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Redox architecture of an Ediacaran ocean margin: Integrated chemostratigraphic ($\delta^{13}C$–$\delta^{34}S$–$^{87}Sr/^{86}Sr$–Ce/Ce*) correlation of the Doushantuo Formation, South China

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ABSTRACT

Early diagenetic silicification and phosphatization of the Ediacaran Doushantuo Formation (ca. 635 to 551 Ma) in South China offer extraordinary taphonomic windows into the early evolution of multicellular eukaryotes, including various algal groups and potentially animals. In order to understand how the ecological and taphonomic distribution of these Ediacaran eukaryotes was controlled by oceanic redox conditions, it is critical to reconstruct the redox architecture of the sedimentary basin. Recently two alternative redox models have been proposed to account for the geochemical and sedimentary features of the Doushantuo Formation. One argues that the unit was deposited on a continental margin where a metastable sulfidic wedge was dynamically maintained by a sulfate concentration gradient between shelf and basinal environments. The other contends that the sulfidic water mass was largely restricted to the intra-shelf basin behind a rimmed margin. These two models make different predictions about the stratigraphic completeness and correlation of the Doushantuo Formation. To test these predictions, we generated high-resolution time-series trends of multiple isotopic and elemental tracers, including $\delta^{34}S$, $^{87}Sr/^{86}Sr$ and Ce/Ce*, to facilitate an integrated chemostratigraphic correlation between inner shelf (Xiaofenghe), intra shelf (Jiulongwan), and outer shelf (Yangjiaping and Zhongling) sections. Our correlations suggest that both the inner and outer shelf sections are stratigraphically incomplete relative to the intra shelf section. The euxinic wedge model should be reconsidered insofar as it is based on a miscorrelation between sections. Viewed from our revised chemostratigraphic framework, euxinic conditions on the platform appear to have been largely restricted to the intra shelf basin. Carbonates in the upper Doushantuo Formation at Jiulongwan and their stratigraphic equivalents are characterized by a profound negative carbon isotope anomaly (i.e., the Shuram Excursion) coincident with a drop in pyrite sulfur isotope values and a significant rise in $^{87}Sr/^{86}Sr$ from 0.7080 to 0.7090. The integrated stratigraphic data from South China suggest that the onset of the Shuram Excursion is associated with enhanced oxidative continental weathering that delivered radiogenic strontium, as well as sulfate, to the Ediacaran basin.

1. Introduction

The unrestricted Modern ocean is pervasively oxygenated from the surface to the abyssal deep (with oxygen content ranging from 3.5 to 7 mL/L depending on the salinity and temperature of various ocean masses) with the exception of oxygen minimum zones where the remineralization of particulate organic matter by aerobic bacteria draws the breathing gas to its lowest concentration (ca. 0.2 mL/L) (Deutsch et al., 2011). Nitrate can also become limiting in these zones as denitrifying bacteria use the oxidant for respiration. Animals living in oxygen minimum zones must either have a reduced metabolic rate or be very efficient at extracting O_2 from seawater. Some of these animals have evolved to have large gill surface areas, resulting in short diffusion distances from the water to the blood. Given that even the simplest animals require a few percent of present atmospheric levels (Mills et al., 2014) and more complex organisms need much more to engage in more active life styles, it is important to understand the redox state of the water column and how oxygen contents in shallow marine ecosystems might be modified by future global warming (Mora et al., 2013).

Determining the redox architecture of ancient ocean margins is particularly important in the Ediacaran Period (635 to 541 Ma) when the first large complex life forms (including animals) evolved (Xiao and

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Laflamme, 2009), assuming the Ediacara biota required O_2 for their metabolic activities and acquired the gas through diffusion (Laflamme et al., 2009). Most, if not all, fossils of the Ediacara biota appear in the sedimentary record following a profound negative carbon cycle anomaly known as the Shuram Excursion (Grotzinger et al., 2011; Macdonald et al., 2013) named after strata in Oman where the event was first described (Burns and Matter, 1993). During this event the carbon isotopic compositions of bedded carbonates, including some oolitic and stromatolitic facies (cf. Melezhik et al., 2009; Lu et al., 2013), fell to a nadir of less than −10‰ and stabilized for millions of years before returning to pre-event conditions. This profound negative carbon cycle anomaly has been interpreted in various ways, including 1) modification of global seawater compositions through oxidation of dissolved organic compounds in the oceans (Rothman et al., 2003), fossil organic carbon exposed on land (Kaufman et al., 2007), or methane in clathrates (Bjerrum and Canfield, 2011), 2) mixing of normal seawater precipitates with authigenic carbonates of anomalous isotopic composition formed through anaerobic metabolic activities (Schrag et al., 2013), or 3) alteration of carbonate sediments through interaction with diagenetic fluids of terrestrial origin (Knauth and Kennedy, 2009; Derry, 2010).

