



Pyrite multiple-sulfur isotope evidence for rapid expansion and contraction of the early Paleoproterozoic seawater sulfate reservoir



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ABSTRACT

Earth's oxygenation is often described in terms of two unidirectional steps at the beginning and end of the Proterozoic Eon, separated by a long-lived intermediate redox state. Recent work defines a more complicated path to oxygenation, exemplified by an apparent drop in oxidation state following the early Paleoproterozoic Lomagundi carbon isotope excursion. The timing of this proposed drop in oxidation state is not well constrained, and it is not clear how it relates to redox conditions during the remainder of the Proterozoic. Here we present a study of pyrite multiple-sulfur isotopes, supported by Fe speciation and organic carbon isotopes, from early Paleoproterozoic black shales. We find evidence for the rapid expansion of the seawater sulfate reservoir during the Great Oxidation Event at ca. 2.3 Ga followed by a subsequent contraction in the size of the seawater sulfate reservoir at ca. 2.05 Ga. This scenario is consistent with the emerging view of a rise and fall in surface oxidation state during the early Paleoproterozoic. Comparison of our new data to other records of the seawater sulfate reservoir suggests that the elevated sulfate concentrations that characterize the early Paleoproterozoic did not return until the late Neoproterozoic.

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1. Introduction

The oxygenation of Earth's atmosphere and oceans is a major focus of Precambrian biogeochemistry. Early models for Earth's oxygenation called upon two unidirectional steps at the beginning and end of the Proterozoic eon. It is generally agreed upon that permanent atmospheric oxygenation (a switch to $>10^{-5}$ present atmospheric levels (PAL); Pavlov and Kasting, 2002) occurred between 2.47 and 2.32 Ga (Holland, 2002; Bekker et al., 2004) during the onset of the so-called 'Great Oxidation Event' [GOE]. A second step in surface oxygenation likely occurred in the late Neoproterozoic (Scott et al., 2008; Sahoo et al., 2012). Because this second oxygenation event is roughly coincident with the first appearance of macroscopic metazoans in the rock record, a causal relationship is commonly evoked. Given the likelihood of Neoproterozoic deep-water oxygenation (Canfield, 2005), estimates for atmospheric oxygen in the immediate aftermath of this second oxygenation event are at minimum between 40%–60% PAL (e.g.,

Canfield, 1998; Ozaki and Tajika, 2013). In between these two steps Earth is believed to have experienced a long-lived intermediate state, more oxidized than the Archean (Canfield, 1998; Scott et al., 2008), but insufficiently oxygenated to allow for the evolution of animals (Narbonne, 2005).

Emerging work describes a more complicated picture of oxygenation, particularly in the Paleoproterozoic era, and it is increasingly clear that oxygenation did not occur as a single, unidirectional step (Canfield, 2005; Frei et al., 2009; Bekker and Holland, 2012; Planavsky et al., 2012; Partin et al., 2013). This new scenario raises a number of important questions. First, what was the magnitude and duration of the GOE? Goldblatt et al. (2006) predicted an abrupt transition from oxygen-free to oxygen-rich conditions across the GOE, and Planavsky et al. (2012) provided evidence for sulfate-rich oceans during the GOE and a contraction of the seawater sulfate reservoir (SSR) following the Lomagundi carbon isotope excursion. Conversely, Kump et al. (2011) argued for a progressive oxygenation that culminated before 2.05 Ga. Second, when did the surface oxidation state rebound and to what degree? Canfield (2005) and Frei et al. (2009) argued for a gradual drop in surface oxidation state prior to the return of iron formations at ca. 1.9 Ga but implied that Earth's surface oxidation state soon returned to early Paleoproterozoic levels. Finally, does the emerging picture of

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fluctuating surface oxidation state in the Proterozoic undermine the proposed link between late Neoproterozoic oxygenation and the evolution of animals?

The apparent rise and fall in the Earth's oxidation state during the early Paleoproterozoic is coincident with the GOE and the Lomagundi carbon isotope excursion (LCIE), a massive ($\sim +10\%$) and long-lived (~ 2200 to 2100 Ma) seawater carbon isotope excursion that is captured in sedimentary carbonates from numerous Paleoproterozoic basins distributed worldwide (Schidlowski et al., 1976; Karhu and Holland, 1996; Bekker et al. 2003a, 2003b). The LCIE has been interpreted as reflecting increased organic carbon burial, which could have released $>20\times$ the amount of oxygen in the present atmospheric reservoir (Karhu and Holland, 1996). This pulse of oxygen must have influenced the chemical composition of seawater.

Because there is a direct, although complicated, relationship between the oxidation state of Earth's surface environments and the concentration of sulfate in seawater, our understanding of Earth's progressive oxygenation has often utilized records of the SSR. Three principal approaches have been used to estimate the size of the Precambrian SSR: the preservation of sulfate evaporites minerals in shallow-marine deposits (e.g., Schröder et al., 2008) or their absence from the record when evidence for other evaporite deposits is preserved (Pope and Grotzinger, 2003), variability in the concentration and isotopic composition of carbonate-associated sulfate (e.g., Kah et al., 2004; Gellatly and Lyons, 2005; Planavsky et al., 2012), and the isotopic composition of sedimentary pyrite sulfur (e.g., Canfield, 1998; Canfield et al., 2010). Since the rock record is incomplete, it is important to investigate each of these sulfur cycle proxies both independently and collectively in order to best describe the evolution of the SSR.

In this paper we present a multi-proxy study of early Paleoproterozoic black shales with a focus on the multiple-sulfur isotope (^{32}S , ^{33}S , and ^{34}S) record of pyrite sulfur. In support of our sulfur isotope data we also present Fe speciation and bulk organic carbon isotope data. These new data provide insight into the size of the SSR in the early Paleoproterozoic oceans during and immediately after the GOE and thus contribute to the developing picture of fluctuating surface redox conditions in the early Paleoproterozoic.

