The formation of marine red beds and iron cycling on the Mesoproterozoic North China Platform

**Dongjie Tang**<sup>1,2,*</sup>, Jianbai Ma<sup>3</sup>, Xiaoying Shi<sup>1,3</sup>, Maxwell Lechte<sup>4</sup>, and Xiqiang Zhou<sup>5</sup>

1State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences (Beijing), Beijing 100083, China
2Institute of Earth Sciences, China University of Geosciences (Beijing), Beijing 100083, China
3School of Earth Sciences and Resources, China University of Geosciences (Beijing), Beijing 100083, China
4Department of Earth and Planetary Sciences, McGill University, 3450 University Street, Montréal, Quebec H3A 0E8, Canada
5Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

**Abstract**

Marine red beds (MRBs) are common in sedimentary records, but their genesis and environmental implications remain controversial. Genetic models proposed for MRBs variably invoke diagenetic or primary enrichments of iron, with vastly different implications for the redox state of the contemporaneous water column. The Xiamaling Formation (ca. 1.4 Ga) in the North China Platform hosts MRBs that offer insights into the iron cycling and redox conditions during the Mesoproterozoic Era. In the Xiamaling MRBs, well-preserved, nanometer-sized flaky hematite particles are randomly dispersed in the clay (illite) matrix, within the pressure shadow of rigid detrital grains. The presence of hematite flake aggregates with multiple face-to-edge (“cardhouse”) contacts indicates that the hematite particles were deposited as loosely bound, primary iron oxyhydroxide floccs. No greenalite or other ferrous iron precursor minerals have been identified in the MRBs. Early diagenetic ankerite concretions hosted in the MRBs show non-zero I/(Ca+Mg) values and positive Ce anomalies (>1.3), suggesting active redox cycling of iodine and manganese and therefore the presence of molecular oxygen in the porewater and likely in the water column during their formation. These observations support the hypothesis that iron oxyhydroxide precipitation occurred in moderately oxygenated marine waters above storm wave base (likely <100 m). Continentally sourced iron reactivated through microbial dissimilatory iron reduction, and distal hydrothermal fluids may have supplied Fe(II) for the iron oxyhydroxide precipitation. The accumulation of the Xiamaling MRBs may imply a slight increase of seawater oxygenation and the existence of long-lasting adjacent ferruginous water mass.

**Keywords:** Marine red beds, hematite, ferruginous, dissimilatory iron reduction, Xiamaling Formation, oxygenation

**Introduction**

Marine red beds are sedimentary successions deposited from seawater that are enriched in iron oxides, imparting a characteristic red color (e.g., Hu et al. 2012). Although MRBs contain less iron (typically containing Fe < 15 wt%) and simpler iron mineral assemblages than iron formations, ancient MRBs have been widely used as important tracers for surface-system redox conditions through geological time. However, the iron cycling processes responsible for the deposition of MRBs—and thus their paleoenvironmental significance—remain elusive.

The enrichment of iron oxides in MRBs has been variably ascribed to detrital, primary, early or late diagenetic origins (e.g., Franke and Paul 1980; Hu et al. 2006, 2012; Song et al. 2017; Liu et al. 2019a; Zou et al. 2019), and each of these hypotheses has vastly different implications for reconstructing ancient seawater chemistry. Detrital-sourced iron oxide is responsible for iron enrichment in some marine sediments (e.g., Franke and Paul 1980), but the observation of MRBs intercalated with iron-poor turbidites suggests that the supply of terrestrial iron oxides is not the controlling factor for MRB deposition (Hu et al. 2012). More recent interpretations suggest that the oxidation of Fe(II) in a ferruginous seawater column may have been important in the deposition of MRBs, such as the abiotic oxidation of Fe(II) following the ocean anoxic events (Song et al. 2017). This hypothesis requires an anoxic event to accumulate Fe(II) in seawater, followed by marine oxygenation to oxidize Fe(II) and precipitate poorly crystalline hydrous ferric oxide phases that can be converted to hematite during diagenesis (Song et al. 2017). However, the duration of red bed deposition could be in the order of millions of years (Hu et al. 2012): the Fe(II) accumulated during ocean anoxic events would be rapidly exhausted during marine oxygenation because of the short residence time of Fe(II) in oxygenated seawater (100–200 yr, Johnson et al. 1997). Alternatively, seawater Fe(II) oxidation could have been microbially mediated (Préat et al. 2008); the activity of microaerobic Fe(II)-oxidizing bacteria near the water–sediment interface has been suggested as the major cause for iron oxide enrichment in several Phanerozoic marine limestones (Mamet and Préat 2006). Early diagenetic origin is argued as the model for some carbonate