fig. 1) (Post and Bish 1988; Post et al. 2003), is the principal Mn mineral species in deep-sea nodules transformed after deposition (Burns and Burns 1978a). Pure todorokite occurs typically in submarine hydrothermal fields (Usui et al. 1986) and late diagenetic nodules (Martin-Barajas et al. 1991). However, in most common early diagenetic nodules todorokite coexists with buserite (Arrhenius and Tsai 1981; Ito et al. 1998), a phyllomanganate which also has a 10 Å *d*-spacing (Giovanoli et al. 1975). Buserite is a two-water (2W) layer hydrated form of the 7 Å mineral birnessite (Fig. 2) (Post and Veblen 1990; Kuma et al. 1994; Drits et al. 1997; Lanson et al. 2000). Synthetic buserite loses one water-layer (1W) and collapses to 7.1 Å at room temperature when it is exchanged with Na^+. When exchanged with Mg^{2+} or Ca^{2+}, synthetic buserite collapses only at 110 °C or in vacuum, a result of the higher ionic potential and greater negative enthalpy of hydration of small divalent cations (Paterson et al. 1986; Johnson and Post 2006). Terrestrial buserites, which generally contain a high proportion of Ca in their interlayer, collapse to 7.1 Å upon dehydration (Usui and Mita 1995; Manceau et al. 2007). Most intriguingly, mineralogical analyses of marine buserites show that they only partly collapse, which has been a source of uncertainty in their characterization (Burns et al. 1983; Lei 1996; Bilinski et al. 2002). This partial collapse could not be understood by X-ray diffraction (XRD), because the natural buserites are turbostratically disordered in the *c* direction (no *hkl* reflections), similarly to vernadite (Giovanoli 1980; Chukhrov et al. 1987). For this reason and to be consistent with our previous terminology (Manceau et al. 2007), the terms 10 Å vernadite and 7 Å vernadite are used henceforth for randomly stacked buserite and randomly stacked birnessite, respectively. Note that the nonstoichiometric MnO_{2-x} nanosheets occur only as monolayers in Fe-vernadite, which is the reason why this heterogeneous phase has no basal reflection in XRD.

The explanation for why marine buserites do not collapse completely is provided by high-resolution transmission electron microscopy (HRTEM). Images of natural todorokites show that the dimension of the tunnels is uniformly equal to three chains of edge-shared $[MnO_6]$ octahedra in the [001] direction, as expected from the X-ray crystal structure, but is variable in the [100] direction ranging from double (T[3,2]) to nonuple (T[3,9]) octahedral chains (Fig. 1) (Chukhrov et al. 1979, 1985; Turner and Buseck 1979, 1981; Turner et al. 1982; Siegel and Turner 1983; Bodeï et al. 2007; Xu et al. 2010). This observation has been linked to the loss of interlayer contractibility of marine buserite, and interpreted in terms of structural transformation during diagenetic reactions (Usui et al. 1989; Mellin and Lei 1993). In seawater, crystallographic rearrangement would begin

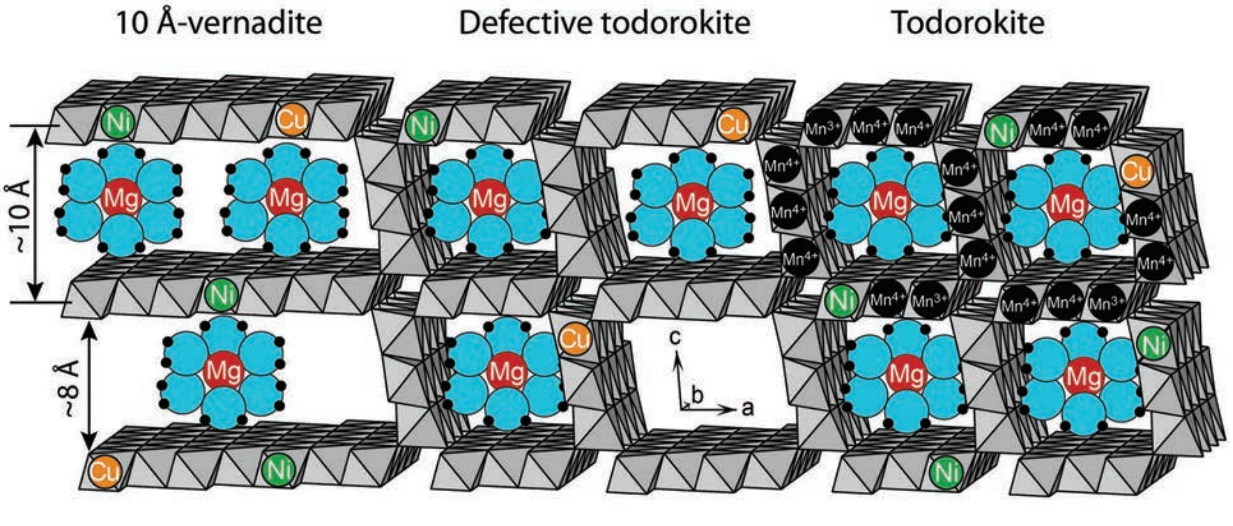

FIGURE 1. Schematic representation of the topotactic transformation of 10 Å vernadite to todorokite. Tetravalent manganese cations likely occupy the central and edge sites of the triple chains from the todorokite framework, and the larger trivalent manganese and divalent nickel and copper cations the edge sites, exclusively (Bodeï et al. 2007). (Color online.)

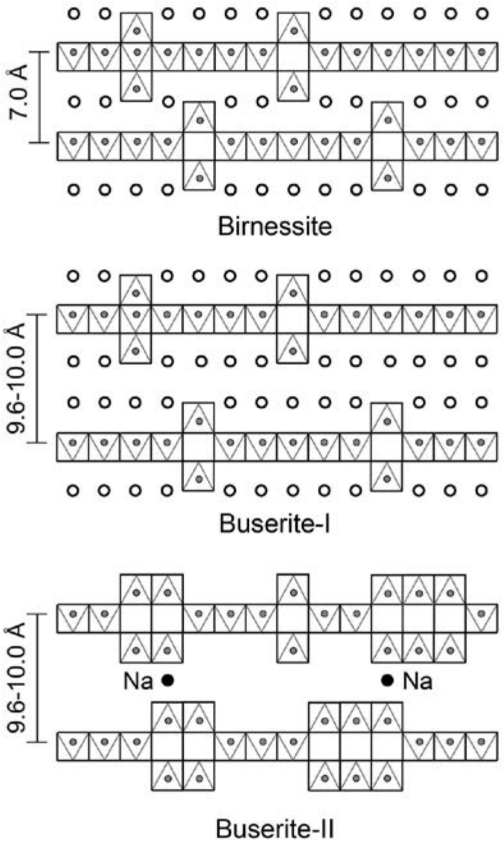

FIGURE 2. Structural models for the two 10 Å manganates, buserites-I and -II. Buserite-I is a two-water layer hydrate, which transforms into the 7 Å manganate birnessite after losing one water layer either in air, upon heating to 105–110 °C, or in vacuum. Buserite-II contains a high amount of interlayer cations above vacancy sites, which prevents it from collapsing to 7 Å. The structure models are adapted from Pal'chik et al. (2011). Note the unlikely absence of hydratation water bound to Na in buserite-II.

with Mg-saturation of 10 Å vernadite and proceed gradually to ideal todorokite. Because the hydrated diameter of the Mg ions (8.6 Å) matches the nominal [3 × 3] tunnel size of todorokite, the Mg ions act as spacers between the pillars of the transforming octahedral sheets (Fig. 1). Thus, the Mg density in the [100] direction is essential in controlling the lateral width of the tunnels (Bodeï et al. 2007). The amount of Mg^{2+} is a function of the layer charge, which itself depends on the extent of Mn^{3+} for Mn^{4+} substitution in the octahedral sheets. In addition, the Mn^{3+} cations, similarly to Ni^{2+} and Cu^{2+}, likely enhance the stability of todorokite by occupying the larger edge sites of the triple chains, and therefore also play a key role in the authigenic formation of todorokite (Burns et al. 1985; Post and Bish 1988; Post et al. 2003; Bodeï et al. 2007; Cui et al. 2008).

Todorokite has been crystallized from a 10 Å phyllomanganate precursor in the laboratory (Golden et al. 1986; Feng et al. 2004; Cui et al. 2006, 2010). This does not mean, however, that all stable marine 10 Å manganates are either todorokite or pillared vernadites. Some authors consider that 10 Å vernadite is composed of two populations, one called "buserite-I," which transforms to 7 Å vernadite upon dehydration, and another called "buserite-II" that contains a high amount of interlayer cations above vacancy sites, which prevents this variety of phyllomanganate from collapsing to 7.1 Å (Fig. 2) (Novikov and Bogdanova 2007; Pal'chik et al. 2011). Yet another mineralogical complexity and source of confusion is the occurrence of asbolane and mixed-layer absolane-buserite as additional 10 Å manganates oxide phases in some marine ferromanganese concretions (Chukhrov et al. 1982, 1983; Manceau et al. 1992).

The crystal chemistry of Co, Ni, Ce, and Pb in marine ferromanganese oxides is generally well known, in contrast to Cu, which has not been explored. It is established that Co is trivalent and incorporated into the phyllomanganate layer of Fe-vernadite by replacement of Mn, whereas Pb is bound to both the Fe and Mn components of Fe-vernadite (Burns 1976; Takahashi et al. 2007). Ce is tetravalent and also associated with the vernadite component, like Co (Takahashi et al. 2000), but how it is incorporated in the phyllomanganate structure is unknown, in contrast to Co (Manceau et al. 1997). Nickel is inside the MnO_2 layers of marine 7 and 10 Å vernadite, and also in the todorokite structure (Figs. 1 and 3) (Bodeï et al. 2007; Peacock and Sherman 2007a). Burns et al. (1985) postulated that Cu^{2+}, like Ni, occupies edge sites in todorokite. Cu also may be substituted for Mn in the vernadite layer, as suggested from Cu-sorption experiments on δ-MnO_2 (synthetic vernadite) conducted at pH 8 (Sherman and Peacock 2010).

