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Oxygenation of a Cryogenian ocean (Nanhua Basin, South China) revealed by pyrite Fe isotope compositions

Feifei Zhang[a,b], Xiangkun Zhu[a,*], Bin Yan[a], Brian Kendall[c], Xi Peng[a], Jin Li[a], Thomas J. Algeo[d,e], Stephen Romaniello[b]

[a] MLR Key Laboratory of Isotope Geology, State Key Laboratories of Continental Tectonics and Dynamics, Institute of Geology, Chinese Academy of Geological Sciences, Beijing 100037, China
[b] School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-6004, USA
[c] Department of Earth and Environmental Sciences, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, N2L 3G1, Canada
[d] State Key Laboratories of Biogeology and Environmental Geology and Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, China
[e] Department of Geology, University of Cincinnati, Cincinnati, OH 45221-0013, USA

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ABSTRACT

The nature of ocean redox chemistry between the Cryogenian Sturtian and Marinoan glaciations (ca. 663–654 Ma) is important for understanding the relationship between environmental conditions and the subsequent emergence and expansion of early animals. The Cryogenian-to-Ediacaran stratigraphic succession of the Nanhua Basin in South China provides a nearly complete sedimentary record of the Cryogenian, including a continuous record of interglacial sedimentation. Here, we present a high-resolution pyrite Fe isotope record for a ∼120-m-long drill-core (ZK105) through Sturtian glacial diamictites and the overlying interglacial sediments in the Nanhua Basin to explore changes in marine chemistry during the late Cryogenian. Our pyrite Fe isotope profile exhibits significant stratigraphic variation: Interval I, comprising middle to upper Tiesi'ao diamictites (correlative with the Sturtian glaciation), is characterized by light, modern seawater-like Fe isotope compositions; Interval II, comprising uppermost Tiesi'ao diamictites and the basal organic-rich Datangpo Formation, is characterized by an abrupt shift to heavier Fe isotope compositions; and Interval III, comprising organic-poor grey shales in the middle Datangpo Formation, is characterized by the return of lighter, seawater-like Fe isotope compositions. We infer that Interval I pyrite was deposited in a predominantly anoxic glacial Nanhua Basin through reaction of dissolved Fe^{2+} and H_2S mediated by microbial sulfate reduction (MSR). The shift to heavier pyrite Fe isotope values in Interval II is interpreted as partial oxidation of ferrous iron to ferric iron and subsequent near-quantitative reduction and transformation of Fe-oxyhydroxides to pyrite through coupling with oxidation of organic matter in the local diagenetic environment. In Interval III, near-quantitative oxidation of ferrous iron to Fe-oxyhydroxides followed by near-quantitative reduction and conversion to pyrite in the local diagenetic environment was likely responsible for the return of lighter, seawater-like Fe isotope compositions in pyrite. Our pyrite Fe isotope profile thus records increased oxygenation in the Nanhua Basin between the Sturtian and Marinoan glaciations.
The increased oxygenation of Nanhua Basin seawater deduced from pyrite Fe isotopes could have resulted from either local or global controls. Further work will be needed to determine whether this increasing oxygenation extended to the global scale.

1. Introduction

The Neoproterozoic Era (1000 to 542 Ma) is a key transitional period in Earth history—notable for its climatic extremes, as a threshold for multicellular life, and for concomitant changes in the chemistry of the oceans and atmosphere. Studies over decades have sought links among these climatic, biological, and environmental events, with an emphasis on trying to understand the co-evolution of oceanic–atmospheric conditions and the origin and development of early animals (Nursall, 1959; Holland, 1984; Fike et al., 2006; Canfield et al., 2007; McFadden et al., 2008; Scott et al., 2008; Frei et al., 2009; Dahl et al., 2010; Planavsky et al., 2010; Shields-Zhou and Och, 2011; Sahoo et al., 2012;

* Corresponding author.
E-mail addresses: xiangkunzhu@163.com, xiangkun@cags.ac.cn (X. Zhu).

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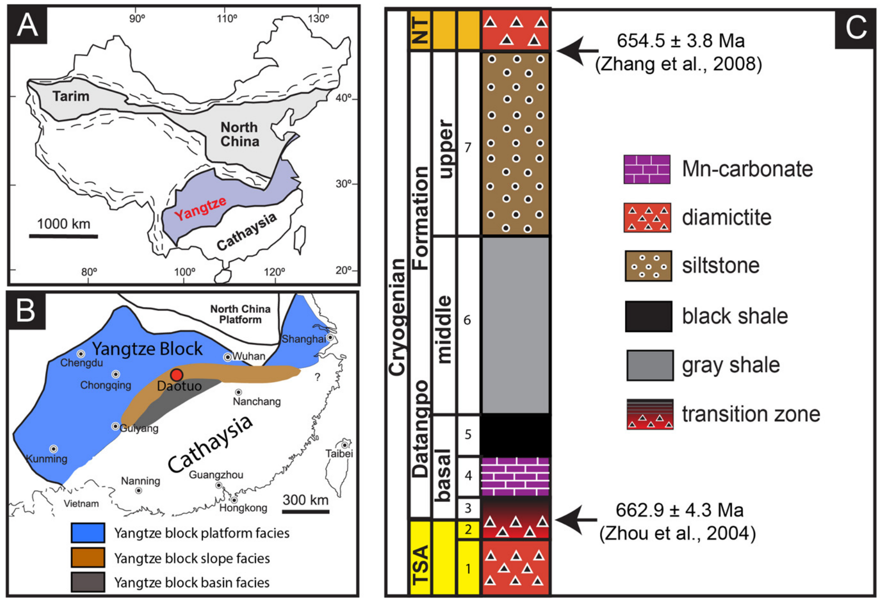

