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Methane-derived authigenic carbonate from the lower Doushantuo Formation of South China: Implications for seawater sulfate concentration and global carbon cycle in the early Ediacaran ocean

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ABSTRACT

Authigenic carbonate associated with anaerobic oxidation of methane (AOM), usually *via* microbial sulfate reduction (MSR) or ferric iron reduction, is generally characterized by extremely low $\delta^{13}C$ values (<−30‰, VPDB). This has been used as one of the major diagnostic features for the recognition of hydrocarbon seep carbonate in the geological past. Previous reports on Precambrian authigenic carbonates are rare, limiting our understanding of the effects of their deposition on the Earth's carbon isotopic mass balance. In this study, mainly based on petrographic features and pronounced negative $\delta^{13}C$ values as low as −38.1‰, we discovered authigenic calcite cement immediately above the cap dolostone in the basal Ediacaran Doushantuo Formation in the Jiulongwan section, Yangtze Gorges area, South China. Our observations not only provide direct evidence for the involvement of AOM during carbonate precipitation in the early Ediacaran (~635 Ma), but also suggest that the seawater sulfate concentrations in the early Ediacaran may have been higher than previously thought.

1. Introduction

Authigenic carbonate refers to carbonate minerals (*e.g.*, calcite, aragonite, dolomite, and siderite) that are precipitated inorganically and *in situ* within sedimentary pore waters or at the sediment–water interface (Kastner, 1999; Schrag et al., 2013). Carbonate precipitation commonly retains the C- and S-isotope signatures of the waters from which it precipitates. Whereas carbonate precipitated from well-mixed marine waters typically have $\delta^{13}C$ values near 0‰, authigenic carbonate precipitated from fluid with alkalinity produced from the anaerobic oxidation of methane (AOM) or organic carbon *via* microbial sulfate reduction (MSR) or ferric iron reduction generally have $\delta^{13}C$ values that are strongly low with respect to coeval marine waters (Campbell et al., 2002; Lein, 2004). It is these extremely negative values that are commonly used as a hallmark for the recognition of these carbonate phases (*e.g.*, Jiang et al., 2003; Wang et al., 2008). In the modern ocean, the oxidation of methane and/or organic carbon through MSR typically results in production of alkalinity within sediments and consequent precipitation of authigenic carbonate. This has been discovered in seafloor sediments of all water depths and in different climatic zones (from polar to tropical) (Lein, 2004; Jørgensen and Kasten, 2006). Although authigenic carbonate mineralization could be inhibited by high dissolved O_2 concentration in modern seawater resulting from decreased carbonate saturation during oxic respiration and oxidation of reduced compounds, the reservoir of authigenic carbonate has been proposed to account for at least 10% of global carbonate deposition in modern oceans (Sun and Turchyn, 2014). Phanerozoic authigenic carbonate associated with submarine fluid seepage are characterized by $\delta^{13}C$ values ranging from −76‰ to +24‰, with most values much lower than 0‰ (*cf.* Roberts and Aharon, 1994; Greinert et al., 2001; Campbell et al., 2002; Campbell, 2006). The broad ranges of $\delta^{13}C$ values, both within individual sites and across the deposits of different geological ages (Campbell et al., 2002), indicate that they may have been controlled by multiple processes, including mixing of variable carbon sources (*i.e.*, seawater inorganic carbon, residual CO_2 from methanogenesis, sedimentary organic diagenesis, thermogenic and biogenic methane) (Campbell et al., 2002; Campbell, 2006). Nevertheless, the recognition of ancient methane-derived authigenic carbonate generally relies on their ^{13}C-depleted carbon isotopic signatures (*e.g.*, $\delta^{13}C < -30‰$) that are diagnostic of anaerobic oxidation of methane (Bristow and Grotzinger, 2013).

