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^{17}O-depleted barite from two Marinoan cap dolostone sections, South China

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ABSTRACT

Distinct, non-mass-dependent ^{17}O depletion was reported in barite from Marinoan cap dolostones (~635 Ma) in South China, and has been interpreted as an indication of an extremely high-pCO$_2$ atmosphere (Bao et al., 2008). There is a significant variation in the magnitude of the ^{17}O anomaly even among samples from the same outcrops. Understanding the origins of this barite and particularly the source of sulfate is critical to interpreting the anomalous ^{17}O signature and its implication on sulfur and oxygen cycles at the aftermath of Marinoan glacial meltdown. In this study, we analyzed 160 micro-sampled barite samples from 20 hand specimens collected from two cap dolostone sections in South China. Together with field, petrographic, and Sr isotope data, the expanded dataset 1) confirms the large variability in Δ^{17}O (from −0.09‰ to −0.87‰, VSMOW), δ^{18}O (+13.3‰ to +23.5‰, VSMOW), and δ^{34}S (+20.0‰ to +45.5‰, VCDT) of barite; 2) demonstrates a hyperbolic relationship between the Δ^{17}O and δ^{34}S of various barite samples with more negative Δ^{17}O values generally corresponding to lower δ^{34}S values; 3) reveals that individual barite crystal fans and fans of the same layer possess a well-clustered set of δ^{18}O, Δ^{17}O, and δ^{34}S values; and 4) shows, correspondingly, that barite crystal fans of different layers bear different sets of Δ^{17}O, δ^{18}O, and δ^{34}S values. The study suggests that ^{17}O-depleted barite crystals were formed under supersaturation when Ba^{2+} from sulfate-free deepwater came to mix with sulfate-bearing shallow water. There were multiple upwelling episodes which resulted in multiple barite layers. The large variability in sulfur and triple-oxygen isotope composition and the high ^{87}Sr/^{86}Sr ratios indicate that the two sites from South China were sufficiently close to the continent so that the isotopic composition of sulfate was easily influenced by changes in riverine flux when seawater sulfate concentration at that time was exceedingly low. Our depositional model for the barite is consistent with the proposed sequence of events after the meltdown of Marinoan glaciation in South China by Zhou et al. (2010), and is also consistent with the proposed atmospheric origin of sulfate ^{17}O depletion by Bao et al. (2008).

1. Introduction

Bao et al. (2008) reported a distinctive, non-mass-dependent ^{17}O depletion in a sedimentary mineral – barite – from Marinoan cap dolostones in South China and West Africa. The barite occurs in dolostones capping Marinoan glacial diamictites, dated at *ca.* 635 Myr old (Condon et al., 2005; Zhou et al., 2010) when the most severe glaciation in Earth history is thought to have abruptly ended (Hoffman et al., 1998). It was further proposed that the anomalous ^{17}O signal was transferred to sulfate from tropospheric O$_2$ through oxidative weathering, and the highly ^{17}O-depleted atmospheric O$_2$ was most likely the result of an extremely high-pCO$_2$ atmosphere at the immediate aftermath of the Marinoan glaciation (Bao et al., 2008). This is consistent with the hard snowball Earth hypothesis (Hoffman et al., 1998). A closer inspection of Bao et al.'s (2008) data reveals a large variability in the magnitude of the ^{17}O depletion in barite samples from South China, even for those from a single hand specimen. Thus, spatial heterogeneity is suspected and micro-analysis in a clear petrographic context is warranted for the barite.

In addition to South China, barite was also found deposited on the top of the cap dolostones in Taoudéni Basin, northwest Africa (Shields et al., 2007) and Mackenzie Mountains, northwestern Canada (Hoffman and Schrag, 2002; James et al., 2001). The occurrence of barite associated with cap carbonates thus may be a global phenomenon. Shields et al. (2007) advocates a sedimentary exhalative origin for the barite in Taoudéni Basin associated with methane seepage after glaciation. Their model was based on a wide range of δ^{34}S and contemporaneous seawater ^{87}Sr/^{86}Sr ratio for their barite samples. The barite from South China, however, was deposited at the onset of a transgression after the initially deposited cap dolostones had been exposed and disrupted. It was clearly deposited earlier than the calcite bearing methane hydrate signature (Zhou et al., 2010). Therefore, understanding the origins of

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barite in South China's cap dolostones can help to understand if the barite deposition, as well as the proposed sequence of events at the aftermath of Marinoan meltdown (Zhou et al., 2010) is of global significance.

A good model for the origin of barite should be able to 1) explain the heterogeneity of barite's sulfur and triple-oxygen isotope composition, 2) identify the source of sulfate and barium, 3) explain its peculiar position in the sequence of events, and 4) offer clues to local depositional condition as well as global ocean chemistry at the aftermath of Marinoan glaciation. To achieve this objective, we selected two sites in South China, Songlin in Guizhou Province and Baizhu in Hubei Province (Fig. 1), where barite is well exposed in Marinoan cap dolostones. After examining polished slabs and thin-sections of these barite-bearing dolostones, we used a high-resolution sampling approach by which barite can be analyzed with spatial resolution at millimeters for its $\Delta^{17}O$, $\delta^{18}O$, and $\delta^{34}S$. This means that multiple samples can be obtained from individual barite crystal fans within the same barite layer or among different layers. Since $^{87}Sr/^{86}Sr$ ratios and $\delta^{34}S$ have been used to distinguish the various types of the barite deposits (Torres et al., 2003), the $^{87}Sr/^{86}Sr$ ratios of selected barite samples were measured as additional evidence of the barium source and the depositional environment.

