



Decline in oceanic sulfate levels during the early Mesoproterozoic



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ABSTRACT

Multiple-sulfur isotope compositions (³²S, ³³S, ³⁴S and ³⁶S) were analyzed for paired carbonate-associated sulfate (CAS) and disseminated pyrite (PY) from the ~1.6-Ga Gaoyuzhuang Formation of the North China Craton to reconstruct the history of sulfate levels in Proterozoic oceans. The 200-m-thick study interval yielded relatively constant values for $\delta^{34}\text{S}_{\text{CAS}}$ ($13.0 \pm 1.8\%$), $\delta^{34}\text{S}_{\text{PY}}$ ($8.0 \pm 2.3\%$), and $\Delta^{34}\text{S}_{\text{CAS-PY}}$ ($\sim 5\%$), as well as relatively constant $\Delta^{33}\text{S}$ ($0 \pm 0.05\%$) and $\Delta^{36}\text{S}$ ($0.35 \pm 0.15\%$) for both CAS and pyrite. Limited variation in $\delta^{34}\text{S}_{\text{PY}}$ and slightly lower $\Delta^{33}\text{S}$ of pyrite relative to CAS suggest water-column precipitation of pyrite. Limited fractionation of sulfur during microbial sulfate reduction (as documented by $\Delta^{34}\text{S}_{\text{CAS-PY}}$) implies low seawater sulfate concentrations in the early Mesoproterozoic ocean. We quantitatively constrained paleo-seawater $[\text{SO}_4^{2-}]$ using a novel modeling approach based on measured values of $\Delta^{34}\text{S}_{\text{CAS-PY}}$ and $\partial\delta^{34}\text{S}_{\text{CAS}}/\partial t(\text{max})$. For the study unit, $\Delta^{34}\text{S}_{\text{CAS-PY}}$ is $5.4 \pm 1.4\%$ ($n = 17$), and $\partial\delta^{34}\text{S}_{\text{CAS}}/\partial t(\text{max})$ is $6.8\text{--}34\%$ Myr^{-1} based on sedimentation rates of $30\text{--}150\text{ m Myr}^{-1}$. These data indicate early Mesoproterozoic seawater $[\text{SO}_4^{2-}]$ of ~ 0.1 to 0.35 mM (with a maximum possible concentration of 1.8 mM), a range that is lower and more tightly constrained than earlier estimates for the Mesoproterozoic. Compilation of published data suggests that low seawater sulfate concentrations began about $\sim 1.7\text{ Ga}$ and persisted until at least the mid-Mesoproterozoic ($\sim 1.4\text{ Ga}$), documenting a distinct early Mesoproterozoic perturbation in ocean chemistry that may have been related to a decline in atmospheric $p\text{O}_2$ after Great Oxidation Event I.

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1. Introduction

Atmospheric oxygen concentrations ($p\text{O}_2$) were very low ($<10^{-5}$ of present atmospheric level, or PAL) during the Archean, as indicated by distinct mass independent fractionation (MIF) of sulfur isotopes (Farquhar et al., 2000; Pavlov and Kasting, 2002). Oxygenation of Earth's surface environments is traditionally inferred to have occurred in two unidirectional steps: Great Oxidation Event (GOE) I during the Paleoproterozoic and GOE II in the late Neoproterozoic (Holland, 2002; Bekker et al., 2004; Fike et al., 2006; Guo et al., 2009). However, recent studies suggest that the Earth's oxygenation history was more complex than previously thought (e.g.,

Kah et al., 1999, 2001; Frei et al., 2009; Kump et al., 2011; Planavsky et al., 2012; Crowe et al., 2013; Scott et al., 2014; reviewed in Lyons et al., 2014), and that $p\text{O}_2$ may have declined significantly and lasted for a prolonged interval ($>1\text{ Gyr}$) after GOE I (Bekker and Holland, 2012; Lyons et al., 2014; Planavsky et al., 2014).

