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Dynamic evolution of the Ediacaran ocean across the Doushantuo Formation, South China

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ABSTRACT

Oceanic redox conditions and atmospheric oxygenation likely played a crucial role in the evolution of macroscopic multicellular eukaryotes during the early Ediacaran period. However, the oxidation mechanism and magnitude of the Ediacaran ocean–atmosphere system remain controversial. To constrain the oceanic redox conditions and the contemporaneous oxygenation of the atmosphere, we present a comprehensive investigation of redox-sensitive elements (e.g., Mo and U), Fe speciation and S isotopes of pyrite from the platform, slope and basin sections across the Doushantuo Formation in South China. Our results suggest a redox-stratified Ediacaran ocean with a fluctuating chemocline from the slope to platform location across the Doushantuo Formation. In particular, euxinic/intermittently euxinic conditions developed not only at the platform and slope but also in the deep basin. Furthermore, these euxinic conditions indicate that high sulfate concentrations may have accumulated not only at the ending of the Ediacaran Doushantuo Formation but also at the middle and beginning. Thus, these results suggest that the extensive euxinic conditions associated with the continuous oceanic sulfate input were in response to progressive oxygenation of the atmosphere during the early Ediacaran period. Integrated with previously published results, if the dissolved organic carbon (DOC) reservoir existed, different mechanisms may be responsible for the oxidation of deep ocean in each part of the studied sections across the Doushantuo Formation. One mechanism is oxidation by sulfate through a bacterial sulfate reduction (BSR) process under anoxic conditions. Another mechanism is oxidation by dissolved free oxygen under oxic/suboxic conditions. Finally, a dynamic evolution model of the Ediacaran ocean–atmosphere system across the Doushantuo Formation, South China, was suggested.

1. Introduction

The increasing oxygen levels and progressive oxygenation of the deep oceans throughout the entire Ediacaran (635–542 Ma) likely stimulated the radiation of macroscopic multicellular eukaryotes (Fike et al., 2006; Canfield et al., 2007; McFadden et al., 2008; Sahoo et al., 2012). Early animal evolution and diversification were commonly followed by an increased atmospheric oxygen concentration (e.g., Neoproterozoic Oxygenation Event) and a fluctuating marine environment. These have been intensively studied on the basis of multiple geochemical methods, such as carbon, sulfur, strontium, iron, chromium, uranium and molybdenum isotopes, redox-sensitive elements and iron speciation (Fike et al., 2006; Canfield et al., 2007, 2008; Jiang et al., 2007, 2011; Kaufman et al., 2007; Shields, 2007; McFadden et al., 2008; Scott et al., 2008; Shen et al., 2008; Frei et al., 2009; Li et al., 2010; Sahoo et al., 2012; Och and Shields-Zhou, 2012; Fan et al., 2014; Kendall et al., 2015). Although the mechanism and magnitude of the Neoproterozoic Oxygenation Event are still uncertain, a rise in atmospheric oxygen concentration has been widely recognized (Canfield and Teske, 1996; Canfield, 2005; Shen et al., 2008; Frei et al., 2009; Campbell and Squire, 2010; Sahoo et al., 2012; Och and Shields-Zhou, 2012). Nevertheless, the redox condition of the Ediacaran ocean remains open to debate and is the focus of conflicting viewpoints, such as whether there was an oxic or anoxic (ferruginous or euxinic) deep ocean. Several studies with investigations of Fe speciation, redox-sensitive elements and carbon, sulfur and nitrogen isotopes, have proposed that the Ediacaran deep ocean was widely oxygenated (Canfield, 1998; Fike et al., 2006; Canfield et al., 2007; Scott et al., 2008; Ader et al., 2014). However, other studies using similar geochemical approaches, have suggested a redox-stratified ocean (Jiang et al., 2007, 2011; Canfield et al., 2008; Shen et al., 2008; Ader et al., 2009; Li et al., 2010; Fan et al., 2014; Wood et al., 2015). Taking an example from the Ediacaran Doushantuo Formation in South China, alternative oceanic redox models have been proposed in recent years, such as the metastable zone of the euxinic water column sandwiched within anoxic open deep water at the platform and slope locations (Li et al., 2010; Wang

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et al., 2012; Fan et al., 2014), or the strongly stratified shelf lagoon and open ocean with oxic shallow water and anoxic/euxinic deep water (Jiang et al., 2007, 2011).

