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Paired carbonate and organic carbon isotope variations of the Ediacaran Doushantuo Formation from an upper slope section at Siduping, South China

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ABSTRACT

Intensive carbon isotope analyses from the Doushantuo Formation (ca. 635–551 Ma) in South China reveal decoupled carbonate and organic carbon isotopes ($\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$) that have been interpreted as recording a large dissolved organic carbon (DOC) reservoir in the Ediacaran ocean or chemoautotrophic-methanotrophic recycling/modification of organic matter in a redox-stratified ocean. Existing paired $\delta^{13}C_{carb}$–$\delta^{13}C_{org}$ data, however, are mostly from sections of an intrashelf lagoon near the Yangtze Gorges area where basin restriction may have resulted in local isotope departure from the open ocean. To better understand the spatial and temporal variations of the Ediacaran $\delta^{13}C$ excursions, we have conducted high-resolution, paired $\delta^{13}C_{carb}$–$\delta^{13}C_{org}$ analyses of the Doushantuo Formation from an upper-slope section at Siduping, Hunan Province, South China. The data reveal three negative $\delta^{13}C_{carb}$ excursions at the basal, middle, and upper Doushantuo Formation. Two prominent negative $\delta^{13}C_{org}$ anomalies are also observed in black shales and shaly dolostones at the base and top of the Doushantuo Formation. For the majority of the Doushantuo Formation, however, $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ values are decoupled, similar to those observed in the Yangtze Gorges area. Both $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ show large (up to 10‰) variations among shallow- and deep-water sections that are consistent with a large carbon isotope gradient in a stratified Ediacaran ocean. The large $\delta^{13}C_{carb}$ gradient between shallow- and deep-water sections implies the availability of sulfate in deep-water environments where the addition of authigenic carbonate films/cements into surface-ocean-derived carbonate particles in anoxic water column or pore-water led to more negative $\delta^{13}C_{carb}$ values. Significant spatial $\delta^{13}C_{org}$ variations suggest that the decoupled $\delta^{13}C_{carb}$–$\delta^{13}C_{org}$ may not have been resulted from direct buffering of a large DOC reservoir but from recycling of organic matter by chemoautotrophs and methanotrophs. Compilation of available paired $\delta^{13}C_{carb}$–$\delta^{13}C_{org}$ data from the Yangtze platform reveals alternating intervals of coupled and decoupled $\delta^{13}C_{carb}$–$\delta^{13}C_{org}$ values up to the early Cambrian ($\leq$520 Ma). Intervals with coupled $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ coincide with evidence for ocean oxygenation events. This phenomenon may be explained by episodic growth and oxidation of a moderate DOC reservoir 6–12 times of the modern ocean. The upper Doushantuo $\delta^{13}C_{carb}$ anomaly temporally crosses a major stratigraphic unconformity, indicating that part of the upper Doushantuo-Shuram $\delta^{13}C_{carb}$ excursion was formed during sea-level regression. Large spatial and temporal variations of the upper Doushantuo $\delta^{13}C_{carb}$ excursion may record a mixed signature of open-ocean seawater overprinted by facies-dependent isotope variation, stratigraphic truncation and authigenic/diagenetic modification along the unconformity. The real primary $\delta^{13}C_{carb}$ excursion may be shorter-lived than previously thought.

1. Introduction

The Ediacaran Period (ca. 635–541 Ma; Knoll et al., 2006) following the Marinoan 'snowball' Earth glaciation witnessed fundamental ocean redox changes (e.g., Scott et al., 2008; Och and

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Shields-Zhou, 2012; Sahoo et al., 2012; Lyons et al., 2014) and biological innovations including the appearance and diversification of primitive metazoans (e.g., Xiao and Laflamme, 2009; Xiao, 2014; Droser and Gehling, 2015). Associated with these ocean chemical and biotic changes are large perturbations of the global carbon cycle. Negative carbon isotope ($\delta^{13}C_{carb}$) excursions with minimum $\delta^{13}C_{carb}$ values down to ≤ -10‰ have been reported from many Ediacaran successions globally (e.g., Calver, 2000; Corsetti and Kaufman, 2003; Halverson et al., 2005; Fike et al., 2006; Le Guerroué et al., 2006; Kaufman et al., 2006; Jiang et al., 2007; Prave et al., 2009; Grotzinger et al., 2011; Husson et al., 2012, 2015; Macdonald et al., 2013). The origin of these $\delta^{13}C_{carb}$ excursions, particularly that of the Shuram $\delta^{13}C_{carb}$ excursion and its correlative equivalents, has been highly debated, with interpretations varying from meteoric/burial diagenesis (e.g., Knauth and Kennedy, 2009; Derry, 2010a,b; Swart and Kennedy, 2012), to oxidation of a large oceanic dissolved organic carbon (DOC) reservoir (e.g., Rothman et al., 2003; Fike et al., 2006; Jiang et al., 2007; McFadden et al., 2008) or methane (Bjerrum and Canfield, 2011), and to authigenic carbonate precipitation from early diagenetic pore fluids (Higgins et al., 2009; Schrag et al., 2013).

