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Hexagonal magnetite in Algoma-type banded iron formations of the ca. 2.52 Ga Baizhiyan Formation, North China: Evidence for a green rust precursor?

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Abstract

Banded iron formations (BIFs) are iron-rich marine chemical sedimentary rocks, and their mineralogy and geochemistry can be used to gain insights into ancient ocean chemistry and biospheric evolution. Magnetite is the major iron-bearing mineral in many BIFs (particularly in the Archean) and is variably interpreted to be of primary, early diagenetic, or metamorphic origin. Different genetic interpretations for magnetite lead to divergent pictures of the Precambrian Earth system and its evolutionary models through time. The Baizhiyan Formation of the Neoarchean Wutai Group (Shanxi, North China) features magnetite-bearing, Algoma-type BIFs deposited ca. 2.52 Ga, in the lead-up to a major period of global iron formation deposition in the Paleoproterozoic. Abundant magnetite crystals found in the silica-rich bands of these BIFs show euhedral, hexagonal morphology. We suggest that this hexagonal magnetite likely represents pseudomorphs after green rust, a mixed-valence iron hydroxysalt formed in the water column. The rare earth element composition of the BIFs shows negligible to slightly positive Ce anomalies ($Ce_{SN}/Ce_{SN}^* = 1.03 \pm 0.07$), which is characteristic of a dominantly anoxic water column. The presence of positive Eu anomalies ($Eu_{SN}/Eu_{SN}^* < 3.9$) suggests a substantial influence from proximal hydrothermal fluids. The co-occurrence of siderite layers associated with the magnetite-bearing strata may indicate iron cycling associated with ferruginous bottom seawater conditions. Geochemical signatures of the Baizhiyan BIFs are consistent with the interpretation that the magnetite was transformed from metastable green rust. This green rust could have formed via several processes, including the partial oxidation of Fe(II) by molecular oxygen/photoferrotrophs, the reaction of settling ferrihydrite with Fe(II)-rich hydrothermal fluids under anoxic conditions, or local dissimilatory iron reduction. In all cases, the contribution of primary green rust to BIF formation requires iron redox cycling, and similar pseudomorphs in the form of hexagonal magnetite may be more common in the geological record. Our findings support the models in which green rust was an important primary constituent of the Precambrian iron cycle, and the potential interactions of green rust with other elements (e.g., phosphorus) should be taken into consideration when reconstructing Precambrian biogeochemical cycles.

Keywords: Ferrihydrite, iron redox cycling, ferruginous, Ce anomalies, Eu anomalies, hydrothermal fluid activity