

Jianshuiite in oceanic manganese nodules at the Paleocene-Eocene boundary

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ABSTRACT

Synchrotron powder X-ray diffraction and scanning electron microscopy examinations of manganese oxide concretions/nodules (~0.3–1.0 mm diameter) from ODP Site 1262 on Walvis Ridge in the Southeastern Atlantic Ocean revealed that they consist primarily of the layered Mn oxide phase jianshuiite $[(\text{Mg}, \text{Mn}, \text{Ca})\text{Mn}_3^{4+}\text{O}_7 \cdot 3\text{H}_2\text{O}]$. The nodules are from an interval with severe carbonate dissolution that represents the Paleocene/Eocene (P/E) thermal maximum (~55.8 Ma). Most nodules from the middle of the carbonate dissolution interval contain internal open space, and consist almost entirely of euhedral plate-like jianshuiite crystals, 2–4 μm in diameter and ~0.1–0.5 μm thick. Backscattered electron images and energy-dispersive X-ray analyses revealed stacks of interleaved Al-rich and Al-poor jianshuiite crystals in some nodules. The crystals in other nodules contain predominantly Mg (with trace K and Al) in addition to Mn and O, making them near “end-member” jianshuiite. Rietveld refinements in space group $R\bar{3}$ confirmed the isostructural relationship between jianshuiite and chalcophanite, with Mg occupying the interlayer position above and below the vacant sites in the Mn/O octahedral sheet, and coordinated to 3 octahedral layer O atoms (1.94 Å) and 3 interlayer water O atoms (2.13 Å). Final refined occupancy factors suggest that small quantities of Ni and possibly Mn^{2+} are located on the Mg site. The transient appearance of the Mg-rich birnessite-like phase jianshuiite, probably abiotically produced, must indicate an exceptional transient change in the chemistry of the pore fluids within deep ocean sediments directly following the P/E boundary, possibly as a result of decreasing oxygen levels and pH, followed by a return to pre-event conditions.

Keywords: Jianshuiite, birnessite, paleocene-eocene thermal maximum (PETM), X-ray diffraction

INTRODUCTION

Site 1262 was drilled on Ocean Drilling Program Leg 208 on the northwestern flank of Walvis Ridge in the Southeastern Atlantic Ocean, west of South Africa (Zachos et al. 2004). Lower Cenozoic sediments at Site 1262 consist mainly of foraminifera-bearing, carbonate-rich nannofossil ooze with minor clay and volcanic ash. The Paleocene/Eocene (P/E) boundary occurs at an abrupt contact between nannofossil ooze and a red clay (Zachos et al. 2005; McCarren et al. 2008) (Fig. 1). This clay layer corresponds to a period of severe carbonate dissolution at the onset of the most extreme global warming event in the Cenozoic, the Paleocene/Eocene Thermal Maximum (PETM), dated at ~55.8 Mya (e.g., McNerney and Wing 2011; Dunkley-Jones et al. 2013). The warming was triggered by a massive injection of isotopically light carbon into the ocean-atmosphere system (e.g., Dickens et al. 1995; Thomas and Shackleton 1996). The source of the carbon, its nature (CH_4 or CO_2 or a mixture), and the mechanisms and duration of release are still debated (McNerney and Wing 2011; Dickens 2011; Dunkley-Jones et al. 2013). The strong increase in atmospheric pCO_2 caused by the release of thousands of gigatons of carbon compounds over <10 000 yr caused global warming by

5–8 °C (Dunkley-Jones et al. 2013) and severe ocean acidification, and these events in turn led to an abrupt shallowing of the carbonate compensation depth (Zachos et al. 2005; Ridgwell and Schmidt 2010; Hoenisch et al. 2012; Winguth et al. 2012).

The >38 μm size fraction of the sediment in the carbonate-free section at Site 1262 (paleodepth ~3500 m; Zachos et al. 2005; Foster et al. 2013) consists primarily of Mn oxide “nodules,” along with fish detritus (Fig. 2a). The nodules measure ~1–5 mm or smaller in diameter. They comprise only a minor fraction of the bulk sediment, with only <1 wt% of the bulk sediment in the >38 μm size fraction. The concentration of Mn in the bulk clay layer is ~20 $\mu\text{mol/g}$ (Chun et al. 2010).

For this study, we investigated the mineralogy of the Mn nodules in the sedimentary record at Site 1262 as well as similar nodules at other sites on Walvis Ridge (e.g., Site 1265, Zachos et al. 2004). Our analyses of the nodules from the PETM clay interval at Site 1262 revealed the predominance of jianshuiite, a Mg-rich phyllosulfate, with unusually high crystallinity. For the first time, we present a full structure refinement and characterization of this rare Mn oxide mineral. Since the PETM represents an extreme climatic anomaly in the Cenozoic, unusual minerals within the sediments associated with this event, and their geographic and bathymetric occurrence, may provide important clues to explain the origin of the warming episode.

