

Distribution and evolution of manganese minerals in polymetallic nodules from the Clarion-Clipperton Fracture Zone: implications for nickel and copper enrichment

Zedong Fan^{a,b}, Xiaohu Li^{a,b,*}, Yanhui Dong^b, Bruno Lanson^c, Zhongkuan Wu^d, Weilin Ma^b, Zhenggang Li^b, Junming Zhou^e, Yi Ding^f, Hao Wang^b, Zhimin Zhu^b, Jie Li^b, Xingwei Meng^b, Huaiming Li^b, Fengyou Chu^b

^a School of Oceanography, Shanghai Jiao Tong University, 200240 Shanghai, China

^b State Key Laboratory of Submarine Geoscience, Second Institute of Oceanography, Ministry of Natural Resources, Hangzhou 310012, China

^c Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, IRD, Univ. Gustave Eiffel, ISTERre, F-38000 Grenoble, France

^d College of Environment, Zhejiang University of Technology, Hangzhou 310014, China

^e Hong Kong Branch of Southern Marine Science and Engineering Guangdong Laboratory (Guangzhou), Hong Kong University of Science and Technology, Hong Kong SAR 999077, China

^f Changzhi University, Changzhi 046011, China

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ABSTRACT

Mn oxides in polymetallic nodules act as pivotal reservoirs for Ni and Cu, governing the biogeochemical cycling of these metals in marine environments. However, accurate identification of Mn-oxide phases—such as buserite, asbolane, and todorokite—remains challenging due to their similar X-ray diffraction characteristics. By applying an integrated mineralogical approach, this study elucidates the distribution and mineralogical controls of Ni and Cu in two diagenetic nodules from the Clarion-Clipperton Fracture Zone. Our results demonstrate a distinct mineralogical zonation: todorokite is predominantly concentrated in the inner layers (constituting up to ~ 68% of the Mn-oxide assemblage), while the outer layers are dominated by 10 Å vernadite (buserite) and asbolane. XANES analysis reveals a significantly higher proportion of Mn(III) in the inner layers (15–25%) compared to the outer layers (8–10%). This Mn(III) enrichment, which we interpret as resulting from early nodule growth under high-productivity-driven suboxic conditions, likely promotes the transformation of 10 Å vernadite into todorokite. This mineralogical transition induces to a 40–50% decrease in Ni content in the inner layer, consistent with the lower compatibility of Ni in the todorokite structure. In contrast, Cu²⁺, as a Jahn-Teller active element, appears to be compatible with the todorokite structure and exhibits similar contents in both todorokite and asbolane. As nodule growth proceeds into more oxic environments, the Increased Stability of Mn(IV), most likely inhibited tectomanganate formation and may have favored the phyllosmanganate stability. Furthermore, the precipitation metal (hydr)oxides in phyllosmanganate interlayers could have led to the asbolane formation. Collectively, our findings underscore that fine-scale mineralogical characterization is indispensable for deciphering the distinct biogeochemical behaviors of Ni and Cu governed by specific Mn oxides.

1. Introduction

In marine ferromanganese nodules, the predominant Mn-bearing minerals systematically exhibit a ~ 10 Å periodicity (Burns and Burns, 1978). These mineral species are enriched in transition metal elements, such as Ni, Cu (Hein et al., 2020), and Zn (Marcus et al., 2004), at levels up to ~ 10⁶ times greater than those in seawater (Koschinsky and Hein,

2003), and thus serve as a significant sink and source for these elements within the modern marine geochemical cycle (e.g. Atkins et al., 2016; Du et al., 2025).

Although Mn-oxide mineralogy in polymetallic nodules has long been confusing and controversial, 10 Å manganates that prevail in these environments have been categorized into two main types for decades: layered (phyllosmanganates) and tunnel-structured (tectomanganates)

* Corresponding author at: School of Oceanography, Shanghai Jiao Tong University, 200240 Shanghai, China.

E-mail address: xhli@sio.org.cn (X. Li).

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Mn oxides (Burns et al., 1983; Post and Bish, 1988; Bodeř et al., 2007; Peacock and Sherman, 2007). The most common tectomanganate identified in ferromanganese nodules, todorokite that ideally exhibits a 3×3 tunnel structure, has consistently been recognized to originate from phylломanganate precursors (Burns and Burns, 1978; Bodeř et al., 2007; Cui et al., 2009; Feng et al., 2010; Xu et al., 2010; Węgorzewski et al., 2020). Due to the coexistence of different tunnel sizes (Siegel and Turner, 1983; Post et al., 2003; Bodeř et al., 2007), its signature peaks in X-ray diffraction (XRD) patterns are usually poorly resolved, with peaks typical for the ~ 10 Å periodicity being most prominent and the sole to be clearly defined (Węgorzewski et al., 2015). These ~ 10 Å peaks, and harmonics thereof, are common however to todorokite and some phylломanganate species (Burns et al., 1983; Bodeř et al., 2007; Feng et al., 2010; Wu et al., 2021), often leading to an ambiguous identification of ~ 10 Å manganates in natural samples (e.g. Węgorzewski and Kuhn, 2014; Węgorzewski et al., 2015; Li et al., 2020; Su et al., 2023; Cheng et al., 2023).

The mineral transformation involving phylломanganate precursors and todorokite, along with their interactions with elements like Cu and Ni, exerts a key control on nodule mineralogy, the distribution of these transition metals, and their geochemical cycling (Manceau et al., 2014; Atkins et al., 2016). Recent studies have further demonstrated that the phyllo- to tectomanganate transformation also governs the selective isotopic fractionation of Ni (Little et al., 2020; Chen et al., 2025). The initial presence of Cu (II) and Mn (III) in phylломanganate precursors favor the formation of tectomanganate “walls” as the migration of these Jahn-Teller distorted cations from octahedral MnO_2 layers alleviate steric strains (Atkins et al., 2014; Atkins et al., 2016; Grangeon et al., 2014; Grangeon et al., 2015). Conversely, the presence of Ni, that possesses a symmetrical octahedral coordination, sorbed to the phylломanganate birnessite hampers its transformation to todorokite (Atkins et al., 2016). Furthermore, the presence of Ni species weakly bound [hydrated Ni, Ni (hydr)oxides] to phylломanganates could hinder Mn (III) migration from the octahedral layers, inhibiting subsequent tectomanganate formation (Wu et al., 2020).

Todorokite formation is well-recognized in specific marine settings, such as hydrothermal nodules (Usui et al., 1989; Bodeř et al., 2007), buried nodules (Węgorzewski et al., 2020), and diagenetic microlayers (Siegel and Turner, 1983; Martin-Barajas et al., 1991; Manceau et al., 2014; Zhou et al., 2024). In contrast, surficial manganese nodules, the most widespread deposits globally, are generally thought to be Todorokite-poor (Węgorzewski and Kuhn, 2014; Węgorzewski et al., 2015). This conventional view is attributed to low Mg^{2+} concentrations, which is a cation critical for determining tunnel size during its crystallization (Bodeř et al., 2007), coupled with the low thermodynamic stability of Mn oxides under such oxic conditions (Węgorzewski and Kuhn, 2014; Węgorzewski et al., 2015; Heller et al., 2018; Węgorzewski et al., 2020). However, significant concentrations of Ni and Cu exhibit considerable variations both across global nodule fields (Dymond et al., 1984; Hein et al., 2020) and at a fine scale within individual nodules (Węgorzewski and Kuhn, 2014; Su et al., 2023), suggesting the presence of unresolved mineralogical controls and potential phase changes. Resolving this paradox has been challenging due to the limited number of high-resolution mineralogical studies on surface nodules (Manceau et al., 2014; Węgorzewski et al., 2015). Consequently, the distribution of todorokite in these surficial deposits remains poorly documented, and the primary factors controlling tectomanganate formation and associated transition metal behavior are still inadequately constrained.

Nodules in the Central and Eastern Clarion-Clipperton Fracture Zone (CCFZ), are characterized by high Mn contents (Węgorzewski and Kuhn, 2014; Węgorzewski et al., 2015; Heller et al., 2018; Menendez et al., 2019) and represent a major global province of mixed hydrogenetic-diagenetic origin (Węgorzewski and Kuhn, 2014). They encompass the complete spectrum of Mn oxides formed under hydrogenetic, oxic diagenetic, and suboxic diagenetic processes (Dymond et al., 1984; Hein et al., 2020; Fan et al., 2024). This provides an exceptional foundation

for a detailed mineralogical segmentation of nodule profiles, thus offering insights into the global distribution and mineralization of Mn oxides. In the present study, the mineralogy and crystal-chemistry of two representative diagenetic nodules from the CCFZ was determined using X-ray diffraction combined with a variety of pre-treatments, transmission electron microscopy, and X-ray absorption spectroscopy. In addition, distributions of elements was determined using electron probe micro-analysis and laser-ablation coupled to mass spectrometry. These informations were combined to decipher the environmental factors controlling the nature, distribution, and evolution of Mn oxides in these deep ocean contexts together with the impact of mineral (trans-)formation on the geochemical behavior of Ni and Cu.

2. Manganese mineralogy in ferromanganese nodules

Two different mineral species, the phylломanganate busserite and tectomanganate todorokite have long been recognized as the dominant Mn-bearing phases in polymetallic nodules (Burns et al., 1983). The presence of a third mineral species, asbolane, being reported a few years later by the same group of authors (Burns et al., 1985) based on earlier reports (Chukhrov et al., 1982a; Chukhrov et al., 1982b). All three mineral species exhibit a prominent ~ 10 Å periodicity in their diffraction patterns, thus often rendering their identification ambiguous, especially as, at the time, robust structure models were lacking for these mineral species. Although Wadsley (1950) had reported the formation of a 10 Å Mn oxides from the oxidation of fresh $\text{Mn}(\text{OH})_2$ suspension, the identification of busserite as a phylломanganate hosting two planes of interlayer H_2O molecules, that is a hydrated equivalent of birnessite/vernadite, was proposed only a couple decades later (Giovanoli and Bürki, 1975). At about the same time, the same group of authors hypothesized a similar layered structure for a series of busserite samples exchanged with alkali-earth (Ca^{2+} , Mg^{2+}) and transition metal (Zn^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+}) cations, based on the similarity of their basal reflection positions (Giovanoli et al., 1975). They also noted an apparent increase of hydration stability of these exchanged busserite samples. Although the cation ionic potential strongly influences the hydration state of interlayer cations at given relative humidity conditions, this increased hydration stability may also result from the presence of island-like $\text{Me}(\text{OH})_2$ octahedral sheets in the interlayer region of MnO_2 layers, as in asbolane (Ploquin et al., 2019). Such asbolane structures were determined from HRTEM observations of nodule combined with electron diffraction and other techniques (Chukhrov et al., 1982a; Chukhrov et al., 1982b). In contrast to these two phylломanganates, Burns and Burns (1977) proposed a tunnel structure for todorokite, a hypothesis later confirmed by HRTEM observations revealing 3×3 tunnel units (Chukhrov et al., 1978; Turner and Buseck, 1981). The crystal structure of todorokite was subsequently refined using X-ray diffraction data (Post and Bish, 1988).

Owing to the ~ 10 Å periodicity common to all three mineral species, Burns et al. (1985) proposed to differentiate them using HRTEM, possibly in conjunction with other techniques. Although familiar with HRTEM, Chukhrov et al. (1984) suggested to use XRD on samples heated to ~ 100 °C to differentiate tectomanganate todorokite from phylломanganate busserite, owing to the swift dehydration of the later at this temperature. This method was later applied successfully by Manceau et al. (2007, e.g.). The persistent confusion between the two phylломanganates (busserite and asbolane) led to consider busserite and todorokite as the two main manganates in polymetallic nodules (Burns et al., 1983), asbolane being essentially overlooked despite its early description (Chukhrov et al., 1982a; Chukhrov et al., 1982b). This simple, but incomplete, differentiation between 10 Å tecto- and phylломanganates likely induced misidentifications of asbolane as todorokite. In todorokite, the intensity of the 9.6 – 10.0 Å diffraction maximum is stronger than that of the 4.8 – 5.0 Å peak (Frondelet et al., 1960; Post et al., 2003), whereas the reverse is true for asbolane, where the 9.6 – 10.0 Å peak is weaker than the 4.8 – 5.0 Å reflection (Chukhrov et al.,

1982b; Lorca, 1988; Wu et al., 2020). This contrast provides a basis for their differentiation. For example, the systematic low intensity of the 9.6–10.0 Å maximum compared to its 4.8–5.0 Å counterpart reported by Ching et al. (1999) for Mg-, Ni-, Co-, and Cu-todorokite suggest that synthesized products may in fact be asbolane-like. However, it should be noted that Byles et al. (2015) and Yuan et al. (2019) reported XRD patterns of todorokite in which the 4.8–5.0 Å maximum was significantly more intense than its 9.6–10.0 Å counterpart, despite an unambiguous imaging of the $3 \times n$ tunnel structure using HRTEM. To overcome this remaining ambiguity between asbolane and todorokite, Wu et al. (2019) proposed to combine XRD with an acid treatment designed to dissolve the interlayer island-like $\text{Me}(\text{OH})_2$ octahedral sheets.

Buserite type II is also supposed to exhibit a 10 Å periodicity that persists upon heating to 105–110 °C, similar to asbolane, due to a high density of interlayer cations located above and/or below layer vacancy sites (Novikov and Bogdanova, 2007; Pal'chik et al., 2013; Manceau et al., 2014). Like asbolane, buserite type II would also collapse to ~ 7 Å after the acid treatment proposed by, as a result of interlayer metal cation desorption. However, the structural model of buserite type II remains largely conceptual. To the best of the authors' knowledge, no experimental evidence has confirmed its natural occurrence, despite targeted investigations (Manceau et al., 2014). In addition, meaningfulness of this model is challenged, for example, by the ~ 7 Å periodicity exhibited by the natural phyllosulfate with the highest known Me:Mn ratio (e.g. Zn:Mn = 0.46 in a Zn–Ca phyllosulfate; Lanson et al., 2008).

Finally, Fe-vernadite has been reported to be another major mineral phase in laminated Mn–Fe oceanic crusts (e.g. Lee et al., 2019) and hydrogenetic nodules (e.g. Ren et al., 2022). As proposed by Chukhrov et al. (1987), Fe-vernadite is a nanocomposite material composed of intergrown ferrosulfate ($\delta\text{-FeSO}_4$) and monodispersed phyllosulfate layers having no interlayer Mn (Manceau et al., 2014). However, Fe-vernadite cannot be confused with ~ 10 Å manganates, as this heterogeneous phase exhibits no basal reflections in XRD patterns due to its monodispersed nature (Lee et al., 2019; Manceau et al., 2014).

3. Samples and methods

3.1. Samples and analytical methods

The two nodules investigated in this study, designated E-DY54 and C-DY50, were collected during survey cruises DY54 (2019) and DY50 (2018), respectively (Fig. 1). Nodule E-DY54 was sourced from the Eastern CCFZ (12.61°N, 138.55°W; water depth 4564 m), while nodule C-DY50 originated from the Central CCFZ (12.61°N, 138.55°W; water depth 5022 m) (Fig. 1). Furthermore, geochemical data were compiled (Table S3) from bulk nodules collected at 14 stations within the CCFZ-East. All nodules were collected from water depths systematically exceeding the carbonate compensation depth (~ 4500 m) in a region where siliceous clays represent the predominant sediment type.

Nodule E-DY54 ($10 \times 9.5 \times 5$ cm) is cauliflower-shaped and exhibits a surface texture characterized by grape-like structures. Similarly, Nodule C-DY50 ($6 \times 4 \times 3.6$ cm) is also cauliflower-shaped and displays numerous protuberances, particularly along the equatorial plane at the seawater-sediment interface. Following collection, the nodules were stored at 4 °C to approximate in-situ seafloor conditions prior to analysis.

For analytical preparation, the nodules were embedded in epoxy resin and sectioned longitudinally. Each sample was then divided into two portions: one was micro-drilled to obtain powder samples from individual growth layers for mineralogical analysis, while the other was polished and prepared as thin-sectioned (100 μm) for geochemical characterization.

3.2. Powder X-ray diffraction (PXRD)

The mineralogical composition of the Nodules was determined by XRD using a Bruker AXS D8 Advance diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406$ Å) at the Instrumentation and Service Center for Physical Sciences at Westlake University (Hangzhou). Analyses were conducted on randomly oriented powder samples over a 2θ angular range of 5° to 70° with a step size of 0.02° and a counting time of 0.5 s per step (scan rate of 2.4°/min). These samples were analyzed under three conditions: i) as an untreated powder, ii) after heating to 110 °C and 300 °C, and iii) after acid treatment. For the acid-treated aliquot, 20 mg of sample (previously heated to 110 °C) was placed in an acid-washed ground-mouth Erlenmeyer flask. It was then reacted with 250

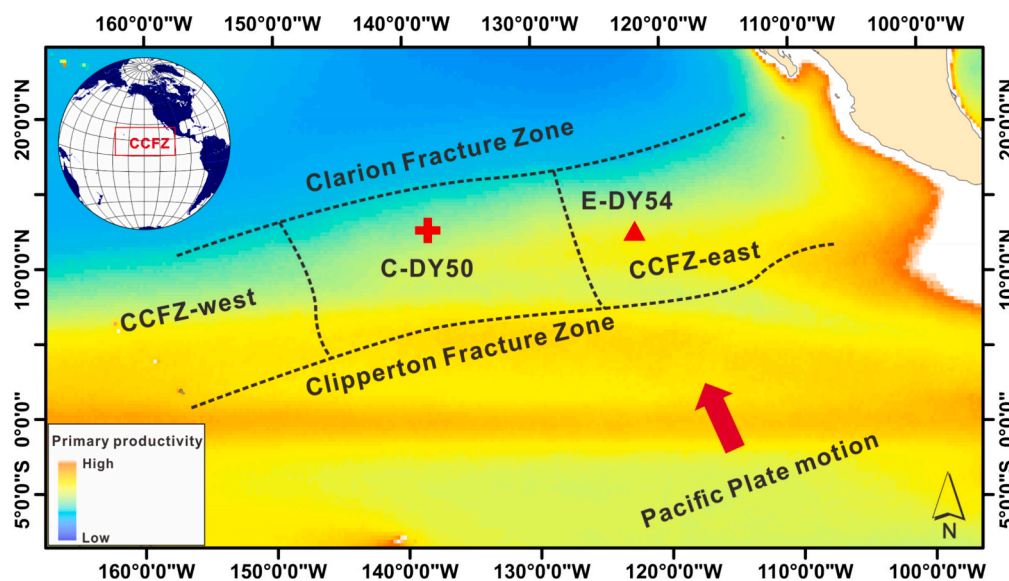


Fig. 1. Sampling locations of the two polymetallic nodules analyzed in this study. The nodules designated as C-DY50 and E-DY54 (marked by a cross and a triangle, respectively) were sampled in an area characterized by significantly higher primary productivity compared to the sampling sites from the western Clarion–Clipperton Fracture Zone (CCFZ–West). The tectonic context of the study area involves the northwestward motion of the Pacific Plate (MacLeod et al., 1996).

mL of a 1 M HNO_3 solution at room temperature under continuous stirring for 36 h. The resulting suspension was filtered through a 0.22 μm membrane, and the residue was dried at 40 °C prior to XRD analysis (Wu et al., 2020). All experimental steps were conducted in an ultra-clean laboratory.