The goal of this study is to better understand the hydrogenetic to diagenetic transformation through microscopic analyses of the chemical composition, mineralogy, and crystal chemistry of a deep-sea ferromanganese nodule. The nodule was examined previously and is representative of abyssal nodules altered by post-depositional remobilization of Mn relative to Fe accompanied by Ni and Cu enrichment (Takahashi et al. 2007). Here, the hydrogenetic-diagenetic interface was characterized at the micrometer scale using X-ray fluorescence (μ-SXRF), X-ray diffraction (μ-XRD), and X-ray absorption spectroscopy (both μ-XANES and μ-EXAFS). Mn and Cu are the main focus of the XAS component of the present study. We used Mn-XANES to seek direct evidence for a redox signature of the transformation of diagenetic Fe-vernadite to 10 Å vernadite and todorokite. Mn-EXAFS was used to determine the local structure of Mn

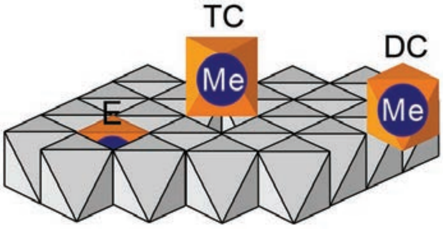

FIGURE 3. Inner-sphere metal (Me) complexes at the δ-MnO_2 surface. E, DC, and TC refer to edge-, double-corner sharing, and triple-corner sharing complexes. The bidentate DC complex is located at the edge of the layer and the tridentate TC complex on the layer surface over a Mn vacancy. The E complex inside the Mn layer shares six edges with the surrounding MnO_6 octaheda. (Color online.)

in Fe-vernadite, and Cu-EXAFS to determine the forms and crystal chemistry of Cu in the hydrogenetic and diagenetic parts of the nodule.

MATERIALS AND METHODS

Experimental sample synthesis

The synthesis procedure and characterization of the birnessite, vernadite (chemical and biogenic δ-MnO_2), and Co- and Ni-containing references were described previously (Manceau et al. 1997; Silvester et al. 1997; Villalobos et al. 2006; Bodeï et al. 2007; Grangeon et al. 2010). A set of Cu-sorbed phyllomanganates were synthesized at different pH, surface loading, and surface area (i.e., layer dimension) to enable the identification of the unknown uptake mechanism of Cu in the diagenetic nodule. The list of reference materials, their synthesis conditions, and the crystal chemistry of Cu within them, are summarized in Table 1. The surface area was varied by using well-crystallized birnessite (HBi and TcBi) and nanoparticulate δ-MnO_2 (dBi) as sorbents. The birnessite platelets have a lateral dimension of 1–2 μm (Tournassat et al. 2002) and the δ-MnO_2 particles 5–10 nm (Grangeon et al. 2012). In HBi, metal sorption is dominated by vacancies on the layer surface, which can be either capped (TC complex) or filled (E complex) by the metal, and in δ-MnO_2 by vacancies and also edge sites at the layer edge owing to the small layer dimension (Manceau et al. 2007; Takahashi et al. 2007).

Deep sea ferromanganese nodule

The abyssal ferromanganese nodule D465 was collected at 5968 m water depth in a central Pacific sedimentary basin (location 09°03.40′N, 174°04.10W) during the Hakurei-maru GH80-5 cruise expedition. The heterogeneous nodule consists of a hydrogenetic core surrounded by a diagenetic rim. The hydrogenetic-diagenetic interface was identified visually and two fragments, each one centimeter in length across the interface, were impregnated in resin. One sample was polished and carbon-coated for electron probe microanalysis (EPMA), and the other bonded to a glass slide, sectioned at a thickness of 30 μm, polished, and peeled off the glass substrate to facilitate transmission-mode μ-XRD. EPMA was performed with a JEOL JXA-8200, running at 15 keV acceleration voltage and using a 5 μm-sized beam. In backscattered electron imaging, the hydrogenetic-diagenetic interface shows numerous interspersed microlayers of each type of accretionary deposit and precipitates with a typical cauliflower-type growth pattern (Supplementary Fig. 1[1]) (Halbach et al. 1982). Four regions, each about 1 mm in lateral dimension, were surveyed and 60 spots in hydrogenetic (opaque gray) and diagenetic (bright gray) regions were selected for analysis. Dark gray regions corresponding to clay phases were not analyzed. Major and minor element concentrations are given in Supplementary Table 1[1].

X-ray data collection and analysis

Synchrotron X-ray measurements were performed in air on the X-ray microprobe 10.3.2 at the Advanced Light Source (ALS) (Marcus et al. 2005). Three SXRF maps were recorded at a scanning resolution of 5 × 5 μm^2 (Map 1, 32 373 pixels), 10 × 10 μm^2 (Map 2, 8775 pixels), and 15 × 15 μm^2 (Map 3, 32 702 pixels), and a beam size adjusted from 10 × 7 μm^2 (Maps 2 and 3) to 5 × 5 μm^2 (Map 1), H × V FWHM, not to over-sample the data. The distributions of Ce, Mn, Fe, Co, Ni, Cu, and Pb were imaged by scanning the sample under a monochromatic beam and measuring the intensity of the $K\alpha$ (Mn, Co, Ni, Cu), $K\beta$ (Fe), and $L\alpha$ (Ce, Pb) fluorescence lines with a 7-element Ge solid-state detector and a counting time of 100–500 ms per pixel. To eliminate fluorescence overlap, the intensities of the Ce$L\alpha$, Co$K\alpha$, and Pb$L\alpha$ lines were measured by recording for each element one map above and another below their absorption edges (5730 and 5714 eV for Ce L_3-edge, 7731 and 7710 eV for Co K-edge, and 12 985 and 13 085 eV for Pb L_3-edge) and calculating the difference maps (Manceau et al. 2002b). The Fe$K\beta$ radiation was measured below the Co K-edge to eliminate the Fe$K\beta$ contamination by the Co$K\alpha$ fluorescence. The fluorescence yield was normalized against the incident intensity I_0 and the counting time. Elemental concentrations were calculated from EPMA, not from SXRF data because of the difficulties inherent to this type of quantification with X-rays.

From visual comparison of elemental distributions, points-of-interest (POIs) were selected for μ-XRD and X-ray absorption measurements at the Mn, Fe, Co, Ni, and Cu K-edges. Transmission-mode μ-XRD patterns were recorded with a Bruker 6000 CCD binned to 1024 × 1024 pixels at 17 keV incident X-ray energy and 16 × 7 μm beam size. The two-dimensional XRD patterns were calibrated with corundum (α-Al_2O_3) and integrated to one-dimensional patterns with the Fit2d code (Hammersley et al. 1996). X-ray absorption spectra were measured in transmission mode at the Mn and Fe K-edge and in fluorescence-yield mode at the Co, Ni, and Cu K-edges. To avoid possible radiation damage, only one spectrum was collected at each spot. Unless otherwise indicated, several single-scan spectra were recorded at distant spots having similar compositions and mineralogy, as seen on the SXRF maps and from μ-XRD patterns, and averaged.

Powder XRD patterns were recorded at ambient condition and in-vacuum with a Bruker D5000 diffractometer equipped with a Cu anode and a Kevex Si(Li) solid-state detector. Samples were mounted in an Anton Paar TTK450 chamber attached to the diffractometer. A first pattern was recorded at ambient condition, then a second after in situ dehydration realized by purging air for six hours with a turbomolecular pump. Some dehydrated samples were rehydrated in situ in air at room temperature for several hours and a new pattern recorded.

RESULTS AND DISCUSSION

Chemical composition

EPMA analyses show a clear inverse relationship of Ni and Cu, on the one hand, and Co, Ce, and Pb, on the other hand, with the Mn/Fe ratio (Fig. 4). Ni and Cu concentrations increase sharply at Mn/Fe ~ 2.5, which divides purely hydrogenetic nodules from those that experienced the beginning of early diagenetic transformation (Halbach et al. 1981), and plateau above Mn/Fe > 10. The average concentrations are Ni = 0.37 (σ = 0.23) and Cu = 0.42 (σ = 0.18) wt% in Mn/Fe < 2.5 regions (n = 26), and Ni = 3.06 (σ = 0.38) and Cu = 2.08 (σ = 0.37) wt% in Mn/Fe >10 regions (n = 12). In contrast, maximum amounts

TABLE 1. List of Cu references

Mineral	Code name	pH	Cu/Mn[a]	Binding mechanism of Cu
Triclinic birnessite[b]	CuTcBi7-10	10	0.0074	Cu substituted for Mn in the octahedral layer (100% E complex)
	CuTcBi7-6	6	0.0071	Cu in the layer (E complex) and interlayer (TC complex)
	CuTcBi7-4	4	0.0072	Cu in the layer (E complex) and interlayer (TC complex)
Hexagonal birnessite[c]	CuHBi11-5	5	0.0112	Cu in the layer (E complex) and interlayer (TC complex)
	CuHBi5-5	5	0.0052	Cu in the layer (E complex) and interlayer (TC complex)
	CuHBi156-4	4	0.156	Cu predominantly in the interlayer (TC complex)
Vernadite[d]	CudBi12-7	7	0.0120	Cu in the layer, interlayer, and on layer edge (DC complex)
	CudBi3-5	5	0.0026	Cu in the layer, interlayer, and on layer edge (DC complex)

[a] Atomic ratio determined by wet chemical analysis following the procedure of Lanson et al. (2002b).

[b] TcBi was synthesized following the procedure of Giovanoli et al. (1970), as described by Drits et al. (1997) and Lanson et al. (2002a). TcBi was doped with Cu, then the pH 10 suspension (CuTcBi10-7) was equilibrated to pH 6 (CuTcBi7-6) and 4 (CuTcBi7-4). TcBi transforms to HBi at acidic pH (Silvester et al. 1997).

[c] The pH 5 samples were prepared by pre-equilibrating TcBi to the sorption pH to transform TcBi to HBi before the dropwise addition of $Cu(NO_3)_2$. The pH 4 sample was characterized previously by XRD (Lanson et al. 2002b) and EXAFS (Manceau et al. 2002a) (sample CuBi156). Cu sorption was achieved by adding $Cu(NO_3)_2$ while equilibrating the TcBi suspension to pH 4.

[d] Synthesis (δ-MnO_2) and Cu sorption were performed following the procedure of Grangeon et al. (2012). δ-MnO_2 was pre-equilibrated at the sorption pH before the dropwise addition of $Cu(NO_3)_2$.

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[1] Deposit item AM-14-1005, Supplementary Figures and Table. Deposit items are stored on the MSA web site and available via the *American Mineralogist* Table of Contents. Find the article in the table of contents at GSW (ammin.geoscienceworld.org) or MSA (www.minsocam.org), and then click on the deposit link.