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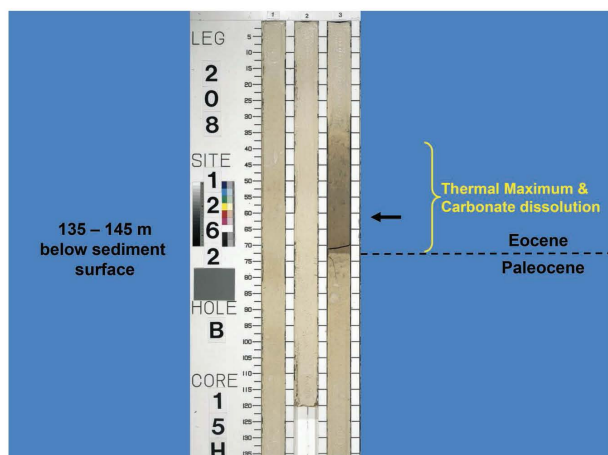


FIGURE 1. Section of Core 208-1262B-15H recovered during Ocean Drilling Leg 208 (Zachos et al. 2004). The Eocene/Paleocene boundary is at the contact between the light-colored calcareous ooze and the dark clay, marking the beginning of the thermal maximum and associated severe carbonate dissolution. The nodule used for the X-ray diffraction study was recovered from the section of the core indicated by the arrow. (Color online.)

EXPERIMENTAL DETAILS

Sample selection

All samples were taken from cores collected during Ocean Drilling Program Leg 208 (March–May 2003) (Zachos et al. 2004). Cores were treated following standard procedure on Ocean Drilling expeditions, i.e., they were split, described, and photographed on-board ship. The Mn nodules were noted during core description onboard ship (Zachos et al. 2004). The core halves were designated as archive half and working half, and placed in plastic D-tubes, with the sediment kept moist by inserting a sponge before closing and taping the D-tube. Cores were kept in cold storage space on the ship, during transport and in the core repository. Some samples were taken onboard ship, others during sampling at the Bremen (Germany) core repository from the working half of the core several months after the cruise. Samples were freeze-dried and wet-sieved following standard paleoceanographic procedure (e.g., McCaren et al. 2008). The nodules were hand-picked from the $>38\ \mu\text{m}$ sieve fraction using a binocular microscope. The individual samples were small (slices 1 cm thick, McCaren et al. 2008), and all nodules were picked from the samples.

Twelve nodules were examined from the $>38\ \mu\text{m}$ sieve fraction recovered from Site 1262 ($27^{\circ}11.15'\text{S}$, $01^{\circ}34.62'\text{E}$; water depth 4755 m), Hole B, Core 15H, Section 3, from the $\sim 30\ \text{cm}$ interval above the P/E contact (Fig. 1), ranging from the bottom to the top of that interval. We also studied similar looking nodules, in size and shape, from older and younger sediments in cores from Site 1262 and nearby Site 1265 ($28^{\circ}50.10'\text{S}$, $02^{\circ}38.35'\text{E}$, depth 3060 m), including: 1262A-4H (Miocene), 1265A-27H (lower Eocene), 1265A-18H (lower Oligocene), and 1262A-17H (mid-Paleocene). We looked for nodules at the shallowest site drilled on Walvis Ridge, Site 1263, which also contains an interval of severe carbonate dissolution across the PETM (Zachos et al. 2005), but the carbonate-free sediments do not contain Mn-oxide nodules. Mn may be present as Mn-carbonate (Chun et al. 2010).

Sample characterization

Scanning electron microscopy. We performed analytical scanning electron microscopy (SEM) using an FEI Nova NanoSEM 600 with a Thermo-Ultrady Silicon drift energy-dispersive X-ray detector in the Department of Mineral Sciences, Smithsonian Institution. The nodules were mounted onto carbon tape on a carbon stub; backscattered electron imaging and energy-dispersive spectroscopy (EDS) analyses were carried out on uncoated samples using the low-vacuum mode and 15 keV accelerating voltage.

X-ray diffraction and crystallographic analysis. We used both conventional and synchrotron powder X-ray diffraction to characterize the minerals in the Mn-oxide nodules from the PETM-clay interval at Site 1262. Initial sample

identification was performed using a Rigaku D-MAX Rapid microdiffractometer with $\text{MoK}\alpha$ radiation and an imaging plate detector. For these experiments, a $\sim 1\ \text{mm}$ nodule (from $\sim 11\ \text{cm}$ above the P/E contact) was mounted with super glue onto a glass fiber and rotated 1° per second during powder diffraction data collection. The synchrotron X-ray diffraction data from the same nodule were collected at beamline 13-BM-C ($\lambda = 0.8265(8)\ \text{\AA}$; CCD detector radius = $95.165\ \text{mm}$) at the Advanced Photon Source (APS), Argonne National Laboratory (ANL), using an exposure time of 30 s. The small, and uniform, jianshuiite crystallite sizes and their “random” arrangement within the nodule provided for good quality diffraction data. Although none was obvious, any possible preferred orientation of the powder was eliminated by full intensity integration of the diffraction rings, as obtained using the program Fit2D (Hammersley et al. 1996) with a polarization factor of 0.99.

