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# Multiple sulfur isotopes in Paleoarchean barites identify an important role for microbial sulfate reduction in the early marine environment

Desiree L. Roerdink [a,*], Paul R.D. Mason [a], James Farquhar [b], Thomas Reimer [c]

[a] Department of Earth Sciences, Utrecht University, Budapestlaan 4, 3584 CD Utrecht, The Netherlands
[b] Department of Geology and ESSIC, University of Maryland, College Park, MD 20742, USA
[c] Bernard-May-Str 43, Wiesbaden, 65203, Germany

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ABSTRACT

Bedded barites from the Barberton greenstone belt (South Africa and Swaziland) preserve a comprehensive record of atmospheric, oceanic and microbial processes involved in the formation and evolution of the Paleoarchean (3.6–3.2 Ga) oceanic sulfate reservoir. Here, we report multiple sulfur isotopic compositions from four of these barite occurrences. Relatively constant mass-independent signatures ($\Delta^{36}S/\Delta^{33}S = -1.0 \pm 0.2$) within deposits support an important role for atmospheric photolysis in the production of oxidized sulfur, whereas $^{34}S$ enrichments relative to the inferred composition of photolytic sulfate suggest drawdown of $^{34}S$ by microbial sulfate reduction. Strong compositional overlap with barites from India and Western Australia indicates the presence of a large-scale and well-mixed marine sulfate pool. Covariation between $\delta^{34}S$ and $\Delta^{33}S$ within individual deposits also suggests a role for processes occurring in semi-closed basins fed by this global reservoir. Based on modeling results, we interpret variations in $\delta^{34}S$ by local microbial sulfate reduction and correlations with $\Delta^{33}S$ by weak inputs of sulfur from magmatic sources, microbial sulfide oxidation or sulfur disproportionation. This agrees with the early occurrence of sulfate reducers in the geological record as inferred from published microscopic pyrite data, and identifies their role as important in both global oceans and local basins in the Paleoarchean.


## 1. Introduction

Multiple sulfur isotopes[1] in sulfide–sulfate mineral pairs from Paleoarchean (3.6–3.2 Ga) greenstone belts preserve evidence for an early sulfur cycle with important roles for atmospheric and microbial processes. Mass-independent isotopic signatures (MIF) found in sedimentary pyrite and barite have been interpreted to reflect photolysis of volcanic $SO_2$ in a low-oxygen atmosphere (Farquhar et al., 2000; Pavlov and Kasting, 2002), suggesting atmospheric deposition of photochemical reaction products sulfate and elemental sulfur. Alternative origins of anomalous isotope fractionation include chemisorption reactions (Lasaga et al., 2008) or thermochemical sulfate reduction with amino acids (Watanabe et al., 2009), but it remains controversial whether these processes were relevant for sulfur-MIF in the Archean rock record (Farquhar et al., 2010; Golding et al., 2011). Moreover, isotopic and textural evidence from sulfides in the Dresser Formation (Western Australia) suggests that different microbial communities existed by 3.5 Ga. At least three types of sulfur metabolic pathways were probably present in the Paleoarchean: dissimilatory sulfate reduction (Shen et al., 2001, 2009; Ueno et al., 2008; Wacey et al., 2010, 2011a), elemental sulfur disproportionation (Philippot et al., 2007; Wacey et al., 2010, 2011a) and chemotrophic and/or phototrophic sulfide oxidation (Wacey et al., 2011b), but preservation of mass-independent signatures suggests limited biological sulfur cycling as this would homogenize and remove MIF-signals.

It remains unclear how these microbial processes were linked to sulfur cycling in the atmosphere and oceans. Disentangling the importance of biological and abiotic aspects of the early sulfur cycle requires information about the compositions of dominant sulfur sources, including multiple sulfur isotopic compositions of photolytic sulfate and elemental sulfur, which are currently poorly constrained because results from atmospheric models (Lyons, 2007, 2009) and experiments (Danielache et al., 2008; Farquhar et al., 2001; Masterson et al., 2011) do not match values found in the rock record. Information is also required about microbial and chemical pathways by which sulfur was transformed, and about the amount of material transferred between different pools in the Paleoarchean sulfur cycle.

Here, we describe the sulfur isotopic record of atmospheric, oceanic and biological processes involved in the formation and evolution of the Paleoarchean marine sulfate reservoir preserved by 3.55–3.23 Ga sedimentary barites from the Barberton greenstone belt in South Africa and Swaziland. Barite occurrences in this area cover the entire time span from which sulfate deposits are known in the

* Corresponding author. Tel.: +31 302535067; fax: +31 302535302.
*E-mail address:* d.l.roerdink@uu.nl (D.L. Roerdink).

[1] $\delta^{34}S = 1000[((^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{V\text{-}CDT}) - 1]$, $\Delta^{33}S = \delta^{33}S - 1000[(1+\delta^{34}S/1000)^{0.515} - 1]$, and $\Delta^{36}S = \delta^{36}S - 1000[(1+\delta^{34}S/1000)^{1.90} - 1]$.

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Paleoarchean (Huston and Logan, 2004) and provide a comprehensive record of the earliest sulfate pools. Data presented in this paper allow us to compare and contrast basin-scale patterns observed within individual deposits, with those observed between units from southern Africa and previously analyzed barites in Western Australia (Farquhar et al., 2000; Shen et al., 2009; Ueno et al., 2008) and India (Hoering, 1989), which might reflect larger-scale or global processes. We explore local sources and sinks of sulfate and their relative importance using a semi-closed reservoir model, and propose that microbial sulfate reduction was important on both a global and basin scale.