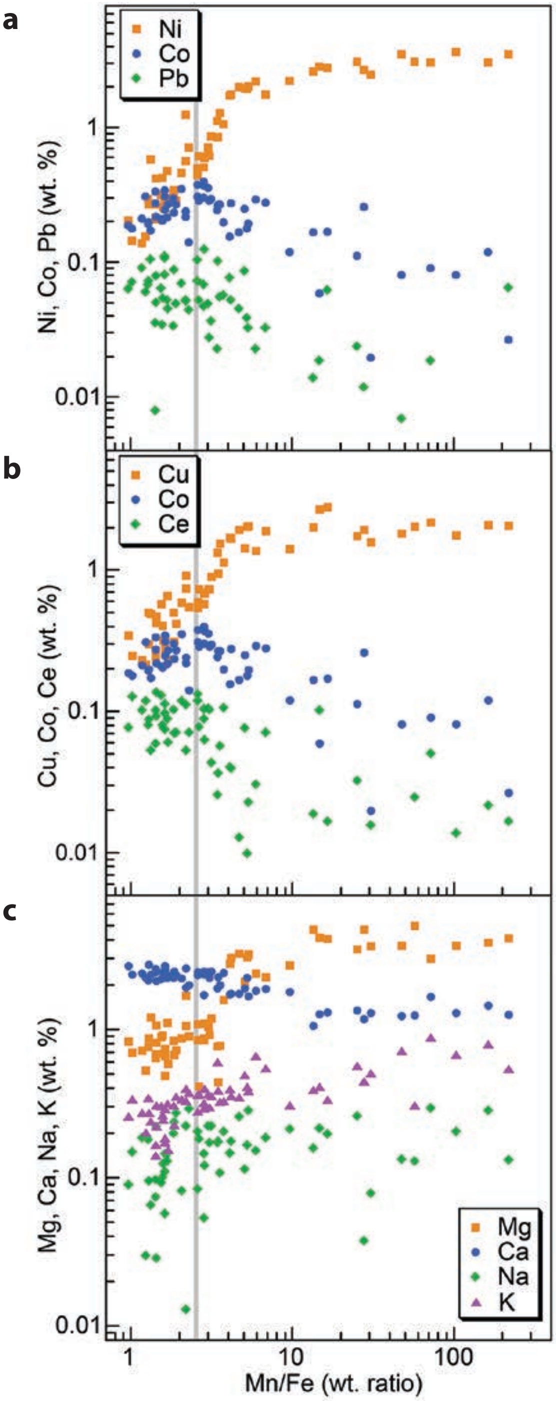


FIGURE 4. EPMA analysis of trace metals and alkali and alkaline earth metal ions in the hydrogenetic-diagenetic nodule as a function of the Mn/Fe ratio. An Mn/Fe ratio of about 2.5 (vertical gray line) divides purely hydrogenetic regions from those that experienced the beginning of early diagenetic transformation (Halbach et al. 1981). Complete analyses are given in Supplementary Table 1[1]. (Color online.)

of Co, Ce, and Pb occur in hydrogenetic regions, where average concentrations are 0.24 ($\sigma = 0.06$), 0.09 ($\sigma = 0.02$), and 0.06 ($\sigma = 0.02$) wt%, respectively. These elements average ⅓ to ½ these amounts in diagenetic regions, but fluctuations are large. The average EPMA results for the five trace metals coincide with previous chemical analyses of seafloor nodules (Piper and Williamson 1981; Dymond et al. 1984; Lei and Boström 1995; Hein and Koschinsky 2012). Interestingly, the change of metal concentration at the onset of the diagenetic transformation is accompanied by a fivefold increase of Mg (0.84 to 4.06 wt%) and a twofold decrease of Ca (2.38 to 1.31 wt%). Because the two alkaline earth divalent cations compensate the layer charge of phyllomanganates (Kuma et al. 1994), Mg is likely exchanged for Ca. However, the exchange is not equimolar; more Mg atoms seem to be introduced than Ca atoms are removed. We will return to this point when discussing the spectroscopic data.

Metal distribution

Micro-SXRF imaging of Mn, Fe, and trace metals confirms the clear chemical distinction of the two general types of nodules (Figs. 5 and 6; Supplementary Fig. 2[1]). Three distinct associations are seen when Ni or Cu is added in red to the bicolor representation of the two elements: green for Fe (gFe) and blue for Mn (bMn). The diagenetic areas appear magenta, the hydrogenetic areas appear violet, and some areas remain green. The green areas also remain unchanged when Ce, Co, or Pb are added in red instead of Ni or Cu. Therefore, the nodule contains two main pools of Fe, one associated with Mn in a Mn/Fe ratio <2.5 wt% and with Ce, Co, and Pb, and one without any Mn and poor in trace metals. Accordingly, the Mn-free Fe pool appears black when only Mn is represented on the SXRF map (bMn image of Fig. 5a). The two Fe pools are also distinguished on the correlation graphs between the $K\alpha$(Fe) and $K\alpha$(Mn) intensities (Fig. 7). They correspond to the groups of points labeled C (clay) and H (hydrogenetic) in Figure 7. Neither the C nor the H fields shows a correlation between Fe and Mn, which suggests that Fe and Mn are in different mineral species. Although depleted in Fe (Mn/Fe >2.5), the diagenetic D field shows a negative relationship between Fe and Mn. This observation provides a hint that two Mn phases likely coexist in diagenetic regions, one associated with Fe similar to the H pool, and another which is Fe-free. We deduce from these observations that Fe and Mn each exists in two distinct mineralogical forms. This inference is confirmed below from the X-ray diffraction and absorption results.

The inverse relationship of Co, Ce, Pb to Ni, Cu as a function of the Mn/Fe ratio observed in Figure 4 by EPMA is neatly demonstrated with bicolor representations. When Ni is green and Co or Pb is red, all colored regions appear monochromatic with no apparent variation in hue (Figs. 5; Supplementary Fig. 2[1]). However, EPMA analysis indicates that the three metals occur everywhere in the Fe-Mn regions. In reality the green and red colors are mixed but secondary hues are faint and cannot been seen by eye alone. A quantitative approach is to calculate correlations of the fluorescence intensities on a pixel-by-pixel basis (Table 2). Calculations show that Ni is moderately anti-correlated with both Pb [r(Ni-Pb) = –0.42 and –0.36] and Co [r(Ni-Co) = –0.37 and –0.42], in agreement with the incomplete separation of metals in the hydrogenetic and diagenetic regions. However,

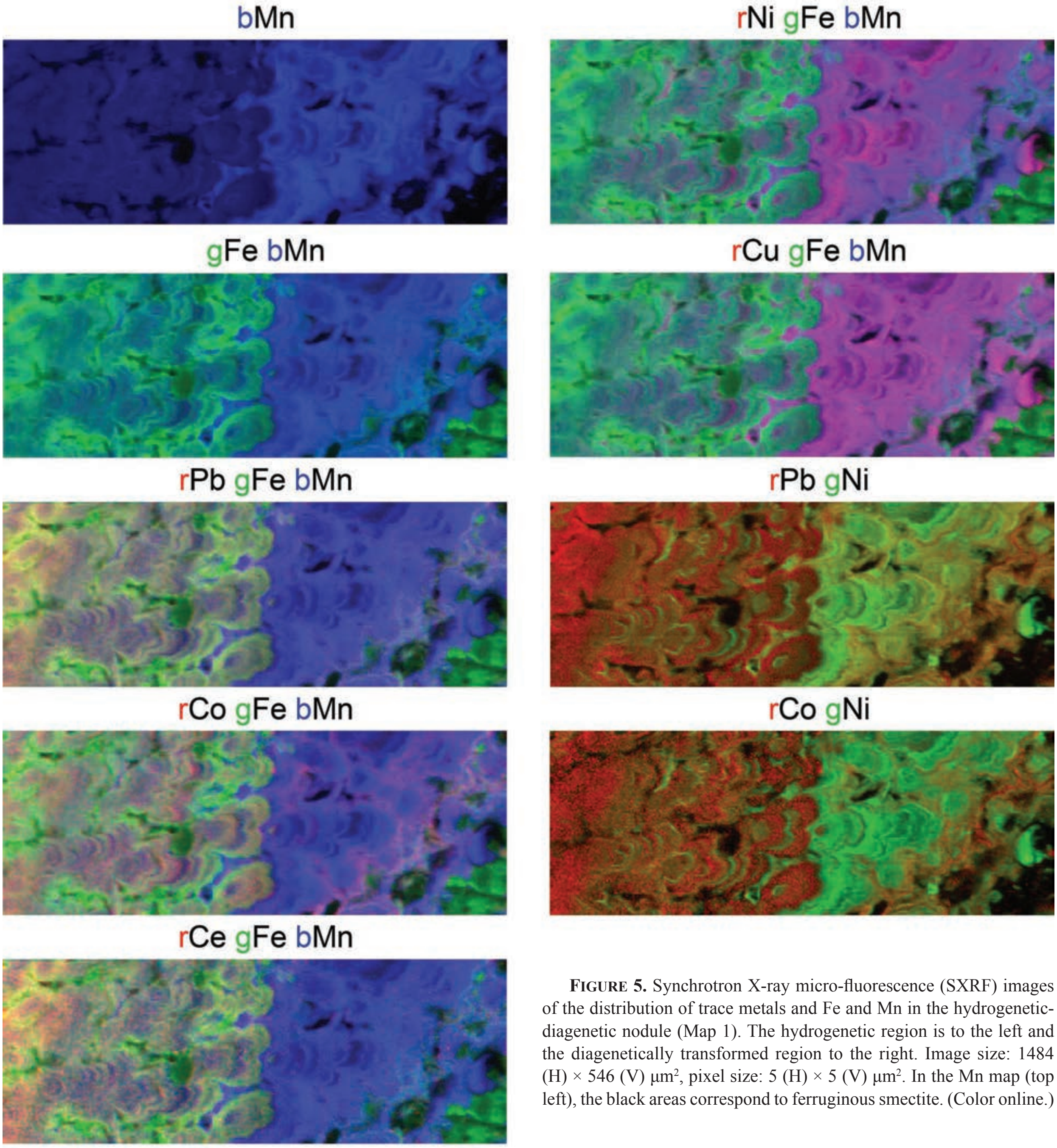


FIGURE 5. Synchrotron X-ray micro-fluorescence (SXRF) images of the distribution of trace metals and Fe and Mn in the hydrogenetic-diagenetic nodule (Map 1). The hydrogenetic region is to the left and the diagenetically transformed region to the right. Image size: 1484 (H) × 546 (V) μm^2, pixel size: 5 (H) × 5 (V) μm^2. In the Mn map (top left), the black areas correspond to ferruginous smectite. (Color online.)

element correlations are misleading in heterogeneous materials that have multiple populations of the same element, each with its own pattern of association. This is the case for Co, which is better correlated to Fe [r(Co-Fe) = 0.77 and 0.54] than to Mn [r(Co-Mn) = –0.16 and –0.44] simply because there are places where Mn is associated with Fe and Co (hydrogenetic regions), and places where Mn occurs alone (diagenetic regions). Early observation of the Co correlation with Fe was interpreted incorrectly to result from the isomorphic substitution of Co^{3+} for Fe^{3+} in ferric oxyhydroxides (Burns and Fuerstenau 1966; Lei and Boström 1995) and from the specific adsorption and oxidation of Co^{2+} to Co^{3+} on siliceous ferric oxyhydroxides particles (Halbach et al. 1982).