Rietveld refinements were performed using the general structure analysis system (GSAS) of Larson and Von Dreele (2006) and EXPGUI interface by Toby (2001). The starting jianshuiite structural parameters were taken from the isostructural chalcophanite structure reported by Post and Appleman (1988). Difference-Fourier maps were calculated using the MnO octahedral layers to locate the Mg atoms and water molecules in the interlayer region. The diffraction pattern backgrounds were fit using a linear interpolation function. Peak profiles

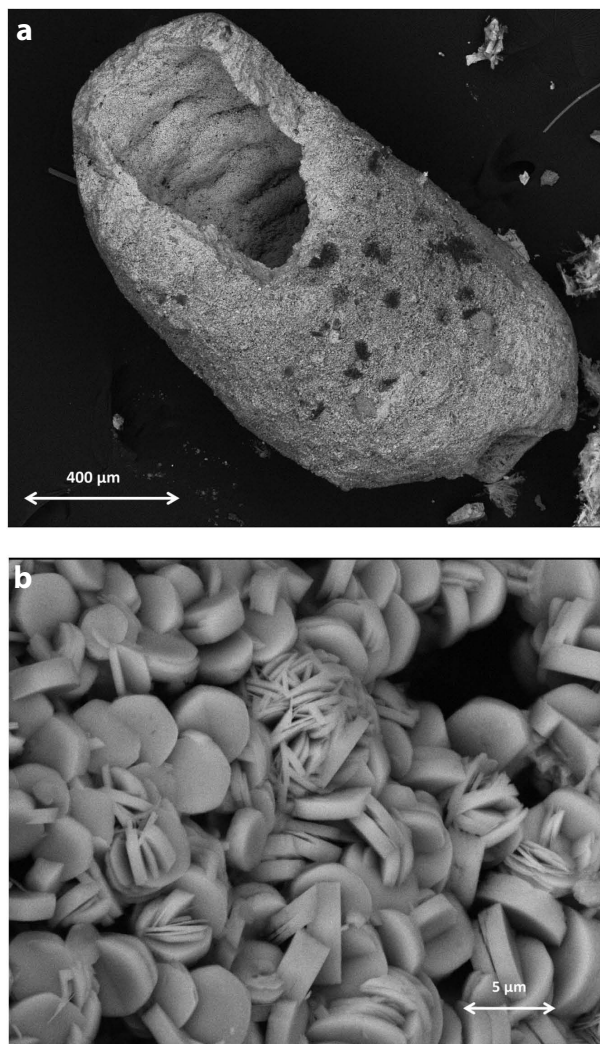


FIGURE 2. Backscattered scanning electron microscope (BSE SEM) images of Mn nodules from $\sim 11\ \text{cm}$ above the Eocene/Paleocene boundary in Core 208-1262B-15H. (a) Complete nodule measuring $\sim 1.2 \times 0.6\ \text{mm}$, showing hollow interior; (b) higher magnification image of the nodule wall reveals that the nodule consists almost entirely of $\sim 5\ \mu\text{m}$ diameter euhedral, plate-like jianshuiite crystals.

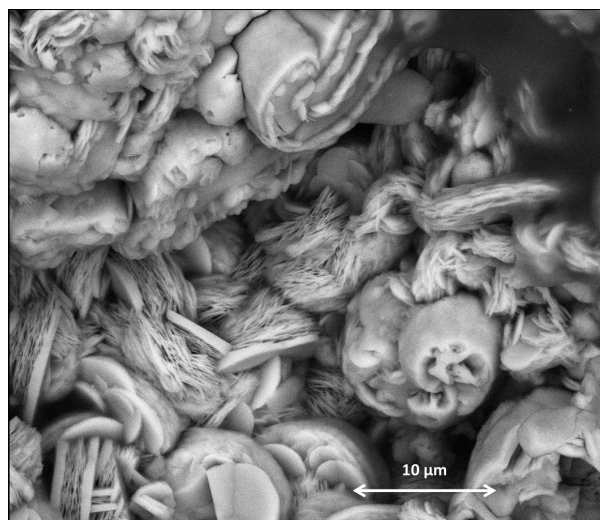
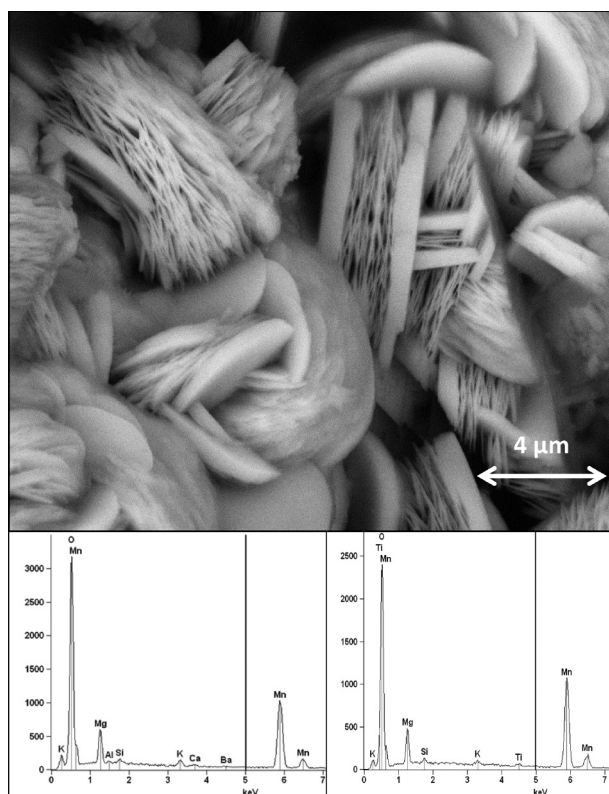


