



Paleoarchean sulfur cycling: Multiple sulfur isotope constraints from the Barberton Greenstone Belt, South Africa



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ARTICLE INFO

Article history:

Received 25 June 2014

Received in revised form 1 June 2015

Accepted 23 June 2015

Available online 2 July 2015

Keywords:

Paleoarchean

Multiple sulfur isotopes

Barberton Greenstone Belt

ABSTRACT

Mass-dependent and mass-independent sulfur isotope fractionation archived in volcanic and sedimentary rocks from the Barberton Greenstone Belt (3550–3215 Ma), South Africa, provide constraints for sulfur cycling on the early Earth. Four different sample suites were studied: komatiites and tholeiites, barite, massive and disseminated sulfide ores, and non-mineralized black shales.

Variable but generally slightly positive $\delta^{34}\text{S}$ values between -0.7 and $+5.2\%$, negative $\Delta^{33}\text{S}$ values between -0.50 and -0.09% , and a negative correlation between $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ as well as between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ for komatiites and tholeiites from the Komati Formation and from the Weltevreden Formation are outside the expected range of unfractionated juvenile sulfur. Instead, results suggest alteration of oceanic crustal rock sulfur through interactions with fluids that most likely derived their sulfur from seawater.

Barite from the Mapepe Formation displays positive $\delta^{34}\text{S}$ values between $+3.1$ and $+8.1\%$ and negative $\Delta^{33}\text{S}$ values between -0.77 and -0.34% . The mass-independent sulfur isotope fractionation indicates an atmospheric sulfur source, notably photolytic sulfate, whereas the positive $\delta^{34}\text{S}$ values suggest bacterial sulfate reduction of the marine sulfate reservoir.

Non-mineralized black shale samples from the presumed stratigraphic equivalent of the Mapepe Formation show positive $\delta^{34}\text{S}$ values between 0.0 and $+1.3\%$ and positive $\Delta^{33}\text{S}$ values between $+0.59$ and $+2.45\%$. These results are interpreted to result from the reduction of photolytic elemental sulfur, carrying a positive $\Delta^{33}\text{S}$ signature.

Positive $\delta^{34}\text{S}$ values ranging from $+0.7$ to $+3.5\%$ and slightly negative $\Delta^{33}\text{S}$ values between -0.17 and -0.12% characterize massive and disseminated sulfides from the Bien Venue Prospect. Results suggest unfractionated juvenile magmatic sulfur source as the primary sulfur source, but a contribution from recycled seawater sulfate, which would be indicative of submarine hydrothermal activity, cannot be ruled out.

Massive and disseminated sulfides from the M'hlati prospect are distinctly different from massive and disseminated sulfide from the Bien Venue Prospect. They show negative $\delta^{34}\text{S}$ values between -1.2 and -0.1% and positive $\Delta^{33}\text{S}$ values between $+2.66$ and $+3.17\%$, thus, displaying a sizeable mass-independent

Abbreviations: GOE, Great oxidation event; BGB, Barberton Greenstone Belt.

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<http://dx.doi.org/10.1016/j.precamres.2015.06.008>

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sulfur isotopic fractionation. Again, these samples clearly exhibit the incorporation of an atmospheric MIF-S signal. The source of sulfur for these samples has positive $\Delta^{33}\text{S}$ values, suggesting a connection with photolytic elemental sulfur.

In conclusion, the sulfur isotope signatures in Paleoproterozoic rocks from the Barberton Greenstone Belt are diverse and indicate the incorporation of different sources of sulfur. For komatiites and tholeiites, barite and massive and possibly also disseminated sulfides from Bien Venue, multiple sulfur isotopes are related to ambient seawater sulfate and its photolytic origin, while massive and disseminated sulfides from M'hlati and non-mineralized black shales are related to a second (photolytic elemental sulfur) end member.

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1. Introduction

The Archean Earth was considerably different from today: it was characterized by a predominance of oceanic over continental crust (Rollinson, 2007); the oceans were anoxic and characterized by ferruginous conditions (Holland, 2002; Canfield, 2004), possibly punctuated by occasional sulfidic intervals in the Neoproterozoic (Anbar et al., 2007; Garvin et al., 2009; Reinhard et al., 2009); the early atmosphere was reducing with abundant carbon dioxide and methane but essentially devoid of free atmospheric oxygen (Holland, 2006; but see Ohmoto et al., 2014 for a different view); life was entirely microbial in nature and is believed to have exclusively inhabited the marine realm (Holland and Turekian, 2004 and references therein).

The low atmospheric oxygen concentration is thought to have prevailed until early Paleoproterozoic time when the first significant rise in atmospheric oxygen abundance occurred around 2.4–2.3 Ga ago (Pufahl and Hiatt, 2012). This point in time is commonly referred to as the Great Oxidation Event (GOE), and it is thought to reflect a singular increase in atmospheric oxygen concentration above a level of 10^{-5} PAL (present atmospheric level; cf. Pavlov and Kasting, 2002). Contrasting studies, however, report the enrichment of redox sensitive metals as well as redox-related changes in their stable isotopic composition (such as Mo or Cr; e.g., Anbar et al., 2007; Frei et al., 2009; Crowe et al., 2013) suggesting an early onset of oxidative continental weathering, notably the presence of atmospheric oxygen some 50–100 or probably as early as 600 million years prior to the GOE.