2. Geological setting

2.1. 2200–2100 Myr old Sengoma Argillite Formation, Pretoria Series, Lobatse, Botswana

The Sengoma Argillite Formation (SAF) is up to 700 m thick and is divided into two upward-shallowing sequences by mafic volcanics. Each sequence is composed of carbonaceous and pyritic argillite with siltstones, minor chert, carbonate, and fine-grained, hematite-rich quartz sandstone layers. Argillites often have convoluted bedding and sandstone dikes. It was deposited in the open-marine, epicontinental Transvaal basin in deltaic to offshore environments and experienced greenschist facies metamorphism.

To date, there are no direct geochronologic constraints on the SAF. However, carbonate rocks above and below the SAF have ^{13}C -enriched carbon isotope compositions indicating their deposition during the peak of the Lomagundi Event (Schidlowski et al., 1976). In addition to this chemostratigraphic constraint, the SAF has also been correlated with the Silverton Formation of the Pretoria Group in South Africa (Key, 1983; Bekker et al., 2008). The Pretoria Group, including the Silverton Formation, is unconformably overlain by felsic volcanic rocks of the Rooiberg Group and intruded by the Bushveld Complex, both having an age of 2.05–2.06 Ga (Walraven, 1997; Olsson et al., 2010). The maximum age is constrained by the underlying 2.22 Ga Hekpoort volcanics (Cornell et al., 1996) and a

2316 ± 7 Ma Re–Os isochron pyrite age for the Rooihoogte-lower Timeball Hill formations (Hannah et al., 2004), which are stratigraphically below the Hekpoort volcanics. We therefore infer that the Sengoma Argillite Formation was deposited between 2.2 and 2.1 Ga, during the peak of the Lomagundi carbon isotope excursion. Samples were collected from the drill-hole STRAT 2 collared near Lobatse (Key, 1983) and represent the carbonaceous argillites from the upper sequence.

2.2. 2100–2000 Myr old Zaonega Formation, Ludikovian Series, Karelia, Russia

The Zaonega Formation consists of a 1500-m-thick sequence of basaltic tuffs, siltstones, mudstones, and cherts and is divided into two subformations: a lower, carbonate–argillite subformation (LZ) and an upper, volcano-sedimentary subformation (UZ) in which the bulk of organic-rich rocks are hosted (Medvedev et al., 2001). The Zaonega Formation experienced greenschist facies metamorphism (Melezhik et al., 1999). In the Lake Onega area, the LZ rests disconformably on Upper Jatulian Series carbonates (Tulomozero Formation) that carry high ($>+10\%$) ^{13}C -enrichments typical of the ca. 2.2–2.1 Ga Lomagundi carbon isotope excursion (Karhu and Holland, 1996; Melezhik et al., 1999; Master et al., 2010), while carbonates of the LZ show ^{13}C -enrichments up to $+7.9\%$ (Yudovich et al., 1991; Tikhomirova and Makarikhin, 1993), suggesting that deposition of the UZ black shales occurred during the late stages of the Lomagundi Event. A minimum age for the Zaonega Formation is constrained by 1983 ± 6.5 and 1984 ± 8 Ma U–Pb ages of the Koikary-Svyatnavolok and Pudozhgora dolerite sills (Filippov et al., 2007). These sills are considered to be co-magmatic with sills and mafic volcanics of the Suisar Formation, which directly overlies the Zaonega Formation with an erosional contact allowing significant age difference between these units.

The UZ is subdivided into three units. Unit 1 consists of dark-grey to black volcanoclastic sandstone, siltstone, and mudstone having ubiquitous carbonate seams and lenses and disseminated sulfides. The unit contains three shungite-bearing shale horizons (I–III) varying in thickness from 12 to 35 m. Unit 2 is composed of organic-rich shale, siltstone, dolomite and basaltic lava flows and contains six 5- to 20-m-thick shungite-bearing shale horizons (IV–IX). Unit 3 is composed of shungite-bearing siltstone with dolomite layers. Samples analyzed in this study were selected from two drill cores. C-175 (219.8 m deep) was collared in the Tolvuya syncline near the Tetyugino shungite occurrence, approximately 500 m to the northwest of the FARDEEP drill-holes 12A and 12B (Kump et al., 2011) and capture the Vth to IXth shungite-bearing horizons of the UZ Unit 1. C-5190 (842 m deep) was drilled southwest of Padma, capturing the IIIrd and IVth shungite-bearing horizons of UZ Unit 2, with all samples below 86.9 m belonging to the IIIrd horizon (see supplementary materials for additional details).

3. Analytical methods

3.1. Pyrite sulfur isotope analysis

Powdered shale samples were subjected to Cr-reduction, and liberated H_2S was trapped in a solution of 10% (w/w) zinc acetate (Canfield et al., 1986). ZnS was subsequently converted to Ag_2S with the addition of ~ 1 mL of 0.2 M AgNO_3 . Ag_2S was then reacted in a nickel reaction vessel overnight at $\sim 250^\circ\text{C}$ in the presence of excess F_2 . The resulting SF_6 was purified, first cryogenically and then with a gas chromatograph. Purified SF_6 was introduced to a ThermoFinnigan MAT 253 dual-inlet gas-source isotope-ratio mass-spectrometer where sulfur isotope abundances were measured by monitoring the $^{32}\text{SF}_6^+$, $^{33}\text{SF}_6^+$, $^{34}\text{SF}_6^+$, and $^{36}\text{SF}_6^+$ ion beams at mass to charge ratio of $m/z = 127, 128, 129,$ and $131,$

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