FIGURE 3. (a) Jianshuiite crystals from 9 cm above the P/E contact appear to have “exfoliated,” perhaps resulting from delamination caused by cation-exchange. EDS analyses (below image) show that thick “caps” contain predominantly Mn, Mg, and O with minor K and Ba (labeled as Ti) (EDS spectrum on lower right), whereas the thin central sheet-like layers contain greater amounts of K and Ca and some Ba (EDS spectrum on lower left). (b) BSE image showing a range of particle morphologies, all mainly Mn, O, and Mg, but darker areas are more Al-rich and contain minor Ni and Co.

were modeled by a pseudo-Voigt profile function as parameterized by Thompson et al. (1987) with asymmetry corrections by Finger et al. (1994) and microstrain anisotropic broadening terms by Stephens (1999).

During the initial cycles of refinement, only the background, scale, peak profile, and unit-cell parameters were allowed to vary. After convergence, all atom positions, displacement factors, and appropriate occupancy factors (e.g., of the Mg and Mn sites) were refined. Difference patterns revealed a small amount of quartz in the sample, consistent with SEM observations. Rietveld refinement that included quartz improved the fit and revealed its abundance as <2 wt% of the sample.

RESULTS

Nodule characterization by microscopy

The Mn-rich nodules from the clay interval at Site 1262 typically were dark brown and ovoid, ranging in length from ~0.3 to ~1 mm along the longest axis. Most of the nodules contained an internal open space (Fig. 2a) with walls measuring ~100 μm in thickness. The sizes and shapes of the hollow nodules were not obviously suggestive of pseudomorphism after a precursor mineral or organism, such as foraminiferal tests (B. Huber, personal communication), but some could have been pseudomorphs of fecal pellets.

Backscattered electron images at high magnification revealed that the nodule walls consist of euhedral crystals with apparently hexagonal symmetry, measuring 3–5 μm across, with a thickness of 0.1 to 1 μm (Fig. 2b). Because of the small size of the crystals, it was not possible to obtain quantitative electron microprobe analyses, but EDS analyses of the crystals showed predominantly Mn and O, with Mg and various amounts of Al, and minor K, Ca, Ba, Si, Ni, and Co. These analyses led to an initial identification of the material composing the nodular walls as the magnesian

birnessite-like phase jianshuiite: $\text{MgMn}_3^{4+}\text{O}_7 \cdot 2.80 \text{H}_2\text{O}$ (Guiyin et al. 1992). Some of the jianshuiite crystals (Figs. 3a and 3b) appear to have separated into thin layers, reminiscent of a vermiculite crystal that swells and expands upon heating. EDS analyses of the expanded regions showed higher concentrations of Ca, K, and Ba, and less Al and Ni, than did the more compacted portions of the crystals (Fig. 3a).

Although micronodules that were apparently similar in shape, color, and size were observed throughout the cores of several sites drilled on Walvis Ridge (Zachos et al. 2004), the jianshuiite crystals were observed only in nodules from within the horizon immediately above the P/E boundary, corresponding to the Core 1262A-15H-3 interval between ~73 and 40 cm, where carbonate dissolution was greatest. We examined by SEM/EDS five nodules that spanned this interval and observed variations in the proportions of carbonate nanofossils and Mn oxides, and in the type of Mn oxide.

A nodule from ~1 cm above the P/E contact contained numerous carbonate nanofossils and other mineral grains, including clays, such as illite, quartz, and barite. The jianshuiite crystals in this nodule were subhedral to rarely euhedral in shape. A nodule from ~9 cm above the contact was devoid of carbonates, and it consisted predominantly of euhedral jianshuiite, but many of the crystals were exfoliated into thin layers that were more K- and Ca-rich than the bulk jianshuiite (Figs. 3a and 3b). A nodule from ~11 cm above the contact was composed almost entirely of euhedral jianshuiite crystals, with scattered grains of quartz and K- and Mg-rich silicates (likely clays) and apatite. This nodule was used for our crystal structure refinement of jianshuiite. In a nodule from 22 cm above the P/E boundary, carbonate nanno-

fossils reappear, and euhedral jianshuiite crystals line vugs and the interior cavity wall. A nodule from 32 cm above the contact contained abundant carbonate nannofossils with euhedral jianshuiite crystals in small cavities and vugs (Fig. 4).

We also examined several nodules from other cores at Site 1262 and nearby Site 1265 that were recovered from sediments older and younger than the PETM. These nodules exhibited comparable sizes and shapes as those from the PETM described above, but appeared to the eye to be lighter colored. SEM images revealed that they consisted predominantly of carbonate nannofossils, and minor Ca-rich Mn oxides, likely todorokite (Fig. 5). Jianshuiite was only observed in the nodules from the PETM horizon in Core 1262B-15H-3.

XRD identification of jianshuiite

Chalcophanite and jianshuiite. Powder X-ray diffraction patterns collected from individual nodules in the carbonate dissolution interval associated with the PETM in Section 1262B-15H-3 revealed minor amounts of quartz, illite, and other clays, but the dominant mineral belonged to the family of 7 Å birnessite-like phases with hexagonal symmetry. The chalcophanite ($\text{ZnMn}^{4+}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$) structure (Wadsley 1955; Post and Appleman 1988; Post and Heaney 2014) offered a close match. However, the EDS analyses revealed that Mg rather than Zn was the most abundant cation after Mn, confirming that the primary phase composing the nodules was nearly end-member jianshuiite.