3.3. High-resolution transmission electron microscopy (HRTEM)

The crystal structures of Mn oxides in the nodules were further characterized using an FEI Talos F200S field-emission transmission electron microscope at the Sinoma Institute of Materials Research (Guangzhou) Co., Ltd (SIMR). The instrument, operated at an acceleration voltage of 200 keV, was equipped with two SuperX high-resolution energy-dispersive X-ray spectroscopy (EDS) detectors and a high-angle annular dark-field (HAADF) detector, providing a spatial resolution of approximately 0.16 nm in scanning transmission electron microscopy (STEM) mode.

A focused ion beam (FIB) was used to prepare a thin section from sample E-DY54-L1 (Fig. 2a). The specimen was initially thinned to ~150 nm using a 30 kV ion beam and subsequently cleaned and further thinned to 50–70 nm at 5 kV for high-resolution TEM observation

3.4. Laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS)

The major and trace element contents and their spatial distributions within the nodules were determined by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) using a NWR 193 nm ArF excimer laser system coupled to an iCAP RQ ICP-MS. The laser was operated with a spot size of 100 μm , a scan speed of 120 $\mu\text{m/s}$, a fluence of 3.5 J/cm², and a repetition rate of 15 Hz. The ICP-MS was calibrated using NIST 610 and NIST 612 reference glasses. The resulting spatial data were processed using Iolite software and subsequently segmented according to the distinct growth layers of the nodules in ArcMap 10.8 for stratified analysis.

3.5. Electron microprobe analysis (EMPA)

In-situ microanalysis of major elements was conducted using a JEOL JXA-iSP100, an accelerating voltage of 15 kV, a beam current of 20 nA (Li et al., 2020), and a beam spot size of 5 μm . All data were baseline-corrected using the ZAF method. The calibration standard samples included the MAC mineral/metal standards and GSB Chinese national standard. Regions of interest were selected from relatively homogeneous

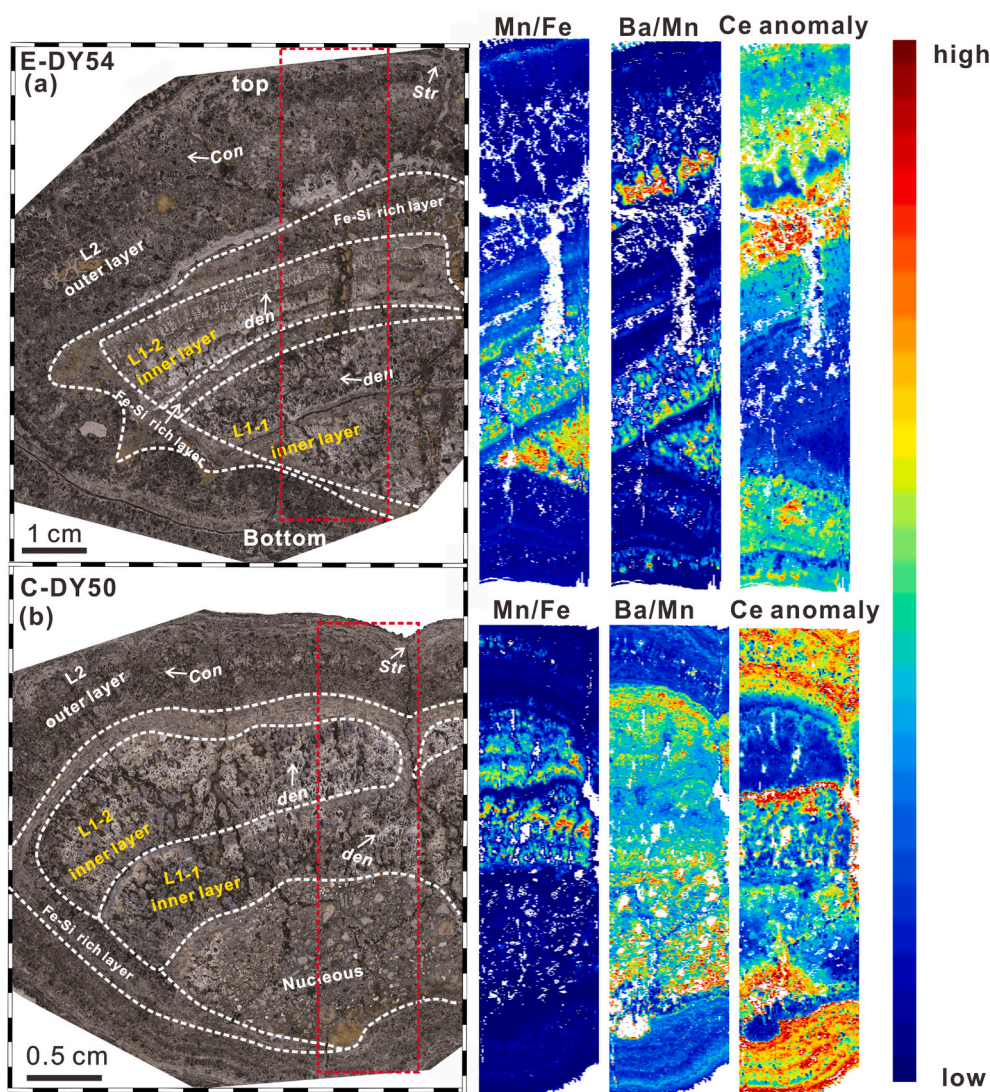


Fig. 2. Nodule photographs under reflective light (a, b); dashed lines represent boundaries between the main growth layers, red boxes denote the areas scanned using LA-ICP-MS, den: dendritic structures; con: concentric structures; str: stromatolite structures.

areas of Mn-oxides within the nodules.

3.6. X-ray absorption spectroscopy (XAS)

The oxidation state and local coordination environment of manganese were characterized using X-ray absorption spectroscopy at beamline 4B9A of the Beijing Synchrotron Radiation Facility (BSRF). Measurements were performed in transmission mode at room temperature, with energy calibration referenced to a Mn foil standard.

The Mn Average Oxidation State (AOS) and the relative proportions of Mn(II), Mn(III), and Mn(IV) in individual growth layers were determined using the Combo method (Manceau et al., 2012). This method involves linear fitting of the first-derivative Mn K-edge X-ray absorption near-edge structure (XANES) spectra using spectra of reference materials with known valence states, with an estimated error of $\pm 4\%$. The Mn K-edge extended X-ray absorption fine structure (EXAFS) data was

processed using the Athena software, covering a k -range of 3.06–12.7 $\text{\AA}^{-1}$. Path simulations were carried out in Artemis in R -space from 1 to 4 $\text{\AA}$, with an amplitude reduction factor (S_0^2) set to 0.8 (Grangeon et al., 2010). In addition, Linear Combination Fitting (LCF) was applied to the Mn K-edge EXAFS spectra of layers L1 and L2, using reference spectra of layer-structured hexagonal birnessite (Bir Hex) and tunnel-structured todorokite (Tod), respectively, to quantify mineral phase proportions. The fitting was performed in k -space over the range of 3–12 $\text{\AA}^{-1}$.

4. Results

Both nodules comprise two primary growth layers, designated L1 (inner layer) and L2 (outer layer), which extend continuously from the nucleus to the outer surface (Fig. 3a and b). A prominent hiatus and angular unconformity are evident between L1 and L2, accompanied by the development of an intervening Fe–Si-rich layer (Fig. 3a and b).

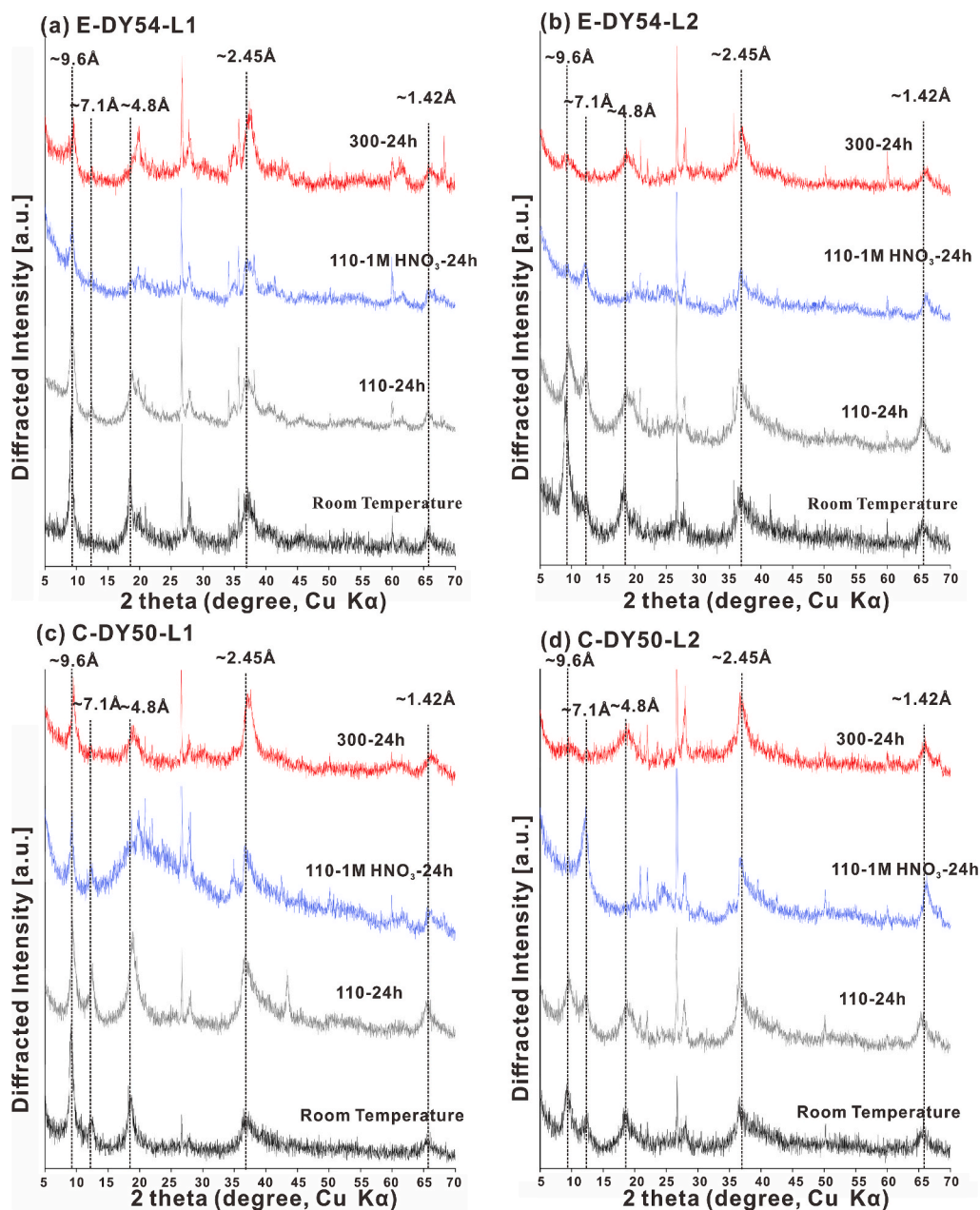


Fig. 3. XRD patterns of E-DY54 (a, b) and C-DY50 (c, d). For each sample, patterns were collected after drying at room temperature (black), after heating to 110 °C for 24 h (grey), after acid leaching of the sample previously heated to 110 °C for 24 h (blue), and after heating of the sample to 300 °C (red).

Internally, L1 is characterized by dendritic textures and high porosity, while L2 displays stromatolitic and concentric structures.

4.1. Mineralogy of individual growth layers in nodules

4.1.1. XRD

The powder XRD patterns of both nodules are dominated by prominent reflections at ~ 9.6 Å, ~ 4.8 Å, ~ 2.45 Å, and ~ 1.42 Å (Fig. 4), consistent with 10 Å manganates such as todorokite, busserite, and asbolane, as commonly identified in marine polymetallic nodules (e.g. Manceau et al., 2014; Wegorzewski et al., 2020). A ~ 7.1 Å peak is also observed in samples C-DY50 (Fig. 4c and d) and E-DY54-L2 (Fig. 4b), indicating the presence of 7 Å phyllomanganates (e.g. birnessite/vernadite). Additional sharp peaks at ~ 3.34 Å and ~ 3.66 Å further suggest the occurrence of quartz and phillipsite.

After drying at 110°C , the intensity of the ~ 9.6 Å peak decreased in all samples except E-DY54-L1 (Fig. 4a), accompanied by a slight shift toward smaller d-spacings and an enhancement of the ~ 7.1 Å reflection. This collapse is attributed to the loss of one interlayer water plane from 10 Å phyllomanganate (busserite/10 Å vernadite), resulting in the transformation to birnessite (e.g. Wadsley, 1950; Burns et al., 1983; Post and Veblen, 1990; Shen et al., 1993). Upon further heating to 300°C , the intensity of the ~ 9.6 Å reflection decreased in the L1 of both nodules, whereas the ~ 4.8 Å reflection remained largely unchanged. Collectively, these results indicate that the 10 Å manganate phase is the dominant component in both L1 and L2, yet their thermal behaviors differ significantly.

Based on the distinct thermal behaviors observed between the layers, the nitric acid treatment method proposed by Wu et al. (2019) was employed to remove island-like (hydr)oxide octahedral sheets from the phyllomanganate interlayers. This treatment resulted in a near-complete collapse of the ~ 9.6 Å reflection in both C-DY50-L2 and E-DY54-L2,

accompanied by a pronounced increase in intensity of the ~ 7.1 Å peak (Fig. 4b and d). In contrast, samples from L1 (C-DY50-L1 and E-DY54-L1) showed negligible changes in both the ~ 9.6 Å and ~ 7.1 Å peak intensities (Fig. 4a and c).

The marked difference in acid response suggests that the L2 layers contain a higher proportion of asbolane-like phyllomanganates. These phases demonstrate relatively high thermal stability under mild heating ($\sim 110^\circ\text{C}$) compared to busserite, yet their interlayer (hydr)oxide islands are susceptible to acidic dissolution, leading to structural collapse. Conversely, the L1 layers are likely enriched in todorokite, whose tunnel-like framework is thought to confer greater resistance to both thermal and acid treatments.

4.1.2. Mn K-edge XAS

Compositional and spectral analyses reveal distinct manganese oxidation states and local structures in the two growth layers. The Mn Average Oxidation State (AOS) is notably lower in L1 (3.70–3.81) than in L2 (3.89–3.91), corresponding to a higher proportion of Mn^{3+} in L1 (16–26%) relative to L2 (8–10%; Table 2). These differences suggest contrasting redox environments during layer formation.

The Mn K-edge EXAFS spectra further reflect structural divergence between the layers. L1 exhibits reduced amplitude, peak splitting, and a low-k shoulder near $\sim 8\text{--}9\text{ Å}^{-1}$, features characteristic of todorokite (Fig. 5a). In contrast, L2 shows sharper oscillations at $\sim 6.8\text{ Å}^{-1}$, $\sim 8.0\text{ Å}^{-1}$, and $\sim 9.3\text{ Å}^{-1}$, indicative of more ordered phyllomanganate layers with hexagonal symmetry (McKeown and Post, 2001; Manceau et al., 2002) (Fig. 5a). Linear Combination Fitting (LCF) confirms a substantially higher todorokite content in L1 (28–68%) compared to L2 (0–8%; Table 3).

The Fourier-transformed Mn K-edge EXAFS spectra (Fig. 5b) exhibit two dominant peaks at approximately 1.5 Å and 2.5 Å ($R + \Delta R$). The first peak corresponds to the first-shell Mn–O scattering path, with a fitted

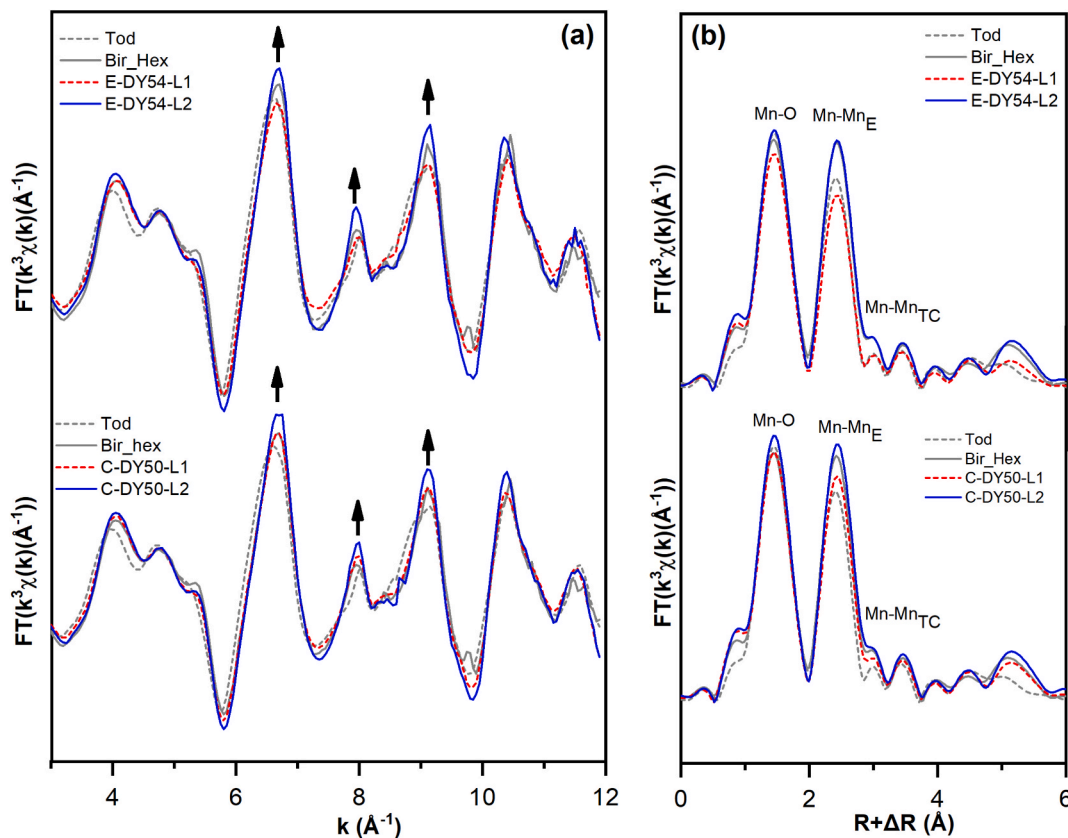


Fig. 4. Comparison of the Mn K-edge EXAFS spectra (a) and of corresponding Fourier transforms magnitudes (b) obtained on samples from different growth layers (L1, L2) with those of todorokite (Tod) and hexagonal birnessites (Bir_hex) references.

Table 1

Structural and Diffraction Characteristics of Mn oxides.

Mineral	Structure	Basal reflection	Thermal (100 °C)	Acid Treatment
Buserite type I	Phyllomanganate (hydrated)	~10 Å, ~4.8 Å	Collapses to ~ 7 Å	Collapses to ~ 7 Å
Buserite type II	Interlayer cations located above and/or below layer vacancy sites	~10 Å, ~4.8 Å	Stable	Collapses to ~ 7 Å
Fe-vernadite	Nanocomposite	No basal reflection	N/A	N/A
Asbolane	Phyllomanganate with interlayer Me(OH) ₂	~10 Å, ~4.8 Å	Stable	Collapses to ~ 7 Å
Todorokite	Tectomanganate (3 × 3 tunnel)	~10 Å, ~4.8 Å	Stable	Stable

Notes: N/A = Not Applicable.

Table 2

Fractional and average valence states of Mn in nodule individual layers obtained from the first derivative fitting of Mn K-edge XANES spectra (Combo method with an error of ± 4% – Manceau et al., 2012).