Oceanic sulfate plays a key role in the biogeochemical cycles of S, C, O, and Fe (Planavsky et al., 2012; Shen et al., 2002), e.g., via the role of microbial sulfate reduction (MSR) in remineralization of organic matter and oxidation of the sedimentary methane flux (Jørgensen, 1982; Valentine, 2002). Oceanic sulfate concentrations are also an important proxy for seawater chemistry and the oxygenation history of the Precambrian atmosphere and oceans (Canfield, 2004; Kah et al., 2004; Kah and Bartley, 2011; Scott et al., 2014). The Archean ocean is thought to have had very low sulfate concentrations due to extremely low $p\text{O}_2$, possibly $<0.2\text{ mM}$, as inferred from limited sulfur isotopic fractionation ($<10\%$) between sulfates and sulfides (Habicht et al., 2002). On the basis of deposition of sulfate evaporite minerals on carbonate platforms, oceanic

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sulfate is thought to have increased significantly (to >2.5 mM) during the ~2.2–2.1-Ga Lomagundi–Jatuli event (LJE) of the Paleoproterozoic (Schröder et al., 2008; Reuschel et al., 2012; Planavsky et al., 2012). The subsequent history of oceanic sulfate is poorly documented, although recent studies have suggested a decline after the LJE (Planavsky et al., 2012; Scott et al., 2014) followed by a gradual rise to ~0.5–2.4 mM during the late Paleoproterozoic (Shen et al., 2002) and ~1.5–4.5 mM during the Mesoproterozoic (Kah et al., 2004; Gellatly and Lyons, 2005; Chu et al., 2007; Canfield et al., 2010). A detailed reconstruction of secular variation in oceanic sulfate concentrations would have the potential to provide valuable constraints on the oxygenation history of the Precambrian atmosphere and oceans.

The magnitude of sulfur isotope fractionation has been used as a proxy for ancient seawater sulfate concentrations, with smaller fractionations associated with lower sulfate levels (Brüchert, 2004; Gomes and Hurtgen, 2013). MSR has been shown to result generally in only limited sulfur isotope fractionation when sulfate levels are low (<1 mM; Cameron, 1982; Harrison and Thode, 1958; Habicht et al., 2002). Paired analyses of sulfate and pyrite sulfur isotopes in geologic archives may be an effective proxy for the magnitude of the sulfur isotope effect, but these have been undertaken in relatively few studies (e.g., Ohmoto et al., 1993; Habicht et al., 2002; Strauss, 2003; Fike et al., 2006). Here, we report the results of new measurements for multiple-sulfur isotope compositions (^{32}S , ^{33}S , ^{34}S , and ^{36}S) of paired carbonate-associated sulfate (CAS) and disseminated pyrite in the early Mesoproterozoic Gaoyuzhuang Formation of the North China Craton (~1.6–1.55 Ga), as well as pyrite sulfur isotope compositions for the ~1.65 Ga Paradise Creek Formation, the ~1.45–1.47 Ga Helena and Newland formations, and the ~1.2 Ga Mescal Limestone (for which CAS sulfur isotope compositions were previously reported by Gellatly and Lyons, 2005). We used these data, combined with previously published sulfate and sulfide sulfur isotope analyses of other late Paleoproterozoic and Mesoproterozoic marine units, to quantitatively model variation in oceanic sulfate concentrations between 2.0 and 1.0 Ga. These constraints on seawater sulfate concentrations provide new insights into the oxygenation history of the contemporaneous atmosphere and oceans.

2. Materials and methods

2.1. Geological background

The Yanshan-Taihangshan Aulacogen is an intracontinental rift basin within the North China Craton (Lu et al., 2008) that was connected with the open ocean during the Proterozoic (Fig. 1) (Qiao and Gao, 2007). It accumulated a ~9-km-thick succession of sediments that has been dated to the late Paleoproterozoic and early Mesoproterozoic (>1.65 to ~1.3 Ga) (reviewed in Luo et al., 2014). This succession includes carbonate and siliciclastic sediments belonging, in ascending order, to the Changcheng Group, Gaoyuzhuang Formation (or Group), Jixian Group, and Qingbaikou Group (Lu et al., 2008). These sedimentary units have experienced only low-grade (prehnite-pumpellyite facies) metamorphism (Chu et al., 2007). The Gaoyuzhuang Formation, the target unit of this study, mainly consists of dolostone and limestone with a thickness of ~1000 m (Guo et al., 2010). Sedimentary structures suggest that this formation was deposited in shallow-marine environments ranging from the supratidal zone to the distal shelf (Guo et al., 2010). The Gaoyuzhuang Formation is subdivided on the basis of lithology into four members, with the third member, the emphasis of this study, consisting mainly of bedded muddy dolomite and laminated limestone. The samples from the third member analyzed in this study were collected from exposures in Pingquan County, Hebei Province

(Fig. 1). Large (~2 kg), unweathered samples were taken from the active quarries for the purpose of geochemical analysis.