Chalcophanite originally was indexed to a triclinic cell (Wadsley 1955), and because the powder X-ray diffraction pattern for jianshuiite closely resembles that of chalcophanite, Guinyin et al. (1992) first described jianshuiite as a triclinic structure with Mg as the dominant interlayer cation. Their wet chemical analyses yielded the following formulas for two samples: $(\text{Mg}_{0.51}\text{Mn}_{0.44}\text{Ca}_{0.08})\text{Mn}_{3.05}^{4+}\text{O}_{7.1} \cdot 2.90\text{H}_2\text{O}$ and $(\text{Mg}_{0.85}\text{Mn}_{0.05})\text{Mn}_{3.15}^{4+}\text{O}_7 \cdot 2.80\text{H}_2\text{O}$. Our chemical analyses of jianshuiite from the PETM cores are consistent with the near end-member jianshuiite composition, but indexing of the powder diffraction pattern and subsequent structure refinement has suggested a different symmetry for this mineral. We report here the first complete crystal structure for jianshuiite, and in the correct trigonal unit cell.

The parameters determined by our Rietveld refinement using the synchrotron X-ray diffraction data for jianshuiite are listed in Table 1. Atom positions are reported in Table 2, and selected bond distances are reported in Table 3. The final observed, calculated, and difference patterns for the Rietveld refinement using the synchrotron data are plotted in Figure 6. (CIF available¹.) The standard

deviations calculated by GSAS for the lattice parameters are likely smaller than the true errors (Post and Bish 1989). Finally, Figure 7 is a structure drawing of jianshuiite.

As with chalcophanite (Post and Appleman 1988), we refined jianshuiite in space group $R\bar{3}$. One out of every seven octahedral sites in the Mn-O sheet was vacant. The Mg (Zn in chalcophanite) cations were located above and below the vacancies. The

¹ Deposit item AM-16-25347, CIF. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to <http://www.minsocam.org/MSA/AmMin/TOC/>).

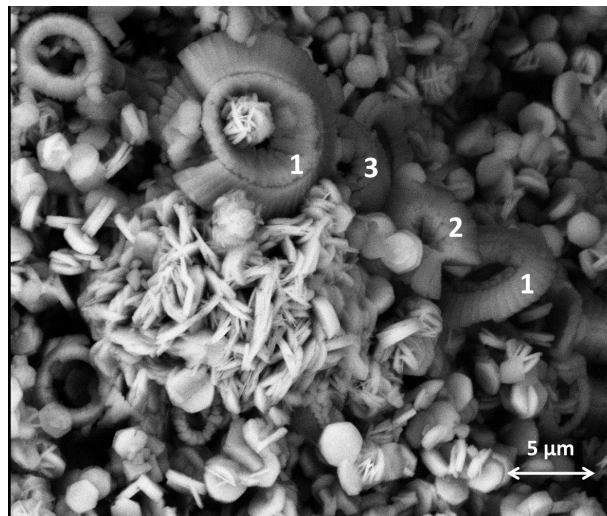


FIGURE 4. BSE SEM image of jianshuiite crystals from 32 cm above the P/E contact with calcareous nannofossils: (1) *Coccolithus pelagicus* (a solution-resistant taxon), (2) *Prinsius* sp., (3) possibly *Toweyus* sp. The other rings are probably remnants of more complex placoliths that are partially dissolved (identification by I. Raffi).



FIGURE 5. BSE SEM image of a nodule from nearby Site 1265 (sample 1265A-18H-CC, earliest Oligocene) composed primarily of calcareous nannofossils with clusters of needle-like crystals of Mn oxide, presumably todorokite.

TABLE 1. Final Rietveld refinement parameters for jianshuiite

Space group	$R\bar{3}$
Unit cell	
a (Å)	7.5409(4)
b (Å)	7.5409(4)
c (Å)	20.8079(14)
V (Å ³)	1024.73(14)
Refinement	
No. of data points	1146
No. of reflections	176
Diffraction range (2 θ)	13.5–47.3°
No. of variables	41
R (F^2)	0.128
R_{wp}	0.0205
χ^2	3.54

^a $\lambda = 0.8265(8)$ Å.

TABLE 2. Atomic coordinates and isotropic displacement factors for jianshuiite

Atom	x	y	z	Site occupancy factor	U_{iso}
Mn	0.7201(6)	0.5793(5)	0.00019(22)	1.0	0.003
Mg	0	0	0.10011(34)	1.073(12) ^a	0.003
O(1)	0.5312(21)	0.6125(22)	0.0493(5)	1.0	0.005
O(2)	0.2315(22)	0.1981(24)	0.0498(5)	1.0	0.005
O(3)	0	0	0.7103(7)	1.0	0.005
O(4)	0.1756(15)	0.9414(17)	0.1678(8)	1.0	0.02116(16)

Note: U_{iso} for O1, O2, O3, Mg, and Mn atoms were fixed to given values and not refined.

