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The sulfur isotope signatures of Marinoan deglaciation captured in Neoproterozoic shallow-to-deep cap carbonate from South China

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ABSTRACT

We present high-resolution sulfur and carbon isotope records from the cap carbonate of the Doushantuo Formation, South China, a unique suite of depositional facies spanning across a pronounced paleo-oceanic depth gradient. The $\delta^{34}S$ of carbonate-associated sulfate (CAS) decreases across a shelf-to-slope depth transect. We propose that the deeper-water slope profile represents syn-glacial sulfur isotope compositions of the seawater sulfates with impact of ^{34}S-depleted hydrothermal sulfur inputs, while the $\delta^{34}S$ of the shallow inner-shelf were dominantly controlled by the ^{34}S-enriched terrigenous input. We suggest that the terrigenous sulfur inputs were mainly from weathering and erosion of the pre-Marinoan Datangpo Formation—glacially ground and then freshly exposed during rapid deglaciation. The widespread Datangpo Formation, deposited between the Sturtian and Marinoan glacial intervals, is noted for the unusually high $\delta^{34}S$ values of its pyrite.

The low sulfate conditions in the ocean allowed for strong local controls and consequent heterogeneities in seawater chemistry. The post-Marinoan ocean was stratified in the immediate wake of glaciation, with anoxic deep waters overlain by an oxic, melt-water layer. During the transgression, the shallow water was disturbed by upwelling. The oxidation of dissolved organic carbon (DOC) from deep water would lead to transiently enhanced ^{13}C depletions but ^{34}S enrichments in the shallow waters.

1. Introduction

Lines of sedimentologic and geochemical evidence indicate that four glaciations (from oldest to youngest, the Kaigas, Sturtian, Marinoan, and Gaskiers) occurred during Neoproterozoic period, with Sturtian and Marinoan records preserved global-wide (Kirschvink, 1992; Kennedy et al., 1998; Knoll, 2000; Shields, 2005; Zhang et al., 2009). Cap carbonate facies overlying Marinoan glacial deposits yield an age of ca. 635 million years for the end of the glacial conditions (Hoffmann et al., 2004; Condon et al., 2005). The cap is typically 1–6 m thick and shows a unique suite of sedimentary structures and textures, including megaripples, peloids, tepee-like structures, tube structures, and barite fans (Kennedy et al., 1998, 2001a; James et al., 2001; Hoffman and Schrag, 2002; Jiang et al., 2003a, 2006a; Xiao et al., 2004). Cap dolostone and limestone are characterized by strong ^{13}C depletions with $\delta^{13}C$ values mostly ranging from 0‰ to −5‰ and some even lower values (Kennedy, 1996; Kennedy et al., 1998, 2001b; Kaufman et al., 1997; Hoffman et al., 1998; James et al., 2001; Hoffman and Schrag, 2002; Leather et al., 2002; Corsetti and Kaufman, 2003; Jiang et al., 2003a; Nogueira et al., 2003; de Alvarenga et al., 2004; Halverson et al., 2004; Xiao et al., 2004). The global distribution of cap carbonates suggests severe climatic changes in the immediate wake of the Marinoan glaciation (Grotzinger and Knoll, 1995; Hoffman et al., 1998; Knoll, 2000; Hoffman and Schrag, 2002; Shields, 2005).

Characteristic cap carbonates directly overlying glacial deposits and their chemical and isotopic features are informative proxies for the change of the ocean chemistry during the transition from Marinoan glaciation to the following Ediacaran, remarked by the first proliferation of animal life and dramatic shifts in ocean-atmosphere oxygenation (Planavsky et al., 2010; Sahoo et al., 2012). As such, the $\delta^{34}S_{CAS}$ of the cap carbonates from different depositional

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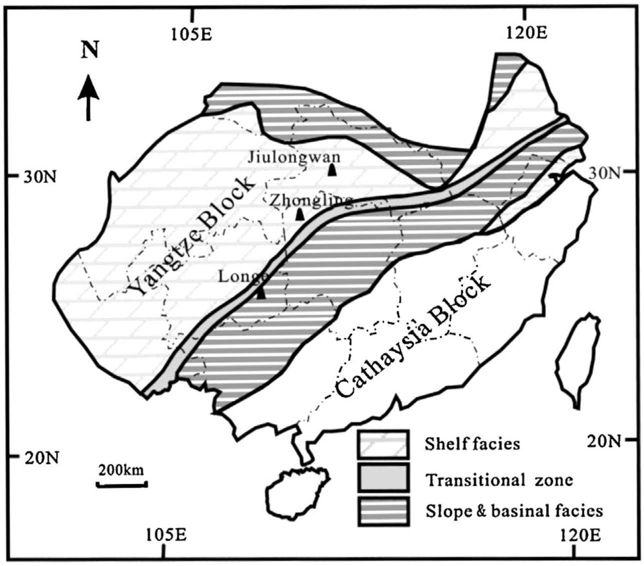

Fig. 1. Simplified geological map showing exposures of Neoproterozoic strata in the Yangtze platform of South China, position of the late Proterozoic platform margin and location of studied cap carbonate sections.