	E-DY54-L1	E-DY54-L2	C-DY50-L1	C-DY50-L2
Mn(II) (at.%)	3	1	2	1
Mn(III) (at.%)	26	10	16	8
Mn(IV) (at.%)	72	90	83	91
Mn-AOS	3.70	3.89	3.81	3.91

distance of ~ 1.90 Å (Table 4), while the second peak arises from edge-sharing Mn–Mn (Mn–Mn_E) interactions, fitted at ~ 2.89 Å (McKeown and Post, 2001; Webb et al., 2005). This Mn–Mn_E distance is consistent with the linkage between adjacent MnO₆ octahedra in both phyllomanganate layers and tectomanganate tunnel walls. A weaker third peak near 3.0 Å (R + ΔR) is attributed to corner-sharing Mn–Mn (Mn–Mn_C) scattering, with a modeled distance of 3.50–3.52 Å. This Mn–Mn_C signal may originate from Mn atoms at triple-corner sites above or below vacancies, double-corner sites at particle edges in phyllomanganates, or from the edges of triple-chain tunnel walls in todorokite (Manceau et al., 2007).

A comparative analysis between layers L1 and L2 reveals a distinct structural contrast. The intensity of the ~ 2.5 Å peak (Mn–Mn_E) is markedly lower in L1 than in L2 for both nodules, whereas the ~ 3.0 Å peak (Mn–Mn_C) is more pronounced in L1. Consistently, the fitting results show lower coordination numbers for edge-sharing Mn–Mn (CN_E) in L1. This reduction in CN indicates a smaller domain size of contiguous edge-sharing linkages, which is a structural signature typical for tunnel tectomanganates such as todorokite.

4.1.3. HRTEM

Mn oxides in L1 of E-DY54 exhibit a needle-like morphology (Fig. 5a), with a corresponding selected area electron diffraction (SAED) pattern displaying diffraction rings at ~ 5 Å, 2.4 Å and 1.4 Å (Fig. 5b). These rings indicate a defective crystal structure typical for manganates. At higher resolution (Fig. 5b), needles appear heterogeneous with alternation of tunnel-like and layered domains (Fig. 5c). Within the 10 Å phyllomanganate domains (Fig. 5c, D1), [MnO₆] octahedral sheets appear regularly spaced at ~ 9.6 Å intervals along the c* axis with a weaker contrast in between these sheets that possibly correspond to incomplete Me(OH)₂ octahedral sheets. The large extent of these domains also appears inconsistent with the presence of Fe-vernadite which is a nanocomposite material composed of intergrown ferroxhyte (δ-FeOOH) and monodispersed phyllomanganate layers, thus lacking periodicity perpendicular to the layer plane. Consistently, FFT patterns of these domains exhibit typical periodicity ~ 9.6 Å along the c* axis but the absence of discrete spots in other directions, typical for layer stacking disorder (Fig. 5d). On the other hand, the tunnel-like structures observed in the tectomanganate domains (Fig. 5c, D2) exhibit variable 3 × x tunnel sizes, with x varying typically from 3 to 5 [MnO₆] octahedral chains. Powder samples from L2 were also analyzed using HRTEM, but no tunnel-like structures or trilling of fiber-shaped crystals twinned at n × 120° from each other were observed (Fig. S2).

4.2. Chemical composition of individual growth layers in nodules

Geochemical analyses reveal systematic variations in elemental composition both regionally and within individual nodules. CCFZ-East nodules exhibit significantly higher concentrations of elements including Ni (1.17–1.59 wt%), Cu (0.90–1.53 wt%), Mg (1.53–2.27 wt%), and Ba (0.26–0.76 wt%), along with lower contents of Co (1744–2770 ppm) and rare earth elements plus yttrium (REY; 515–916 ppm) compared to hydrogenetic nodules from the Cook Islands region (Hein et al., 2015). CCFZ-West nodules display intermediate compositions, representing a transitional signature between the diagenetic (CCFZ-East) and hydrogenetic (Cook Islands) end-members (Fig. 6a).

LA-ICP-MS mapping reveals systematic geochemical contrasts between layers L1 and L2, consistent with EMPA trends in Mn/Fe ratios. The L1 layer is enriched in diagenetically sourced components, exhibiting higher Mn and Ba but lower Co and REY contents relative to L2 (Fig. 7b and c). A detailed comparison of Ni and Cu contents versus Mn/Fe ratios further indicates that L1 contains less Ni (E-DY54: ~0–1.7 wt%; C-DY50: ~0–3 wt%) yet similar Cu contents (~0–2.5 wt%) compared to L2 (Fig. 8c and d), resulting in significantly higher Cu/Ni ratios in L1 (Fig. 8e, f). Mn/Fe ratios are markedly higher in L1 (E-DY54: 0–75; C-DY50: 0–150) than in L2 (0–30 in both nodules; Fig. 7). Growth rate estimates derived from an empirical formula ($13.8 \times \text{Mn/Fe}^2 + 0.75$; Hun and Ku, 1984) indicate that L1 grew approximately ten times faster than L2, in agreement with its more pronounced diagenetic signature.

The origin of studied nodules may be deduced from the Mn–(Ni + Cu + Co) × 10–Fe ternary diagram of Bonatti et al. (1972). As shown in Fig. 8a, CCFZ-East nodules fall predominantly within the diagenetic field, in clear contrast to those from the CCFZ-West and Cook Islands regions which are mainly hydrogenetic.

Elemental profiling of nodule E-DY54 indicates a mixed hydrogenetic–diagenetic origin for both layers L1 and L2. However, L1 exhibits a substantially stronger diagenetic signature, marked by higher Mn content, lower total metal content (Ni + Cu + Co), and a lower average Mn oxidation state relative to L2 (Fig. 8b). These features are consistent with a greater contribution from suboxic diagenetic processes during the formation of L1.

5. Discussion

5.1. Improved determination and distribution of Mn mineralogy in ferromanganese nodules

Accurate determination of Mn oxide mineralogy in marine environments remains challenging owing to their similar XRD signature. These phases are primarily characterized by peaks at 9.6–10.0 Å and 4.8–5.0 Å, along with more diffuse peaks/bands corresponding to periodicities within octahedral layer fragments (~2.45 and ~ 1.42 Å) (e.g. Burns et al., 1983, 1985; Wegorzewski et al., 2020). To improve identification, additional treatments such as thermal treatment (Chukhrov et al., 1984) or acidic treatment (Wu et al., 2020) have been proposed. To our knowledge, this study represents the first application of a comprehensive suite of such treatments for the mineralogical characterization of Mn oxides in ferromanganese nodules.

Based on the XRD data (Fig. 3), L1 thus appears to contain significant

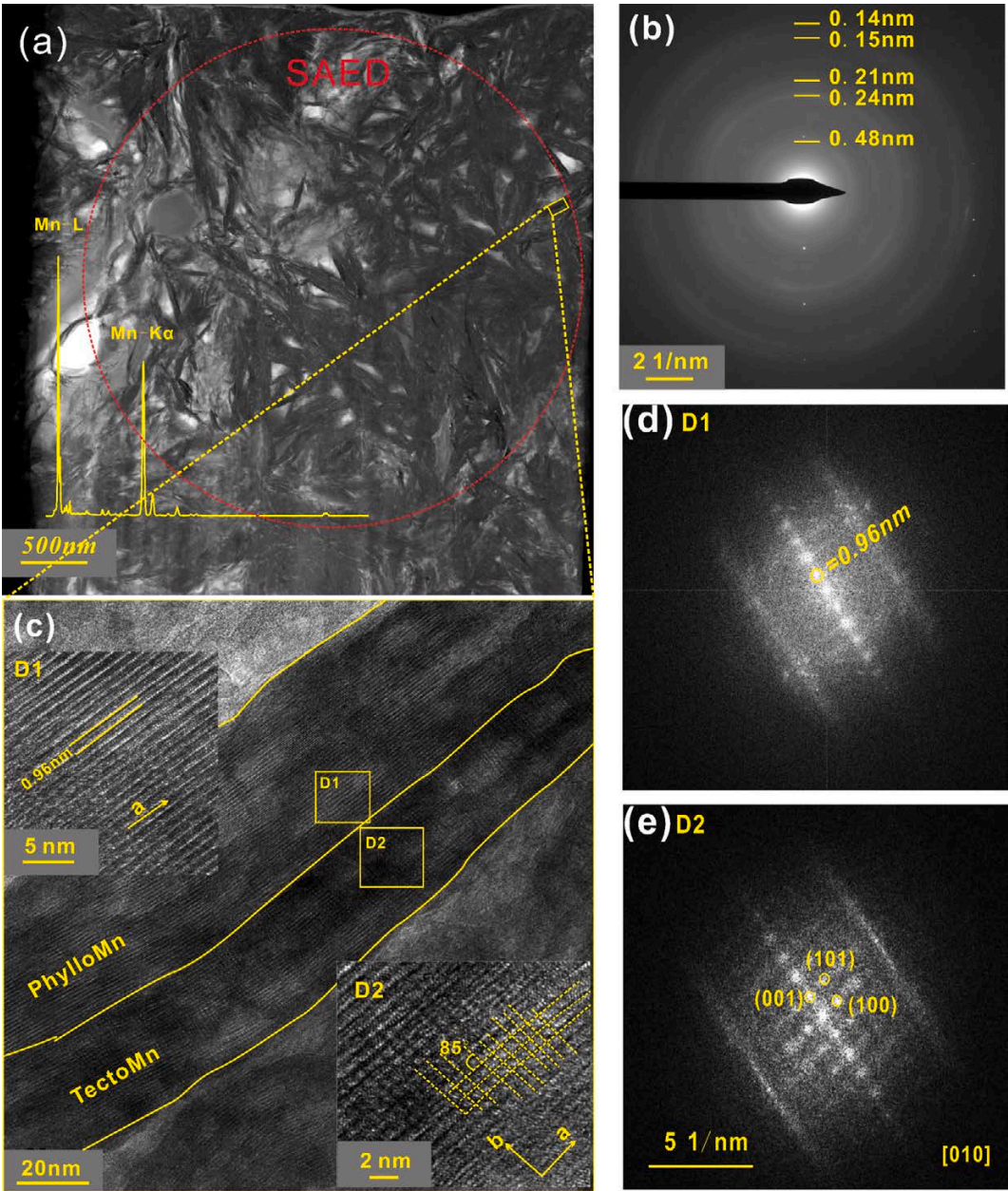


Fig. 5. Microstructural characterization of Mn oxides in the inner layer (L1) of nodule E-DY54. (a) TEM image of a FIB-prepared section. (b) SAED pattern acquired from the region marked by the red circle in (a), displaying polycrystalline diffraction rings corresponding to d-spacings of approximately 5 Å, 2.4 Å, and 1.4 Å, indicative of nanocrystalline Mn oxides. (c) HRTEM image from the area outlined in yellow rectangle in (a), revealing distinct domains of tunnel-structured tectomanganate (D2) and 10 Å phyllomanganate (D1). (d, e) (FFT) patterns derived from domains D1 and D2 in (c), respectively, confirming the periodicities of the layered and tunnel structures.

Table 3

Relative proportions of todorokite and 10 Å phyllomanganate in nodule individual layers as derived by fitting (LCF) Mn K-edge EXAFS spectra with todorokite and hexagonal birnessite reference spectra (Wu et al., 2020).

Reference mineral contribution	E-DY54-L1	E-DY54-L2	C-DY50-L1	C-DY50-L2
Todorokite (%)	68	8	28	0
Hexagonal birnessite (%)	32	92	72	100
Error	0.07	0.06	0.01	0.06

amounts of tectomanganates (todorokite), characterized by the persistence of the ~ 9.6 Å peak and its harmonics, independent of the treatment. This finding is notable, as todorokite is not commonly reported in

surface nodules from the CCFZ (e.g., Węgorzewski and Kuhn, 2014; Węgorzewski et al., 2015, 2020; Fan et al., 2024; Li et al., 2024).

In contrast, L2 is predominantly composed of phyllomanganates, encompassing both buserite (10 Å vernadite), which dehydrates readily upon mild heating (110 °C), and asbolane, which remains stable under the same conditions. Consistent with previous observations by Ploquin et al. (2019), the layer-to-layer distance of asbolane present in L2 decreases only slightly upon mild heating, whereas heating to 300 °C leads to a major decrease in intensity of the ~ 9.6 Å peak, with the second harmonics being much less affected (Fig. 3b and d). The ~ 10 Å layer-to-layer distance collapses to ~ 7 Å upon acidic treatment due to the dissolution of the island-like interlayer octahedral Me(OH)₂ sheets (Wu et al., 2020). These observations indicate that the thermodynamically stable phyllomanganate in L2 could be most likely asbolane, a phase that

Table 4

Structural parameters derived from the path simulation of Mn K-edge EXAFS fitting over 1–4 Å.

Atomic pairs		E-DY54-L1	E-DY54-L2	C-DY50-L1	C-DY50-L2
Mn-O _{1st}	CN	4.8 (8)	5.3 (9)	5.0 (8)	5.3 (9)
	R (Å)	1.90 (1)	1.90 (1)	1.90 (1)	1.90 (1)
	δ^2 (Å ²)	0.004 (1)	0.004 (1)	0.004 (1)	0.004 (2)
Mn-O _{2nd}	R (Å)	3.67 (12)	3.67 (12)	3.67 (12)	3.68 (12)
	CN	4.5 (13)	5.0 (11)	4.8 (12)	5.1 (11)
	R (Å)	2.89 (1)	2.89 (1)	2.89 (1)	2.89 (1)
Mn-Mn _E	δ^2 (Å ²)	0.007 (3)	0.006 (2)	0.006 (2)	0.006 (2)
	CN	2.6 (8)	2.4 (8)	2.4 (8)	2.3 (9)
	R (Å)	3.50 (8)	3.51 (8)	3.51 (8)	3.52 (8)
Mn-Mn _C	CN	2.6 (8)	2.4 (8)	2.4 (8)	2.3 (9)
	R (Å)	3.50 (8)	3.51 (8)	3.51 (8)	3.52 (8)
	R-factor	0.006	0.006	0.006	0.007

The parameters correspond to the following structural features: E (Edge-sharing), metals within the MnO₆ sheet; C (Corner-sharing), which includes DC (Double-corner; bidentate, at edge) and TC (Triple-corner; tridentate, over vacancy); CN, coordination number; R (Å), bond length (Å); δ^2 (Å²), Debye-Waller factor (Å²); E₀ (eV), energy shift (eV).

has been largely overlooked in previous studies.

The distinct distribution of Mn oxides between the two layers is corroborated by EXAFS spectroscopy, which indicates a substantially higher proportion of tectomanganates (todorokite) in L1 (28–68%)

compared to L2 (0–8%), where phyllosulfates (buserite and asbolane) dominate (Table 1). This distribution is further supported by the analysis of Mn–Mn scattering paths in R-space, which shows significantly higher CNs for edge-sharing Mn–Mn (Mn–Mn_E) paths in L2 relative to L1 (Table 4). The elevated CN values suggest that the phyllosulfates in L2 contain few layer vacancies, a feature inconsistent with buserite type II (Pal'chik et al., 2011). Additional confirmation of the mineralogical contrast is provided by HRTEM, which identified tectomanganates exclusively in L1 (Fig. 6, S2).

Moreover, the extensive development of phyllosulfate domains perpendicular to the layer plane, observed in both L1 (Fig. 5c) and L2 (Fig. S2), appears inconsistent with the presence of Fe-vernadite. The latter is characterized by its occurrence as Mn octahedral monolayers (Chukhrov et al., 1987; Manceau et al., 2014) and thus lacks periodicity perpendicular to the layer plane. The local chemical analysis of these domains (Table S1) further supports the absence of Fe-vernadite, as they were found to be devoid of Fe. Together with complementary microscopic and spectroscopic techniques, the combination of thermal and acid treatments used in the present study brings however a more insightful determination of the complex Mn mineralogy commonly observed in polymetallic nodules (e.g. Burns and Burns, 1977; Chukhrov et al., 1982b; Wegorzewski et al., 2015; Siegel and Turner, 1983; Hein et al., 2020).

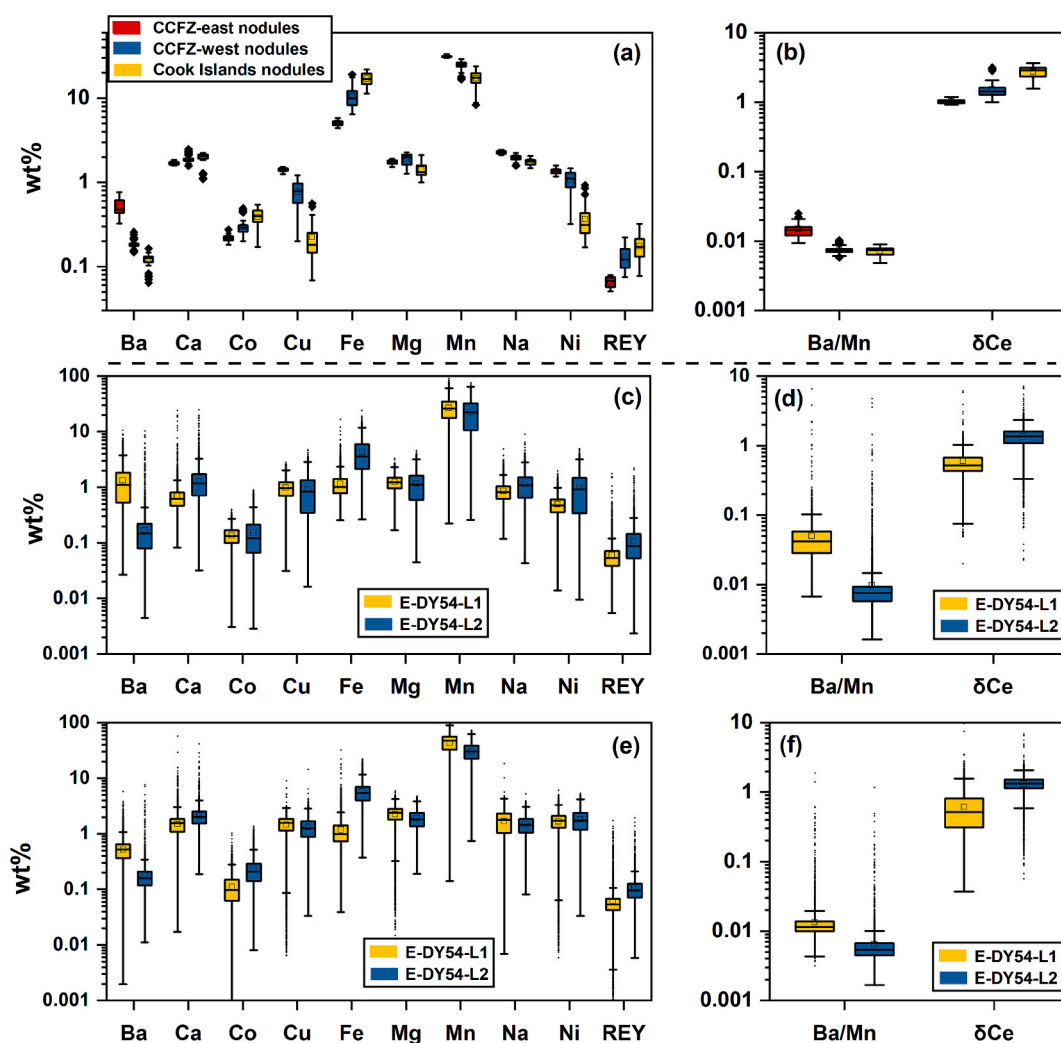


Fig. 6. Box plots of elemental geochemical data: (a, b) whole-rock composition of the nodules from CCFZ-East, CCFZ-West and Cook Islands nodules (data from Hein et al., (2015)); (c–f) LA-ICP-MS mapping data from nodules E-DY54 and C-DY50. Ba/Mn and Ce anomaly are used as proxies for primary productivity and redox conditions, respectively (see discussion 5.2 for details).

