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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 [$(Mg,Mn,Ca)Mn_3^{4+}O_7 \cdot 3H_2O$]. 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