settings may provide extensive information on the seawater chemistry at different water depths in the immediate aftermath of the Marinoan glaciation (Hurtgen et al., 2006; Shen et al., 2008). Hurtgen et al. (2006) studied cap carbonates of Maieberg Formation in Namibia and suggested that ^{34}S on the shallower restricted shelf was enriched due to the bacterial sulfate reduction (BSR), while ^{34}S on the deeper open shelf was depleted due to the oxidation of H_2S released from the deep ocean. Shen et al. (2008) investigated isotopic signatures of the Zhamoketi cap carbonate in Northwest China and suggested otherwise, that ^{34}S in the deep ocean might be more enriched compared to the surface ocean. They argued specifically that the deep ocean was impacted by BSR that elevated the $\delta^{34}S$ values, while the surface ocean was dominated by continental weathering with low $\delta^{34}S$. Recently, Shen et al. (2011) studied cap dolostone overlying the Hankalchough diamictite in the Quruqtagharea of Northwest China, which is younger than the Marinoan diamictite and possibly correlates with the ~582 Ma Gaskiers diamictite, and found that $\delta^{34}S_{CAS}$ became more negative and more scattered from offshore to onshore sections. They suggested that the sulfur isotope gradient was caused by pronounced terrestrial input of ^{34}S-depleted sulfate in shallower profile, mainly from the oxidation of continental pyrite deposits. Because the post-glacial sulfur isotope records could be strongly impacted by localized factors discussed above, a systematic study on various geological settings is desired to unravel the chemical structure of the ocean in the aftermath of the Marinoan glaciation.

In this study, we present high-resolution chemostratigraphic records of the cap carbonates from three post-Marinoan sections in South China, spanning from shallow to deep ocean depositional settings. Together with previously published data (McFadden et al., 2008; Huang et al., 2009, 2011), our data suggest a stratified ocean and its evolution immediately after the Marinoan glaciation in South China, which are controlled by both global (e.g. hydrothermal input) and local (e.g. weathering input) factors during deglaciation.

2. Geological background

The Ediacaran System in South China is distributed on a passive continental margin along the Yangtze Block (Wang and Li, 2003; Jiang et al., 2006a; Zhou and Xiao, 2007) (Fig. 1). It is composed of Doushantuo and Dengying formations, which overlie the Nantuo glacial diamictite that formed during the termination of the Marinoan glaciation at 635 Ma (Chu et al., 2005; Condon et al., 2005; Yin et al., 2005; Zhang et al., 2005). A 3–6 m thick cap carbonate overlies the Nantuo diamictite and is defined as the basal member of the Doushantuo Formation. The cap carbonate in South China is correlated with the post-Marinoan caps in Australia (Kennedy, 1996), Namibia (Hegenberger, 1987; Kennedy et al., 2001a), eastern California (Cloud et al., 1974), and Norway (Siedlecka and Roberts, 1992). The cap is overlain by alternating shales and carbonates of Doushantuo and Dengying formations with thicknesses of approximately <250 to 1000 m.

Guided by the paleogeographic reconstruction of a southeast-facing late Neoproterozoic Yangtze platform (Jiang et al., 2003b), we collected cap carbonate samples from the Jiulongwan section in Yichang, Hubei Province, Zhongling section in Shimen, Hunan Province, and Longe section in Liping, Guizhou Province that represent inner-shelf, outer-shelf, and slope facies, respectively (Fig. 2). The Ediacaran strata are well developed in the Yangtze area. In the shelf-facies region, such as the Jiulongwan and Zhongling sections, the cap carbonates are 5–6 m thick, which are overlain by alternating shales and carbonates of Doushantuo Formation and carbonates of Dengying Formation. In the slope and basin-facies region, such as the Longe section, the cap carbonates are 2–3 m thick, which are overlain by shales of Doushantuo Formation and cherts of Laobao Formation.

Hoffman et al. (2007) studied the Keilberg cap dolostone (635 Ma) across the Otavi carbonate bank and down a contiguous submarine slope in northern Namibia, in which the petrology and geochemistry records suggest that those Ediacaran cap carbonates are diachronous. However, unlike Keilberg cap dolostone, the Doushantuo cap carbonate successions have similar thickness (3–6 m) in South China, and they do not contain wave-generated bedforms in the slope facies (Jiang et al., 2006a). In addition, the $\delta^{13}C_{carb}$ values of Doushantuo cap carbonate from slope to shelf do not collectively describe a sigmoidal $\delta^{13}C$ curve over time with a net decline or increase (Shen et al., 2005; Jiang et al., 2007; this study). Therefore, the Doushantuo cap carbonates in South China are likely isochronous, and thus the cap carbonates from the sections we studied are correlated.

Jiang et al. (2006a, 2006b) divided Doushantuo cap carbonate into three members based on sedimentological features. The base of the cap carbonate (C1) consists of cliff-forming, buff- to yellow-weathering microcrystalline dolomite with localized bedding disruption, brecciation, cavities and early cementation. The middle interval (C2) is laminated dolomite with local tepee-like structures. The uppermost part (C3) commonly consists of thinly laminated, silty and shaly limestone. C1, C2, and C3 are easily distinguished from each other in Jiulongwan section, but no distinct laminated limestone of C3 can be found in Zhongling and Longe sections (Fig. 2). The $\delta^{13}C$ values of C3 in Jiulongwan section are higher than 0‰, while all $\delta^{13}C$ values from Zhongling and Longe sections are lower than 0‰ (Wang et al., 2008; this study). Thus, we are able to correlate the C1 and C2 parts in all three sections based on their similar carbon isotope properties (Fig. 2).

These three sections are well exposed with fresh outcrops, which are critical for isotopic analyses. The stratigraphic continuity allows high-resolution, integrated sulfur and carbon isotope investigations of the post-Marinoan cap carbonates in different settings deposited under different water depths.

3. Methods

We collected all the carbonates in outcrop as large hand-specimens to ensure sufficient quantities for geochemical analysis. Petrographic observation and chromium reduction tests indicated