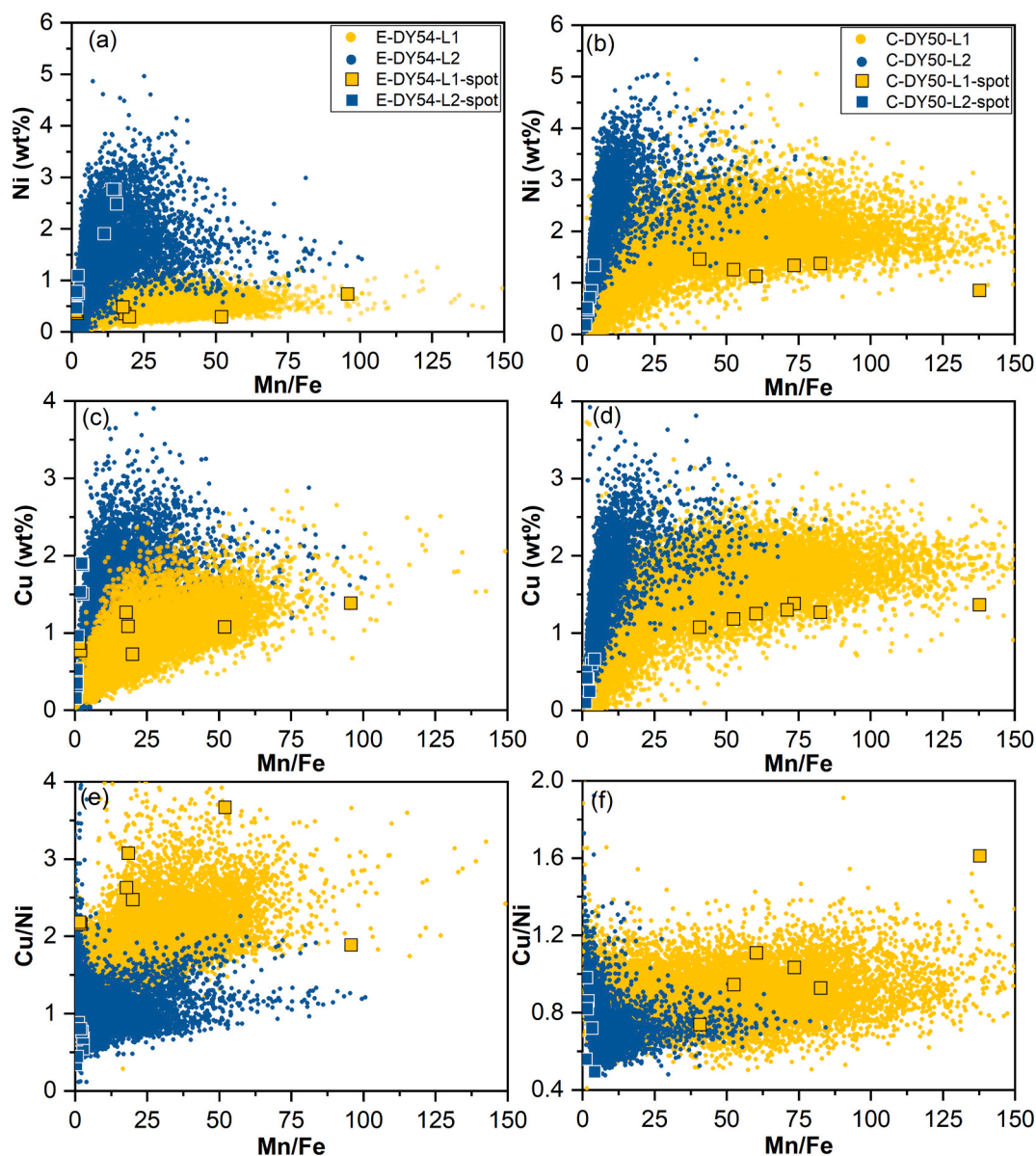


Fig. 7. Co-variance plots of Ni vs Mn/Fe, Cu vs Mn/Fe, and Cu/Ni vs Mn/Fe for nodules E-DY54 (a, c, e) and C-DY50 (b, d, f). All datasets are derived from LA-ICP-MS mapping; the specific extraction methods are described in Section 3.4. Blue and yellow squares denote EMPA data obtained from the same layers.

5.2. Controls on the formation of todorokite

The transformation of phyllo-manganates to tectomanganates is strongly driven by the presence and abundance of Mn^{3+} (Grangeon et al., 2014, 2015; Atkins et al., 2016; Wu et al., 2019). It is now widely recognized that the abundance of Mn(III) in the precursor phyllo-manganates governs their transformation potential into tunnel structures (Cui et al., 2008; Grangeon et al., 2014; Grangeon et al., 2015). For instance, Wu et al. (2019) observed that birnessite containing 26% Mn (III) can completely transform into tectomanganate todorokite. This view is further supported by the systematic correlation between todorokite occurrence and Mn(III) content in studied nodules. As determined by Combo fitting of the XANES data (Table 4), the L1 layer in both nodules exhibits a significantly higher Mn(III) content (16–26%) compared to L2 (8–10%). The presence of todorokite in L1 consistently corresponds to these elevated Mn(III) levels. Such a correlation aligns fully with experimentally established transformation pathways of Mn oxides (Golden et al., 1986; Feng et al., 1995, 2004; Wu et al., 2019). Mechanistically, the Jahn–Teller distortion of $[\text{Mn}^{3+}\text{O}_6]$ octahedra

likely triggers migration of Mn^{3+} from layers to interlayers, thereby alleviating steric strain and contributing to the assembly of tecto-manganate “walls” (Grangeon et al., 2014; Manceau et al., 2014; Grangeon et al., 2015; Atkins et al., 2016; Wu et al., 2019).

Despite similar Mn contents in L1 and L2 (Fig. 6c, e), the pronounced difference in their Mn^{3+} contents indicate distinct redox conditions during their formation. This difference most likely resulted from a contrast in paleoproductivity, which is consistent with the reported association between todorokite and biogenic debris in nodules from central CCFZ (Siegel and Turner, 1983). We hypothesize that increased primary productivity increases the flux of organic matter to the seafloor, which in turn accelerates oxygen consumption in the underlying sediments. This process drives the upward migration of the Oxid–Suboxic Front (OSF) (Wegorzewski and Kuhn, 2014; Mewes et al., 2014) and establishes a suboxic environment that is essential for Mn oxides recycling (Dymond et al., 1984; Wegorzewski et al., 2020). To test this hypothesis, Ba was employed as a paleoproductivity proxy (Chu et al., 2025), an elevated Ba content in nodules reflecting the supply and preservation of biogenic barite (BaSO_4) to the seafloor, a process directly

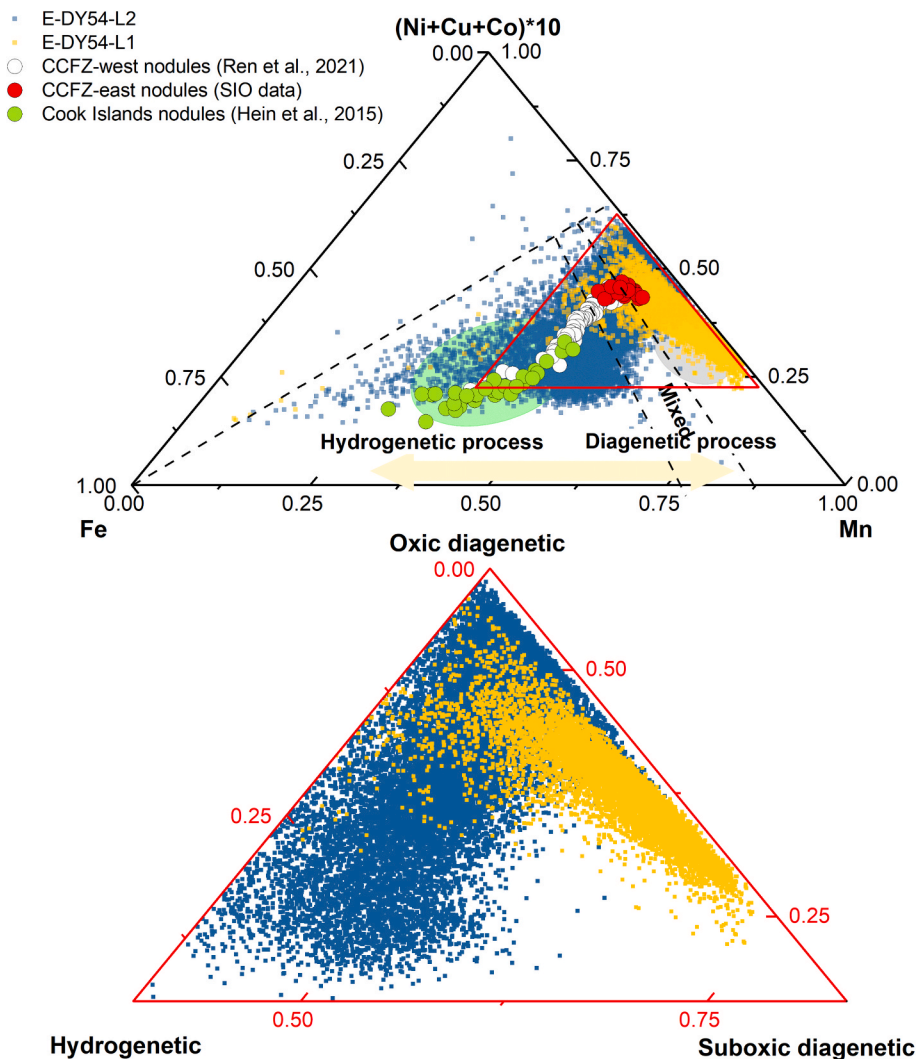


Fig. 8. Three-component genetic diagram (Fe-Mn-10×(Ni + Cu + Co)) for nodule E-DY54, adapted from Bonatti et al. (1972). The upper panel outlines compositional fields for typical hydrogenetic (green) and buried suboxic-diagenetic (gray; Fan et al., 2024) deposits. The lower panel offers an enlarged view of the red-triangular area, clearly highlighting the geochemical distinction between the inner layer L1 (orange) and the outer layer L2 (blue). The position of L1 indicates a stronger suboxic-diagenetic signature (Fan et al., 2024), whereas L2 falls within the oxic-diagenetic field (Fan et al., 2024) and trends toward the hydrogenetic end-member.

linked to high surface ocean productivity. The Ba/Mn ratio was specifically used to minimize adsorption-related bias (Manceau et al., 2007) and to better constrain the enrichment of biogenic Ba relative to the Mn oxide matrix. The substantially higher Ba/Mn ratios measured in L1 compared to L2 thus support formation of L1 under elevated primary productivity conditions. Consistently, paleomagnetic and ^{10}Be isotope dating indicate CCFZ nodule ages exceeding 4 Ma (Yi et al., 2020), a period during which the CCFZ was influenced by the equatorial high-productivity zone (Menendez et al., 2019) due to the ongoing expansion of the East Pacific Rise (Von Stackelberg and Beiersdorf, 1991; Macleod et al., 1996). The prevalence of suboxic conditions linked to high productivity during L1 formation is further supported by a weaker Ce anomaly and higher growth rates:

1) As Ce is highly sensitive to redox changes (e.g. Ling et al., 2013; Zhang and Shields, 2022, 2023), a high flux of organic matter into sediments enhances oxygen consumption, suppresses Ce^{3+} oxidation, and aligns its geochemical behavior with that of other trivalent rare earth elements (e.g. Takahashi et al., 2007; Bau et al., 2014), thus weakening the Ce anomaly in L1.

2) L1 grew an order of magnitude faster than L2, with mean growth rates peaking at 463 mm/Ma (Fig. S4). Such high growth rates indicate that Mn oxides mainly derived from the oxidation of Mn^{2+} in sediment pore waters (Koschinsky and Hein, 2017; Su et al., 2023; Fan et al., 2024), rather than from slow colloidal chemical precipitation processes in the deep-sea water (Hein et al., 2020; Ren et al., 2024). Extensive Mn reduction in suboxic sediments establishes strong concentration gradients, driving upward Mn^{2+} diffusion and re-oxidation at the OSF (Dymond et al., 1984; Mewes et al., 2014; Węgorzewski and Kuhn 2014). This process fuels nodule growth and supplies transient Mn^{3+} via comproportionation with Mn^{4+} (Elzinga, 2016; Zhao et al., 2016; Grangeon et al., 2017). Additionally, microbially mediated or EPS-facilitated oxidation pathways may promote further Mn^{2+} to Mn^{3+} conversion (Tebo et al., 2004). As the nodule location shifted away from high-productivity zones during L2 growth, lower Mn/Fe ratios and higher Co and Ce contents reflect more oxic conditions and a greater contribution from hydrogenetic precipitation (Koschinsky and Hein, 2003; Koschinsky and Hein, 2017; Hein et al., 2020). These oxic conditions hamper Mn^{3+} generation, thereby inhibiting todorokite formation.

In addition to the quantity of Mn(III), pH (Shen et al., 2005) and temperature (Golden et al., 1986) are also critical variables that influence the mineral transformation process in laboratory synthesis of todorokite. However, in marine polymetallic nodules, the relatively stable precipitation environment of deep-sea ferromanganese nodules, characterized by high pressure, low temperature (4°C), and slightly alkaline conditions, renders these variables less relevant to account for the contrasting mineralogy in L1 and L2.

Mg is also widely recognized as an efficient and specific interlayer templating ion for Mn oxides (Golden et al., 1986), owing to the good match between its hydrated diameter and the dimension of todorokite 3×3 tunnels. Furthermore, elevated Mg concentrations in marine sedimentary settings are generally considered crucial for the formation of marine authigenic tectomanganates (Bodeř et al., 2007; Manceau et al., 2014; Wegorzewski et al., 2015). However, in the present study, both the average Mg contents and their variation ranges in L1 and L2 are nearly identical (Fig. 7c and e). This observation suggests that, under the same sedimentary conditions, Mg may not be the primary factor controlling the transformation from phyllomanganates to todorokite, although its presence likely modulates tunnel dimensions once tectomanganate structures are formed (Bodeř et al., 2007). Therefore, we propose that the transformation of authigenic phyllomanganates to todorokite in marine environments is primarily controlled by high primary productivity-driven suboxic diagenetic processes.

5.3. Mn oxide mineralogy control on elemental distribution of Ni and Cu

The near-constant Cu concentrations suggest that Cu is largely retained during the mineral transformation, a process that can be promoted by the Jahn–Teller activity of Cu^{2+} in Mn-oxide structures (Bodeř et al., 2007; Manceau et al., 2014), thereby favoring the incorporation of Cu into the resulting todorokite. The rapid release of Cu during acidic treatment (Fig. S9), with kinetics comparable to Mg^{2+} , points to its occurrence in readily soluble forms. We infer that this behavior reflects two principal occurrence modes: (1) as an outer-sphere complex within tectomanganate tunnels in L1, consistent with previous Cu K-edge EXAFS studies (Peña et al., 2015; Wegorzewski et al., 2020), and (2) as inner-sphere complex (surface-sorbed species) or interlayer hydroxides in asbolane-like phyllomanganates.

Ni and Cu are expected to have a similar geochemical behavior in marine manganese deposits (Bonatti et al., 1972; Halbach et al., 1981; Wegorzewski and Kuhn, 2014). However, the higher contents of Ni measured in L2 compared to L1 (Fig. 7c and e Fig. 8, S8), consistent with the early reports of Siegel and Turner (1983), suggest that part of the Ni initially present in the layers of phyllomanganates is released during their conversion to tectomanganates. Consistently, Atkins et al. (2016) showed experimentally that part of Ni initially sorbed to birnessite (7 Å vernadite) is released into solution during its transformation to todorokite, thus suggesting a limited ability of todorokite to incorporate Ni into its structure. In line with these postulates, Ni in polymetallic nodules is commonly enriched in phyllomanganates compared to tectomanganates (e.g. Bodeř et al., 2007; Wegorzewski et al., 2020). In these settings, Ni was assumed to be isomorphically substituted for Mn in the Mn octahedral layers (Peacock and Sherman, 2007; Manceau et al., 2014).

In contrast, the Ni leaching rates during acidic treatment in the L1 and L2 were intermediate between those of Co and Cu (Fig. S9). Given that Co is consistently recognized to be incorporated into the Mn octahedral layers via isomorphic substitution (e.g. Manceau et al., 1997; Takahashi et al., 2007; Manceau et al., 2014; Wu et al., 2019), this observation implies that, besides isomorphic substitution, a considerable fraction of Ni in polymetallic nodules likely resides in adsorbed forms or as weakly bound species ($\text{Ni}(\text{OH})_2/\text{Ni}(\text{H}_2\text{O})_6$). This proposition is supported by Atkins et al. (2016), whose Ni K-edge EXAFS analysis revealed Ni in a tridentate corner-sharing (TC) configuration, suggesting its presence as an adsorbed species on todorokite. Similarly,

Wegorzewski et al. (2020) reported similar Ni K-edge EXAFS signatures as an outer-sphere complex within todorokite tunnels.

If some Ni is present in phyllomanganates as weakly bound species, the formation of island-like $\text{Ni}(\text{OH})_2$ domains within the interlayers of L2 may also occur. This possibility is supported by the experimental findings of Wu et al. (2020), which demonstrated that such structures form under elevated Ni concentrations and promote asbolane crystallization. The correlation between higher Ni content and asbolane occurrence in L2 could therefore be partly attributed to this mechanism. Furthermore, the presence of these interlayer species might also hinder the transformation of phyllomanganates to todorokite, consistent with previous observations (Wu et al., 2020).

We hypothesize that isomorphic substitutions of Ni occur in phyllomanganates (Peacock and Sherman, 2007; Manceau et al., 2014) when Ni contents are low (a few wt%). In contrast, as Ni content increases, polymerization of $\text{Ni}(\text{OH})_2$ in phyllomanganate interlayers may be kinetically favored over the migration of Jahn–Teller-distorted cations (Mn^{3+} and possibly Cu^{2+}) from octahedral layers. This preferential process is considered to promote the formation of asbolane (Wu et al., 2020). However, this hypothesis remains to be fully validated in natural systems. To our knowledge, reports documenting adsorbed or weakly bound Ni in phyllomanganate are scarce in natural marine deposits. Therefore, applying Ni K-edge EXAFS to elucidate the precise speciation of Ni across different Mn oxides in such settings is essential to assess our hypotheses.

5.4. Ni and Cu enrichment mechanisms in marine manganese deposits

Based on the published data on marine surficial manganese deposits, it is possible to posit global distribution patterns for Mn, Ni, and Cu (Fig. 9). These patterns reveal a significant positive correlation among contents of Ni, Cu, and Mn. Hydrogenetic manganese deposits (e.g. hydrogenetic crusts and selected hydrogenetic nodules from the Cook Islands (Hein et al., 2015) and the West Pacific Seamount Basin (Ren et al., 2022)) and oxic diagenetic nodules (e.g. CCFZ-West nodules) define distinct enrichment trends. Hydrogenetic crusts form slowly on hard substrates via precipitation from seawater (e.g., Halbach et al., 1982; Ren et al., 2022; Ren et al., 2024). Their growth proceeds through colloidal precipitation of Mn oxides (Fe–vernadite/7 Å vernadite) (Lee et al., 2019; Koschinsky and Hein, 2003), which scavenge Ni and Cu via surface sorption (Hein et al., 2013; Hein et al., 2020). In contrast, enrichment of Ni and Cu in nodules follows a multi-stage process. During the initial oxic diagenetic stage (Stage 1), as observed in oxic diagenetic nodules from CCFZ-West (Dymond et al., 1984; Fan et al., 2024), 10 Å manganates precipitate from sediment porewaters (Wegorzewski and Kuhn, 2014), incorporating Ni and Cu released during the degradation of deeply buried Mn oxides (Dymond et al., 1984; Heller et al., 2018). This process could result in Ni contents that are significantly higher than those in crusts and hydrogenetic nodules (Halbach et al., 1981).