The Doushantuo Formation (ca. 635 Ma to $\geq$551 Ma) in South China is one of the critical stratigraphic units that serve as a window for understanding the origin of Ediacaran $\delta^{13}C$ excursions and their potential causal link with ocean chemical-biological changes. Intensive $\delta^{13}C$ chemostratigraphic studies from this unit revealed two important features of the Ediacaran $\delta^{13}C$ record: (1) decoupled carbonate-organic carbon isotopes ($\delta^{13}C_{carb}$–$\delta^{13}C_{org}$) for the majority of the Doushantuo Formation (e.g., Guo et al., 2006, 2007; McFadden et al., 2008; Xiao et al., 2012; Cui et al., 2015) and (2) a regionally persistent but highly variable negative $\delta^{13}C_{carb}$ excursion from the upper Doushantuo Formation (e.g., Guo et al., 2007; Jiang et al., 2007; Ader et al., 2009; Wang et al., 2012a; Zhu et al., 2007, 2013; Lu et al., 2013). The decoupled $\delta^{13}C_{carb}$–$\delta^{13}C_{org}$ pattern has been used to support the existence of a large Ediacaran DOC reservoir (Rothman et al., 2003; Fike et al., 2006; McFadden et al., 2008) and the upper Doushantuo negative $\delta^{13}C_{carb}$ excursion was interpreted as resulting from oxidation of this inferred DOC reservoir (e.g., Jiang et al., 2007; McFadden et al., 2008; Ishikawa et al., 2013). Alternatively, decoupled $\delta^{13}C_{carb}$–$\delta^{13}C_{org}$ and their spatial heterogeneity were interpreted as recording isotope signature of chemoautotrophically-methanotrophically recycled/modified carbon in a redox-stratified ocean (Ader et al., 2009; Jiang et al., 2010, 2012; Hohl et al., 2015) and the upper Doushantuo $\delta^{13}C_{carb}$ excursion might record burial diagenetic (Derry, 2010a) or hydrothermally altered (Derkowski et al., 2013) isotope signature.

The veracity of a large DOC reservoir has been challenged by the spatial limitation of paired $\delta^{13}C_{carb}$–$\delta^{13}C_{org}$ data. In spite of intensive carbon isotope analyses from the Doushantuo Formation, current studies have focused mainly on the Yangtze Gorges area or adjacent sections. Paleogeographic reconstructions (e.g., Vernhet and Reijmer, 2010; Jiang et al., 2011; Zhu et al., 2013) indicate that most of the sections that have paired $\delta^{13}C_{carb}$–$\delta^{13}C_{org}$ data, including Jiulongwan (McFadden et al., 2008), Xiaofenghe (Xiao et al., 2012), Zhongling (Li et al., 2010; Cui et al., 2015), and Yangjiaping (Ader et al., 2009; Cui et al., 2015), are located in an intrashelf lagoon or near the lagoonal side of the shelf margin shoal complex (loc. 2, 4, 5, and 6 in Fig. 1). Paired $\delta^{13}C_{carb}$–$\delta^{13}C_{org}$ data from deep-water sections are limited to a condensed section at Yanwutan (loc. 8 in Fig. 1), where the Doushantuo Formation is about 60 m thick (Guo et al., 2006, 2007; also see Hohl et al., 2015). This limitation raises uncertainties about whether the decoupled $\delta^{13}C_{carb}$–$\delta^{13}C_{org}$ pattern documented from the Doushantuo Formation records an open-ocean seawater isotope signature. In addition, the Xiaofenghe section (loc. 2; Fig. 1) has only the lower-middle Doushantuo Formation and the Zhongling/Yangjiaping sections (loc. 5 and 6; Fig. 1) may have significant stratigraphic truncation at the top of the Doushantuo Formation (Cui et al., 2015). Therefore, these sections may not have a complete $\delta^{13}C_{carb}$–$\delta^{13}C_{org}$ record across the upper Doushantuo/Shuram $\delta^{13}C_{carb}$ excursion.