Our present understanding about the anoxic nature of the Archean and early Paleoproterozoic atmosphere is generally based on the multiple sulfur isotope record. The discovery of mass-independently fractionated sulfur isotopes (MIF-S) by Farquhar et al. (2000; and subsequent reports, recently reviewed, e.g., by Johnston, 2011), expressed as distinctly positive and negative $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ signatures ($>\pm 0.3\%$) and preserved in terrestrial rocks of Archean and early Proterozoic rocks older than 2.4 Ga, has become key evidence in our quest for reconstructing the temporal evolution of atmospheric oxygen.

This study investigates the multiple sulfur isotopic composition of different rock types that were derived from the 3.2 to 3.5 Ga old Barberton Greenstone Belt of South Africa and samples should collectively provide an understanding of Paleoproterozoic sulfur cycling. Specifically, we studied four different lithologies: (1) komatiites and tholeiites were selected as a potential archive of isotopically unfractionated juvenile sulfur pool (“mantle sulfur”); (2) barite is assumed to reflect the sulfur isotopic composition of ambient oceanic sulfate; (3) carbonaceous black shales without obvious signs of sulfide mineralization could reveal a biological signal; and (4) mineralized sulfidic black shales could have archived a hydrothermal signal. The prime scientific objective is to identify the principle sulfur sources and to characterize pertinent processes of inorganic and/or microbial sulfur cycling during Archean times.

2. Multiple sulfur isotope systematics and applications to the early Archean sulfur cycle

Multiple stable sulfur isotopes (^{32}S , ^{33}S , ^{34}S , ^{36}S) provide an unprecedented opportunity for identifying different sulfur sources and for reconstructing diverse (bio)geochemical processes that all characterize the pre-2.4 Ga sulfur cycle. Archived in sedimentary sulfide and sulfate minerals that formed in ancient Earth surface environments, mass-dependent and mass-independent sulfur isotopic fractionations may be utilized to deduce terrestrial as well as atmospheric processes. Conclusions based solely on the $\delta^{34}\text{S}$ record include (i) an unfractionated sulfur isotope signature in magmatic rocks (Clark and Fritz, 1997; Ono et al., 2003; Seal, 2006), (ii) slightly positive $\delta^{34}\text{S}$ values in hydrothermal precipitates reflecting a mixture between an unfractionated juvenile sulfur source and a contribution from recycled seawater sulfate (e.g., Peters et al., 2010), (iii) variable, yet generally positive $\delta^{34}\text{S}$ values in seawater precipitates, i.e. evaporitic sulfates and carbonate-associated sulfate (e.g., Kampschulte and Strauss, 2004), and (iv) highly variable, yet frequently negative $\delta^{34}\text{S}$ values in sedimentary sulfides attributed to biological sulfur cycling, notably bacterial sulfate reduction (e.g., Strauss, 1997; Canfield, 2001). Considering respective observations and underlying systematics of sulfur isotopic fractionation (reviewed, e.g., in Canfield and Raiswell, 1999; Johnston, 2011), the sedimentary records of Archean $\delta^{34}\text{S}_{\text{sulfate}}$ and $\delta^{34}\text{S}_{\text{sulfide}}$ have been regarded as generally reflecting (i) a low-sulfate ocean (Habicht et al., 2002; Crowe et al., 2014), whereas (ii) controversial views exist with respect to an early activity of biological sulfur cycling. Notably, the absence of consistently sizeable fractionations in ^{34}S has been regarded as evidence for a limited importance of biological sulfur cycling in Archean sedimentary surface environments (e.g., Strauss et al., 2003), despite individual reports of highly ^{34}S -depleted pyrite in Paleoproterozoic sedimentary rocks (e.g., Ohmoto et al., 1993; Shen et al., 2001, 2009; Philippot et al., 2007; Wu and Farquhar, 2013) and the notion from molecular biology that bacterial sulfate reduction represents an ancient metabolic pathway (Shen and Buick, 2004; Blumenberg et al., 2006; Philippot et al., 2007; Ueno et al., 2008; Shen et al., 2009; Johnston, 2011). Several recent reports of highly ^{34}S -depleted pyrite occurrences of early Archean age (e.g., Philippot et al., 2007; Ueno et al., 2008; Shen et al., 2009; Wacey et al., 2011a,b; Roerdink et al., 2013) strengthen the case for early biological sulfur cycling, even utilizing diverse metabolic pathways such as bacterial sulfate reduction, elemental sulfur reduction, elemental sulfur disproportionation, and sulfide oxidation.

The recognition that mass-independently fractionated sulfide and sulfate sulfur (MIF-S, i.e., non-zero $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values) were present in a large number of Archean and early Proterozoic (>2.4 Ga) sedimentary rocks (e.g., Farquhar et al., 2000) provided an additional dimension in understanding sulfur isotope geochemistry.

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