2. Sedimentological and petrographic contexts of the ^{17}O-depleted barite

Barite occurs in several horizons throughout the Neoproterozoic Ediacaran System in South China. Blocky, void-filling barite occurs in some of the Doushantuo cap dolostones and basal Dengying Formation dolostones (e.g., at Wuhe in eastern Guizhou Province). Barite nodules are also seen in lower Doushantuo Formation black shales in the Yangtze Gorges area, Hubei Province. We have not found distinct ^{17}O anomalies in these barite deposits. The barites studied in this paper, however, are exclusively sea-floor barite, being associated with Marinoan cap dolostone at the base of the Doushantuo Formation in the Songlin (27°43′ N, 106°39′E) and Baizhu (31°42′ N, 110°56′E) areas (Fig. 1). Note that here we regard barite coatings around blocks of brecciated dolostones as “sea-floor” barite as well (Zhou et al., 2010), which differs from some papers which label the barite coatings or “crusts” as “early diagenetic barite” as is referred in Hoffman (2011). These sea-floor barites, occasionally silicified, occur in two different growth forms, 1) B1: larger, dendritic crystal fans within a dolomite matrix, with the height of individual fans ranging from 2 to 5 cm (Figs. 2A and B, 3C, and 4A); and 2) B2: smaller, denser clusters of crystal fans with the height of individual fans ranging from 0.1 cm to 2 cm (Figs. 2C–F, 3B, and 4B–D). Field observations show that there are many layers of barite growth, e.g. up to 4 layers within 3 cm (Figs. 2F and 3A and B). Optical microscope examination on thin sections often reveals multiple layers within an apparent single layer seen on hand specimen (Fig. 6A and E). In Songlin, the 2–3 m thick cap dolostones consist mainly of pink dolostone, capping the gray diamictite of the Nantuo Formation. They are overlaid by purple muddy dolostones and black shale of the Doushantuo Formation. Here the well exposed outcrops show B1 barite blading in the dolostone matrix (Fig. 2A and B) and B2 barite coating the surfaces of the disrupted cap dolostones (Fig. 2C–F). In Baizhu, B2 barite occurs ~0.5 m above the B1 barite layer, sandwiching a dolostone with wavy laminated structures (Fig. 3A). The Songlin and Baizhu cap dolostones are believed to deposit in shallow platform environment (Zhu et al., 2003). The barite was deposited at the onset of a regional transgression after the basal dolostones were deposited, exposed, and disrupted (by dissolution), as outlined in Zhou et al. (2010).

3. Analytical methods

We analyzed 160 micro-sampled barite samples from 20 hand specimens collected from several sections in Songlin and Baizhu. Hand specimens were first cut and polished and thin-sections were made accordingly. Different barite crystal fans or layers were identified before being micro-sampled by a dental drill. A 2 M HCl solution was then added to ~100 mg powders to dissolve and remove any

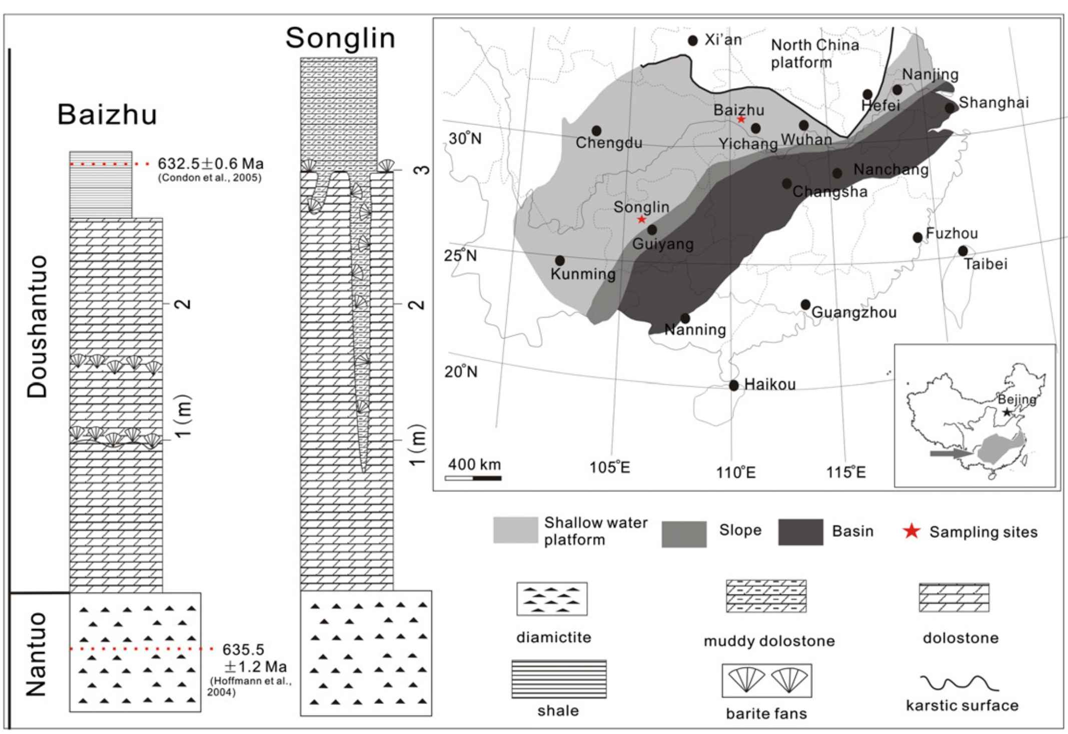

Fig. 1. Simplified stratigraphic column of the cap dolostone unit at Baizhu and Songlin, and paleogeography of the Yangtze Block during late Neoproterozoic to Cambrian times illustrating the location of the Songlin and Baizhu sections (modified after Zhu et al., 2003).