Mineralogy

Fe phases. Sixteen μ-XRD patterns and μ-SXRF spectra were recorded at POIs in Fe regions from the three SXRF maps shown in Figures 5 and 6, and Supplementary Figure 2[1]. Iron is essentially present in association with vernadite in the H regions and with dioctahedral smectite in the C (clay) regions (Fig. 8a).

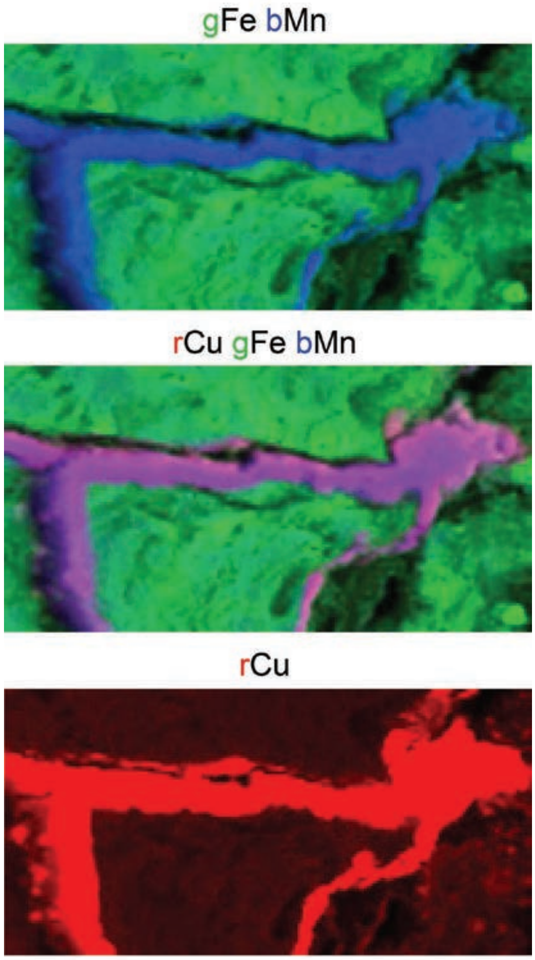


FIGURE 6. Synchrotron X-ray micro-fluorescence (SXRF) images of the distribution of Cu, Fe, and Mn in a diagenetic vein and the surrounding hydrogenetic matrix (Map 2). Image size: 1350 (H) × 650 (V) μm^2, pixel size: 10 (H) × 10 (V) μm^2. (Color online.)

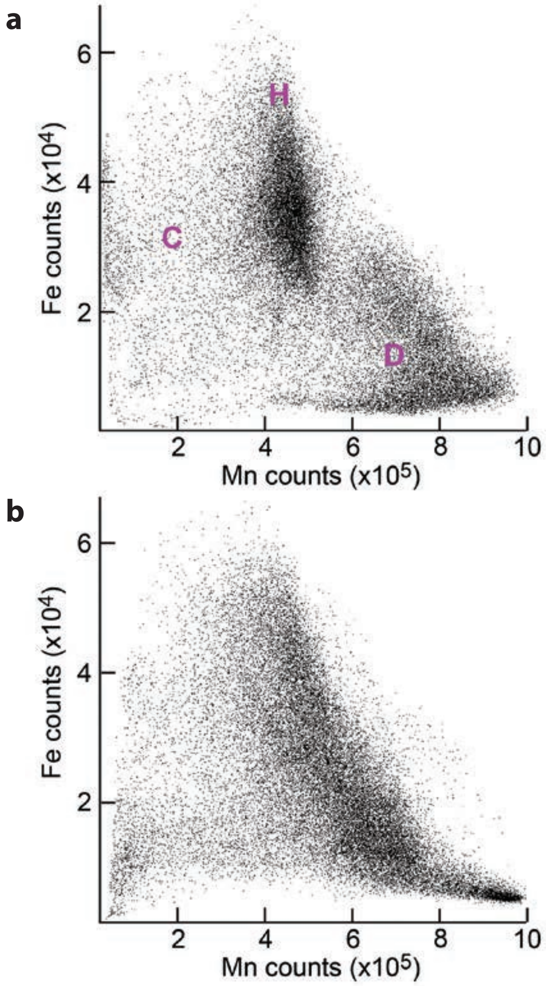


FIGURE 7. Scatter plots for Mn*K*α and Fe*K*β fluorescence lines for the images shown in Figure 5 (Map 1) (**a**) and Supplementary Figure 2[1] (Map 3) (**b**). The pattern suggests that there are two chemically distinct populations of Fe. Complementary analysis by micro-XRD and EXAFS indicate that Fe is associated with dioctahedral smectite in C (clay) areas and speciated as feroxyhite (δ-FeOOH) in H areas. (Color online.)

TABLE 2. Pearson *r* values for X-ray fluorescence intensities between elements, taken pixel-by-pixel

	Mn	Fe	Ce	Co	Ni	Cu	Pb
				Map 1			
Mn	1						
Fe	−0.61	1					
Ce	−0.30	0.70	1				
Co	−0.16	0.77	0.59	1			
Ni	0.87	−0.74	−0.46	−0.37	1		
Cu	0.92	−0.75	−0.52	−0.38	0.92	1	
Pb	−0.03	0.59	0.69	0.70	−0.42	−0.25	1
				Map 3			
Mn	1						
Fe	−0.51	1					
Ce	−0.23	0.62	1				
Co	−0.44	0.54	0.63	1			
Ni	0.78	−0.54	−0.27	−0.42	1		
Cu	0.89	−0.61	−0.39	−0.54	0.87	1	
Pb	−0.10	0.75	0.66	0.70	−0.36	−0.35	1

Note: This correlation is a quantitative measure of the degree of association between two elements.

Goethite also was detected in some spots. The Fe-vernadite pattern is characterized by broad reflections at 2.455(1) Å (100 reflection) and 1.420(1) Å (110 reflection) from the phyllomanganate component, and two broad reflections at ~2.20 and 1.70 Å from the Fe oxyhydroxide component (Varentsov et al. 1991; Manceau et al. 1992, 2007). When observed, the basal reflections at 9.6 Å (001) and 4.8 Å (002) from the vernadite component are faint because the stacking of the Mn layers is disrupted by the epitaxial intergrowth of the Fe nanoparticles (Burns and Burns 1975, 1979; Golden et al. 1988; Manceau and Combes 1988). The composite assemblage has a *K*α(Mn)/*K*α(Fe) ratio ranging typically from 1.0 to 1.2, consistent with EPMA analysis (Fig. 8b). The nature of the Fe nanophase was further characterized by Fe *K*-edge EXAFS spectroscopy. The best spectral match to our Fe (oxyhydr)oxide database (Manceau and Drits 1993) was obtained with feroxyhite (δ-FeOOH) (Supplementary Fig. 3[1]). Ferrihydrite, which has a distinct EXAFS signature at $k = 5.30$ and 7.60 Å^{-1} (Manceau 2011), is an incompatible model.

In C regions, diffraction maxima and scattering profiles at 10–13, 4.48, 2.57, 2.40, and 1.50 Å match known 001 and *hk*0

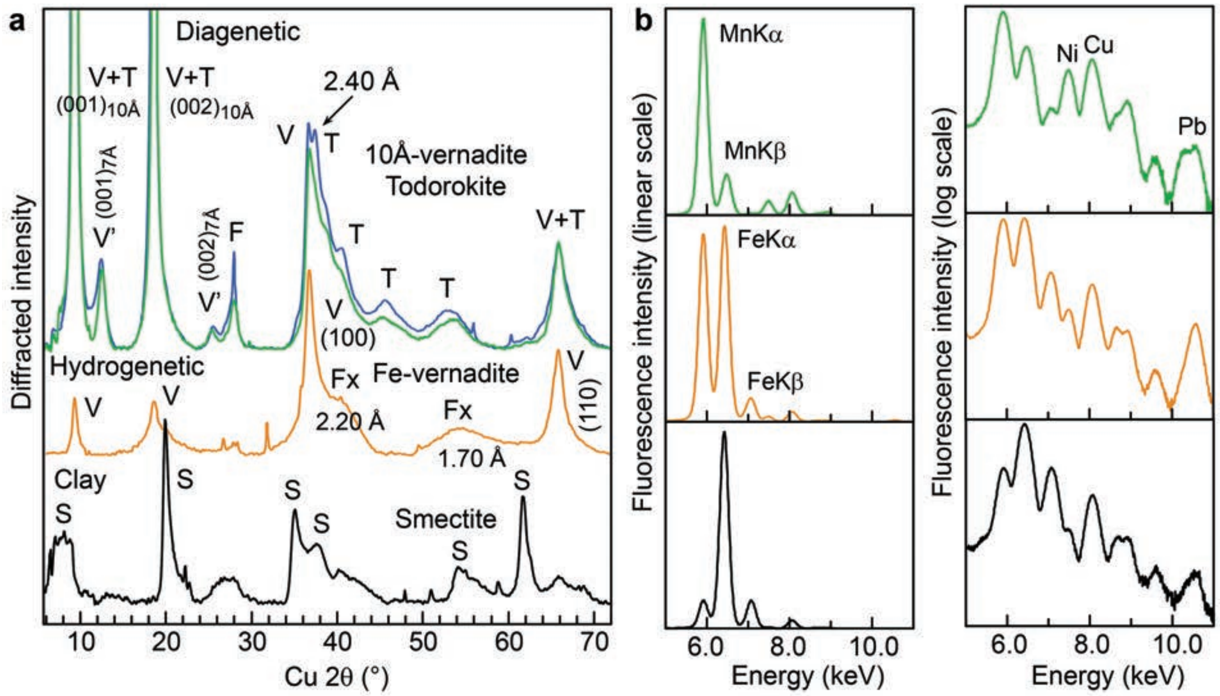


FIGURE 8. Representative micro-XRD patterns (**a**) and point SXRF spectra (**b**) collected at 17 keV in the clay (C), hydrogenetic (H), and diagenetic (D) regions of the nodule. The C areas have major dioctahedral smectite, the H areas have major Fe-vernadite, and the diagenetic areas have variable proportions of 10 Å vernadite (two-water layer phyllomanganate) and todorokite. The amount of todorokite increases as the hydrogenetic to diagenetic transformation increases (Supplementary Fig. 5[1]). Peaks labeled V′ correspond to the 001 and 002 reflection of pure vernadite crystallites with one-water layer (7 Å phyllomanganate). In vacuum or upon heating, the removal of one water layer from 10 Å vernadite causes the ~10 Å reflection to shift to ~7 Å (Supplementary Fig. 6[1]) (Usui and Mita 1995; Manceau et al. 2007). Peaks labeled S, V, T, Fx, and F refer to smectite, vernadite, todorokite, feroxyhite, and feldspar, respectively. (Color online.)