Time-series variation of carbon isotopes in carbonate carbon and organic carbon has been widely used to trace the evolution of global carbon cycle and infer the oxidation state of the Earth's surface. For instance, a pronounced negative $\delta^{13}C$ excursion as low as −12‰ has been recorded globally in middle Ediacaran strata (Grotzinger et al., 2011) and interpreted as caused by oxidation of large amounts of

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organic matter (Rothman et al., 2003; Fike et al., 2006; McFadden et al., 2008) or methane (Bjerrum and Canfield, 2011). In addition, Schrag et al. (2013) proposed that authigenic carbonate may have played an important role in the carbon cycle of the geological past, especially in the Proterozoic and specific time intervals in the Phanerozoic featured by widespread ocean anoxia. During these intervals, authigenic carbonate precipitation may have been enhanced *via* anaerobic respiration of organic carbon (Higgins et al., 2009). However, geological evidence of authigenic carbonate in the Proterozoic and early Paleozoic is rare.

Compilation of data from ancient seep carbonates in the geological record (Campbell, 2006; Bristow and Grotzinger, 2013) reveals that highly ^{13}C-depleted carbon isotopic signatures are absent in pre-Carboniferous carbonate rocks. The only documented Precambrian example of highly ^{13}C-depleted cement (as low as −48‰, Jiang et al., 2003; Wang et al., 2008) was reported from the post-Marinoan cap dolostone deposits from South China, but was later reinterpreted as representing abiotic thermogenic methane signals overprinted millions of years after deposition (Bristow et al., 2011). Based on a one-dimensional biogeochemical reaction-transport model simulation, Bristow and Grotzinger (2013) proposed that low seawater sulfate and high DIC in the early Paleozoic and Precambrian may account for the absence of strongly ^{13}C-depleted authigenic carbonate older than Mesozoic. However, authigenic calcite cement with low δ^{13}C values (down to −33‰) in the Ediacaran upper Doushantuo Formation at the Yangjiaping section has recently been reported and interpreted to reflect AOM by sulfate reduction (Cui et al., 2016b; Furuyama et al., 2016).

Our present study reveals methane-derived authigenic carbonate immediately above the post-Marinoan cap dolostone in the basal Ediacaran Doushantuo Formation. This new finding not only provides direct evidence for the AOM-driven precipitation of authigenic carbonate in the early Ediacaran, but also implies that the sulfate concentrations in the post-Marinoan ocean may have been higher than previously thought.

2. Geological background

The Ediacaran Period represents a key transitional time interval between the termination of the Neoproterozoic global glaciation and the explosive radiation of metazoans in the early Cambrian (Butterfield, 2007; Narbonne et al., 2012). In the past few decades, the Ediacaran Doushantuo Formation in South China, especially in the Yangtze Gorges area (Fig. 1), has received intensive geological investigations owing to its well-preserved fossils and the potential for investigating the co-evolution of eukaryotes and their living environments during this key transitional period (Zhou et al., 2007; McFadden et al., 2008; Liu et al., 2014; Xiao et al., 2014 and references therein). Age constraints measured from three volcanic ash layers bracketing the entire formation suggest that the Doushantuo Formation was deposited between *ca.* 635 Ma and *ca.* 551 Ma (Condon et al., 2005). However, based on an updated stratigraphic correlation, the age of 551 ± 0.7 Ma previously placed in the uppermost Doushantuo Formation has been re-assigned to the lower Shibantan Member of the overlying Dengying Formation (An et al., 2015). If correct, the Doushantuo Formation may represent deposition during a relatively shorter time interval than previously thought. The Doushantuo Formation in the Yangtze Gorges area was deposited in a shelf lagoon (Jiang et al., 2011) or shelf basin (Zhu et al., 2013) environment, although radical speculation of a non-marine basin has also been proposed (Bristow et al., 2009), and then falsified (Huang et al., 2013).

The Doushantuo Formation in the Yangtze Gorges area has been divided lithologically into four members. Member I is composed of a 3–5 m cap dolostone unit characterized by abundant sheet cracks, tepee-like structures, and barite fans (Jiang et al., 2006; Zhou et al., 2010). Member II is ~80 m thick, and consists of interbedded dolostone and black shale. Member III (~60 m thick) is characterized by medium- to thin-bedded carbonate rocks, and Member IV (~10 m thick) is composed of organic-rich black shale (*cf.* Zhou and Xiao, 2007). Chert nodules occur in members II and III, and yield a microfossil assemblage mainly consisting of abundant and diverse spiny acritarchs (*cf.* Zhang et al., 1998; Zhou et al., 2007; Liu et al., 2014). Diverse macroscopic fossils preserved as carbonaceous compressions have been reported from Member IV black shale (*e.g.*, Xiao et al., 2002).