^a Site also contains minor Ni, Co, and Ba, but was refined as Mg.

vacant Mn sites were fully ordered. The Mn^{4+} -O octahedra were distorted, with bond distances ranging from 1.85 to 2.00 Å in jianshuiite, caused by displacement of Mn toward the vacancy in the octahedral sheet; in chalcophanite, the distances range from 1.86 to 1.97 Å (Post and Appleman 1988). The mean Mn-O distance for jianshuiite (Table 3) was 1.93 Å, slightly larger than the value of 1.91 Å reported for chalcophanite, but still indicating that the Mn is tetravalent (Shannon 1976).

Interlayer structure. Our refinements indicated that Mg cations (and minor Ca and possible Mn^{2+} cations) occupy sites above and below the vacancies in the octahedral sheets and are coordinated to three O atoms and three water O atoms. The mean Mg-O distance was 2.03 Å; as is the case for Zn in chalcophanite, the Mg-O bonds to the water oxygen atoms were longer (2.13 Å) than those to the O atoms in the octahedral layer (1.94 Å). By analogy with ernienickelite—the Ni-rich structural analog to chalcophanite (Grice et al. 1994)—the trace Ni cations revealed by EDS likely are located on the Mg site, perhaps accounting for the observation that the refined occupancy factor for Mg exceeded unity [$Mg_{occ} = 1.07(1)$]; Co, however, likely substitutes for some of the octahedral Mn^{4+} (Manceau et al. 1992). Unfortunately, the limitations in our chemical analyses, the small quantities of minor elements, and the similarity of X-ray scattering factors among Mn, Ni, and Co make definitive site assignments impossible. Because Ba is significantly larger than Mg [crystal radii of 1.49 vs. 0.86 Å (Shannon 1976)], it is likely that any Ba is located closer to the center of the interlayer region, as is the case in synthetic Ba-rich birnessite-like phases (Lopano et al. 2007).

DISCUSSION

Other occurrences of jianshuiite

Guiyin et al. (1992) named jianshuiite after its locality (Lu Village, Janshui County, Yunnan Province, China), where they observed it as a hypogene phase associated with terrestrial manganese ores. Another reported occurrence is in the Ojos Negros iron mines near Aragón Spain (Calvo 2008). As part of a paleomagnetic study of upper Paleocene silty red sediments in Baja California, Larson and Walker (1975) characterized locally abundant Mn-rich concretions with major concentrations of Mg and Ba, and minor Fe, Al, Ca, and Ti. Their low-analytical totals suggested that the phase contained a significant amount of water. The mineral was informally named “hydrosilomelane.” Potter and Rossman (1979) analyzed this material using X-ray powder diffraction and infrared spectroscopy, and they concluded that the Mn oxide phase had the chalcophanite structure. Using analytical data of Larson and Walker (1975), they calculated the chemical

TABLE 3. Selected bond lengths for jianshuiite (Å)

Mn-O(1)	1.869(10)
Mn-O(1)	2.001(13)
Mn-O(1)	1.994(13)
Mn-O(2)	1.976(10)
Mn-O(2)	1.849(14)
Mn-O(3)	1.916(7)
<Mn-O>	1.93
Mg-O(2)	1.941(16) ×3
Mn-O(4)	2.126(13)
<Mg-O>	2.03

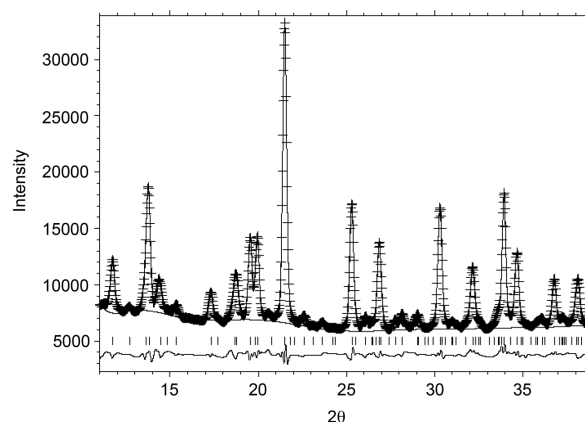


FIGURE 6. Final observed (black crosses), calculated (solid line), and difference (solid line below) powder X-ray diffraction patterns from the Rietveld refinement for jianshuiite. The Bragg reflections are marked by the set of small vertical lines.

formula as $(Mg_{0.6}Ba_{0.1}Fe_{0.1})(Mn_{3.0}Al_{0.1}) \cdot 2H_2O$, and proposed that “hydrosilomelane” is, in fact, a Mg analog of chalcophanite. Although they did not formally recognize it as a new mineral, this work first reported the Mn oxide phase later described as jianshuiite. In addition, jianshuiite was identified by XRD as a minor phase in ferromanganese nodules in Miocene carbonate-mud mounds in the Gulf of Cadiz (González et al. 2009, 2012). The authors argue that ferromanganese minerals including siderite-rhodochrosite grew diagenetically, fueled by anaerobic oxidation of thermogenic hydrocarbons, and were replaced by Fe-Mn oxyhydroxides when seawaters became more oxygen-rich, possibly microbially induced.