Building upon the initial geochemical divergence, our data reveal a more complex scenario. We reinterpret the well-documented decrease in the Ni/Mn ratio with increasing abundance of 10 Å manganates—a trend observed in the Peru Basin and other highly diagenetic settings (Halbach et al., 1981; Von Stackelberg, 1997; Cheng et al., 2023). We propose that this inflection point likely marks a critical phase boundary: the transformation of phyllomanganates into tectomanganates (todorokite). Based on the refined mineralogical zonation identified in this study, we classify the subsequent enrichment mechanisms of Ni and Cu into two distinct stages (Stage 2 and Stage 3).

Stage 2 (Fig. 10) is characterized by Mn enrichment alongside limited enrichment in Ni and Cu. In the present L1 ($\text{Mn}/\text{Fe} > 10$), Ni and Cu contents are essentially independent of Mn concentration (Fig. 7a–d). A similar phenomenon has also been documented in hydrothermal deposits and high-productivity pelagic sediments (Fleischmann et al., 2023). These deposits reflect rapid Mn oxide precipitation under Mn^{2+} fluxes from sediment pore water significantly higher than in

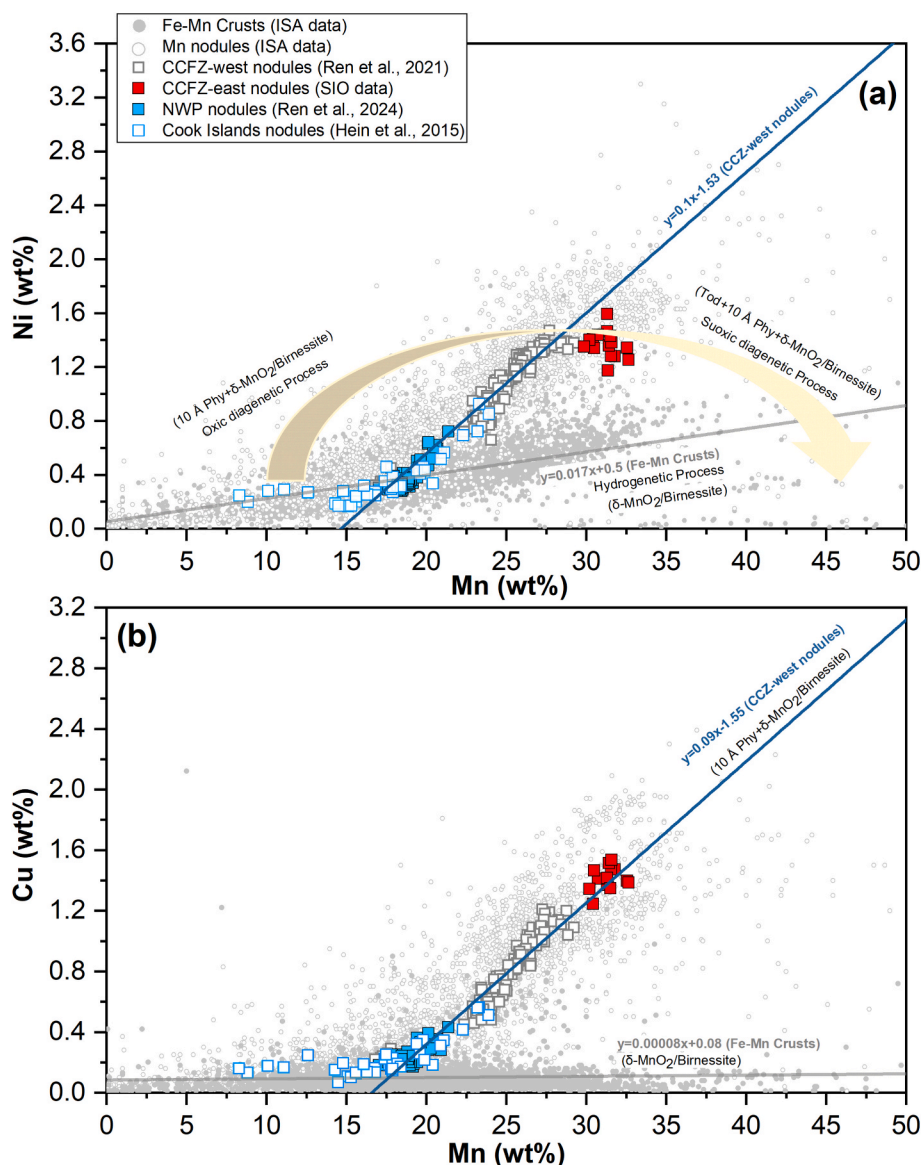


Fig. 9. Co-variance plots of Mn vs. Ni and Mn vs. Cu in manganese deposits from the Pacific Ocean. Data sources: NWP nodules (Northwest Pacific seamount basin): Ren et al. (2024); Cook Islands: Hein et al. (2015); Fe–Mn crusts and Fe–Mn nodules: complete unfiltered ISA database (2010). Solid blue lines represent linear regression fits for bulk nodules analyses of Western CCFZ nodules, respectively. The Eastern CCFZ nodules are characterized by a higher abundance of todorokite, whereas Western CCFZ nodules are dominated by phyllomanganates (Fan et al., 2024; Li et al., 2024). The yellow arrow illustrates the proposed diagenetic transition from oxalic to suboxic conditions, which explains the unique trend observed in Eastern CCFZ nodules: despite higher Mn content, Ni does not accumulate due to todorokite formation and associated Ni release.

hydrogenetic process (Halbach et al., 1981; Hein et al., 2020). As Mn oxides undergo reductive dissolution during burial (consuming oxygen from organic matter), Mn^{2+} is released together with associated Ni and Cu (Heller et al., 2018). This mobilized Mn^{2+} then migrates upward and re-oxidizes above the OSF (Mewes et al., 2014), redistributing associated Ni and Cu into newly formed Mn oxides.

Stage 3 (Fig. 10) involves the suboxic, diagenetically driven secondary migration of Ni, typically linked to the transformation of 10 Å vernadite to todorokite under suboxic conditions associated with high primary productivity. Additionally, with increasing distance from these high-productivity regions (Menendez et al., 2019), more oxic conditions prevail (Wegorzewski and Kuhn, 2014), thus impeding todorokite formation. Concurrently, progressive Ni enrichment may promote the polymerization of Ni in phyllomanganate interlayers via hydrolysis leading to the formation of asbolane-like minerals, which in turn inhibits any subsequent transformation of phyllomanganates to todorokite

(Fig. 9).

6. Conclusion

This study deciphers the mineralogical architecture of polymetallic nodules from the CCFZ and its fundamental control on Ni and Cu distribution. By combining thermal and acid treatments prior to XRD analysis with complementary microscopic and spectroscopic techniques, our integrated methodology enabled a thorough and unambiguous determination of the complex Mn mineralogy commonly found in ferromanganese nodules. The analyzed nodules exhibit two distinct growth layers: an inner layer (L1) and an outer layer (L2). The primary mineral composition of L1 includes 10 Å vernadite/buserite and todorokite (23–68%), whereas L2 is dominated by 10 Å phyllomanganates (10 Å vernadite/buserite and asbolane), with todorokite being virtually absent.

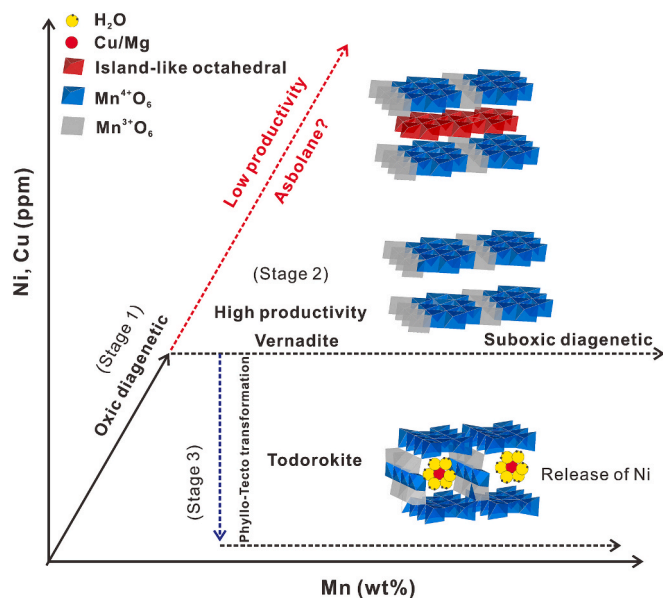


Fig. 10. Conceptual model of the geochemical behavior of Ni and Cu during the transformation from 10 Å vernadite to todorokite in ferromanganese nodules. Stage 1 represents the initial enrichment of Ni and Cu during oxic diagenetic processes. Stage 2 depicts the bottleneck in element enrichment caused by the high Mn^{2+} flux under high primary productivity conditions leading to formation of Mn^{3+} through Mn comproportionation. Stage 3 shows the phyllo-manganate transformation to tectomanganate (todorokite) under suboxic conditions. This transformation may induce the remobilization of Ni, leading to their depletion in newly formed tectomanganates and their enrichment in deep-sea waters thus promoting the formation of Me-rich phyllo-manganates such as asbolane. Blue, grey, red, and yellow octahedra represent Mn^{4+}O_6 , Mn^{3+}O_6 , Ni, and Cu, respectively.

This mineralogical contrast likely stems from differences in physico-chemical conditions during nodule formation. During early mineralization stages, 10 Å phyllo-manganates form systematically. Subsequent transformation of these precursors into todorokite may occur if sufficient Mn(III) is present. Mn(III) content is enhanced under reducing conditions in suboxic sediment pore waters, which result from substantial inputs of organic material. Under such reducing conditions, Mn^{3+} is generated through comproportionation between Mn^{2+} and Mn^{4+} , promoting the crystallization of todorokite. In contrast, under more oxic conditions, low Mn^{3+} availability, coupled with metals sequestration into asbolane via the formation of island-like interlayers, suppresses todorokite crystallization in the outer layer.

Critically, this mineralogical transformation governs the differential metal enrichment, the 40–50% depletion of Ni in layer L1 is linked to its expulsion during the phyllo-to-tectomanganate transformation. Conversely, a substantial fraction of Cu is retained within the todorokite structure. Incorporated into the mineral lattice as a Jahn-Teller active element, likely within the tunnel sites, Cu exhibits negligible remobilization throughout this process.

Data availability

Data is available through Mendeley data at <https://doi.org/10.17632/jx6hw8rryf.1>.

CRediT authorship contribution statement

Zedong Fan: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Xiaohu Li:** Writing – review & editing, Visualization,

Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Yanhui Dong:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Bruno Lanson:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Formal analysis, Data curation, Conceptualization. **Zhongkuan Wu:** Writing – review & editing, Visualization, Investigation, Formal analysis, Data curation, Conceptualization. **Weilin Ma:** Writing – review & editing, Supervision, Methodology, Investigation, Data curation, Conceptualization. **Zhenggang Li:** Writing – review & editing, Supervision, Formal analysis, Data curation, Conceptualization. **Junming Zhou:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Yi Ding:** Conceptualization, Methodology, Supervision. **Hao Wang:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Zhimin Zhu:** Writing – review & editing, Supervision, Software, Data curation, Conceptualization. **Jie Li:** Writing – review & editing, Methodology, Formal analysis, Data curation, Conceptualization. **Xingwei Meng:** Writing – review & editing, Supervision, Software, Data curation, Conceptualization. **Huaiming Li:** Writing – review & editing, Funding acquisition, Conceptualization. **Fengyou Chu:** Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

This file contains supplementary data supporting the geochemical and mineralogical findings reported in the main text. Included are: detailed chemical compositions and regional geochemical comparisons for 71 polymetallic nodules from the CCFZ; electron microprobe analyses (EMPA) characterizing microscale heterogeneity between the L1 and L2 layers; Mn K-edge XANES spectra used to quantify manganese oxidation states and phase distributions; LA-ICP-MS maps illustrating the spatial distribution of key elements and growth rates of the L1 and L2 layers; and results from metal leaching experiments comparing the dissolution behaviors of different mineral phases.

Supplementary material to this article can be found online at <https://doi.org/10.1016/j.gca.2026.04.016>.

References

- Atkins, A.L., Shaw, S., Peacock, C.L., 2014. Nucleation and growth of todorokite from birnessite: implications for trace metal cycling in marine sediments. *Geochim. Cosmochim. Acta* 144, 109–125.
- Atkins, A.L., Shaw, S., Peacock, C.L., 2016. Release of Ni from birnessite during transformation of birnessite to todorokite: implications for Ni cycling in marine sediments. *Geochim. Cosmochim. Acta* 189, 158–183.
- Bau, M., Schmidt, K., Koschinsky, A., Hein, J., Kuhn, T., Usui, A., 2014. Discriminating between different genetic types of marine ferro-manganese crusts and nodules based on rare earth elements and yttrium. *Chem. Geol.* 381, 1–9.

