Precambrian Research 307 (2018) 218–228

Contents lists available at ScienceDirect

Precambrian Research

journal homepage: www.elsevier.com/locate/precamres

Ediacaran negative C-isotopic excursions associated with phosphogenic events: Evidence from South China

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ARTICLE INFO

Keywords:
Ediacaran
C-isotopic excursion
Phosphorite
Upwelling
Yangtze platform

ABSTRACT

The Yangtze platform of South China preserves relatively continuous strata of the Ediacaran Period and has been one of the key areas to explore Neoproterozoic Earth history. In this study, high-resolution carbon isotope ($\delta^{13}C$) and oxygen isotope ($\delta^{18}O$) data of 701 samples were reported for sedimentary rocks spanning the entire Ediacaran Period using a continuous drill core collected from Wangji, South China. The C-isotopic data of the Doushantuo Formation are consistent with previous work, showing three negative $\delta^{13}C$ excursions that can be correlated intra-basinally. A large negative $\delta^{13}C$ excursion from +8.16‰ to −7.20‰ identified at the top of the Doushantuo Formation, which is equivalent to the "Shuram Negative Excursion", allows us to correlate the $\delta^{13}C$ profile globally. In the overlying Dengying Formation, we identified two distinct $\delta^{13}C$ intervals with an average value of +3.32‰ and of +0.40‰, respectively. As well, we observed a negative $\delta^{13}C$ excursion in the middle Dengying Formation, which has not been reported previously.

Three major negative $\delta^{13}C$ excursions, two in the Doushantuo Formation and one in the Dengying Formation, are tightly associated with phosphorite deposits. The temporal correlation between the negative $\delta^{13}C$ excursions and the phosphorite deposits suggests a potential link between carbon and phosphorus cycling in the Ediacaran oceans. We argue that multiple periods of strong upwelling may have played an important role in C and P cycling in the Ediacaran oceans. Oxidative processes of the ^{13}C-depleted dissolved organic carbon (DOC) transported into oxic near-surface waters by upwelling resulted in the negative $\delta^{13}C$ excursions, and contributed to synchronous burial of abundant phosphorites in the inner shelf areas. The different magnitudes of the negative $\delta^{13}C$ excursions observed in the Doushantuo and Dengying formations may reflect spatial changes of DOC reservoir and variations of upwelling intensity and mixing processes.

1. Introduction

The Ediacaran Period (635–541 Ma) witnessed dramatic changes in the environment as well as in biological evolution. During this period, the Earth's surface environment is thought to have experienced the "Second Great Oxidation Event" (Campbell and Squire, 2010; Och and Shields-Zhou, 2012), which might have contributed to the transition from an anoxic to more oxygenated state of the deep ocean (e.g., Sahoo et al., 2012). This redox change likely served as an ecological trigger that paved a way for emergence of early macroscopic animals (Johnston et al., 2012b; Kendall et al., 2015; Sperling et al., 2015). The carbon isotopic ($\delta^{13}C$) composition of carbonate rocks has been utilized in reconstructing a series of extreme climate events such as the Sturtian glaciation and the Marinoan glaciation, known as "Snowball Earth" events in the Neoproterozoic (Hoffman et al., 1998, 2017; Hoffman and Schrag, 2002). Specifically, the $\delta^{13}C$ record of the Ediacaran strata is characterized by several extremely positive and negative excursions (Kaufman and Knoll, 1995; Bartley and Kah, 2004; Halverson et al., 2005, 2010). However, the origins of the C-isotope excursions in the Ediacaran Period remain debated. For example, one of the leading hypotheses to explain the negative $\delta^{13}C$ excursions is that they may have resulted from intermittent periods of oxidation of a large DOC pool in the deep ocean (Rothman et al., 2003). The hypothesis of Rothman et al. (2003) was supported by paired C-isotope data of carbonate and organic carbon and paired S-isotope data of pyrite and carbonate-associated sulfate from Oman and South China, respectively (Fike et al., 2006; McFadden et al., 2008). However, the availability of sufficient oxidants has been questioned (Bristow and Kennedy, 2008), and the coupling or decoupling between $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ is more complicated than previously thought (Swanson-Hysell et al., 2010; Johnston et al., 2012a).