Jianshuiite formation and implications for changes in Eh and/or pH in PETM pore waters

The jianshuiite nodules observed within the PETM clay layer differ fundamentally from superficially similar micronodules in older and younger sediments, which contain mainly carbonate material and some minor Mn oxide phases, likely todorokite. The ocean and/or pore water conditions during the PETM at Site 1262 differed from those during other time periods, specifically in a lower pH [i.e., lower carbonate saturation, Ω , leading to the dissolution of $CaCO_3$; Zachos et al. (2005); Foster et al. (2013)] and higher temperatures (McCarren et al. 2008). Before and shortly after the PETM, the bottom waters at the depth of Site 1262 were generally well-oxygenated, but at the PETM itself, oxygen levels might have decreased (Chun et al. 2010). Climate modeling generally agrees with the geochemical data,

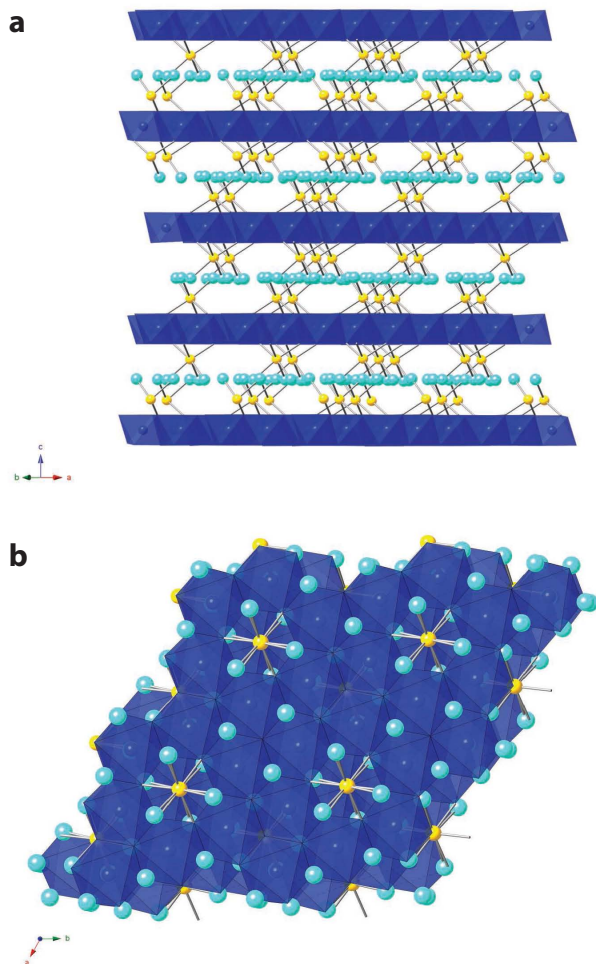


FIGURE 7. Structure drawing of jianshuiite. Mn-O octahedra are colored dark blue, and Mg cations are shown as small yellow spheres. The water O atoms are indicated by larger light-blue spheres. (a) The *c* axis is vertical and (b) looking normal to the Mn-O octahedral sheets. (Color online.)

indicating lowered oxygen in the SE Atlantic due to temperature rise and circulation changes (e.g., Winguth et al. 2012). It is not clear whether a decreased delivery of organic matter to the sea floor, and thus decreased oxidation of organic matter, could have counteracted the tendency toward lower oxygen levels (Ma et al. 2014).

The behavior of Mn in pore waters in Pleistocene-Recent sediments at a Walvis Ridge location close to that from which the present PETM cores were taken, was studied by Ginge and Kasten (1994). In general, dissolved Mn^{2+} migrates upward in sediment pore waters to the oxic/suboxic boundary, where it oxidizes and precipitates, unless the supply of organic matter atop the seafloor is sufficiently high that the bottom ocean waters are reduced (Mangini et al. 2001). Chun et al. (2010) argued that reducing conditions characterized the onset of the PETM, and could have mobilized Mn as Mn^{2+} . The Mn in jianshuiite is in the 4+ oxidation state. Thus, the precipitation of jianshuiite

may represent a diagenetic event that occurred once oxidizing conditions returned later—either during or after the main part of the PETM, possibly similar to the sequence of events reported by González et al. (2012). Mn oxide nodules are absent at shallower Site 1263, because conditions there were less oxidizing than at Site 1262 before, during and after the PETM (Chun et al. 2010). The formation of chalcophanite may provide an analogous genetic pathway, since it forms in Zn-rich oxidized zones of terrestrial Mn-rich deposits. Mn oxidation can also occur at constant solution Eh through a rise in pH (e.g., Takeno 2005), and therefore, the transition from dissolved Mn^{2+} to Mn^{4+} might have resulted from an increase in pH of pore waters after the acidification event at the P/E boundary ended.

Any carbonate phases in the Walvis Ridge sediments (derived from the pelagic calcifiers in the surface waters) would have dissolved early in the PETM, potentially leaving sediment pore space and voids. The nodule morphology might be attributed to the growth of jianshuiite crystals on cavity walls, as Mn in the pore fluid was oxidized, forming a hollow shell such as that in Figure 2a. Alternatively, the jianshuiite might have crystallized on the walls of burrows, or on the outside of fecal pellets, or of calcareous tests that later dissolved. Previous studies (Chun et al. 2010; Paelike et al. 2014) suggest that carbonate dissolution preceded the reoxidation, so calcareous tests dissolved long before oxic fluids would have precipitated dissolved Mn. This consideration might support the hypothesis that increases in pore water pH induced the precipitation of jianshuiite during a later diagenetic event.