The Ediacaran Doushantuo Formation, one of the best-preserved sedimentary sequences in the world, has been highly investigated in relation to its biological evolution, its stratigraphic correlation and the evolution of the ocean–atmosphere system (Xiao et al., 2002; Zhao et al., 2004; Zhou et al., 2007; McFadden et al., 2008; Xiao and Laflamme, 2008; Li et al., 2010; Jiang et al., 2011; Sahoo et al., 2012; Zhu et al., 2013). Fortunately, a number of integrated stratigraphy (including chemo- and chrono-) and paleogeography reviews have documented a wealth of fundamental information about the Doushantuo Formation (Zhou and Xiao, 2007; Zhu et al., 2007; Jiang et al., 2011; Xiao et al., 2012). Among the numerous geochemical efforts during the past decades, prominently negative carbonate carbon isotope ($\delta^{13}C_{carb}$) excursions have been characterized for the Doushantuo Formation in the Yangtze Three Gorges (Zhou and Xiao, 2007; Zhu et al., 2007; Jiang et al., 2007, 2011; McFadden et al., 2008). These were often correlated with other Ediacaran systems, such as those in Oman, Australia, Canada, Namibia, India, and the United States (Calver, 2000; Hoffman and Schrag, 2002; Jiang et al., 2002, 2003; Halverson et al., 2005; Fike et al., 2006; Kaufman et al., 2007; Le Guerroué and Cozzi, 2010). Several different hypotheses have been proposed for the origin of these unusually negative $\delta^{13}C_{carb}$ excursions, such as mantle-derived sources (Hoffman et al., 1998; Hoffman and Schrag, 2002), methane hydrate release (Kennedy et al., 2001; Jiang et al., 2003, 2006a; Bjerrum and Canfield, 2011), seawater overturn/upwelling (Kaufman et al., 1991; Knoll et al., 1996; Grotzinger and Knoll, 1995; Shields, 2005; Schröder and Grotzinger, 2007; Fan et al., 2014), and the oxidized weathering of terrigenous and marine organic-rich sediments (Kaufman et al., 2007; Higgins and Schrag, 2006). Additionally, another model has also been suggested which includes the oxidation of the deep oceanic dissolved organic carbon (DOC) reservoir (Rothman et al., 2003; Fike et al., 2006; Jiang et al., 2007; McFadden et al., 2008). If this DOC reservoir existed, the remineralization of deep oceanic DOC was likely related to the oxygenation of the Ediacaran ocean–atmosphere system (Fike et al., 2006; Jiang et al., 2007; McFadden et al., 2008; Fan et al., 2014). Furthermore, S isotopes, Fe speciation and redox-sensitive elements have also been used to reconstruct the paleoceanographic environment of the Ediacaran Doushantuo Formation. Despite the lower-resolution samples and the lack of comparison among different sedimentary sections, these geochemical data have still provided relevant information for continued investigation of the ocean redox conditions and atmospheric oxygenation in the Ediacaran (McFadden et al., 2008; Shen et al., 2008; Li et al., 2010; Sahoo et al., 2012).

To constrain the oceanic redox conditions and the atmospheric oxygenation during the Ediacaran Doushantuo period, the high resolution variations in redox-sensitive elements (e.g., Mo and U) coupled with Fe speciation and S isotope data of the comprehensive sedimentary facies including platform, slope and basin sections, all from the Doushantuo Formation, were investigated in this contribution. Based on our data in combination with previously published results, we would like to suggest a dynamic evolution model of the Ediacaran ocean–atmosphere system across the Doushantuo Formation, South China.