Stratigraphically continuous $\delta^{13}C_{carb}$–$\delta^{13}C_{org}$ data from open-ocean sections are needed to test the veracity of a large Ediacaran DOC reservoir and to explore the origin of the upper Doushantuo/Shuram $\delta^{13}C_{carb}$ excursion. In this paper we report high-resolution, paired $\delta^{13}C_{carb}$–$\delta^{13}C_{org}$ data of the Doushantuo Formation from an upper-slope section in Siduping, Hunan Province, South China (loc. 7 in Fig. 1). In combination with available data in literature, we discuss the possibility of and constraints on a large Ediacaran oceanic DOC reservoir and the heterogeneity of the upper Doushantuo $\delta^{13}C_{carb}$ anomaly.

2. Geological background and sampling section

The Ediacaran Yangtze platform developed over a late Neoproterozoic rifted continental margin that is inferred to have initiated at the southeastern side of the Yangtze Continental Block (or craton) at ca. 820 Ma (Li et al., 1999; Wang and Li, 2003). A passive continental margin setting has been inferred for the Ediacaran Doushantuo and Dengying/Liuchapo formations on the basis of stratigraphic pattern and thickness variation (Jiang et al., 2003a, 2011). The majority of the Doushantuo Formation was thought to have deposited in a rimmed carbonate shelf, with a shelf margin shoal complex separating an intrashelf lagoon from the open ocean (Fig. 1; Jiang et al., 2011).

In the Yangtze Gorges area (e.g., the Jiulongwan section; loc. 4 in Fig. 1), the Doushantuo Formation is divided into four lithostratigraphic members (Members I–IV). Member I refers to the 2–6-m-thick cap carbonate. Member II consists of interbedded shale and limestone with pea-sized chert nodules that contain abundant acanthomorphic acritarchs (e.g., Zhou et al., 2007; McFadden et al., 2008, 2009; Liu et al., 2013). Member III is composed of thin- to thick-bedded dolostone and limestone, from which the upper Doushantuo negative $\delta^{13}C_{carb}$ excursion was documented and correlated with the Shuram/Wonoka $\delta^{13}C_{carb}$ anomaly (Zhou and Xiao, 2007; Jiang et al., 2007; Zhu et al., 2007, 2013; McFadden et al., 2008; Sawaki et al., 2010; Tahata et al., 2013; Lu et al., 2013). Member IV refers to the 5–10-m-thick organic-rich black shales at the top of the Doushantuo Formation. U–Pb zircon ages of 635.2 ± 0.6 Ma from the cap carbonate (Member I) and 551 ± 0.7 Ma from the Miaohe Member (thought to be time-equivalent with the Doushantuo Member IV; but see An et al., 2015, for discussions) constrain the Doushantuo Formation as ca. 635 to $\geq$551 Ma (Condon et al., 2005; Zhang et al., 2005).

The Doushantuo Formation shows significant facies change toward the shelf margin (e.g., Yangjiaping; loc. 6 in Fig. 1). Except for the cap carbonate and its immediate overlying black shales that are similar to those of the Yangtze Gorges areas, the majority of the Doushantuo Formation in the shelf margin is composed of thin- to thick-bedded shallow-water carbonates (Jiang et al., 2011). The top of the Doushantuo Formation is marked by 5–10-m-thick phosphoritic limestone and dolostone. The Member IV organic-rich black shales seen in the Yangtze Gorges area are partially or entirely missing in shelf-margin sections.

The upper-slope sections of the Doushantuo Formation (e.g., Tianping and Siduping) consist mainly of microcrystalline dolostone, cherty dolostone, and shaly dolostone with abundant syndepositional folds, slump blocks, and olistostrome breccias (Jiang et al., 2003a, 2006; Vernhet et al., 2006, 2007; Zhu et al., 2007). The lower-slope deposits of the Doushantuo Formation (e.g., Wuhe section; Jiang et al., 2007) are dominated by black shales with