Fig. 1. (A) Geological map of China, with the Yangtze Craton highlighted in color. (B) Paleogeographic map of South China craton during the Late Neoproterozoic (Jiang et al., 2011). Red dot marks the location of the section discussed in this paper. (C) The stratigraphic column shows the stratigraphic succession of drillcore ZK105. TSA indicates Sturtian equivalent Tiesi'ao Formation, and NT indicates Marinoan equivalent Nantuo Formation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Lenton et al., 2014; Meysman, 2014; Kendall et al., 2015). Neoproterozoic successions worldwide provide robust evidence of episodes of increased ocean oxygenation during the Ediacaran Period (635–542 Ma), which is assumed to have stimulated the evolution of macroscopic multicellular animals (= metazoans). However, the redox state of the ocean during the Cryogenian (∼750–635 Ma) is still poorly known. Any appreciable increase in atmosphere–ocean oxygenation during this time likely had a strong influence on the appearance and diversification of the earliest metazoans (Planavsky et al., 2014).

The cycling of iron (Fe) is intimately linked to the redox state of Earth's surface environments, and the isotopic composition of Fe in seawater (as inferred from sedimentary archives) depends on the redox state of the ocean (Anbar, 2004; Anbar and Rouxel, 2007; Johnson et al., 2008). Increasing ocean oxygenation through time has led to dramatic changes in the Fe cycle because of the high reactivity of Fe with oxygen. These changes are reflected in the Fe isotopic composition of sedimentary pyrite, which is the principal sink for reduced and reactive iron in marine sediments, thus providing a tool for tracking the long-term history of ocean redox conditions (Rouxel et al., 2005; Archer and Vance, 2006; Anbar and Rouxel, 2007; Fehr et al., 2008; Severmann et al., 2008; Zhu et al., 2008; Duan et al., 2010; Nishizawa et al., 2010; Owens et al., 2012; Planavsky et al., 2012; Asael et al., 2013; Zhang et al., 2013; Busigny et al., 2014).

In this study, we report pyrite Fe isotope data for Cryogenian sedimentary rocks from a recently completed drill core. (ZK105, completed in early 2013 and drilled by the 103 Geological Party, Guizhou Bureau of Geology and Mineral Exploration and Development) from the Nanhua Basin, South China. The new data shed insights on ocean paleoredox conditions during the Sturtian glaciation and subsequent interglacial interval.

2. Geological setting and sample description

2.1. Geological setting

The Nanhua Basin of South China contains a continuous Cryogenian-to-Middle Cambrian succession, providing one of the most complete sedimentary records of this interval in the world. Previous studies have generated a highly detailed regional stratigraphic framework (Wang, 1985; Wang and Li, 2003; Zhang et al., 2003; Zhu et al., 2003; Zhou et al., 2004; Condon et al., 2005; Zhang et al., 2005, 2008; Steiner et al., 2007) within which high-resolution chemostratigraphic studies have been undertaken (e.g., Li et al., 2010; Jiang et al., 2011, 2012; Zhu et al., 2013). This study area is thus suitable for the exploration of changes in ocean chemistry during the Cryogenian glacial period and its aftermath.

The Nanhua Basin sedimentary record contains two major glacial diamictite intervals—the older Tiesi'ao Formation and the younger Nantuo Formation, which are separated by the interglacial Datangpo Formation (Fig. 1). The Tiesi'ao Formation principally comprises glacial–marine diamictites and is correlative with Sturtian glacial deposits globally (Zhang et al., 2003; Macdonald et al., 2010). The Nantuo Formation is primarily composed of thick diamictites, siltstones, and sandstones, and is correlative with Marinoan glacial deposits elsewhere (Zhang et al., 2005; Condon et al., 2005). The Datangpo Formation is in conformable contact with both the underlying Tiesi'ao Formation and the overlying Nantuo Formation and contains no known intraformational unconformities (Fig. 1). Thus, this unit may record the entire sedimentary history of the Nanhua Basin between the Sturtian and Marinoan glacial intervals. U–Pb zircon ages of 662.9 ± 4.3 Ma (Zhou et al., 2004) and 654.5 ± 3.8 Ma (Zhang et al., 2008) for tuffaceous beds in the basal and upper Datangpo Formation, respectively, provide time constraints for the interglacial interval. As there is an unconformity between the Datangpo and Nantuo formations in the section dated by Zhang et al. (2008), the Datangpo Formation covers a time interval of at least 8.5 Ma.

The Tiesi'ao Formation exhibits pronounced internal stratigraphic variation. The middle-upper part of the formation (Unit 1, Fig. 1) is composed of poorly sorted, grey diamictites containing variable amounts of mm- to cm-sized clasts or pebbles of varying lithology. The clasts or pebbles are generally subangular to subrounded and comprise ∼10–15% of the diamictite by volume. The uppermost part of the formation (Unit 2, Fig. 1) consists of a layer of gray to black, organic-rich sandstone with minor small pebbles (Fig. 2a). Pyrite is abundant in the diamictites, with euhedral crystals dominating in Unit 1 and nodules ranging from a few mm to a few cm in diameter dominating in Unit 2.