2. Geological backgrounds

The Ediacaran Doushantuo Formation, which constrained between 635.2 ± 0.6 Ma and 551.1 ± 0.7 Ma by zircon U–Pb ages of interbedded volcanic ash, is underlain closely by the Cryogenian Nantuo Formation and is deposited at a passive continental margin setting, without tectonic events and igneous activities, in South China (Fig. 1; Condon et al., 2005; Jiang et al., 2011). The sediment of the Doushantuo Formation commonly starts with the cap carbonate and terminates with organic-rich black shale. Whether on the platform or in the slope and basin facies, the similar lithology and geochemical characteristics of the cap carbonate make it a lithostratigraphic marker bed at the base of the Doushantuo Formation (Jiang et al., 2006b, 2011). After the cap carbonate, the sedimentary facies and the thickness of the Doushantuo Formation exhibit large variations from the platform, to the slope to the basin (Zhu et al., 2007; Jiang et al., 2011; Wang, 2012). In general, the platform section is dominated by interbedded carbonate and black shale, whereas the main lithology of black shale is characterized for the slope and basin locations (Zhu et al., 2007; Jiang et al., 2011; Wang, 2012). At the top of the Doushantuo Formation, the organic-rich black shale is recommended as another regional lithostratigraphic marker bed because it can distinguish the Doushantuo Formation from the overlying Dengying/Liuchapo/Laobao Formations (Jiang et al., 2011; Wang, 2012).

In this work, two well-studied sections (the platform, Jiulongwan, and the slope, Wuhe) and one new basin section (Xiangtan) are included and provide a comprehensive comparison across the Doushantuo Formation (Fig. 1). The Jiulongwan section, one of the most well-known sections, is located in the Yangtze Gorges area with a rough thickness of 155 m, and it can be divided into four members as follows. Member 1 consists of cap carbonate with a thickness of approximately 5 m at the base of the Doushantuo Formation. Member 2 (ca. 80 m) contains interbedded carbonates and organic-rich black shale accompanied by numerous pea-sized chert nodules. Member 3 (ca. 60 m) is primarily characterized by carbonates with bedded chert layers and minor shale beds. Member 4 (ca. 10 m) is mainly deposited as the organic-rich black shale at the top of the Doushantuo Formation (Fig. 2; McFadden et al., 2008; Li et al., 2010; Jiang et al., 2011; Wang, 2012).

Nevertheless, these distinctive features and divisions in the Jiulongwan platform section are not identified in the Wuhe slope and Xiangtan basin sections due to the absence of correlation of the biostratigraphy and lithostratigraphy. Therefore, the variations of geochemical lines are expected to provide rough evolutionary stages in this study. The Doushantuo Formation in the Wuhe section, with a thickness of approximately 120 m, has approximately 2.5 m of cap carbonate and 5 m of organic-rich black shale, which are distributed at the base and top of the Doushantuo Formation, respectively. The remainder of the Wuhe section is mainly characterized by interbedded black shale and carbonates, with a few olistostrome layers (Fig. 3; Jiang et al., 2007; Sahoo et al., 2012; Wang, 2012). Regarding the Xiangtan basin section, the overall thickness of the Doushantuo Formation is approximately 190 m, and black shale is the predominated feature. The distinctive markers of the Doushantuo Formation in the Xiangtan section, distinguishing it from the underlying Nantuo Formation and the overlying Liuchapo Formation, are mainly based on the distributions of the underlying cap carbonate and the overlying chert layer (Fig. 4).

3. Samples and methods

3.1. Samples

All of the studied black shale samples were freshly collected from the Jiulongwan (30°48′54″N, 110°3′20″E, 36 samples, platform, Fig. 2), Wuhe (26°45′57″N, 108°24′59″E, 48 samples, slope, Fig. 3) and Xiangtan (27°58′24″N, 112°49′51″E, drill-hole samples, 52 samples, basin, Fig. 4) sections. These samples were ground to minus 200 mesh in an agate mortar for further elemental analysis. The Fe speciation and S isotope of the Jiulongwan section were cited from Li et al. (2010) and McFadden et al. (2008). Another data of Mo, U and Fe speciation of the upper part of the Jiulongwan section (Member 4) were cited from Kendall et al. (2015) (Fig. 2). In addition, other further 25 data points for black shale samples from the base (21 samples from 2.4–8.6 m) and the top (4 samples from 117 to 120 m) of the Wuhe section were taken from Sahoo et al. (2012) and Wang (2012), respectively (Electronic Appendix Table 1).