- Bodei, S., Manceau, A., Geoffroy, N., Baronnet, A., 2007. Formation of todorokite from vernadite in Ni-rich hemipelagic sediments. *Geochim. Cosmochim. Acta* 71, 5698–5716.
- Bonatti, E., Kraemer, T., Rydell, H., 1972. Classification and genesis of submarine iron-manganese deposits. In: Horn, D. (Ed.), *Ferromanganese Deposits on the Ocean Floor*. National Science Foundation, Washington, pp. 149–165.
- Burns, R.G., Burns, V.M., 1977. The mineralogy and crystal chemistry of deep-sea manganese nodules, a polymetallic resource of the twenty-first century. *Phil. Trans. R. Soc. Lond. A* 286, 283–301.
- Burns, R.G., Burns, V.M., 1978. Post-depositional metal enrichment processes inside manganese nodules from the north equatorial Pacific. *Earth Planet. Sci. Lett.* 39, 341–348.
- Burns, R.G., Burns, V.M., Stockman, H.W., 1983. A review of the todorokite-buserite problem: implications to the mineralogy of marine manganese nodules. *Amer. Mineral.* 68, 972–980.
- Burns, R.G., Burns, V.M., Stockman, H.W., 1985. The todorokite-buserite problem: further considerations. *Amer. Mineral.* 70, 205–208.
- Byles, B.W., West, P., Cullen, D.A., More, K.L., Pomerantseva, E., 2015. Todorokite-type manganese oxide nanowires as an intercalation cathode for Li-ion and Na-ion batteries. *RSC Adv.* 5, 106265–106271.
- Ching, S., Krukowska, K.S., Suib, S.L., 1999. A new synthetic route to todorokite-type manganese oxides. *Inorg. Chim. Acta* 294, 123–132.
- Chu, Y., Li, X., Yi, L., Dong, Y., Xie, R.C., Fan, Z., Hein, J.R., Little, S.H., Liu, Y., Matsuzaki, H., Zhang, W., Meng, X., Ma, W., Li, Z., Wang, H., Li, J., 2025. A shift in ocean circulation drives variations in paleoproductivity in the North Pacific Ocean. *Earth Planet. Sci. Lett.* 671, 119669.
- Cui, H.J., Feng, X.H., Tan, W.F., He, J., Hu, R.G., Liu, F., 2009. Synthesis of todorokite-type manganese oxide from Cu-buserite by controlling the pH at atmospheric pressure. *Micropor. Mesopor. Mat.* 117, 41–47.
- Cui, H.J., Liu, X.W., Tan, W.F., Feng, X.H., Liu, F., Ruan, H.D., 2008. Influence of Mn(III) availability on the phase transformation from layered buserite to tunnel-structured todorokite. *Clays Clay Miner.* 56, 397–403.
- Chen, L., Downey, A.R., Archer, C., Little, S.H., Homoky, W.B., Peacock, C.L., 2025. Mineralogical controls of the oceanic nickel cycle. *Nat. Commun.* 16, 1–12.
- Cheng, Y., Xu, Y., Yi, L., Li, D., Lin, F., Yin, X., Wang, A., 2023. Chronology and critical metals enrichment mechanism of ferromanganese nodules from the Parece Vela Basin. *Philippine Sea. Chem. Geol.* 630, 121494.
- Chukhrov, F.V., Gorshkov, A.I., Sivtsov, A.V., Berezovskaya, V.V., 1978. Structural varieties of todorokite. *Izv. Akad. Nauk SSSR Ser. Geol.* 12, 86–95.
- Chukhrov, F.V., Gorshkov, A.I., Drits, V.A., 1982a. New structural variation of asbolane. *Izv. Akad. Nauk SSSR Ser. Geol.* 6, 69–77.
- Chukhrov, F.V., Gorshkov, A.I., Vitovskaya, I.V., Drits, V.A., Sistov, A.V., Rudnitskaya, Y. S., 1982b. Crystallochemical nature of Co-Ni asbolane. *Int. Geol. Rev.* 24, 598–604.
- Chukhrov, F.V., Gorshkov, A.I., Drits, V.A., Sivtsov, A.V., Uspenskaya, T.Y., Sakharov, B. A., 1984. Structural models and methods of study of buserite. *Int. Geol. Rev.* 26, 1350–1360.
- Chukhrov, F.V., Drits, V.A., Gorshkov, A.I., 1987. Structural transformations of manganese oxides in ferromanganese nodules. *Int. Geol. Rev.* 29, 110–121.
- Du, J., Haley, B.A., McManus, J., Blaser, P., Rickli, J., Vance, D., 2025. Abyssal seafloor as a key driver of ocean trace-metal biogeochemical cycles. *Nature* 642, 620–627.
- Dymond, J., Lyle, M., Finney, B., Piper, D.Z., 1984. Ferromanganese nodules from MANOP sites H, S, and R-control of mineralogical and chemical composition by multiple accretionary processes. *Geochim. Cosmochim. Acta* 48, 931–949.
- Elzinga, E.J., 2016. ^{54}Mn radiotracers demonstrate continuous dissolution and reprecipitation of vernadite ($\delta\text{-MnO}_2$) during interaction with aqueous Mn(II). *Environ. Sci. Technol.* 50, 8670–8677.
- Fan, Z., Li, X., Li, Z., Ma, W., Zhu, Z., Li, J., Wang, H., Yang, K., Li, H., Chu, F., Dong, Y., 2024. Geochemical behavior of shallow buried nodules from Clarion-Clipperton Fracture Zone in the East Pacific: a LA-ICP-MS mapping analysis perspective. *Minerals* 14, 80.
- Feng, Q., Kanoh, H., Miyai, Y., Ooi, K., 1995. Metal ion extraction/insertion reactions with todorokite-type manganese oxide in the aqueous phase. *Chem. Mater.* 7, 1722–1727.
- Feng, X.H., Tan, W.F., Liu, F., Wang, J.B., Ruan, H.D., 2004. Synthesis of todorokite at atmospheric pressure. *Chem. Mater.* 16, 4330–4336.
- Feng, X.H., Zhu, M.Q., Ginder-Vogel, M., Ni, C.Y., Parikh, S.J., Sparks, D.L., 2010. Formation of nano-crystalline todorokite from biogenic Mn oxides. *Geochim. Cosmochim. Acta* 74, 3232–3245.
- Fleischmann, S., Du, J., Chatterjee, A., McManus, J., Iyer, S.D., Amonkar, A., Vance, D., 2023. The nickel output to abyssal pelagic manganese oxides: a balanced elemental and isotope budget for the oceans. *Earth Planet. Sci. Lett.* 619, 11.
- Fronzel, C., Marvin, U.B., Ito, J., 1960. New occurrences of todorokite. *Amer. Mineral.* 45, 1167–1173.
- Giovanoli, R., Bürki, P., 1975. Comparison of X-ray evidence of marine manganese nodules and non-marine manganese ore deposit. *Chimia* 29, 266–269.
- Giovanoli, R., Bürki, P., Giuffredi, M., Stumm, W., 1975. Layer structured manganese oxide/hydroxides. IV: the buserite group; structures stabilization by transition elements. *Chimia* 29, 517–520.
- Golden, D.C., Chen, C.C., Dixon, J.B., 1986. Synthesis of todorokite. *Science* 231, 717–719.
- Grangeon, S., Fernandez-Martinez, A., Warmont, F., Gloter, A., Marty, N., Poulain, A., Lanson, B., 2015. Cryptomelane formation from nanocrystalline vernadite precursor: a high energy X-ray scattering and transmission electron microscopy perspective on reaction mechanisms. *Geochim. Trans.* 16, 12.
- Grangeon, S., Lanson, B., Lanson, M., 2014. Solid-state transformation of nanocrystalline phyllomanganate into tectomanganate: influence of initial layer and interlayer structure. *Acta Crystallogr. B* 70, 828–838.
- Grangeon, S., Lanson, B., Miyata, N., Tani, Y., Manceau, A., 2010. Structure of nanocrystalline phyllomanganates produced by freshwater fungi. *Amer. Mineral.* 95, 1608–1616.
- Grangeon, S., Warmont, F., Tournassat, C., Lanson, B., Lanson, M., Elkaïm, E., Claret, F., 2017. Nucleation and growth of feitknechtite from nanocrystalline vernadite precursor. *Eur. J. Mineral.* 29, 767–776.
- Halbach, P., Giovanoli, R., Borstel, D.V., 1982. Geochemical processes controlling the relationship between Co, Mn, and Fe in early diagenetic deep-sea nodules. *Earth Planet. Sci. Lett.* 60, 226–236.
- Halbach, P., Scherhag, C., Heibisch, U., Marchig, V., 1981. Geochemical and mineralogical control of different genetic types of deep-sea nodules from the Pacific Ocean. *Mineral. Deposita* 16, 59–84.
- Hein, J.R., Koschinsky, A., Kuhn, T., 2020. Deep-ocean polymetallic nodules as a resource for critical materials. *Nat. Rev. Earth Environ.* 1, 158–169.
- Hein, J.R., Mizell, K., Koschinsky, A., Conrad, T.A., 2013. Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: comparison with land-based resources. *Ore Geol. Rev.* 51, 1–14.
- Hein, J.R., Spinardi, F., Okamoto, N., Mizell, K., Thorburn, D., Tawake, A., 2015. Critical metals in manganese nodules from the Cook Islands EEZ, abundances and distributions. *Ore Geol. Rev.* 68, 97–116.
- Heller, C., Kuhn, T., Versteegh, G.J.M., Wegorzewski, A.V., Kasten, S., 2018. The geochemical behavior of metals during early diagenetic alteration of buried manganese nodules. *Deep-Sea Res. Pt. I* 142, 16–33.
- Koschinsky, A., Hein, J.R., 2003. Uptake of elements from seawater by ferromanganese crusts: solid-phase associations and seawater speciation. *Mar. Geol.* 198, 331–351.
- Koschinsky, A., Hein, J.R., 2017. Marine ferromanganese encrustations: archives of changing oceans. *Elements* 13, 177–182.
- Lanson, B., Marcus, M.A., Fakra, S., Panfil, F., Geoffroy, N., Manceau, A., 2008. Formation of Zn-Ca phyllomanganate nanoparticles in grass roots. *Geochim. Cosmochim. Acta* 72, 2478–2490.
- Lee, S., Xu, H., Xu, W., Sun, X., 2019. The structure and crystal chemistry of vernadite in ferromanganese crusts. *Acta Cryst. B Struct. Sci. Cryst. Eng. Mater.* 75, 591–598.
- Little, S.H., Archer, C., McManus, J., Najorka, J., Wegorzewski, A.V., Vance, D., 2020. Towards balancing the oceanic Ni budget. *Earth Planet. Sci. Lett.* 547, 116461.
- Li, D.F., Fu, Y., Sun, X.M., Wei, Z.Q., 2020. Critical metal enrichment mechanism of deep-sea hydrogenetic nodules: insights from mineralogy and element mobility. *Ore Geol. Rev.* 118, 103371.
- Li, J., Jin, Y., Wang, H., Yang, K., Zhu, Z., Meng, X., Li, X., 2024. In-situ analysis of polymetallic nodules from the Clarion-Clipperton Zone, Pacific Ocean: implication for controlling on chemical composition variability. *Front. Mar. Sci.* 11, 1489184.
- Ling, H., Chen, X., Li, D., Wang, D., Shields-Zhou, G.A., Zhu, M., 2013. Cerium anomaly variations in Ediacaran–earliest Cambrian carbonates from the Yangtze Gorges area, South China: implications for oxygenation of coeval shallow seawater. *Precamb. Res.* 225, 110–127.
- Lorca, S., 1988. Nouvelles données sur la composition et la structure des asbolanes (nouvelle-calédonie). *C. R. Acad. Sci. Paris Sér. II* 307, 155–161.
- Manceau, A., Drits, V.A., Silvester, E.J., Bartoli, C., Lanson, B., 1997. Structural mechanism of Co^{2+} oxidation by the phyllomanganate buserite. *Amer. Mineral.* 82, 1150–1175.
- Manceau, A., Lanson, M., Geoffroy, N., 2007. Natural speciation of Ni, Zn, Ba, and As in ferromanganese coatings on quartz using X-ray fluorescence, absorption, and diffraction. *Geochim. Cosmochim. Acta* 71, 95–128.
- Manceau, A., Lanson, M., Takahashi, Y., 2014. Mineralogy and crystal chemistry of Mn, Fe, Co, Ni, and Cu in a deep-sea Pacific polymetallic nodul. *Amer. Mineral.* 99, 2068–2083.
- Manceau, A., Marcus, M.A., Grangeon, S., 2012. Determination of Mn valence states in mixed-valent manganates by XANES spectroscopy. *Amer. Mineral.* 97, 816–827.
- Manceau, A., Marcus, M.A., Tamura, N., 2002. Quantitative speciation of heavy metals in soils and sediments by synchrotron X-ray techniques. *Rev. Mineral. Geochem.* 49, 341–428.
- Marcus, M.A., Manceau, A., Kersten, M., 2004. Mn, Fe, Zn and As speciation in a fast-growing ferromanganese marine nodule. *Geochim. Cosmochim. Acta* 68, 3125–3136.
- Martin-Barajas, A., Lallier-Verges, E., Leclaire, L., 1991. Characteristics of manganese nodules from the Central Indian Basin: relationship with the sedimentary environment. *Mar. Geol.* 101, 249–265.
- McKeown, D.A., Post, J.E., 2001. Characterization of manganese oxide mineralogy in rock varnish and dendrites using X-ray absorption spectroscopy. *Amer. Mineral.* 86, 701–713.
- MacLeod, C.J., Tyler, P.A., Walker, C.L., 1996. Tectonic, magmatic, hydrothermal and biological segmentation of mid-ocean ridges. *Geol. Soc. Lond. Spec. Publ.* 118, 5–20.
- Mewes, K., Mogollón, J.M., Picard, A., Rühlemann, C., Kuhn, T., Nöthen, K., Kasten, S., 2014. Impact of depositional and biogeochemical processes on small scale variations in nodule abundance in the Clarion-Clipperton Fracture Zone. *Deep-Sea Res. Pt. I* 91, 125–141.
- Menendez, A., James, R.H., Lichtschlag, A., Connelly, D., Peel, K., 2019. Controls on the chemical composition of ferromanganese nodules in the Clarion-Clipperton Fracture Zone, eastern equatorial Pacific. *Mar. Geol.* 409, 1–14.
- Novikov, G.V., Bogdanova, O.Y., 2007. Transformations of ore minerals in genetically different oceanic ferromanganese rocks. *Lithol. Min. Resour.* 42, 303–317.
- Pal'chik, N.A., Grigor'eva, T.N., Moroz, T.N., 2013. Natural and synthetic manganese minerals. *Russ. J. Inorg. Chem.* 58, 138–143.

- Peña, J., Bargar, J., Sposito, G., 2015. Copper sorption by the edge surfaces of synthetic birnessite nanoparticles. *Chem. Geol.* 396, 196–207.
- Peacock, C.L., Sherman, D.M., 2007. Crystal-chemistry of Ni in marine ferromanganese crusts and nodules. *Amer. Mineral.* 92, 1087–1092.
- Ploquin, F., Fritsch, E., Guigner, J.M., Esteve, I., Delbes, L., Dublet, G., Juillot, F., 2019. Phyllosilicate vein-infillings in faulted and Al-poor regoliths of the New Caledonian ophiolite: periodic and sequential crystallization of Ni-asbolane, Alk-birnessite and H-birnessite. *Eur. J. Mineral.* 31, 335–352.
- Post, J.E., Bish, D.L., 1988. Rietveld refinement of the todorokite structure. *Amer. Mineral.* 73, 861–869.
- Post, J.E., Veblen, D.R., 1990. Crystal structure determinations of synthetic sodium, magnesium, and potassium birnessite using TEM and the Rietveld method. *Amer. Mineral.* 75, 477–489.
- Post, J.E., Heaney, P.J., Hanson, J.C., 2003. Synchrotron X-ray diffraction study of the structure and dehydration behavior of todorokite. *Amer. Mineral.* 88, 142–150.
- Ren, J., He, G., Deng, X., Deng, X., Yang, Y., Yao, H., Yang, S., 2022. Metallogenesis of Co-rich ferromanganese nodules in the northwestern Pacific: selective enrichment of metallic elements from seawater. *Ore Geol. Rev.* 143, 104778.
- Ren, J., He, G., Yang, Y., Yu, M., Deng, N., Pang, Y., Zhao, B., Yao, H., 2024. Ultraselective enrichment of trace elements in seawater by Co-rich ferromanganese nodules. *Global Planet. Change* 239, 104498.
- Shen, Y.F., Zenger, R.P., DeGuzman, R.N., Suib, S.L., McCurdy, L., Potter, D.L., O'Young, C.L., 1993. Manganese oxide octahedral molecular sieves: preparation, characterization, and applications. *Science* 260, 511–515.
- Siegel, M.D., Turner, S., 1983. Crystalline todorokite associated with biogenic debris in manganese nodules. *Science* 219, 172–174.
- Su, R., Sun, F.Y., Li, X.H., Chu, F.Y., Sun, G.S., Li, J., Wang, H., Li, Z.G., Zhang, C., Zhang, W.Y., Gong, X.H., Dong, Y.H., 2023. Diverse early diagenetic processes of ferromanganese nodules from the Eastern Pacific Ocean: evidence from mineralogy and in-situ geochemistry. *Int. Geol. Rev.* 65, 2131–2147.
- Takahashi, Y., Manceau, A., Geoffroy, N., Marcus, M.A., Usui, A., 2007. Chemical and structural control of the partitioning of Co, Ce, and Pb in marine ferromanganese oxides. *Geochim. Cosmochim. Acta* 71, 984–1008.
- Tebo, B.M., Bargar, J.R., Clement, B.G., Dick, G.J., Murray, K.J., Parker, D., Verity, R., Webb, S.M., 2004. Biogenic manganese oxides: properties and mechanisms of formation. *Annu. Rev. Earth Planet. Sci.* 32, 287–328.
- Hun, C.A., Ku, T.L., 1984. Radiochemical observations on manganese nodules from three sedimentary environments in the north Pacific. *Geochim. Cosmochim. Acta* 48, 951–963.
- Turner, S., Buseck, P.R., 1981. Todorokites: a new family of naturally occurring manganese oxides. *Science* 212, 1024–1026.
- Shen, X.F., Ding, Y.S., Liu, J., Cai, J., Laubernds, K., Zenger, R.P., Vasiliev, A., Aindow, M., Suib, S.L., 2005. Control of nanometer-scale tunnel sizes of porous manganese oxide octahedral molecular sieve nanomaterials. *Adv. Mater.* 17, 805–809.
- Usui, A., Mellin, T.A., Nohara, M., Yuasa, M., 1989. Structural stability of marine 10 Å manganates from the Ogasawara (Bonin) Arc: implication for low-temperature hydrothermal activity. *Mar. Geol.* 86, 41–56.
- Von Stackelberg, U., Beiersdorf, H., 1991. The formation of manganese nodules between the Clarion and Clipperton fracture zones southeast of Hawaii. *Mar. Geol.* 98, 411–423.
- Von Stackelberg, U. (1997) Growth history of manganese nodules and crusts of the Peru Basin. In: *manganese mineralization: geochemistry and mineralogy of terrestrial and marine deposits. Geol. Soc. Spec. Publ.* 119, 153–176.
- Wadsley, A.D., 1950. Synthesis of some hydrated manganese minerals. *Amer. Mineral.* 35, 485–499.
- Webb, S.M., Tebo, B.M., Bargar, J.R., 2005. Structural characterization of biogenic Mn oxides produced in seawater by the marine *bacillus* sp. strain SG-1. *Amer. Mineral.* 90, 1342–1357.
- Wegorzewski, A.V., Kuhn, T., 2014. The influence of suboxic diagenesis on the formation of manganese nodules in the Clarion Clipperton nodule belt of the Pacific Ocean. *Mar. Geol.* 357, 123–138.
- Wegorzewski, A.V., Grangeon, S., Webb, S.M., Heller, C., Kuhn, T., 2020. Mineralogical transformations in polymetallic nodules and the change of Ni, Cu and Co crystal-chemistry upon burial in sediments. *Geochim. Cosmochim. Acta* 282, 19–37.
- Wegorzewski, A.V., Kuhn, T., Dohrmann, R., Wirth, R., Grangeon, S., 2015. Mineralogical characterization of individual growth structures of Mn-nodules with different Ni+Cu content from the central Pacific Ocean. *Amer. Mineral.* 100, 2497–2508.
- Wu, Z.K., Peacock, C.L., Lanson, B., Yin, H., Zheng, L., Chen, Z., Tan, W.F., Qiu, G., Liu, F., Feng, X.H., 2019. Transformation of Co containing birnessite to todorokite: effect of Co on the transformation and implications for Co mobility. *Geochim. Cosmochim. Acta* 246, 21–40.
- Wu, Z.K., Lanson, B., Feng, X.H., Yin, H., Qin, Z.J., Wang, X.M., Tan, W.F., Chen, Z.J., Wen, W., Liu, F., 2020. Transformation of Ni-containing birnessite to tectomanganate: influence and fate of weakly bound Ni(II) species. *Geochim. Cosmochim. Acta* 271, 96–115.
- Wu, Z.K., Lanson, B., Feng, X.H., Yin, H., Tan, W.F., He, F., Liu, F., 2021. Transformation of the phyllosilicate vernadite to tectomanganates with small tunnel sizes: favorable geochemical conditions and fate of associated Co. *Geochim. Cosmochim. Acta* 295, 224–236.
- Xu, H.F., Chen, T.H., Konishi, H., 2010. HRTEM investigation of trilling todorokite and nano-phase Mn-oxides in manganese dendrites. *Amer. Mineral.* 9, 556–562.
- Yi, L., Medina-Elizalde, M., Kletetschka, G., 2020. The potential of marine ferromanganese nodules from Eastern Pacific as recorders of Earth's magnetic field changes during the past 4.7 Myr: a geochronological study by magnetic scanning and authigenic ¹⁰Be/⁹Be dating. *J. Geophys. Res.-Solid Earth.* 125, e2019JB019145.
- Yuan, Y., He, K., Byles, B.W., Liu, C., Amine, K., Lu, J., Pomerantseva, E., Shahbazian-Yassar, R., 2019. Deciphering the atomic patterns leading to MnO₂ polymorphism. *Chem* 5, 1793–1805.
- Zhang, K., Shields, G.A., 2022. Sedimentary Ce anomalies: secular change and implications for paleoenvironmental evolution. *Earth Sci. Rev.* 229, 104015.
- Zhang, K., Shields, G.A., 2023. Early diagenetic mobilization of rare earth elements and implications for the Ce anomaly as a redox proxy. *Chem. Geol.* 635, 121619.
- Zhao, H., Zhu, M., Li, W., Elzinga, E.J., Villalobos, M., Liu, F., Zhang, J., Feng, X., Sparks, D.L., 2016. Redox reactions between Mn(II) and hexagonal birnessite change its layer symmetry. *Environ. Sci. Technol.* 50, 1750–1758.
- Zhou, J., Kogure, T., Okumura, T., Takahashi, Y., Liu, J., Yang, S., Yuan, P., 2024. Characterization of submicron-thick layered structure in hydrogenetic ferromanganese nodule suggests short-term redox fluctuation of paleo-ocean. *J. Geophys. Res.-Oceans.* 129, e2023JC020240.

[Distribution of Mn oxides in polymetallic nodules from the Clarion-Clipperton Fracture Zone: Implications for Ni and Cu fate]

Zedong Fan^{a, b}, Xiaohu Li^{a, b} *, Yanhui Dong^b, Bruno Lanson^c, Zhongkuan Wu^d, Weilin Ma^b, Zhenggang Li^b, Junming Zhou^e, Yi Ding^f, Hao Wang^b, Zhimin Zhu^b, Jie Li^b, Xingwei Meng^b, Huaiming Li^b, Fengyou Chu^b

^a School of Oceanography, Shanghai Jiao Tong University, 200240 Shanghai, China

^b State Key Laboratory of Submarine Geoscience, Second Institute of Oceanography, Ministry of Natural Resources, Hangzhou 310012, China.

^c Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, IRD, Univ. Gustave Eiffel, ISTERre, F-38000 Grenoble, France

^d College of Environment, Zhejiang University of Technology, Hangzhou 310014, China

^e Hong Kong Branch of Southern Marine Science and Engineering Guangdong Laboratory (Guangzhou), Hong Kong University of Science and Technology, Hong Kong SAR 999077, China

^f Changzhi University, Changzhi, 046011, China

Corresponding author: Xiaohu Li (xhli@sio.org.cn)

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Table S1.