In the studied Jiulongwan section (Figs. 1, 2), overlying the glaciogenic diamictite of the Cryogenian Nantuo Formation, the Ediacaran Doushantuo Formation has at its base an ~3.3 m thick deposit of cap dolostone (Member I) (Fig. 3a), followed by ~5 m of thin-bedded dolomicrite (Fig. 3b) in the lower part of Member II, which is dominated by medium-bedded dolostone interbedded with black shale up-section. At Jiulongwan, the cap dolostone mainly consists of dolomicrite. The lower part of the cap dolostone is moderately to severely disrupted, with bedding-parallel sheet cracks and centimeter-scale cavities, while the upper part is dominated by laminated dolomicrite. At the top of the cap dolostone, <10-cm-thick silty limestone lenses are present parallel or subparallel to bedding (Wang et al., 2008). The cavities and sheet cracks are generally filled with isopachous dolomites, recrystallized chalcedony, and large blocky calcite cement (Zhou et al., 2010). Carbon isotope analyses indicate that while microcrystalline dolomite matrix yields uniform δ^{13}C values with an average of ~−3‰, the extremely negative δ^{13}C values (from −10‰ to −44‰) were obtained from the calcite cement in sheet cracks and cavities in the lower cap

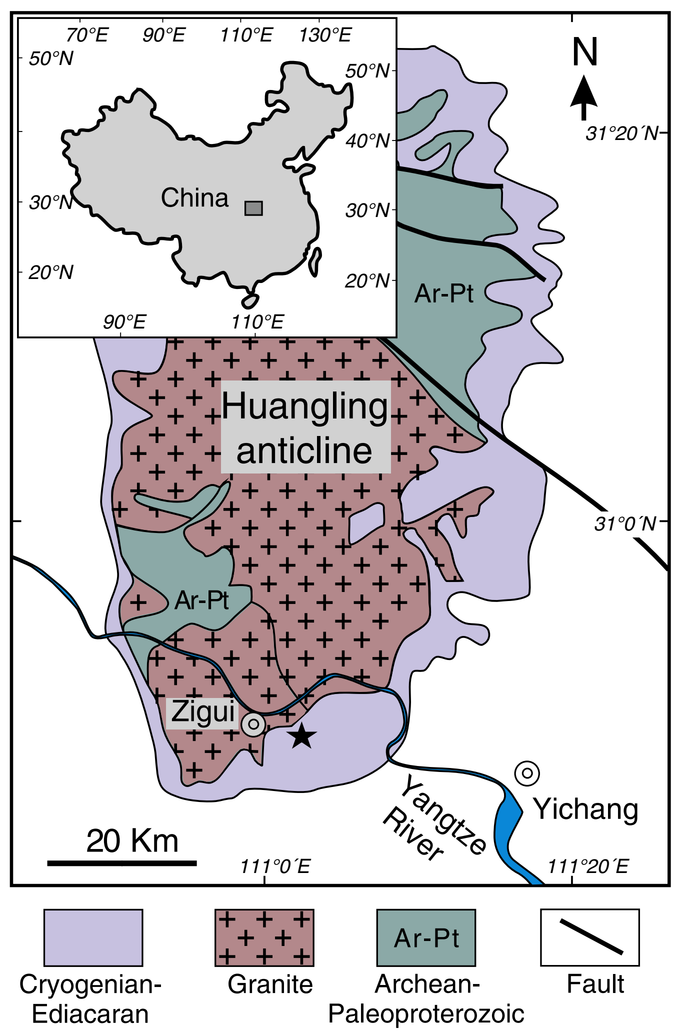

Fig. 1. Geological map showing the location of the studied Jiulongwan section (star) in the Yangtze Gorges area, South China.