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Terminal Proterozoic cyanobacterial blooms and phosphogenesis documented by the Doushantuo granular phosphorites II: Microbial diversity and C isotopes

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ABSTRACT

An unprecedented period of phosphogenesis, along with massive deposition of black shales, major perturbations in the global carbon cycle and the rise of atmospheric oxygen, occurred in the terminal Proterozoic in the aftermath of the Marinoan glaciation. Although causal links between these processes have been postulated, evidence remains challenging. Correlated in situ micro-analyses of granular phosphorites from the Ediacaran Doushantuo Formation in Yichang, South China, suggested that cyanobacteria and associated extracellular polymeric substances (EPS) might have promoted aggregated granule growth and subsequent phosphatization (She et al., 2013). Here, we present new paleontological data for the Doushantuo phosphorites from Yichang, which, combined with Raman microspectroscopy and carbon isotope data, further document links between the biology of cyanobacteria and phosphogenesis. Mapping of microfossils in thin section shows that most phosphatic granules contain microfossils that are dominated by colonies of *Myxococcoides*, along with several filamentous genera generally considered to represent cyanobacterial sheaths. In addition, the phosphorites and associated rocks have $\delta^{13}C_{org}$ values in the range of −26.0 to −29.7‰ VPDB, consistent with photoautotrophic carbon fixation with the Rubisco enzyme. Close association of phosphorites with the Marinoan tillites in stratigraphic level supports a genetic link between deglaciation and phosphogenesis, at least for the Doushantuo occurrence. Our new data suggest that major cyanobacterial blooms probably took place in the terminal Proterozoic, which might have resulted in rapid scavenging of bioavailable phosphorus and massive accumulations of organic matter (OM). Within a redox-stratified intra-shelf basin, the OM-bound phosphorus could have liberated by microbial sulfate reduction and other anaerobic metabolisms and subsequently concentrated by Fe-redox pumping below the chemocline. Upwelling of the bottom waters or upward fluctuation of the chemocline might have brought P-enriched waters to the photic zone, where it was again scavenged by cyanobacteria through their EPS to be subsequently precipitated as francolite. The feedbacks between enhanced continental weathering, cyanobacterial blooms, carbon burial, and accelerated phosphorus cycle thus controlled the marine biogeochemical changes, which led to further oxygenation of the atmosphere and oceans, ultimately paving the way for the rise of metazoans.

1. Introduction

Worldwide phosphogenic events took place in the immediate aftermath of the Neoproterozoic glaciation period, resulting in some of the largest phosphorus deposits in Asia, Australia, Africa and South America (Cook, 1992; Cook and Shergold, 1984). As phosphorus is an essential nutrient and an important driving and regulating force behind biological productivity (Redfield, 1958; Föllmi, 1996), massive deposition of phosphate is generally related to biological accumulation of excess phosphorous. Models have suggested that enhanced post-glacial weathering might have led to blooms of primary producers in the oceans (Kirschvink et al., 2000), which in turn would have promoted phosphogenesis

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(Papineau, 2010). Direct links between biological activity and phosphogenesis have long been proposed (Föllmi, 1996, and references therein). Sulfur isotopes of framboidal pyrite and organic biomarkers from modern phosphorites have documented the importance of bacterial sulfate reduction in the formation of modern phosphatic sediments from the Peruvian and California coast (Arning et al., 2009; Berndmeyer et al., 2012). Other studies have shown that sulfur-oxidizing bacteria can release orthophosphate into pore waters where it accumulates and rapidly precipitated as apatite (e.g., Schulz and Schulz, 2005; Goldhammer et al., 2010; Brock and Schulz-Vogt, 2011). Cyanobacteria have not been specifically targeted in studies of phosphogenesis despite the fact that primary production in today's oceans is provided by a consortium of eukaryotic microalgae and cyanobacteria.

The Doushantuo Formation (ca. 635–551 Ma) in South China is well known because it contains exceptionally well-preserved fossil evidence for putative earliest embryos (Xiao et al., 1998; Chen et al., 2004), which have been variably interpreted as thiomargarita-like sulfur bacteria (Bailey et al., 2007), as algae (Xue et al., 1999) and as encysting protists (Huldtgren et al., 2011). Adult metazoans (Zhu et al., 2008), multicellular algae and acanthomorph acritarchs have also been reported (Xiao, 2004; Xiao et al., 2004, 2014; Yin et al., 2007). Moreover, the Doushantuo Formation preserves a chemostratigraphic record of significant perturbations of the carbon and sulfur cycles that correlate with global tectonic and climate changes and oxygenation of the atmosphere and the oceans (Och and Shields-Zhou, 2012, and references therein). Thus, the Doushantuo Formation presents a unique window for understanding feedbacks between global chemical changes and biological evolution at the dawn of animal life. While the evolution of metazoans has been the focus of most studies, the biogeochemical significance of other organisms, including primary producers, has received less attention. The prior recognition of abundant well preserved in situ microfossils from the Doushantuo phosphorites (Zhongying, 1985; Zhou et al., 2005; She et al., 2013) hints at an intimate relation between primary phosphatization and fossilization of microorganisms. In a recent study, we suggested that cyanobacteria and associated extracellular polymeric substances (EPS) might have promoted accretionary granule growth and provided nucleation sites for rapid crystallization of apatite in the Doushantuo environment (She et al., 2013). Now, we present results of detailed systematic mapping of microfossils in thin section and Raman microspectroscopy and carbon isotope data which suggest that, while other microorganisms such as sulfur bacteria may have played a role in phosphogenesis, cyanobacteria also played important roles in phosphorus cycling and phosphogenesis. This study favors a biological origin for the Doushantuo phosphorites and suggests links between biology, the changing environment, and phosphogenesis at this critical time of Earth history.