The Yangtze platform of South China (Fig. 1A), which preserves relatively continuous strata of the Ediacaran Period, has been one of the key regions to explore Neoproterozoic Earth history. As such,

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https://doi.org/10.1016/j.precamres.2018.01.014
Received 29 March 2017; Received in revised form 22 January 2018; Accepted 27 January 2018
Available online 31 January 2018
0301-9268/

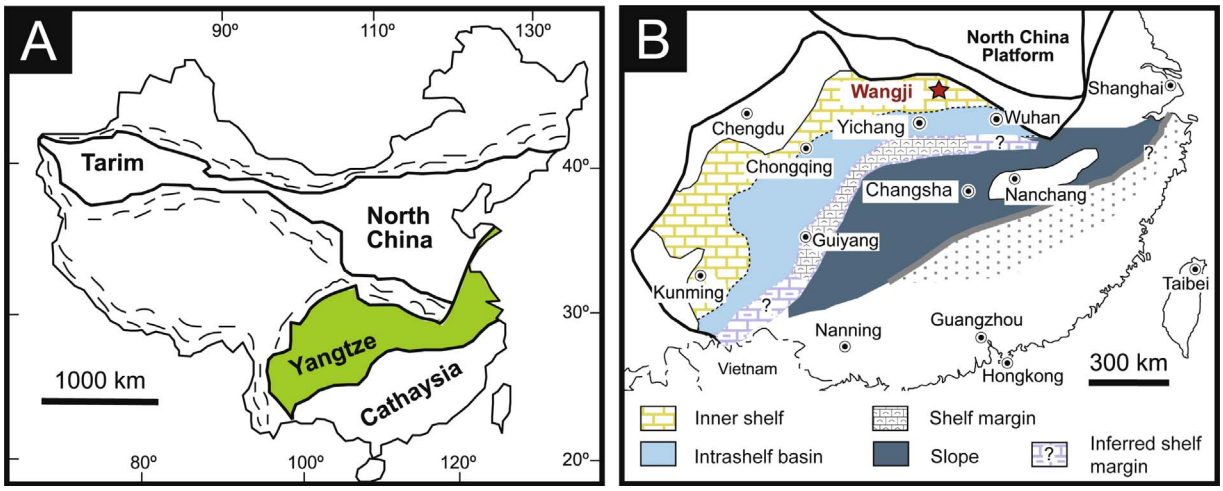

Fig. 1. (A) Generalized geological map of China. (B) The sedimentary facies in the Yangtze platform during the Ediacaran Period (modified after Jiang et al., 2011). The red star shows the drilling site.

paleogeography and C-isotopic chemostratigraphy of the Yangtze platform have been extensively studied (Lambert et al., 1987; Shen and Schidlowski, 2000; Condon et al., 2005; Guo et al., 2007, 2013; Jiang et al., 2007, 2011; Zhou and Xiao, 2007; Zhu et al., 2007, 2013; McFadden et al., 2008; Lu et al., 2013; Tahata et al., 2013; Cui et al., 2015, 2016a,b, 2017; Zhou et al., 2017). Nonetheless, highly variable depositional environments and limited high-resolution C-isotope data often complicate basinal stratigraphic correlations and our understanding of the dynamic carbon cycle in the Ediacaran Period. For example, three major negative C-isotopic excursions, named EN1, EN2 and EN3, were previously reported within the Doushantuo Formation of the Yangtze platform (e.g., Jiang et al., 2007; Zhou and Xiao, 2007; McFadden et al., 2008). However, recent studies showed that there are at least four marked negative $\delta^{13}C$ excursions within the Doushantuo Formation (e.g., Tahata et al., 2013; Zhu et al., 2013) and there is little consensus on the cause(s) of these negative excursions. In addition, C-isotopic values in the overlying Dengying Formation may be more variable than previously thought (e.g., Cui et al., 2016a). Therefore, more high-resolution C-isotope data from continuous successions are needed to better understand intra-basinal correlations, as well as to constrain the carbon cycle during the Ediacaran Period.