## 2. Barite samples

Samples were collected from four barite deposits in the Barberton greenstone belt of South Africa and Swaziland (Fig. 1), as described below.

### 2.1. Londozi

The Londozi deposit is located in the southeastern part of the Barberton greenstone belt close to the South African–Swaziland border (26°11′20″S, 31°0′28″E). It occurs just east of the 3.51–3.50 Ga Steynsdorp pluton, a TTG gneiss dome which has intruded into the strongly deformed and metamorphosed supracrustal rocks of the Theespruit Formation in the lower Onverwacht Group (Kröner et al., 1996). Characteristic lithologies at the base of the succession include variably silicified, finely laminated volcanics and pillow lavas of (ultra)mafic composition, metamorphosed to actinolite–epidote–chlorite schists during amphibolite facies metamorphism (Barton, 1982; Kröner et al., 1996). Above the barite horizon, more felsic volcaniclastics are present together with quartz-muscovite gneisses. Barite occurs in lenses of variable thickness (0.5–10 m) in a zone that can be traced continuously for at least 1.25 km along strike. Its presence is associated with strongly silicified host rocks, and finely crystalline barite is often interbedded with thin layers of brown and green chert (1–5 cm) with some slivers of mafic host rock. Sulfides associated with the deposit include disseminated and layered pyrite, sphalerite and to a lesser extent chalcopyrite and galena (Reimer, 1980). Samples were collected from barite outcrops (08-LON-01) and old quarry waste dumps (08-LON-02).

The abundance of (ultra)mafic and finely laminated volcanics, pillow lavas as well as the absence of andesitic rocks (Kröner et al., 1996) indicates barite deposition in a relatively low-energy marine setting, similar to a modern oceanic plateau or plume-related oceanic island (Kröner et al., 1996), or a back-arc basin in an active convergent margin (Armstrong et al., 1990; de Ronde and de Wit, 1994; Dziggel et al., 2006). Intense silicification of host rocks suggests strong hydrothermal activity and a sedimentary-exhalative origin of the barite (Barton, 1982; Reimer, 1980, 1990).

Intense deformation produced strong foliation and lineation in the surrounding amphibolites, but lithologies can be traced linearly for at least 10 km along the N–S strike (Barton, 1982). Therefore, an age for the barite can be derived from felsic volcanics 3 km north of the deposit, dated at 3547 ± 2 Ma by Kröner et al. (1996). Although it is unclear whether these rocks are syn-volcanic and part of the Theespruit Formation (Kröner et al., 1996), or older and representing a section of tectonically emplaced crust (Armstrong et al., 1990; de Ronde and de Wit, 1994; Dziggel et al., 2006), this does not affect our age estimate because the felsic volcanics occur in the same tectonic unit as the barite horizon. An age of 3.55 Ga for the Londozi barite implies that this is the oldest sulfate deposit currently identified in the geological record.

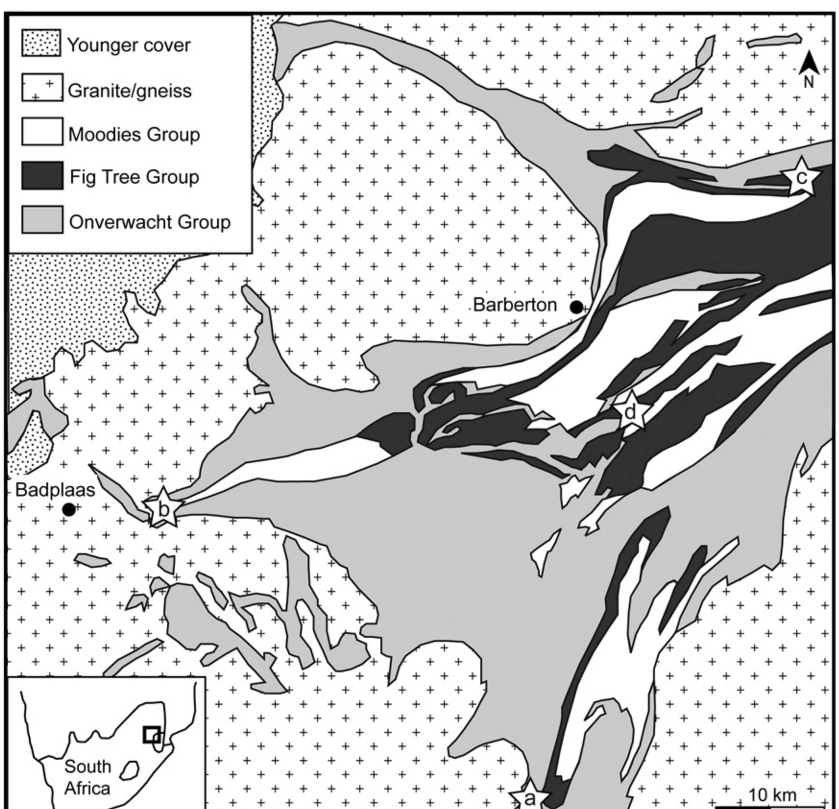


**Fig. 1.** Locations of barite deposits in the Barberton greenstone belt. Simplified geological map of the Barberton greenstone belt modified from Hofmann (2005). Barite deposits indicated: (a) Londozi barite, 3.55 Ga Theespruit Formation, lower Onverwacht Group; (b) Vergelegen barite, ca. 3.41 Ga Kromberg Formation, upper Onverwacht Group; (c) Stentor barite, 3.26 Ga Bien Venue Formation, Fig Tree Group; and (d) Barite Valley, 3.26–3.23 Ga Mapepe Formation, Fig Tree Group.