reflections of aluminous dioctahedral smectites (Fig. 8a). In some cases, the 060 reflection is a doublet with one maximum at 1.500 Å and another at 1.514 Å (Supplementary Fig. 4[1]). The 1.514 Å reflection is intermediate between those of aluminous (1.500 Å) and ferric (1.52 Å) smectites, namely montmorillonite/beidellite and nontronite (Brindley and Brown 1980; Badaut et al. 1985; Srodon et al. 2001). Nontronite with *d*(060) spacings of 1.518 and 1.521 Å was reported in marine Fe-Mn crusts (Dekov et al. 2011). Because of this previous report of nontronite, and because the intensity of the 1.514 Å reflection varied with the intensity of the Fe*K*α signal measured simultaneously on the same spots (Vespa et al. 2010), the 1.514 Å reflection is attributed here to dioctahedral (Fe,Al)-smectite. It follows from coupled μ-XRD and μ-SXRF that Fe occurs in smectite as a subsitutional cation and in the precipitates as nanocrystalline feroxyhite. This is the first time that the two Fe forms have been identified in situ in an intact nodule. Only the second mineral species is potentially metalliferous because μ-SXRF imaging showed that the clay-rich regions have no trace metals.

Mn phases. Micro-XRD patterns were collected on 22 diagenetic spots from the three μ-SXRF maps. A clear relationship was observed between the Fe concentration and the XRD trace. The XRD pattern of the high-Fe end-member resembles the Fe-vernadite pattern, with a decrease in the feroxyhite component as the Fe content declines. The low-Fe end-member is a mixture of 10 Å vernadite and todorokite (Fig. 8a). Todorokite has a prominent diffraction line at 2.40 Å, observed as a second maximum to the right of the 100 reflection from 10 Å vernadite. In addition, todorokite has reflections in the 2.2–1.7 Å interval, which modulate the pattern of vernadite between the 100 and 110 reflections differently from feroxyhite in Fe-vernadite. The increase of todorokite with a decrease of Fe observed at high-diffraction angle is accompanied at low angle by the enhancement of the 001 and 002 basal reflections at 9.6–9.7 and 4.8 Å (Supplementary Fig. 5[1]). The 7.1 Å (001) and 3.5 Å (002) basal reflections from the one-water (1W) layer hydrated form (7 Å vernadite) are observed in some patterns, but the 2W sets of reflections always prevails.

The reinforcement of the 00*l* reflections with increasing amounts of todorokite probably results from the pillaring with triple octahedral chains of the interlayer space of the phyllomanganate, as reported previously for a deep-sea nodule from a low-temperature hydrothermal field (Fig. 1) (Bodeï et al. 2007). The two types of MnO_{2-x} interlayers, those fully hydrated and those whose adjacent layers are bridged with triple chain pillars, can be distinguished by dehydration in vacuum or heating to 80–150 °C, similarly to 2W/1W smectites (Yoshikawa 1991; Ferrage et al. 2005; Manceau et al. 2007). For technical reasons, dehydration could not be performed in situ during the synchrotron measurements, therefore a fragment of nodule taken from the outer region was dehydrated in vacuum in the laboratory. Several marine Mn oxides, chosen to represent the variety of manganese

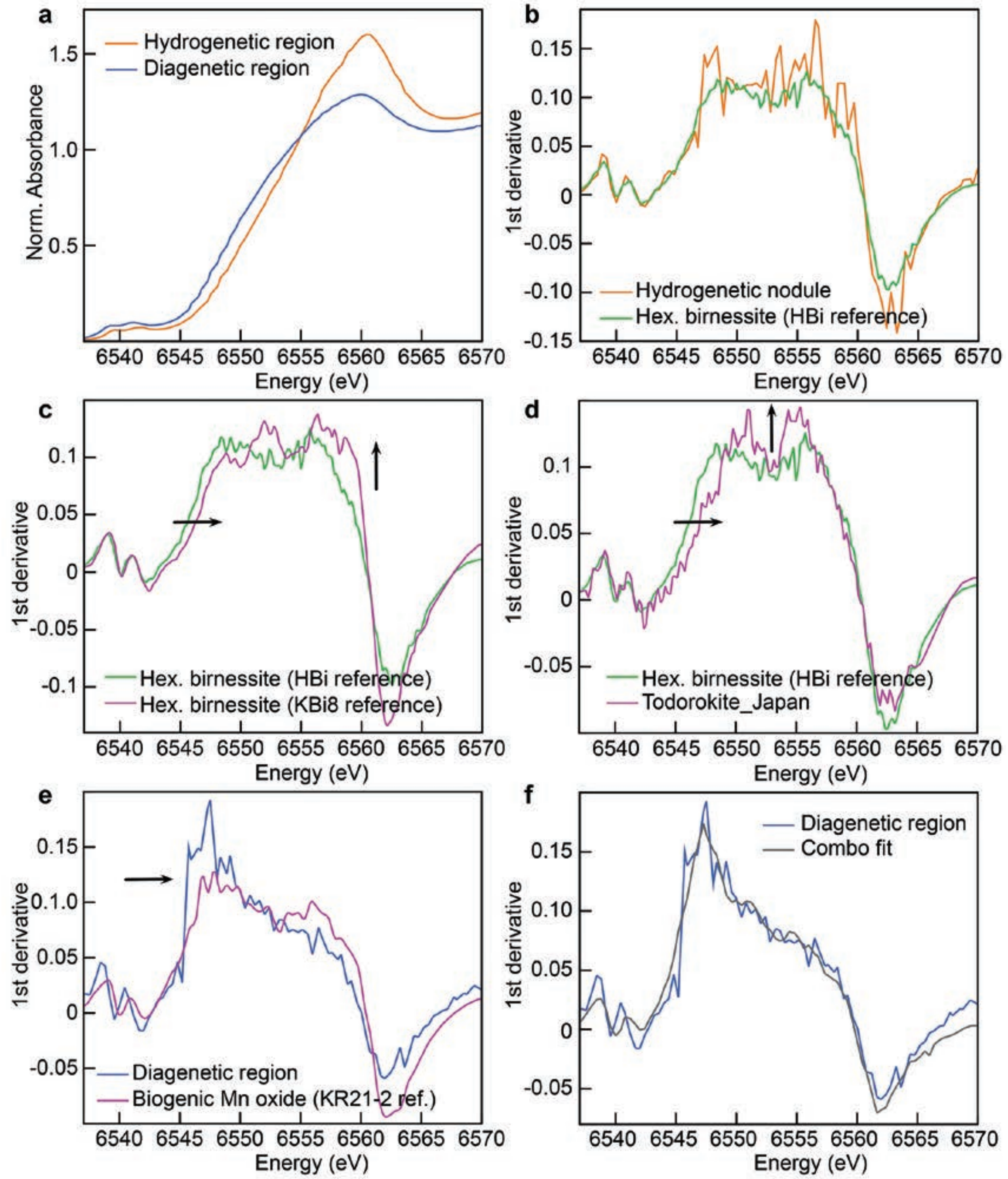
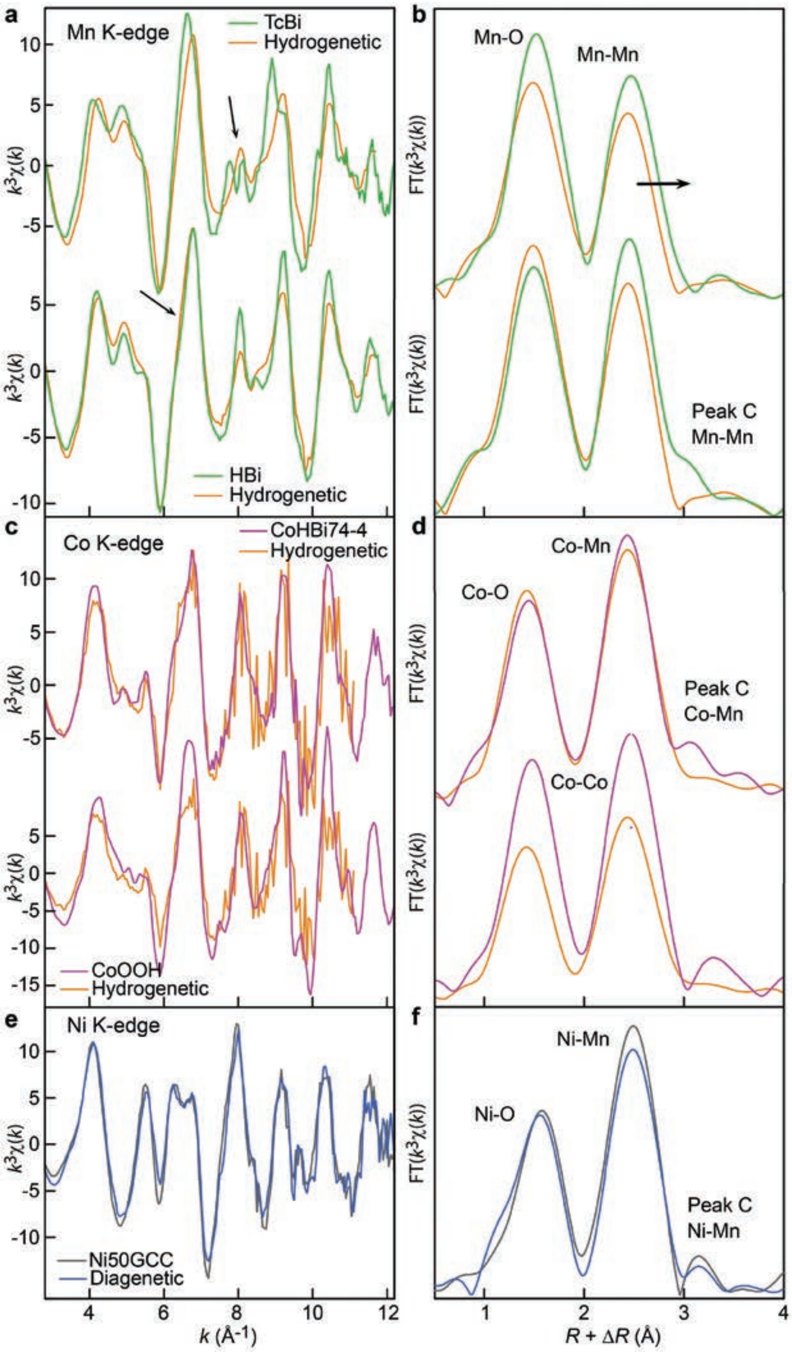