In this study, we present high-resolution carbon and oxygen isotopic data for carbonates of the Doushantuo Formation and the overlying Dengying Formation which were deposited on shallow shelf environment during the Ediacaran Period and of the lower Cambrian Yanjiahe Formation in the Yangtze platform (Fig. 1B). Samples were obtained from a continuous drill core collected near Wangji, South China (Fig. 1B). The objective of this study was to characterize the $\delta^{13}C$ chemostratigraphy of the Ediacaran shallow shelf environment, which could then be used for intra-basinal correlations in South China. In the drill core, we identified several beds of phosphorite in the lower Doushantuo Formation as well as in the middle Dengying Formation (Fig. 2). It has been demonstrated that phosphorus cycling and phosphorite deposition in modern and ancient environments are tightly linked to changes in redox chemistry of both seawater and sediments (e.g., Van Cappellen and Ingall, 1994; Mort et al., 2010; Pufahl and Groat, 2017). The temporal relationships between phosphorite deposits and C-isotope variations in the Wangji core allow us to unravel the possible origins of $\delta^{13}C$ excursions in the Ediacaran strata in the Yangtze platform and shed new light on our understanding of carbon cycling in the Ediacaran oceans.

2. Geological setting and sampling core

Ediacaran strata are extensively distributed throughout the Yangtze platform, which was developed on a rifted continental margin between the Yangtze Block and the Cathaysia Block at ~800 Ma (Li et al., 1999; Wang and Li, 2003). The sedimentary Ediacaran strata represent a range of depositional environments from inner shelf, distal shelf, shelf margin to slope (Jiang et al., 2011; Zhu et al., 2013) (Fig. 1B). The Three Gorges area, which is one of the important regions to investigate the Ediacaran history in South China, is inferred to have been an intrashelf basin at that time (Zhao et al., 1988; Jiang et al., 2011; Zhu et al., 2013) (Fig. 1B).

The Ediacaran strata in the Three Gorges area are subdivided into the Doushantuo Formation and the Dengying Formation (Fig. 2). The Doushantuo Formation overlies the Cryogenian Nantuo tillite, which is equivalent to the global Marinoan tillite (e.g., Zhao et al., 1988). The age of the Doushantuo Formation is bracketed between 635.2 ± 0.6 Ma and 551.1 ± 0.7 Ma using U-Pb zircon dates of volcanic ash beds found near the base and top of the formation, respectively (Condon et al., 2005) (Fig. 2). The dolostone-dominated Dengying Formation overlies black shales of the fourth member of the upper Doushantuo Formation (Fig. 2). Compared with the Doushantuo Formation, the Dengying Formation (~551 Ma to 541 Ma) is much thicker possibly due to an accelerating tectonic subsidence rate (Condon et al., 2005; Zhang et al., 2005). The Dengying Formation is overlain by the carbonates and shales of the Cambrian Yangjiahe Formation (Fig. 2).

In this study, we collected the samples drilled near the town of Wangji (31°28′12.32″ N, 112°13′24.53″ E), Hubei province (Fig. 1B). The drilling location is about 150 km northeast of the city Yichang (Fig. 1B). The drill core contains the sedimentary rocks from the Cryogenian Nantuo tillite through the Doushantuo and Dengying formations to the base of the Cambrian Yanjiahe Formation (Fig. 2). Unlike the Three Gorges area, which represents an intrashelf facies, the Wangji area is further shoreward and represents an inner shelf facies (Zhu et al., 2013). At Wangji, the lower Doushantuo Formation and the middle Dengying Formation contain massive phosphorites, and it is one of the major phosphorite mining areas exploited in South China over the last 30 years (e.g., Zhao et al., 1988).

In the lowermost part of the drill core, a typical Nantuo tillite is identified (Fig. 2). Above the Nantuo glacial deposits in the lower part of the Doushantuo Formation, the rocks are dominantly dolostone for 11.5 m (710.3–698.8 m), followed by 7.3 m of black shale (698.8–691.5 m) (Fig. 2). Dolostone again overlies the black shale and it is 2.3 m in thickness (691.5–689.2 m). Overlying this dolostone is a 129.2 m thick dark grey dolostone (689.2–560.0 m) that contains two phosphorite-bearing dolostone beds (689.2–666.0 m and 637.7–627.3 m, respectively) (Fig. 2). Further upward, the Doushantuo