



Shallow stratification prevailed for ~1700 to ~1300 Ma ocean: Evidence from organic carbon isotopes in the North China Craton



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ABSTRACT

The Late Paleoproterozoic to Early Mesoproterozoic (from ~1700 Ma to ~1300 Ma) was highlighted by the assembly of the Nuna supercontinent, expansion of euxinic marine environments and apparent stasis in the diversity of eukaryotes. The isotopic composition of carbonate carbon ($\delta^{13}\text{C}_{\text{carb}}$) was surprisingly constant during this interval, but little is known about the secular variation in the organic carbon isotopic composition ($\delta^{13}\text{C}_{\text{org}}$). Here we report $\delta^{13}\text{C}_{\text{org}}$ data from the latest Paleoproterozoic (>1650 Ma) to Early Mesoproterozoic (~1300 Ma) succession in North China. The $\delta^{13}\text{C}_{\text{org}}$ values range from -25% to -34% , and are dependent on sedimentary facies. In subtidal and deeper environments $\delta^{13}\text{C}_{\text{org}}$ values are low and constant, ca. -32% , but relatively enriched and more variable in shallower intertidal and supratidal environments. We attribute the facies-dependent variation in $\delta^{13}\text{C}_{\text{org}}$ to the presence of a shallow chemocline. A probable result of a shallow chemocline is that it supported significant contributions of organic matter produced by chemoautotrophic and/or anaerobic photoautotrophic microbes in relatively deep environments from the latest Paleoproterozoic to Early Mesoproterozoic continental shelf of North China.

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1. Introduction

The origin and diversification of organisms on Earth was strongly affected by the evolution of oceanic and atmospheric chemistry (Anbar and Knoll, 2002). A growing body of evidence, both geological and geochemical, suggests that oxidation of Earth's surface first occurred during the transition from the Archean to the Paleoproterozoic, and this paved the way for the origin and diversification of eukaryotic organisms (Holland, 1978; Karhu and Holland, 1996; Farquhar et al., 2000; Bekker et al., 2004; Anbar et al., 2007; Kaufman et al., 2007; Guo et al., 2009; Garvin et al., 2009). It is understandable that a great deal of attention has been paid to the 300 million years (2.4 Ga to 2.1 Ga) that comprise the Great Oxidation Event (GOE) period. However, the details of redox conditions following the GOE remain unclear.

The period from the Late Paleoproterozoic to the Early Mesoproterozoic (~1700 Ma to ~1300 Ma) holds the record of the

assemblage of the supercontinent Columbia or Nuna (Zhao et al., 2004; Zhang et al., 2012), a significant increase in the volume of euxinic waters (Shen et al., 2003; Poulton et al., 2004; Scott et al., 2008), and the stasis in diversity of eukaryotic organisms (Javaux et al., 2001; Knoll et al., 2006; Lamb et al., 2009). To achieve a complete understanding of these events, particularly the evolution of eukaryotic organisms, it is important to characterize the atmospheric and oceanic chemistry through this interval.

On the basis of the overall disappearance of iron formation (IF) in strata younger than 1.8 Ga (except for the short reappearance of IF in the late Neoproterozoic) (e.g. Bekker et al., 2010), the old paradigm was that the ocean transitioned to a largely oxidized state (Cloud, 1972; Holland, 1984). However, Canfield (1998) argued that the deep ocean post-1.8 Ga was anoxic and sulfidic (euxinic) resulting from a substantial increase in oceanic sulfate concentration after the GOE which fueled sulfate reduction. This hypothesis has been largely supported by a series of studies showing euxinic conditions in several basins from latest Paleoproterozoic to Early Mesoproterozoic (e.g., Shen et al., 2003; Arnold et al., 2004; Poulton et al., 2004; Brocks et al., 2005; Reinhard et al., 2013). New lines of evidence suggest that oceanic