FIGURE 9. (**a**) Mn *K*-edge XANES absorption spectra representative of the hydrogenetic and diagenetic regions. The spectra were normalized to unit step in the absorption coefficient from well below to well above the edge. (**b**–**f**) First derivatives compared to reference spectra (**b**,**e**), and Combo fit to an extended database of reference spectra from Manceau et al. (2012) (**f**). (Color online.)

minerals observed in diagenetic and hydrothermal environments (todorokite, hexagonal birnessite, asbolane), also were analyzed by powder XRD at room condition and in vacuum for comparison and to ascertain that no important Mn phases had been missed (Supplementary Fig. 6[1]). At room condition, the D465 powder appears to be composed of Fe-vernadite and 10 Å vernadite. Todorokite is not detected at high-diffraction angle, and only indirectly at low angle from the high intensity of the two basal reflections from 10 Å vernadite. The removal in vacuum of one water layer causes the 10 Å reflection from the 2W layers to shift to 6.7 Å, and the pillared crystallites to collapse to 8.9 Å, thereby revealing the presence of todorokite. In hydrothermal nodules containing a high proportion of well-crystallized todorokite, the basal reflection decreases less in vacuum, from 9.6–9.7 to 9.3–9.4 Å (Supplementary Fig. 6[1]). The greater decrease of 9.6–9.7 to 8.9 Å observed in the D465 nodule is related to the incomplete topotactic transformation of 10 Å vernadite to todorokite at the early stage of the diagenetic reaction. Comparison with the min-



◀**FIGURE 10.** (**a**,**b**) Mn *K*-edge EXAFS spectra of the hydrogenetic nodule and triclinic (TcBi) hexagonal (HBi) birnessites and their Fourier transform magnitudes. The arrow at *k* = 8.1 Å^{-1} denotes the double antinode pattern observed in some bioprecipitates (Webb et al. 2005), and resulting from the ordering of Mn^{3+} and Mn^{4+} in the phyllomanganate layer (Gaillot et al. 2003, 2007; Manceau et al. 2004). The arrow to the right denotes the shift to higher distances of the Mn-Mn peak in TcBi resulting from the presence of Mn^{3+} in the layer. The arrow at *k* = 6.5 Å^{-1} points out the shoulder observed in HBi but absent in the sample because it lacks interlayer MnO$_6$ octahedra that share corners with the layer octahedra around vacancies (TC linkage). In real space, this is reflected by the absence of the Mn-Mn corner-sharing peak C. (**c**,**d**) Co *K*-edge EXAFS spectra and Fourier transform magnitudes of the hydrogenetic nodule (CoD465H) and two references, Co-sorbed birnessite (CoHBi74-4) and CoOOH. The sample has no corner-sharing Co-(Co,Mn) peak, meaning that all Co and Mn atoms are in the manganese layer. (**e**,**f**) Ni *K*-edge EXAFS spectra and Fourier transform magnitudes of the diagenetic nodule from the Central Pacific studied here (NiD465D), and from a hydrothermal metalliferous Fe-Mn deposit collected west of Nicoya Peninsula off Costa Rica (Ni50GCC) (Bodeï et al. 2007, 2008; Steinmann et al. 2012). The crystal chemistry of Ni is nearly identical in the two deep-ocean Fe-Mn deposits. The Co- and Ni-EXAFS data are provided in the Supplementary material[1] as a useful resource for other studies. (Color online.)

eralogy of hydrothermal nodules shows the absence of hexagonal birnessite, which is a *c*-ordered form of 7 Å vernadite (Drits et al. 1997), and also asbolane, which has a mixed-layer structure (Supplementary Fig. 6[1]) (Manceau et al. 1992).

Fe-vernadite and 10 Å vernadite both have a *d*(100)/*d*(110) ratio of 2.455(1)/1.420(1) ~ √3, which indicates that the phyllomanganate layers have hexagonal symmetry with $a = b = 2.84$ Å. This metric parameter needs to be corrected for diffraction effects, which shift the maximum of the two *hk*0 reflections to higher scattering angles (i.e., lower *d* values) for nanosized compared to larger-sized materials (Supplementary Fig. 7[1]) (Manceau et al. 2013). The actual value, obtained by X-ray simulation, is $b = 2.85$ Å. Because Mn^{3+} is larger than Mn^{4+}, the layer dimension can be used to estimate the amount of Mn^{3+} in the MnO$_{2-x}$ octahedral sheets, with the provision that *b* also depends on the density of vacancies. Natural vernadite with no layer Mn^{3+} has an apparent *b* value of 2.83 Å (Manceau et al. 2007), and an actual value of 2.84 Å. Synthetic vernadite (δ-MnO$_2$) equilibrated at pH 10 has 12% layer Mn^{3+}, 10% vacancies, and a corrected *b* parameter of 2.853 Å (Lanson et al. 2000; Manceau et al. 2013).

Synthetic hexagonal birnessite (HBi) equilibrated at pH 4 has 13% Mn^{3+} in its layer, 17% vacancies, and a *b* parameter of 2.848 Å. On the basis of this comparison, the nodule vernadite has about 10–15% layer Mn^{3+}.

The valence states of Mn in Fe-vernadite and 10 Å vernadite were measured by XANES spectroscopy and determined using an extended database of reference spectra (Manceau et al. 2012). The XANES spectra for the two phyllomanganates are compared in Figure 9a. Fe-vernadite has a greater white line corresponding to Mn^{4+}, and 10 Å vernadite a broad shoulder in the rising part of the edge, which is distinctive of Mn^{2+}. Trivalent Mn appears in Mn-XANES spectra as a shoulder below the edge maximum. The rounded maximum of the 10 Å vernadite spectrum is suggestive of a higher proportion of Mn^{3+}. Spectral features are better discerned in the derivative spectra. The derivative of Fe-vernadite closely matches that of the HBi reference, which has the nominal formula $Mn^{3+}_{0.11}Mn^{2+}_{0.055}H^{+}_{0.33}(Mn^{4+}_{0.722}Mn^{3+}_{0.11}\square_{0.167})O_2{\cdot}0.5H_2O$ (Lanson et al. 2000) (Fig. 9b). The valence composition of HBi determined previously by XANES is $0.69Mn^{4+} + 0.24Mn^{3+} + 0.07Mn^{2+}$ (average = 3.62) (Manceau et al. 2012). The sensitivity of the XANES derivatives to the Mn valence is shown in Figures 9c and 9d with the hexagonal birnessite reference KBi8 (average = 3.83) and todorokite (average = 3.72). Triclinic birnessite is an incompatible model because it gives a distinct derivative, as shown in Figure 3 of Manceau et al. (2012). The best agreement between 10 Å vernadite and reference spectra was obtained with a biogenic phyllomanganate of valence composition $0.61Mn^{4+} + 0.23Mn^{3+} + 0.16Mn^{2+}$ (Fig. 9e). However, the 10 Å vernadite spectrum has a lower amplitude at 6557 eV (Mn^{4+}) and a higher amplitude at 6547 eV (Mn^{3+}) than the reference, which is indicative of a more reduced state in the sample. Since the 10 Å vernadite spectrum did not match exactly any entry in our spectral library, its valence composition was calculated by least-squares fitting of its spectrum to our complete database under the constraint of non-negativity in the loadings (Combo fit). This approach is more robust than regression analysis with a limited set of model compounds, because irrelevant references, which give negative loadings, are removed from the fit. The result is $0.39Mn^{4+} + 0.50Mn^{3+} + 0.11Mn^{2+}$ (average = 3.28), in agreement with phenomenological observations (Fig. 9f).

Having shown that Mn had the same average oxidation state in Fe-vernadite and HBi, mineralogical characterization was pursued by comparing its local structure in the two minerals by Mn *K*-edge EXAFS spectroscopy. Not surprisingly, the two spectra resemble those of phyllomanganates with hexagonal layer structure (Fig. 10a) (Villalobos et al. 2006). The Mn^{3+} and Mn^{4+} cations are not ordered in the MnO_2 layer, as in some bioprecipitated Mn oxides (Webb et al. 2005), otherwise the oscillation at $k = 8.1$ Å^{-1} would show the double antinode feature observed in triclinic birnessite (Gaillot et al. 2003, 2007; Manceau 2004). Also, it is known that when there is interlayer Mn octahedra that share corners with the layer octahedra, a shoulder appears at $k = 6.5$ Å^{-1} and a peak in the Fourier transform magnitude at $R + \Delta R = 3$ Å (Manceau et al. 1997; Silvester et al. 1997; Gaillot et al. 2003). The two structural fingerprints are observed in HBi, which has 17% interlayer Mn, but not in the hydrogenetic nodule (Figs. 10a and 10b). The local structure of Mn in the diagenetic nodule was not examined by this technique because Mn is present in 10 Å vernadite and todorokite.