For geological background concerning the ~1.65 Ga Paradise Creek Formation (McNamara Group, NW Queensland, Australia), the ~1.45–1.47 Ga Helena and Newland formations (Belt Supergroup, Montana, USA), and the ~1.2 Ga Mescal Limestone (Apache Group, Arizona, USA), see Gellatly and Lyons (2005).

2.2. Methods

2.2.1. CAS extraction

Each sample was cut into smaller pieces in the laboratory. Fresh chips were chosen and washed with deionized water by ultrasonication, after which the chips were crushed to finer than 200 mesh in a stainless puck mill. The procedure for extraction of carbonate-associated sulfate (CAS) followed that of Luo et al. (2010) with minor changes. For each sample, about 200 g of powder was weighed, leached in a 5.25% NaClO solution for 24 h, and then washed three times with deionized water to remove any organic sulfur and reactive sulfide minerals. The leached powder was re-leached in a 10% NaCl solution for another 24 h and then washed three times with deionized water to remove soluble sulfate. The cleaned and rinsed powder was reacted with 6 M HCl in contact with air to dissolve carbonate, and the solution was then passed through a 1 μm filter paper. The sulfate present in the solution was precipitated quantitatively as BaSO₄ by adding 10–20 ml of a saturated BaCl₂ solution to the sample. The mixed solution was heated for about 1 h and set aside for 12 h, and the precipitated barite was collected the following day. This work was completed in the State Key Laboratory of Geological Processes and Mineral Resources (GPMR) at the China University of Geosciences-Wuhan.

2.2.2. Pyrite extraction

For each sample, ~30 g of powder was decarbonated using 6 HCl. The residue was cleaned with deionized water until neutralized and then dried in an oven at 60 °C for 24 h. Pyrite sulfur was extracted using the chromium reduction method of Canfield et al. (1986), which is briefly described here. A chromous chloride (CrCl₂) solution was prepared by reduction of chromic chloride (CrCl₃) using granulated elemental Zn under a N₂ atmosphere. For each sample, about 1–8 g of the acid residue was placed in a reaction vessel that was connected to an Erlenmeyer flask trap containing 40 ml of zinc acetate. The system was then flushed with N₂ for about 20–30 min, after which 30 ml of chromous chloride (CrCl₂), 20 ml of ethanol, and 20 ml of concentrated HCl were injected into the reaction vessel through a plastic syringe. The mixture was allowed to boil in the reaction vessel for 2 h with an N₂ flow through the system adjusted to maintain a constant flow of 2–3 bubbles per second into the Erlenmeyer flask. The evolved H₂S was collected in the Zn-acetate trap as Zn sulfide (ZnS). Lastly, ~10 ml of silver nitrate (AgNO₃) was added to the Erlenmeyer flask in order to precipitate silver sulfide (Ag₂S). Pyrite extractions for the Gaoyuzhuang Formation were completed in the Department of Earth, Atmospheric and Planetary Sciences at the Massachusetts Institute of Technology (MIT), while those for the Paradise Creek Formation, Helena and Newland formations, and Mescal Limestone were completed in the Department of Earth Sciences, University of California at Riverside (UCR).

2.2.3. Sulfur isotope analysis

For sulfur isotope analysis, the CAS previously recovered as barite from the Gaoyuzhuang Formation was reduced to H₂S using the Kiba reagent (Sasaki et al., 1979), and the evolved H₂S was first precipitated as ZnS and later converted to Ag₂S. The multiple-sulfur isotope compositions (^{32}S , ^{33}S , ^{34}S , and ^{36}S) were measured according to the method of Ono et al. (2012), which is briefly described

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