The Shuram Excursion is well developed in Ediacaran successions throughout South China (Jiang et al., 2007, 2011; Zhu et al., 2007; McFadden et al., 2008; Wang et al., 2012; Lu et al., 2013; Zhu et al., 2013; Tahata et al., 2013), including the well-studied intra-shelf section near Jiulongwan (Fig. 1A, B) where the onset of the carbon isotope event occurs in dolostone and limestone facies immediately above a thick cherty horizon (McFadden et al., 2008). Notably, in both the proximal inner shelf section at Xiaofenghe, as well as the distal outer shelf sections at Zhongling and Yangjiaping, the Shuram carbon isotope anomaly is missing altogether, or is very poorly expressed (Zhu et al., 2007; Li et al., 2010; Kunimitsu et al., 2011; Xiao et al., 2012; Liu et al., 2013; Zhu et al., 2013). Based on iron-speciation analyses and a clear sulfur isotope contrast between sections in the uppermost Doushantuo Formation at Jiulongwan and Zhongling (believed at the time to represent deep water deposition on the continental slope), Li et al. (2010) proposed that a metastable euxinic wedge was maintained dynamically across the ramp by a gradient of sulfate concentration between shallow and deep settings (Fig. 1C). Such redox modeling is based on the assumption that sections of the Doushantuo Formation in inner shelf Jiulongwan and outer shelf Zhongling section are continuous and well correlated (see Fig. S7 of Li et al., 2010). Sedimentary facies analyses, however, suggest that the sections at Zhongling and nearby Yangjiaping accumulated in shallow waters along an elevated margin rim, suggesting that euxinic conditions on the platform may have been restricted to an intra shelf setting (Zhu et al., 2007; Jiang et al., 2011; Zhu et al., 2013). Similar conditions may have also characterized deep-water slope settings distal from the rimmed shelf based on the preponderance of framboidal relative to euhedral pyrite preserved in the sediments and abundances of redox-sensitive trace elements (Fig. 1D; Sahoo et al., 2012; Wang et al., 2012). These observations suggest that euxinia may have been patchy across Doushantuo margin environments, and that the wedge model needs to be reconsidered in light of improved stratigraphic correlation and integrated geochemical data.

To search for the Shuram Excursion in the outer shelf environments preserved at Zhonging and Yangjiaping (~90 km to the southwest of Jiulongwan) where phosphorite is abundant in the upper reaches of the Doushantuo Formation, and to test the hypothesis that the shoal complex in this setting is stratigraphically incomplete, we applied time-series $\delta^{13}C$, $\delta^{34}S$, and $^{87}Sr/^{86}Sr$ isotope data from four sections (with Ce/Ce* from two of these) that span across the platform margin (Fig. 1E). The integrated results provide a systematic framework of chemostratigraphic correlations that allow us to test the two competing redox reconstructions for the Ediacaran basin. In addition, the time-series trends provide environmental context for the Laggerstätten of

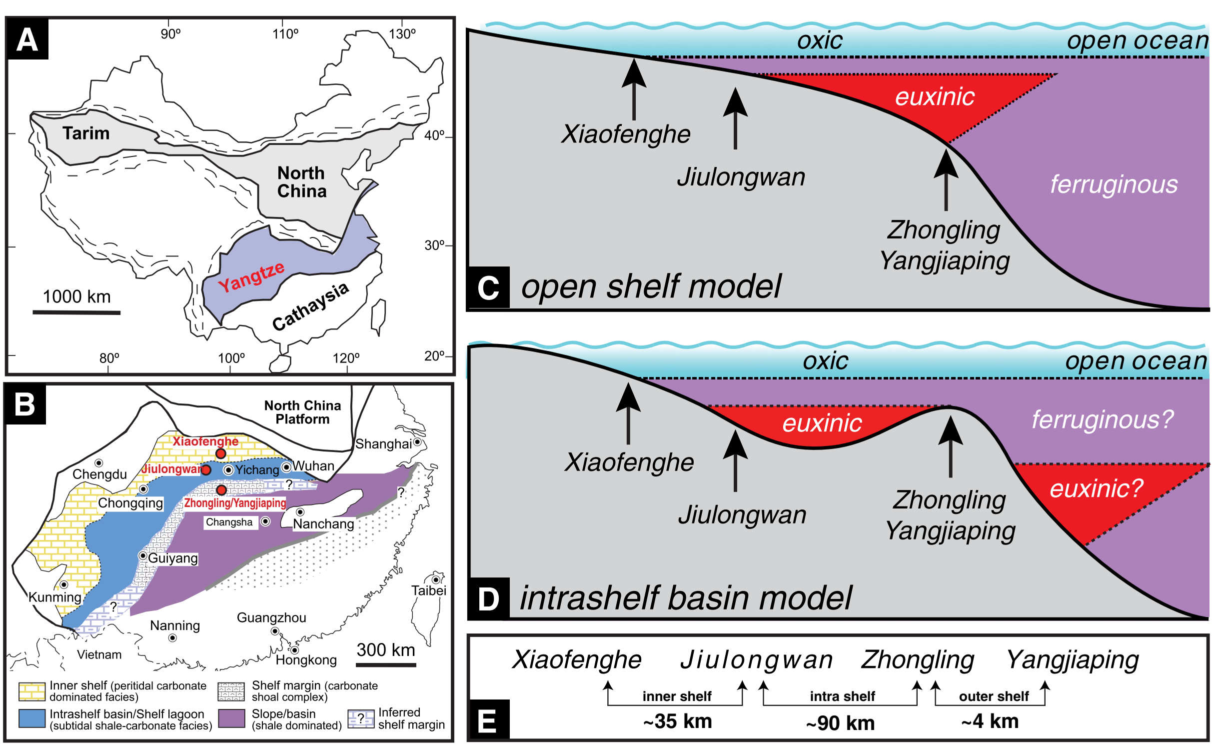

Fig. 1. (A) Geological map of China, with the Yangtze Craton highlighted in color. (B) Reconstructed Ediacaran depositional environments on the Yangtze Craton (Jiang et al., 2011). Red dots mark the location of the four sections discussed in this paper. (C) Open shelf model with a metastable sulfidic wedge maintained dynamically by overall low oceanic sulfate concentrations and a gradient of sulfate concentration between shallow and deep environments (Li et al., 2010). (D) Intra-shelf basin model with euxinic water mass largely restricted in lagoonal and deep basin settings (Jiang et al., 2011; Wang et al., 2012; Sahoo et al., 2012). (E) Distance between each correlated sections.