We conclude from our XRD, Mn-XANES and Mn-EXAFS investigation that the Mn is in the form of a turbostratic phyllomanganate (i.e., vernadite) with no interlayer Mn in the hydrogenetic nodule, and in turbostratic phyllomanganate and todorokite in the diagenetic nodule. The average oxidation state of Mn is 3.62 ± 0.04 v.u. in the first region and 3.28 ± 0.04 v.u. in the second. The fraction of Mn^{3+} to total Mn in Fe-vernadite is estimated to be 10–15% using diffraction (*b* parameter) and 23% using XANES spectroscopy. The difference probably falls within the range of compositional variability of this poorly ordered and non-stoichiometric nanophase. Diagenetic MnO_2 has

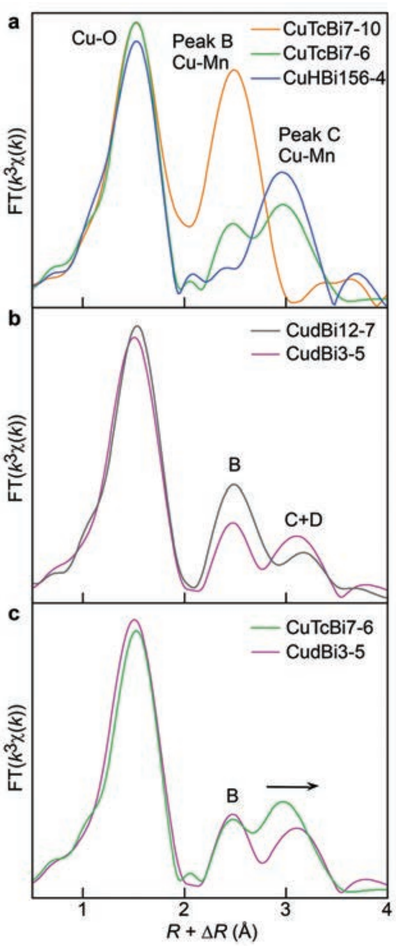


FIGURE 11. Fourier transform magnitudes of Cu *K*-edge EXAFS data for crystalline birnessite and nanoparticulate δ-MnO_2 (synthetic vernadite, dBi) references. (**a**) Three birnessites with contrasted proportions of layer (E complex, peak B) and interlayer (TC complex, peak C) Cu^{2+}. (**b**) Two Cu-sorbed δ-MnO_2 samples showing the influence of sorption pH on the proportions of the layer and interlayer complexes. (**c**) Comparison of spectra for Cu-sorbed on birnessite and δ-MnO_2 showing that peak C is a doublet produced by Cu sorbed on layer vacancies (TC complex) and on layer edges (DC complex) (Fig. 3). This third complex is always present but only detected in δ-MnO_2 because Mn oxide nanosheets have a higher fraction of border sites. The Cu-EXAFS data are provided in the Supplementary material[1] as a useful resource for other studies. (Color online.)

more Mn^{3+} in its structure than Fe-vernadite. The higher charge deficit introduced by Mn^{3+}, but also by Ni and Cu (see below), for Mn^{4+} substitution in diagenetic MnO_2 is consistent with the increase of Mg measured by EPMA (Fig. 4).

Crystal chemistry of trace metals

Cobalt and nickel. We examine now how Co and Ni are incorporated in the ferromanganese nodule. One Co-EXAFS spectrum was recorded in the hydrogenetic region and one Ni-EXAFS spectrum in the diagenetic region of Map 1. Measurements were not repeated on different spots because the two spectra appeared to confirm what was largely expected of the structural forms of the two metals; that is, the incorporation of Co as Co^{3+} into the vernadite layer by replacement of Mn, and the partitioning of Ni between vernadite and todorokite (Bodeï et al. 2007; Takahashi et al. 2007). The first mechanism is demonstrated in Figure 10c by comparing the hydrogenetic Co-EXAFS spectrum with the spectra of two references, a Co-sorbed birnessite of chemical formula:

$$Mn^{2+}_{0.07}Mn^{3+}_{0.04}Co^{3+}_{0.01}(Mn^{4+}_{0.72}Mn^{3+}_{0.11}Co^{3+}_{0.06}\square_{0.11})O_{1.68}(OH)_{0.32}$$

and CoOOH, which has a phyllomanganate-type layered structure (Manceau et al. 1997). The Co-sorbed birnessite reference is the nearest fit for the nodule spectrum. The features in the two spectra are similar, in contrast to those for CoOOH, which show a higher amplitude and also a distinct shape at $k < 8$ Å^{-1}. Fourier transforms indicate that Co-sorbed birnessite has a nearest Co-Mn peak at $R+\Delta R = 2.4$ Å from edge-sharing CoO_6-MnO_6 octahedra in the Mn layer, and a next-nearest Co-Mn peak at $R+\Delta R = 3.1$ Å from TC-sharing between layer CoO_6 octahedra and interlayer $Mn(O,H_2O)_6$ octahedra (Fig. 3). The second peak (peak C) is absent in the nodule spectrum (Fig. 10d). We interpret this result to indicate that the vernadite layer has no Mn or Co in its interlayer, consistent with Mn-EXAFS results. The Co in this spot of the sample is structurally incorporated in the natural vernadite, as is consistent with previous findings (Burns 1976; Manceau et al. 1997).

The Ni-EXAFS spectrum, when compared to those of natural and synthetic references (Supplementary Fig. 8[1]), most closely resembles the 50GCC spectrum from hydrothermal Mn deposits in hemipelagic sediments off Costa Rica (Fig. 10e) (Bodeï et al. 2007, 2008; Steinmann et al. 2012). High-resolution transmission electron microscopy (HRTEM) coupled with microanalysis showed that 50GCC is a mixture of 10 Å vernadite and todorokite with Ni partitioned almost evenly between the two phases (Bodeï et al. 2007). In todorokite, NiO_6 octahedra located in one tunnel wall are corner-linked to MnO_6 octahedra from the adjacent tunnel wall at a Ni-Mn distance of ~3.50 Å. This distance, which appears on the Fourier transform as a peak at $R+\Delta R = 3.2$ Å similar to the Co-Mn and Mn-Mn TC-linkages described previously, is clearly observed on the diagenetic data (Fig. 10f). Consequently, we conclude that Ni coexists in 10 Å vernadite and todorokite in marine ferromanganese nodules transformed by early diagenetic reactions. In 10 Å vernadite, Ni is likely totally incorporated in the vacancy sites of the Mn layer, as observed in other natural phyllomanganates (Manceau et al. 2002c; Peacock and Sherman 2007a).

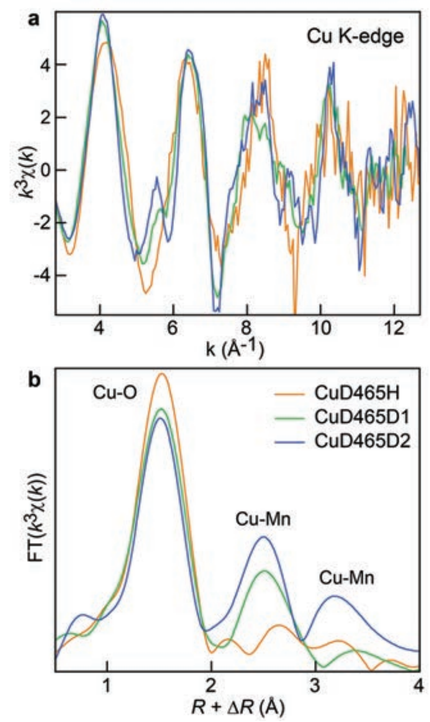


FIGURE 12. Cu *K*-edge EXAFS spectra (**a**) and their Fourier transform magnitudes (**b**) representative of the structural forms of Cu in smectitic regions (CuD465H), in 10 Å vernadite from an early diagenetic region (diagenetic vein, CuD465D1), and in the diagenetic nodule with abundant todorokite (CuD465D2). (Color online.)

Copper. Results from Cu-sorbed phyllomanganates show that Cu uptake on the basal surfaces of birnessite and δ-MnO_2 is pH dependent: it occurs preferentially as a TC complex at acidic pH [peak C at *d*(Cu-Mn) = 3.40 Å], and an E complex at pH circumneutral [peak B at *d*(Cu-Mn) = 2.87 Å] (Fig. 11; Supplementary Fig. 9[1]). The effect of pH on the Cu site occupation is observed regardless of whether or not Cu is added to the birnessite surface at pH ≤ 7, or incorporated initially into the birnessite structure at basic pH (TcBi) and the suspension subsequently equilibrated to lower pH (Table 1; Supplementary Fig. 10[1]). The results are in agreement with previous studies on Cu and Ni sorption on phyllomanganate (Manceau et al. 2007; Peacock and Sherman 2007a, 2007b; Peacock 2009; Sherman and Peacock 2010). However, the Fourier transform of Cu sorbed on δ-MnO_2 at pH 5 (CudBi3-5) shows evidence for a longer Cu-Mn scattering path at $R = 3.68$ Å not described previously, which is the distance expected for Cu sorbing to the edge sites via a bidentate corner-sharing linkage (DC complex) (Fig. 3) (Manceau et al. 2007). An inspection of all data reveals that this contribution is always present, but its contribution to the EXAFS signal is negligible in HBi because the fractional amount of the layer-edge complex is low because of the large layer dimension. Thus, peak C in reality is a doublet made of the TC and DC complexes, which is only resolvable when the sorbent surface has a smaller fraction of vacancy sites (TC complex) relative to edge sites (DC complex) available for surface complexation.

Three micro-Cu-EXAFS spectra were recorded on the nodule thin section: one in regions rich in smectite (Map 1), one in a diagenetic vein rich in 10 Å vernadite and poor in todorokite as indicated by µ-XRD (Map 2), and one on concentrated Cu areas from diagenetic regions containing high amounts of todorokite (Map 1). From the comparison of the three EXAFS spectra shown in Figure 12a, it is clear that Cu is bound differently in the three regions. The EXAFS collected in the organo-clay matrix is featureless with the signal made of only one electronic wave from the Cu-O coordination shell. The two other spectra show a second wave oscillation at $k = 5.5$ Å^{-1}, which occurs when there is a metal shell beyond the oxygen shell. The Fourier transform of the first spectrum confirms that the local order is limited to the nearest-neighbor shell of oxygen, which we attribute to disorder arising from the multiplicity of the binding Cu environments (Fig. 12b). Ferromanganese nodules from abyssal plains typically contain organic matter and biogenic silica, phosphates, and carbonates (Peacock and Sherman 2007a; Hein et al. 2012), which may take up Cu (and also Ni) in addition to aluminosilicates and Fe-Mn oxides (Boström and Nayudu 1974; Boström et al. 1974). The Fourier transform for 10 Å vernadite shows evidence for a Cu-Mn scattering best modeled with 1.6 Mn at 2.88 Å (Supplementary Fig. 10[1]). Copper has become structurally incorporated into the $\mathrm{MnO_2}$ layer by occupying some vacancy sites. However, the low number of Mn neighbors, which nominally should be six if all the Cu were in the $\mathrm{MnO_2}$ layer, suggests that the diagenetic vein has an abundant hydrogenetic component. In the highly diagenetically transformed region of the nodule, a second Mn shell at a distance characteristic of corner-sharing linkage (peak C) is detected. Because the analyzed spots have high amounts of todorokite, the likely origin of this feature is the incorporation of Cu into todorokite, similarly to Ni.