E-DY54-L1 Chemical composition by EDS (wt%)

Area	Element	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit Error (%)
Area#1 (Phyllomanganate)	Mn	92.92	0.82	92.01	0.92	0.47
	Fe	0.00	0.01	0.00	0.01	0.00
	Co	0.16	0.02	0.17	0.02	4.26
	Ni	1.15	0.17	1.21	0.18	0.53
	Cu	5.78	0.80	6.61	0.91	0.26
Area#2 (Todorokite)	Mn	93.31	0.78	92.43	0.89	0.33
	Fe	0.00	0.01	0.00	0.01	0.00
	Co	0.19	0.03	0.20	0.03	1.97
	Ni	0.95	0.14	1.01	0.15	0.70
	Cu	5.55	0.77	6.36	0.88	0.61

Note: Samples were mounted using copper grids and the determined Cu content is thus representative of that of the Mn oxides in nodule E-DY54-L1

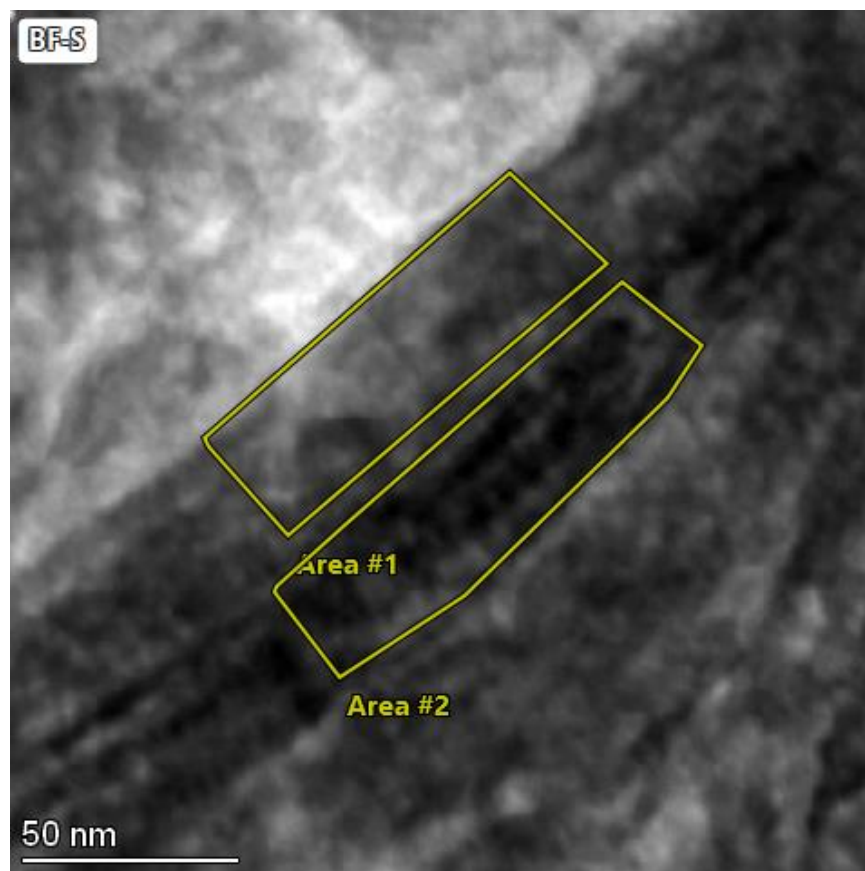


Figure S1. Low magnification TEM image of E-DY54-L1 showing the adjacent areas that were analyzed with energy dispersive spectroscopy (Table S1)

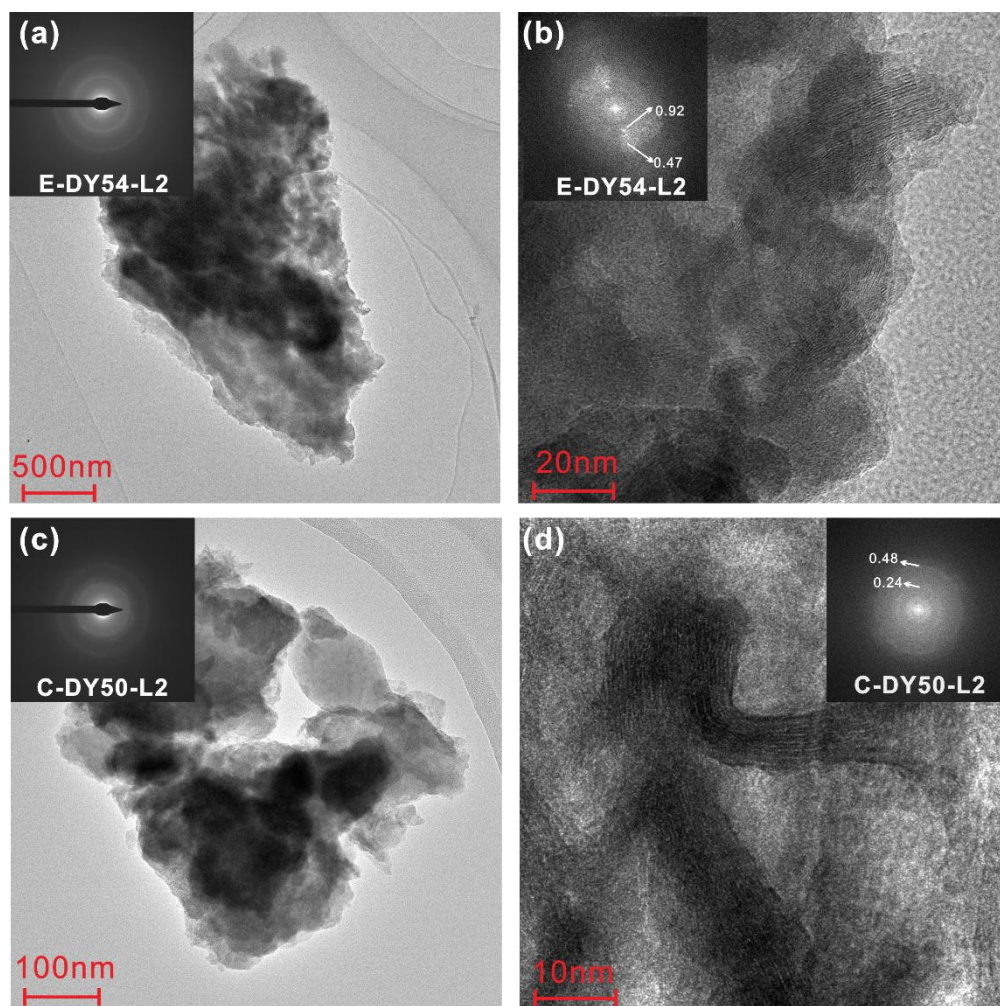


Figure S2. Low magnification TEM image of L2 in E-DY54 (a, b) and C-DY50 (c, d). a and c, SAED displays diffuse diffraction rings, only two $hk0$ reflections are indexed; b and d, 10 Å lattice fringes can be distinguished, which correspond to 10 Å phyllomanganate.

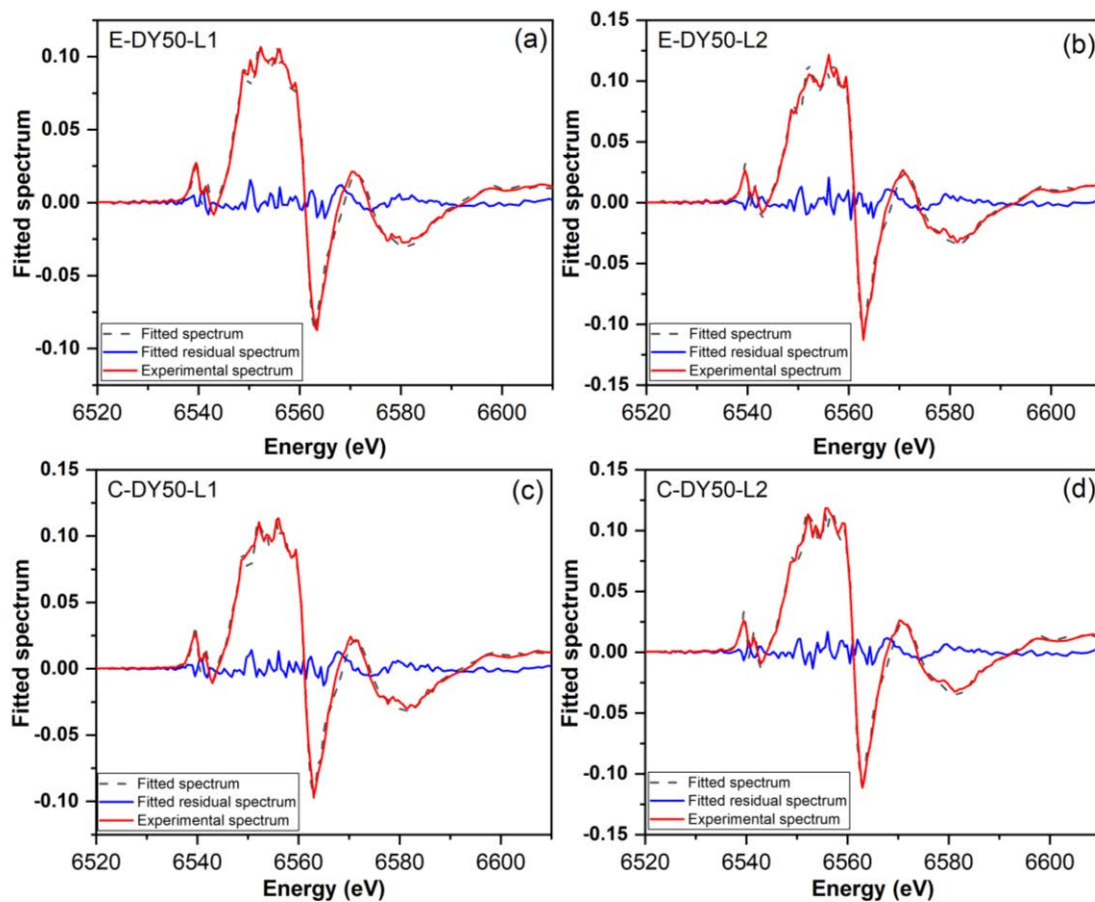


Figure S3. Mn K-edge XANES first derivative fitting using the Combo method (Manceau et al., 2012). The black dashed line represents the experimental spectrum, the solid red line

represents the best fit, and the blue dashed line represents the difference between the two spectra.

The standard samples used for data fitting are from [Manceau et al. \(2012\)](#)

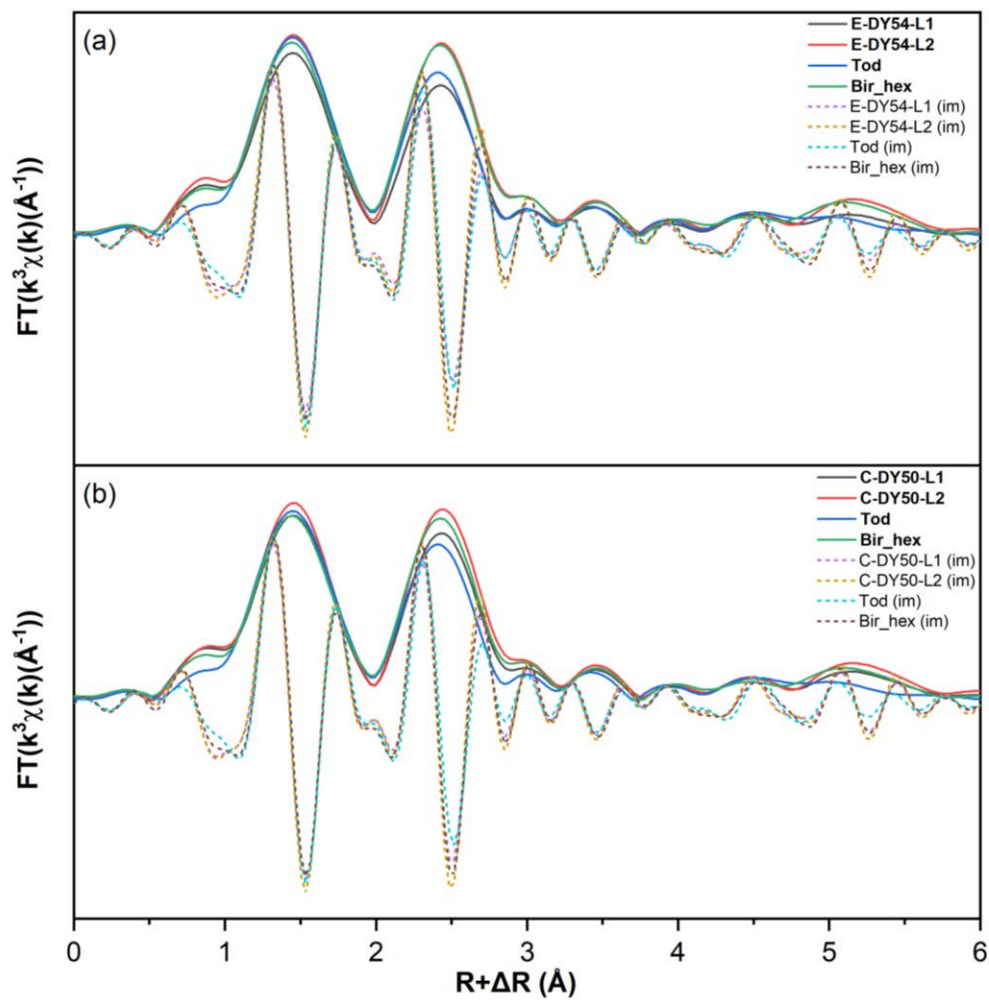


Figure S4. Fourier transforms of the Mn K-edge XANES data, showing the real (solid line) and imaginary (dashed line) parts.

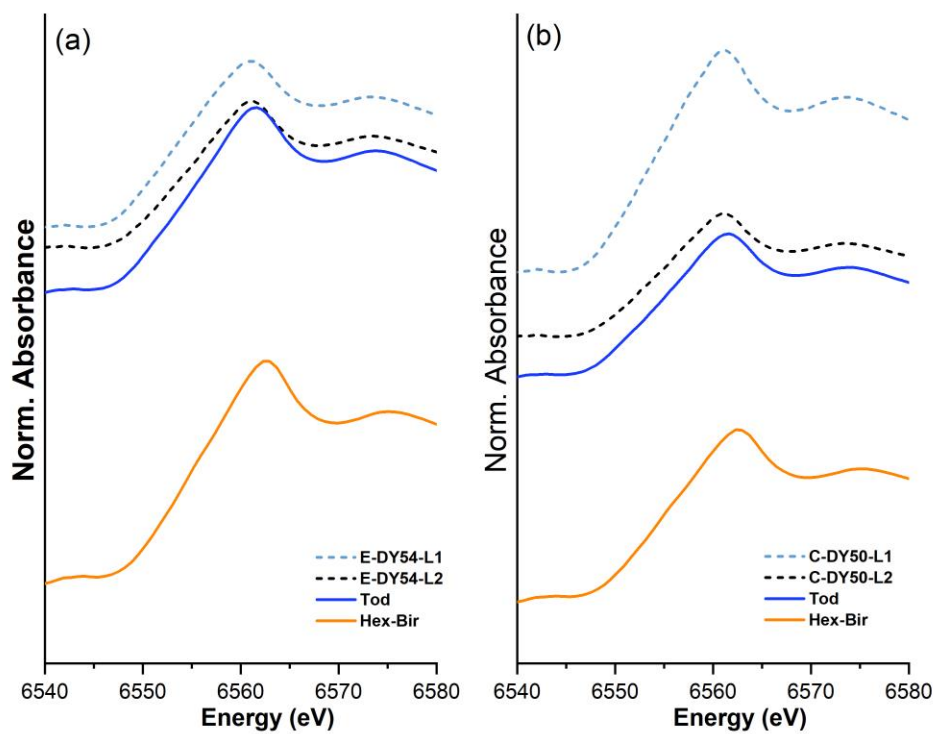


Figure S5. XANES spectra of nodules E-DY54 and C-DY50.

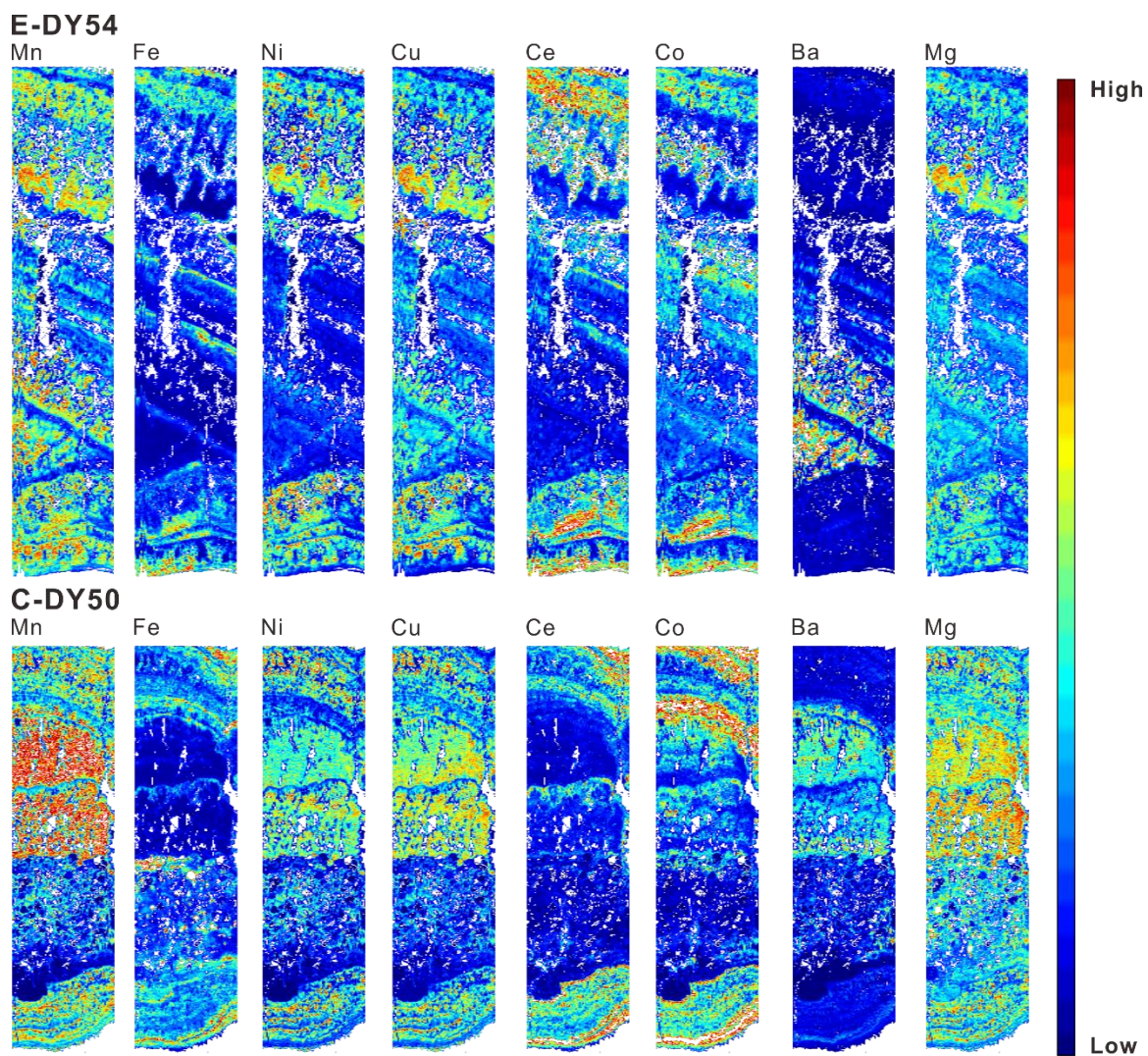


Figure S6. LA-ICP-MS mapping of elemental distributions in nodules E-DY54 and C-DY50.