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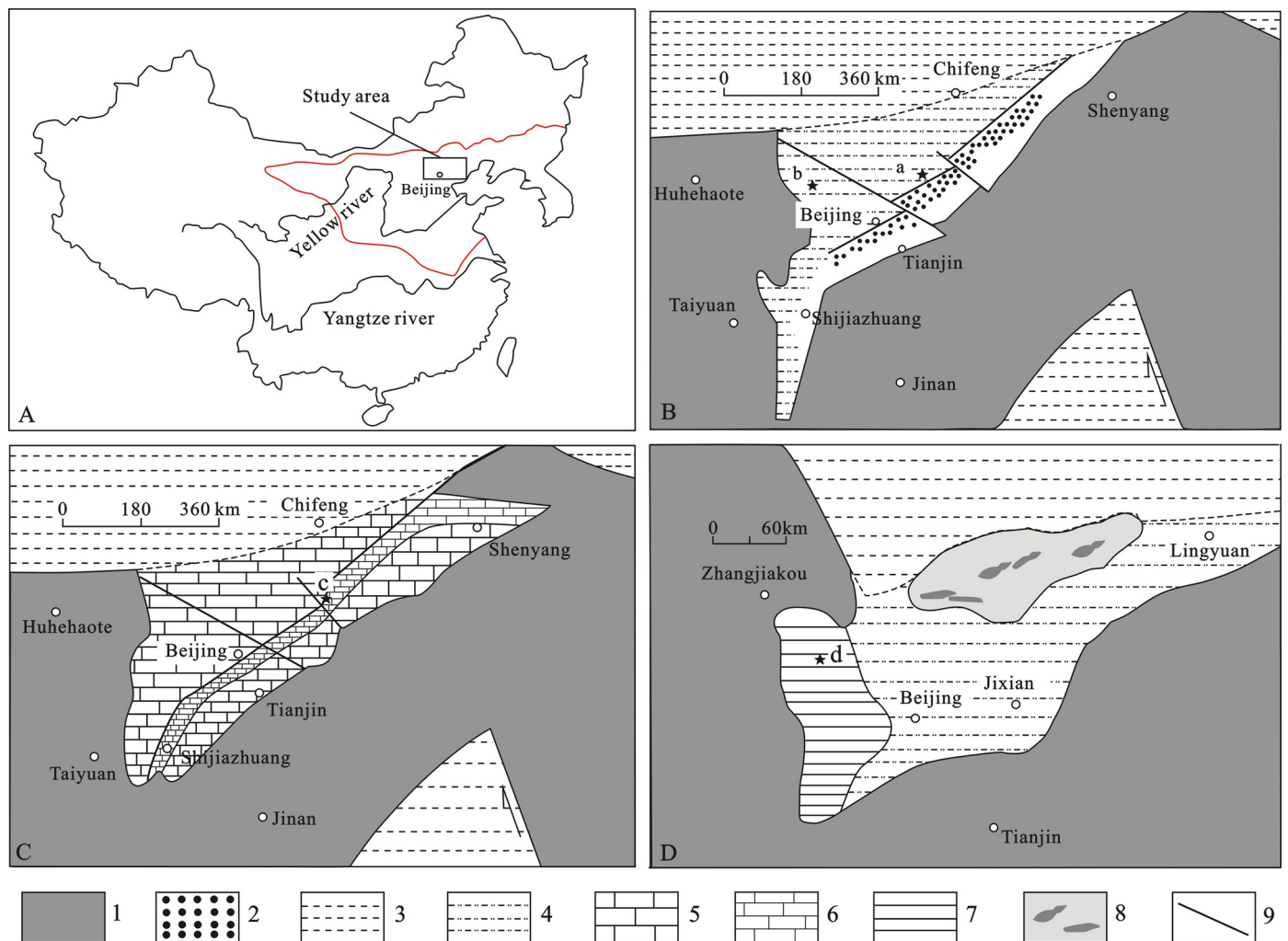