Chemical formulas and metal uptake capacity of todorokites

Because todorokite is the stable phase and its amount is correlated positively with the Mn/Fe ratio, an average chemical formula can be calculated from the three nodule spots with the highest value of the Mn/Fe ratio (>100), as measured by electron microprobe analysis (Fig. 4; Supplementary Table 1[1]). The three point formulas obtained by balancing the charges on the cations in the framework sites (in parentheses) and tunnel sites are:

Mn/Fe (wt%) =216.50

$$\mathrm{Mg^{2+}_{0.222}Ca^{2+}_{0.041}K^{+}_{0.018}Na^{+}_{0.007}(Mn^{4+}_{0.569}Mn^{3+}_{0.310}Co^{3+}_{0.001}Ni^{2+}_{0.078}Cu^{2+}_{0.043})O_2{\cdot}\mathit{n}H_2O}$$

Mn/Fe (wt%) =160.86

$$\mathrm{Mg^{2+}_{0.204}Ca^{2+}_{0.046}K^{+}_{0.026}Na^{+}_{0.016}(Mn^{4+}_{0.568}Mn^{3+}_{0.321}Co^{3+}_{0.003}Ni^{2+}_{0.067}Cu^{2+}_{0.042})O_2{\cdot}\mathit{n}H_2O}$$

Mn/Fe (wt%) =102.00

$$\mathrm{Mg^{2+}_{0.199}Ca^{2+}_{0.042}K^{+}_{0.023}Na^{+}_{0.012}(Mn^{4+}_{0.602}Mn^{3+}_{0.278}Co^{3+}_{0.002}Ni^{2+}_{0.082}Cu^{2+}_{0.036})O_2{\cdot}\mathit{n}H_2O}$$

which average to:

$$\mathrm{Mg^{2+}_{0.208}Ca^{2+}_{0.043}K^{+}_{0.022}Na^{+}_{0.012}(Mn^{4+}_{0.580}Mn^{3+}_{0.303}Co^{3+}_{0.002}Ni^{2+}_{0.076}Cu^{2+}_{0.040})O_2{\cdot}\mathit{n}H_2O.}$$

Based on the crystal structure of todorokite, the cations in the tunnel interior cannot exceed a total of 1.0 cation per unit cell, which corresponds to a ratio of tunnel to framework cations of ⅙ (Post and Bish 1988; Lei 1996). Two chemical formulas have been proposed for terrestrial todorokites, one by Gutzmer and Beukes (2000):

$$\mathrm{Mg^{2+}_{0.07}Ca^{2+}_{0.03}Na^{+}_{0.06}K^{+}_{0.01}(Mn^{4+}_{0.80}Mn^{3+}_{0.17}\square_{0.02}Fe^{3+}_{0.01}Al^{3+}_{0.01})O_2{\cdot}0.55H_2O}$$

and another by Post et al. (2003)

$$\mathrm{Mg^{2+}_{0.07}Ca^{2+}_{0.02}Na^{+}_{0.07}(Mn^{4+}_{0.73}Mn^{3+}_{0.27})O_2{\cdot}0.7H_2O.}$$

In both cases, the amount of tunnel cations is equal to the number of tunnel sites available per formula unit (0.16 ≈ ⅙). The excess of tunnel cations in our calculated formula [(0.208 + 0.043 + 0.022 + 0.012) – ⅙ = 0.12] can be explained by the common association of todorokite with the authigenic zeolite phillipsite in marine nodules (Burns and Burns 1978a; Lei and Lee 1998; Bodeï et al. 2007). Lee and Lee (1998) proposed the following formula for phillipsite in manganese nodules of the northeastern equatorial Pacific basin:

$$\mathrm{Mg^{2+}_{0.3}Ca^{2+}_{0.1}Na^{+}_{1.1}K^{+}_{1.5}(Fe_{0.3}Al_{4.2}Si_{11.8})O_{32}{\cdot}10H_2O.}$$

Assuming that Na, K, Ca and the excess Mg are in phillipsite and other mineral impurities, the chemical formula for the nodule todorokite studied here can be recalculated as:

$$\mathrm{Mg^{2+}_{0.167}(Mn^{4+}_{0.783}Mn^{3+}_{0.099}Co^{3+}_{0.002}Ni^{2+}_{0.076}Cu^{2+}_{0.040})O_2{\cdot}\mathit{n}H_2O.}$$

The proposed formula is supported by the inter-element relationship in Figure 4c, which shows that Na has no, K little, and Ca a negative correlation with the Mn/Fe ratio; hence are not associated with todorokite. By analogy with the nodule todorokite, the hydrothermal marine todorokite studied by Bodeï et al. (2007) also can be considered to be saturated by Mg. Accordingly, its formula proposed originally

$$\mathrm{Mg^{2+}_{0.178}Ca^{2+}_{0.013}K^{+}_{0.019}(Mn^{4+}_{0.612}Mn^{3+}_{0.356}Ni^{2+}_{0.032})O_2{\cdot}\mathit{n}H_2O}$$

can be recalculated as:

$$\mathrm{Mg^{2+}_{0.167}(Mn^{4+}_{0.699}Mn^{3+}_{0.269}Ni^{2+}_{0.032})O_2{\cdot}\mathit{n}H_2O.}$$

The nodule todorokite is strongly enriched in Ni and Cu and has a (Ni+Cu+Co)/Mn ratio of 0.13, which is slightly lower than the ~0.167 (or about ⅙) upper limit suggested by Usui (1979) from bulk nodule analyses. The highest metal uptake capacity is reached when the 0.167 tunnel sites are all occupied by a divalent cation (mostly $\mathrm{Mg^{2+}}$) and when the low-valence octahedral cations that balance the intratunnel charge of +0.33e are all $\mathrm{Ni^{2+}}$ and $\mathrm{Cu^{2+}}$ cations, without $\mathrm{Mn^{3+}}$. Last, it is worthwhile comparing the cationic composition of the todorokite framework $\mathrm{(Mn^{4+}_{0.783}Mn^{3+}_{0.099}Co^{3+}_{0.002}Ni^{2+}_{0.076}Cu^{2+}_{0.040})}$ to the Mn valence composition of 10 Å vernadite $\mathrm{(Mn^{4+}_{0.61}Mn^{3+}_{0.23}Mn^{2+}_{0.016})}$. One notes that $[\mathrm{Mn^{3+}}]$ in 10 Å vernadite $\approx \Sigma([\mathrm{Mn^{3+}}] + [\mathrm{Co^{3+}}] + [\mathrm{Ni^{2+}}] + [\mathrm{Cu^{2+}}])$ in todorokite, which supports the view that these other metals substitute for Mn^{3+} in the edge sites of the todorokite framework (Fig. 1) (Burns et al. 1985; Post et al. 2003).

IMPLICATIONS

To date, there is a regain of interest in mining marine metal deposits (Co, Ni, Cu, Li, Mo, REEs…) to augment the production from land-based deposits (Hein et al. 2013). A good understanding of the forms and enrichment mechanisms of these elements in crust-nodule ferromanganese deposits is a necessary prerequisite for the effective mining and optimal processing of this resource. The present study shows how the mineralogy of polymetallic nodules on sediment-covered abyssal plains controls the concentration of metals and how the mineralogy is modified diagenetically by geochemical reactions that occur in suboxic conditions at the sediment-water interface.

We showed that metallifeous 10 Å vernadite in diagenetic veins of the hydrogenetic nodule is composed of non-collapsable and collapsable (to 7 Å) vernadite crystallites, which we interpret to indicate that the first have Mg^{2+} and todorokite pillars in the interlayer, whereas the second have none of those (Sun et al. 2012). The 10 Å vernadite also has better crystallinity and more reduced Mn cations (Mn^{2+} and Mn^{3+}) than the adjacent Fe-vernadite in the unaltered hydrogenetic nodule, which indicates that 10 Å vernadite precipitated directly from solution. The as-formed 10 Å vernadite is metastable and is eventually replaced by todorokite via topotactic transformation.

Our results do not confirm the suggested existence in authigenic 10 Å vernadite of "buserite-II" phyllomanganate layers, which are characterized by a high proportion of Mn (and possibly other transition metals) as interlayer cation (Fig. 2) (Novikov and Bogdanova 2007; Pal'chik et al. 2011). The absence (or scarcity) of interlayer Mn in unpillared vernadite is consistent with the pH-dependence of the δ-MnO_2 structure, which shows that the proportion of interlayer Mn is low at the seawater pH of ~8 and high at acidic pH (Manceau et al. 2013). Neither orderly stacked birnessite (7 Å manganate) nor asbolane-type mix-layers (10 Å manganate), which occur in hydrothermal deposits (Supplementary Fig. 6[1]), were identified.

Here, we also documented for the first time the diversity of the Cu coordination environments in manganese nodules. In the organo-clay matrix, Cu appears to be bound in several forms, as indicated by the lack of Cu-metal signal by EXAFS. This pool likely includes organically complexed Cu, which eventually becomes available for uptake in authigenic 10 Å vernadite and todorokite during dissimilatory bio-oxidation of organic material and concomitant reduction of hydrogenetic vernadite (Burns and Burns 1978b; Lovley and Philips 1988). The incorporation of Cu^{2+} in Mn^{3+}-containing 10 Å vernadite and todorokite is favored by the Jahn-Teller distortion of the $[CuO]_6$ coordination environment. Finally, the Co, Ni, and Cu *K*-edge EXAFS spectra are provided as supplementary material to facilitate further identification of metal coordination environments in Mn oxides.

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