2. Sample description

Samples of black shales and phosphorites (designated with prefix "TP", Fig. 1) were collected from and near major phosphorus-bearing horizons in the Doushantuo Formation (member II) in the Taopinghe mining area, north of Yichang City (Fig. 1a and b in She et al., 2013). The phosphorus-bearing sequence overlies basal, cap dolostones. It is characterized by interbedded black potassic shale and phosphorite with gradual increasing dolostones upsection (Fig. 1c in She et al., 2013). The phosphorites are mostly black to brownish banded rocks with granular textures that are visible to the naked eye. When observed with a petrographic microscope, individual granules display distinct oncoid-like zoning. They are composed primarily of cryptocrystalline apatite although minor microcrystalline apatite, quartz and carbonate minerals are present as cement or later replacement (She et al., 2013).

Another cherty dolomicrite sample (YG0914, Fig. 1) was collected from the uppermost of cap carbonate (member I) of the Doushantuo Formation near Liantuo Village (GPS coordinates: 30°51′12.5″N, 111°09′11.5″E), ~20 km NW of Yichang. The sample is mainly composed of dolomicrite and is generally brownish gray to dark gray. Black chert nodules are common in this horizon and are often rimmed by brownish "rusted" dolomicrite. There appears to be some chaotic layering in the dolomite matrix which roughly encompass the chert nodules (Fig. 1) that points to an early diagenetic origin for the chert.

According to previously published data, the age of the studied section is constrained to be between 635 and 614 Ma (Condon et al., 2005; Liu et al., 2009), corresponding to the first 20 Myr of the Ediacaran Period. Paleogeographic reconstructions show that the majority of the Doushantuo Formation in the Yangtze platform (the NW part of the South China Craton) was deposited in a restricted basin on a rimmed carbonate shelf (Jiang et al., 2011). Sedimentological and petrographic data have shown that the Yichang phosphorites and black shales were deposited in relatively low energy, shallow water settings (Zhou et al., 2005; She et al., 2013).

3. Methods

3.1. Petrography and documentation of microfossils

Observation and documentation of polished thin sections were performed with an Olympus BX51 optical microscope equipped with a mechanical stage. Identification of microfossils was based on morphological criteria including shape, size and wall structure. For all examined thin sections, important targets including interesting textures and microfossils were documented with exact locations marked on maps of the thin sections and pictures taken for each at 40×, 100×, 400× and 1000× magnifications. Systematic documentation of microfossils in thin section TP0901S was conducted by scanning along linear vertical (Y axis) transects across the thin section at 400× magnification. Each successive transect was separated by displacing the slide ~200 μm along the X axis of the microscope stage, which provide a complete cover of the examined area. Occurrences of different microfossils were marked on the map by different shapes or colors, with pictures taken for each (1379 photos generated). Size frequency distributions of coccoidal microfossils were obtained by measuring the diameters of 15–20 cells for well-preserved colonies in five thin sections. Immersion oil was used only on one thin section for high resolution imaging after Raman micro-spectroscopy.

3.2. Raman micro-spectroscopy

Confocal laser Raman micro-spectroscopy was performed with a WITec alpha 300R system equipped with a 532 nm laser with output power maintained at ~5 mW. Raman hyperspectral scans were performed under a 100× objective (N.A. = 0.9) with a 50 μm diameter optic fiber and collected on a Peltier-cooled EMCCD detector. Spatial resolution was ~360 nm/pixel and spectral resolution was ~0.1 cm^{-1}. Individual spectra shown in this work represent averages of selected regions with similar spectral characteristics. Detailed descriptions of this method can be found in Bernard et al. (2008). Raman hyperspectral analyses were performed 3–10 μm below the thin section surface, therefore ruling out potential artifacts induced by polishing or surface contamination. Raman spectra of different minerals were compared with spectra from the online database http://rruff.info/.