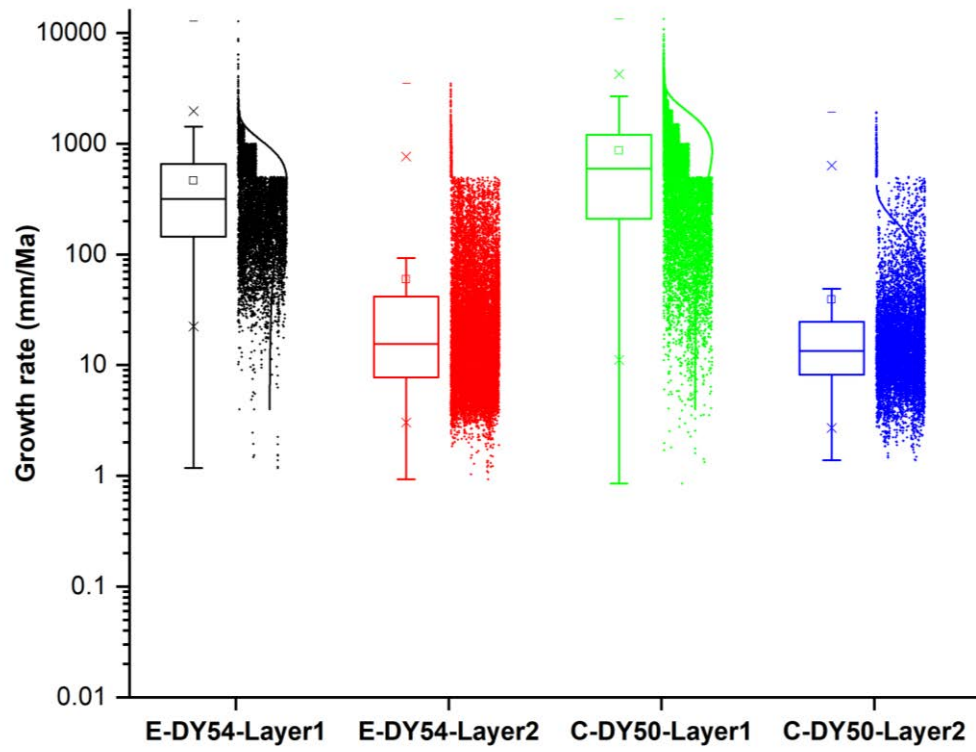


Figure S7. Box plots of nodule growth rates, calculated using the empirical formula $13.8 \times (\text{Mn}/\text{Fe}^2) + 0.75$ (Hun and Ku, 1984). Data sourced from LA-ICP-MS elemental maps.

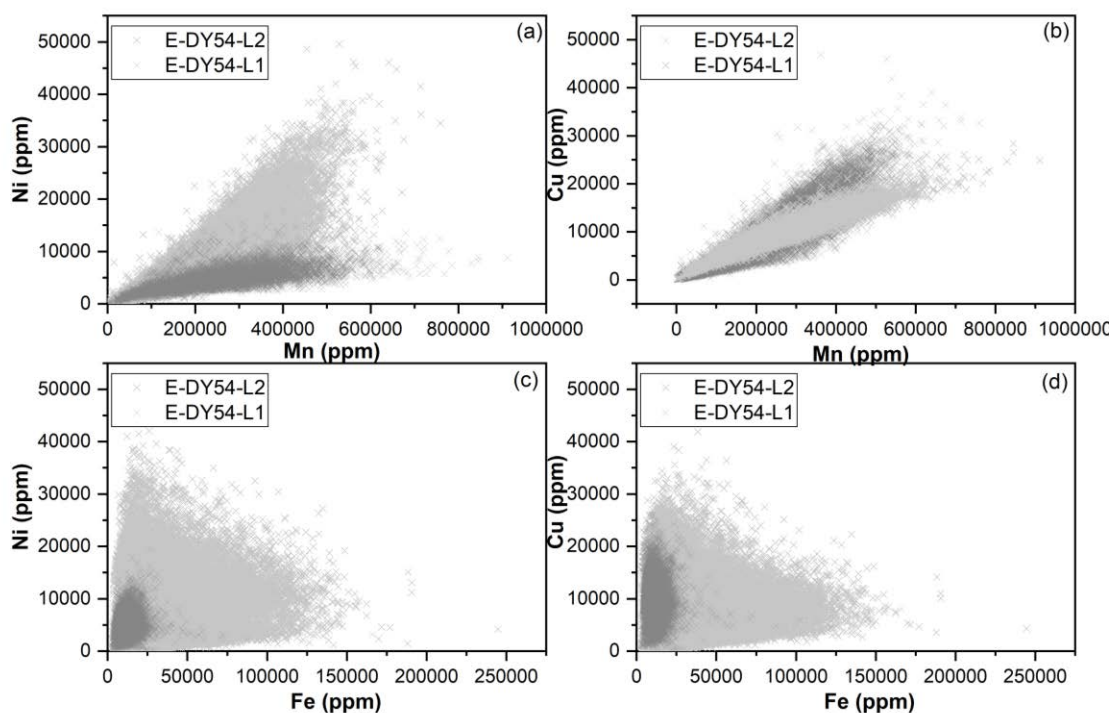


Figure S8. Co-variance plots of Ni and Cu contents Vs Mn and Fe contents in samples E-DY54-L1 and E-DY54-L2

Samples L1 and L2 (100 mg each, in powder form) were separately reacted with 250 mL of 1 M HNO_3 solution. During the reaction, 5 mL aliquots were collected at designated time intervals, filtered through a 0.22 μm membrane, and subsequently analyzed for metal ion concentrations. The analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS, NexION 2000G, PerkinElmer, USA). Calibration standards were prepared by diluting commercial 1000 mg/L ICP-MS standard solutions (Inorganic Ventures, USA) with 2% nitric acid. Element concentrations were quantified using an external calibration method with rhodium (Rh) as the internal standard.

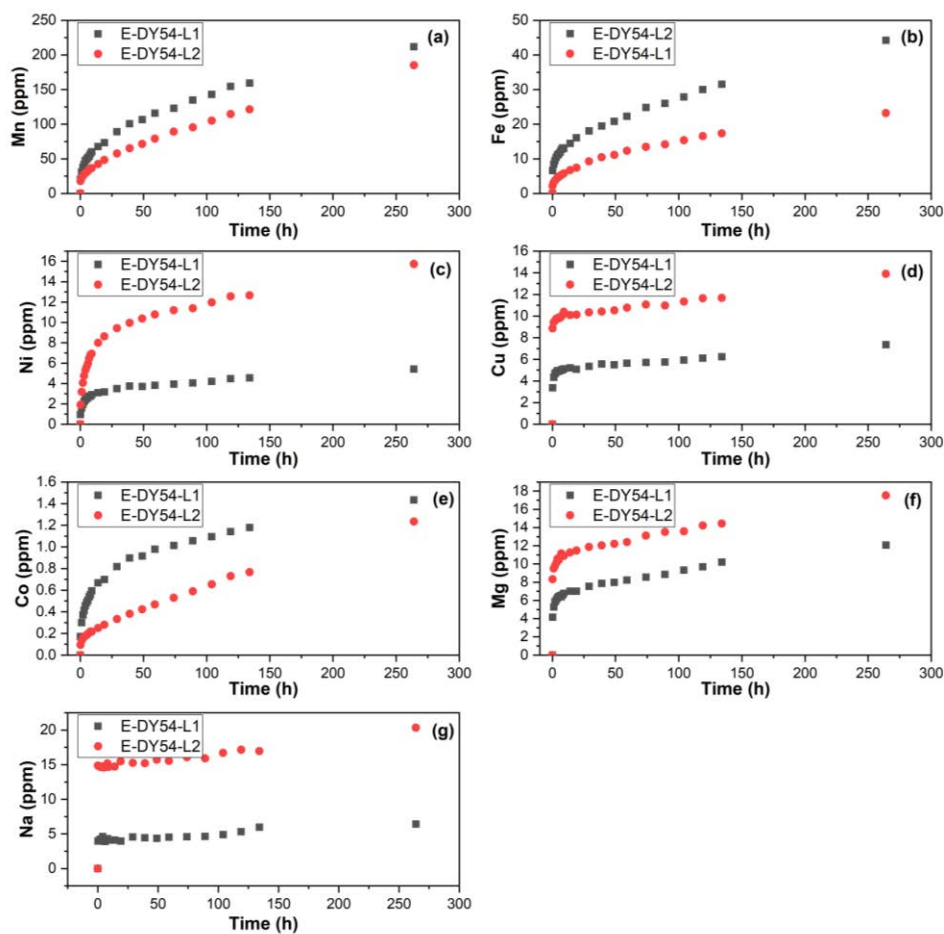


Figure S9. Proportion of metal cations released during nitric acid treatment of samples E-DY54-L1 (solid black squares) and E-DY54-L2 (solid red disks).

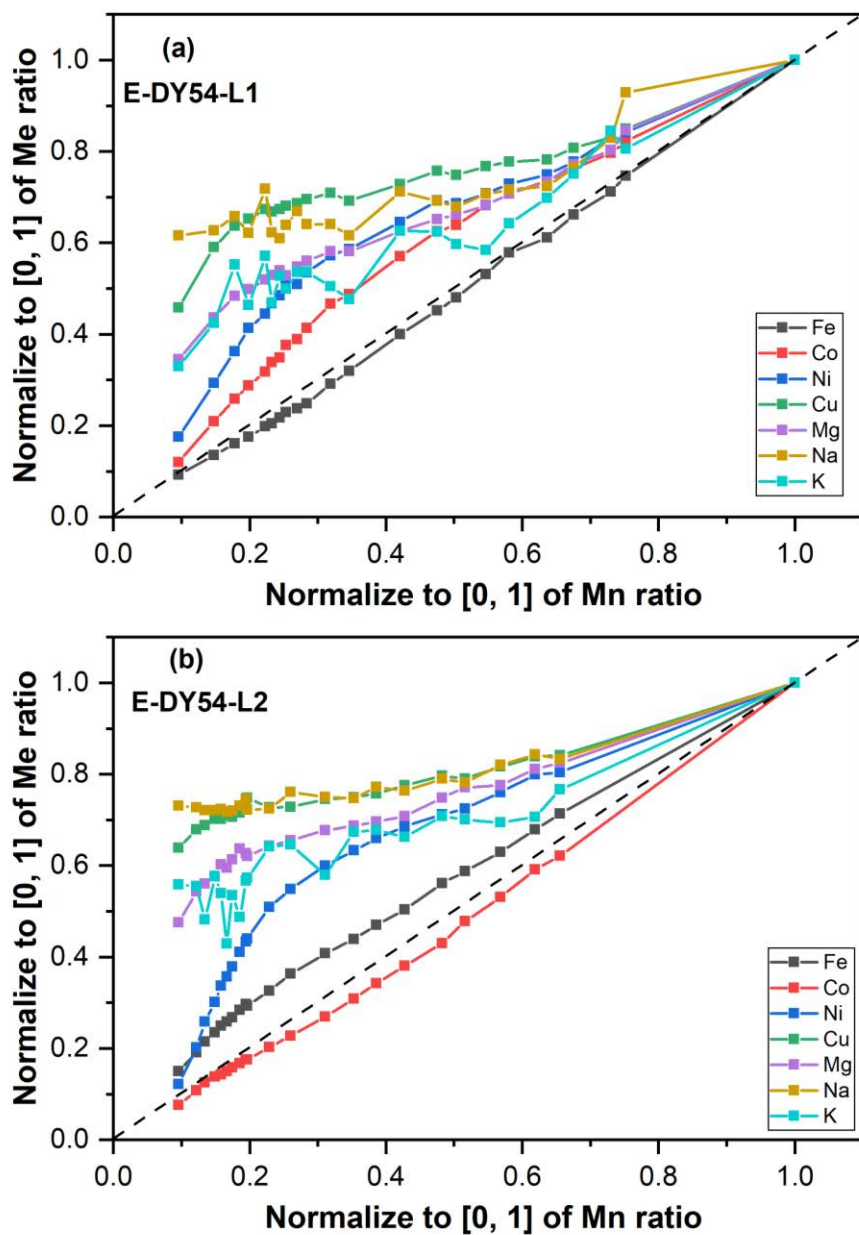


Figure S10. Proportion of metal cations released during the nitric acid treatment of samples (a) E-DY54-L1 and (b) E-DY54-L2 as a function of Mn release. The amount of metal released is normalized to the sample overall metal release during the treatment.

Table S2.

Individual microlayer geochemical data of the nodules analyzed (EMPA data; wt.%).

		Layer	MgO	Al ₂ O	CoO	NiO	CuO	ZnO	FeO	MnO	TiO ₂	Na ₂ O	SiO ₂	K ₂ O	CaO	P ₂ O ₅	BaO	Total
C-DY50	spot1	L1	3.60	2.75	0.21	1.85	1.34	0.15	1.12	45.99	0.19	1.06	4.41	0.85	1.32	0.16	0.77	65.77
	spot2	L1	3.47	0.55	0.12	1.05	1.52	0.27	0.35	56.40	0.04	2.60	1.02	1.54	1.17	0.11	0.36	70.57
	spot3	L1	3.21	1.94	0.14	1.59	1.48	0.20	1.07	56.46	0.19	2.03	4.24	1.51	1.48	0.13	0.77	76.44
	spot4	L1	3.66	1.52	0.06	1.74	1.58	0.19	0.62	51.12	0.07	2.75	2.22	1.48	1.17	0.11	0.32	68.61
	spot5	L1	3.22	1.12	0.10	1.70	1.73	0.15	0.77	56.90	0.07	2.93	1.03	1.18	1.70	0.12	0.39	73.09
	spot6	L1	3.13	0.49	0.03	1.08	1.71	0.24	0.42	57.67	0.05	2.76	0.58	1.41	1.35	0.15	0.58	71.62
	spot7	L1	2.84	0.86	0.44	1.43	1.56	0.11	0.85	51.62	0.09	2.80	2.00	1.31	1.22	0.08	0.52	67.72
	spot8	L2	1.37	1.91	0.46	1.07	0.76	0.13	13.08	42.94	2.35	2.39	6.59	0.73	4.49	0.62	0.24	79.10
	spot9	L2	3.22	0.99	0.09	2.02	2.84	0.37	0.71	50.77	0.08	2.19	1.79	0.71	6.38	0.16	0.16	72.47
	spot10	L2	1.73	2.82	0.38	0.66	0.63	0.04	20.02	27.52	1.61	1.03	11.92	0.49	2.80	0.62	0.25	72.51
	spot11	L2	1.02	2.16	0.41	0.60	0.51	0.06	17.51	34.10	1.70	1.52	10.37	0.57	4.46	0.76	0.14	75.88
	spot12	L2	1.04	1.65	0.51	0.23	0.13	0.07	14.79	18.08	1.29	0.81	6.78	0.36	2.23	0.58	0.09	48.64
	spot13	L2	1.42	2.70	0.79	0.90	0.31	0.07	15.67	40.60	1.37	1.10	8.12	0.79	4.17	0.86	0.26	79.11
	spot14	L2	1.55	1.98	0.73	0.65	0.52	0.12	20.61	34.12	1.79	1.59	8.44	0.47	3.71	0.77	0.27	77.33
	spot15	L2	2.40	3.04	0.34	1.70	0.82	0.11	10.26	43.48	1.01	2.57	8.07	0.95	3.14	0.49	0.14	78.52
E-DY54	spot1	L1	3.23	1.29	0.08	0.93	1.73	0.03	0.59	56.80	0.09	1.47	2.11	1.34	0.97	0.11	1.14	71.90
	spot2	L1	2.62	3.94	0.12	0.45	1.35	0.03	2.59	47.97	0.32	1.06	14.02	1.40	1.05	0.20	3.32	80.43
	spot3	L1	1.97	0.81	0.13	0.37	1.35	0.02	1.11	58.21	0.49	1.24	1.54	1.25	1.23	0.20	4.67	74.58
	spot4	L1	2.01	1.46	0.44	0.45	0.96	0.08	11.88	24.24	0.05	0.83	10.05	0.67	1.23	0.36	0.48	55.16
	spot5	L1	1.89	1.79	0.09	0.37	0.91	0.01	1.40	28.19	0.09	0.80	3.90	0.72	0.50	0.21	0.60	41.46
	spot6	L1	3.17	2.34	0.26	0.61	1.58	0.05	2.78	49.58	0.12	2.12	6.43	1.17	1.09	0.19	0.94	72.42
	spot7	L1	2.35	2.85	0.65	0.51	1.08	0.03	18.52	28.87	0.15	1.73	16.11	0.89	2.21	0.57	0.52	77.01
	spot8	L1	4.20	3.87	0.36	2.02	2.44	0.12	1.40	48.63	0.37	2.43	7.85	0.89	1.30	0.09	0.39	76.36
	spot9	L1	4.17	3.96	0.09	2.59	3.10	0.04	1.85	48.38	0.13	2.56	4.07	0.67	0.88	0.11	0.01	72.62

spot10	Mn-rich	2.74	0.93	0.11	2.11	3.24	0.27	0.41	57.11	0.07	3.45	1.41	0.82	1.48	0.13	0.18	74.44
spot11	Mn-rich	4.72	2.65	0.12	2.11	2.12	0.27	0.46	55.72	0.03	2.16	2.89	1.20	1.24	0.09	0.21	75.98
spot12	L2	5.85	4.83	0.10	3.16	2.99	0.16	1.04	51.17	0.16	2.33	3.82	0.57	1.24	0.11	0.09	77.60
spot13	L2	6.53	3.87	0.24	3.51	1.88	0.22	3.38	51.17	0.42	1.49	2.56	0.44	1.70	0.18	0.13	77.72
spot14	L2	1.48	2.10	0.40	0.61	0.40	0.09	15.21	19.53	1.02	1.35	9.13	0.46	1.61	0.63	0.26	54.26
spot15	L2	1.80	1.69	0.50	0.95	0.66	0.16	17.11	39.62	1.23	1.04	7.38	0.29	3.37	0.66	0.11	76.56
spot16	L2	2.59	2.58	0.93	1.00	0.37	0.08	19.36	35.46	1.78	1.26	9.55	0.47	3.16	0.79	0.24	79.60
spot17	L2	1.00	1.29	0.47	0.59	0.20	0.03	12.43	21.88	1.09	0.47	4.70	0.16	1.69	0.62	0.22	46.83
spot18	L2	1.16	2.94	0.56	1.00	0.44	0.1	18.46	33.65	1.80	1.39	12.59	0.83	2.93	0.82	0.28	78.94

Table S3.

Metal contents of bulk nodules from the CCFZ

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	K ₂ O	P ₂ O ₅
CCFZ-east-N1	16.24	0.52	5.09	8.35	39.29	3.11	2.24	1.41	0.34
CCFZ-east-N2	15.70	0.34	4.45	6.66	40.48	2.54	2.37	1.14	0.31
CCFZ-east-N3	15.17	0.37	4.60	6.69	41.03	2.78	2.38	1.12	0.30
CCFZ-east-N4	14.75	0.46	4.80	7.28	40.44	3.18	2.23	1.20	0.31
CCFZ-east-N5	15.65	0.45	4.92	7.36	39.69	3.05	2.24	1.23	0.31
CCFZ-east-N6	15.45	0.41	4.90	7.59	39.36	2.89	2.57	1.16	0.46
CCFZ-east-N7	14.81	0.36	4.62	6.88	40.73	2.77	2.45	1.08	0.33
CCFZ-east-N8	14.95	0.39	4.75	7.09	40.58	2.89	2.48	1.05	0.33
CCFZ-east-N9	14.93	0.39	4.90	7.11	40.78	2.92	2.45	1.08	0.33
CCFZ-east-N10	14.13	0.38	4.49	6.79	42.03	2.77	2.42	1.09	0.32
CCFZ-east-N11	15.18	0.31	4.54	6.30	42.16	2.71	2.42	1.13	0.30
CCFZ-east-N12	13.30	0.55	4.77	7.75	40.43	3.10	2.37	1.05	0.34
CCFZ-east-N13	14.12	0.45	4.66	7.61	40.70	2.99	2.27	1.08	0.34
CCFZ-east-N14	15.32	0.50	4.94	8.26	39.00	3.00	2.32	1.08	0.35