Jianshuiite formation and implications for high-Mg/Ca ratios in PETM pore waters

One of the most intriguing aspects of the PETM Mn nodules is that they are composed of well-formed microcrystals of the rare Mn oxide mineral jianshuiite. In contrast, the macroscopic Mn nodules that cover broad expanses of the ocean floor (and occur in core samples at Walvis Ridge in older and younger sediments than the PETM) contain phases such as todorokite $[(\text{Na}, \text{Ca}, \text{K})_2 (\text{Mn}^{4+}, \text{Mn}^{3+})_6 \text{O}_{12} \cdot 3-4.5\text{H}_2\text{O}]$, “buserite” $(\text{Na}_4\text{Mn}_{14}\text{O}_{27} \cdot 21\text{H}_2\text{O})$, and vernadite $[(\text{Mn}^{4+}, \text{Fe}^{3+}, \text{Ca}, \text{Na})(\text{O}, \text{OH})_2 \cdot n\text{H}_2\text{O}]$ (Burns and Burns 1977). Moreover, most researchers have concluded that the precipitation of Mn oxides in seafloor nodules is biologically mediated (e.g., Moffett and Ho 1996; Tebo et al. 2004), and these biogenic Mn oxides invariably are fine-grained and poorly crystalline, as is the jianshuiite in the nodules described by González et al. (2009, 2012). The strongly euhedral nature and relatively large sizes of the jianshuiite crystals in the PETM nodules are atypical of known synthetic or natural biogenic Mn oxides. Consequently, we infer that the PETM nodules formed abiotically, possibly induced by the unusually severe changes in oxygenation and pH during the PETM, although organisms or other organic material in the sediments might have contributed to the particular chemical conditions that resulted in the formation of the jianshuiite crystals.

The high concentration of Mg relative to Ca in jianshuiite would seem to reflect pore water chemistries in PETM sediments that contained anomalously high-Mg/Ca ratios, especially because Mg/Ca values in seawater at the time of the PETM may have been much lower than today (e.g., Stanley and Hardie 1998;

Farkas et al. 2007). The transient nature of this high-magnesian pulse is evidenced by the return of organisms with Ca carbonate tests, such as foraminifera and nannofossils, higher in the section.

Intriguingly, the jianshuiite crystals themselves might record changes in the Mg/Ca compositions of fluids through cation-exchange textures that are observable in some crystals. We have documented previously that Cs exchange within the interlayer of Na-birnessite occurs through a delamination-relamination ("delam-relam") mechanism rather than through classic dissolution-reprecipitation pathways (Lopano et al. 2009; Fleeger et al. 2013). The expanded, accordion-like jianshuiite crystals seen in Figure 3 provide strong textural evidence for delam-relam alteration resulting from cation exchange. In the delam-relam process, cation exchange between the aqueous phase and the Mn oxide interlayer occurs via the separation of individual layers followed by the wholesale substitution of the interlayer cations, in contrast to traditional exchange processes that occur by diffusion of substitutional cations from the surface of a crystal to its interior. It seems especially significant that spot EDS analyses of these accordion-like crystals reveal a consistently higher concentration of Ca to Mg in the expanded portions of the crystals than in the compressed regions. The crystals showing possible exchange textures were most obvious in the nodule from ~9 cm above the P/E contact, and above the last appearance of calcareous nannofossils (which are still visible in the nodule 1 cm above the contact). Perhaps the dissolution of carbonates resulted in a rise in Ca concentrations in pore waters (Foster et al. 2013) that deposited the jianshuiite, and these now Ca-rich solutions reacted with the jianshuiite crystals, leading to partial cation exchange.

IMPLICATIONS

As described by models of mineral evolution (Hazen et al. 2008), the appearance of new minerals within the rock record can signify fundamental changes in events that govern Earth processes. Surveys of Mn oxides within modern near-surface environments have uniformly indicated the predominance of poorly crystalline, biologically precipitated Ca-rich Mn oxides, such as buserite and/or rancieite $[(\text{Ca}, \text{Mn})\text{Mn}_4\text{O}_9 \cdot 3\text{H}_2\text{O}]$, vernadite, and todorokite. The transient appearance of the Mg-rich birnessite-like phase jianshuiite must indicate an exceptional change in the chemistry of the pore fluids within deep ocean sediments at the P/E boundary. As is consistent with other transitions during this global warming event, we infer that pulses of fluids with high-Mg/Ca values deposited the jianshuiite within cavities formed by the prior dissolution of carbonate micronodules. The tetravalent oxidation state of the Mn suggests that these depositional fluids were less acidic than those that led to the abrupt carbonate dissolution event at the onset of the PETM. We speculate that jianshuiite might have been mistaken for other Mn oxides at other sites, and it might serve as a marker mineral for climate change events, such as these recorded by González et al. (2012).

Birnessite-like phases are challenging to investigate because they tend to occur as fine-grained, poorly crystalline masses. Chalcophanite, and now jianshuiite, are unusual in the birnessite family because they are exceptionally well-crystallized, sometimes forming crystals up to several millimeters in diameter, as in the case of chalcophanite. Consequently, these phases

serve as excellent crystallographic proxies for the structures and chemical behaviors of the broader group of birnessite-like minerals.

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