Fig. 1. A: Geographic map of the study location (square) and the outline of the North China Craton (NCC). B–D: Paleogeography of the NCC from late Paleoproterozoic to middle Mesoproterozoic (redrawn from Qiao and Gao, 2007; Qiao et al., 2007). B, the Chuanlinggou Formation; C, the Gaoyuzhuang Formation; D, the Xiamaling Formation. The stars represent the location of the study sections. a: the Yamenzi section in Kuancheng county; b: the Pangjingpu section in Huailai county; c: the Pingquan section in Pingquan county; d: the Zhaojiashan section in Huailai county. 1: Paleo-continent; 2: coarse-grained sedimentary rocks; 3: deep oceanic sedimentary rocks; 4: shallow-water mudstone; 5: shallow-water carbonate; 6: relatively deep-water carbonate; 7: deep-water mudstone and black shale; 8: island arc granite; 9: fault.

sulfate concentrations may have been lower than previously recognized (Shen et al. 2002, 2003; Kah and Bartley, 2011), and Slack et al. (2007) suggest that the deep ocean might have even contained low concentrations of dissolved O_2 on the basis of rare earth element data from hydrothermal silica-iron oxide sedimentary rocks from deep-water environments. Continued investigations, including this study, reveal that redox conditions are more complex and spatially heterogeneous (Poulton et al., 2010; Planavsky et al., 2011; Gilleaudeau and Kah, 2013).

Carbon isotopes have been used widely to explore the relationships between the ancient carbon cycle, tectonic events, biological innovation, and changes in the oxidation state of Earth's surface (Schidlowski et al., 1976; Des Marais et al., 1992; Schidlowski, 2001; Eigenbrode and Freeman, 2006; Bekker et al., 2008). Relatively constant carbon isotopic composition of marine carbonate ($\delta^{13}C_{carb}$) characterizes early Mesoproterozoic successions (>1300 Ma) globally. For example, the $\delta^{13}C_{carb}$ of the carbonate sequences from northwestern Australia (Buick et al., 1995; Brasier and Lindsay, 1998), northwestern Siberia (Knoll et al., 1995; Bartley et al., 2007; Khabarov and Varaksina, 2011), Russia (Kah et al., 2007), North America (Frank et al. 1997, 2003) and North China (Xiao et al., 1997; R.W. Li et al., 2003; Chu et al., 2007; Guo et al., 2013) varied gently between -2% and $+1\%$. The lim-

ited variability of $\delta^{13}C_{carb}$ values through the Late Paleoproterozoic to the Early Mesoproterozoic led to this interval to be referred to the duller time in Earth history (Buick et al., 1995), and the 'boring billion' (Brasier and Lindsay, 1998). Compared with the abundant published $\delta^{13}C_{carb}$ data, detailed records of the isotopic composition of organic carbon ($\delta^{13}C_{org}$) are few (Des Marais, 2001; Johnston et al., 2008; Guo et al., 2013) and may help us better understand carbon cycle dynamics during this interesting time in Earth's history.

In this study, we analyzed the $\delta^{13}C_{org}$ of the latest Paleoproterozoic to Early Mesoproterozoic (~ 1670 Ma to ~ 1350 Ma) strata exposed in the North China Craton (NCC). We observed wider variability in $\delta^{13}C_{org}$ during the interval from ~ 1670 Ma to ~ 1350 Ma than $\delta^{13}C_{carb}$, suggesting that this interval was far more dynamic than $\delta^{13}C_{carb}$ suggests alone. Here we aim to unravel the relationship between sedimentary facies and $\delta^{13}C_{org}$, and examine the implications for the ocean redox conditions.

2. Geological background and sedimentary facies

Proterozoic strata with a total thickness of ca. 9000 m are distributed widely in North China (Fig. 1) and divided into the Changcheng Group, Jixian Group and Qingbaikou Group in ascending order (Fig. 2). This sedimentary sequence was deposited in the

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