



Reworking of atmospheric sulfur in a Paleoarchean hydrothermal system at Londozi, Barberton Greenstone Belt, Swaziland



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ABSTRACT

Anomalous fractionation of the minor isotopes of sulfur ($\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$) in Archean pyrite is thought to reflect photochemical reactions in an anoxic atmosphere, with most samples falling along a reference array with $\Delta^{36}\text{S}/\Delta^{33}\text{S} \approx -1$. Small deviations from this array record microbial sulfate reduction or changes in atmospheric source reactions. Here, we argue that reworking of atmospheric sulfur with distinct minor sulfur isotope ratios ($\Delta^{36}\text{S}/\Delta^{33}\text{S} \neq -1$) produced additional variability in sulfide $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ -values in a 3.52 Ga hydrothermal barite deposit at Londozi, Barberton Greenstone Belt, Swaziland. *In situ* measurement of the four stable sulfur isotopes in pyrite revealed $\Delta^{36}\text{S}$ – $\Delta^{33}\text{S}$ relationships and a $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ trend (-3.2 ± 0.4), which is significantly different from the co-variation between $\Delta^{36}\text{S}$ and $\Delta^{33}\text{S}$ in the co-existing barite that reflects ambient Paleoarchean seawater sulfate. This argues against biological or thermochemical sulfate reduction at the time of barite deposition, and requires incorporation of sulfide generated in a chemically distinct atmosphere before 3.52 Ga. We propose a model that combines reworking of this sulfur by hydrothermal leaching, deep mixing with juvenile sulfur and surface mixing with biogenic sulfide to explain the observed variation in $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$. These interactions between abiotic and biological processes in the Londozi hydrothermal system complicate the interpretation of biosignatures based on deviations in $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ from the Archean reference array.

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1. Introduction

Sulfur cycling in seafloor hydrothermal systems involves high-temperature abiotic sulfate reduction by ferrous iron minerals, leaching of sulfur from volcanic host rocks and direct degassing of magmatic SO_2 , as well as microbial sulfate reduction and sulfide oxidation in lower temperature venting areas (Ohmoto and Goldhaber, 1997; Shanks, 2001). The relative importance of these processes can be evaluated from multiple sulfur isotopic compositions ($\delta^{33}\text{S}$, $\delta^{34}\text{S}$, $\delta^{36}\text{S}$) of hydrothermal sulfide and sulfate minerals. Experimental and modeling work has shown that biological transformations, isotope mixing and equilibrium reactions follow slightly different mass-dependent fractionation laws that result in small but measurable variations in $\Delta^{33}\text{S}$ ($\delta^{33}\text{S} - 1000 \times ((1 + \delta^{34}\text{S}/1000)^{0.515} - 1)$) and $\Delta^{36}\text{S}$ ($\delta^{36}\text{S} - 1000 \times ((1 + \delta^{34}\text{S}/1000)^{1.91} - 1)$), and enable identification of sulfur

sources even when $^{34}\text{S}/^{32}\text{S}$ ratios ($\delta^{34}\text{S}$) are inconclusive (Farquhar et al., 2003; Johnston et al., 2007, 2005; Ono et al., 2006). For example, using this multiple sulfur isotope approach, Ono et al. (2007) showed that leaching of basaltic sulfur dominated over biogenic sources of sulfide at sediment-free mid-ocean ridges.

The same principle can be applied to assess roles of abiotic and biological processes in the formation of sulfide minerals in Archean (3.8–2.5 Ga) hydrothermal environments. However, Archean sulfide sources carry additional variation in $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ due to mass-independent fractionation of sulfur isotopes (S-MIF) during SO_2 photolysis in the anoxic early atmosphere (Farquhar et al., 2000; Pavlov and Kasting, 2002). Many sulfide samples older than ca. 2.45 Ga define a negative correlation between the minor isotope signatures, which is described by $\Delta^{36}\text{S}/\Delta^{33}\text{S} \approx -1$ and is assumed to reflect a common photochemical reaction pathway for nearly two billion years (Farquhar et al., 2000; Johnston, 2011; Kaufman et al., 2007; Thomassot et al., 2015). Small deviations from this array corresponding with large mass-dependent sulfur isotope fractionation ($\delta^{34}\text{S}$) measured in pyrite have been cited as evidence for early microbial activity in hydrothermally-influenced marine

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settings (Roerdink et al., 2013; Shen et al., 2009; Ueno et al., 2008). Alternatively, larger variations in $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ at specific time intervals in the rock record have been interpreted to reflect temporal changes in atmospheric chemistry (Farquhar et al., 2007), for example due to biogenic methane production (Domagal-Goldman et al., 2008; Zerkle et al., 2012) or changes in volcanic fluxes of reduced and oxidized sulfur species (Halevy et al., 2010). Recent work demonstrated that such shifts may have already occurred in the early Paleoproterozoic (Wacey et al., 2015).

Assuming that contributions of non-seawater-derived sulfide were equally important in the Archean as in modern seafloor hydrothermal systems, these fluctuations in atmospheric conditions raise the question whether reworking of older atmospheric sulfur from host rocks could have generated additional variability in $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ in ancient hydrothermal sulfide minerals. Although the preservation of S-MIF signatures implies that biological or magmatic redox cycling of atmospheric sulfur species must have been limited on the early Earth (Halevy et al., 2010), non-zero $\Delta^{33}\text{S}$ -values were observed in 2.7 Ga komatiite-hosted Fe–Ni sulfide deposits formed by magmatic assimilation of older atmospheric sulfur in volcano-sedimentary rocks (Bekker et al., 2009). In addition, observation of S-MIF in geologically young diamond- and olivine-hosted igneous sulfides suggests that dilution with mantle-derived sulfur does not necessarily erase atmospherically-derived isotope signatures (Cabral et al., 2013; Farquhar et al., 2002). As such, reworking of surface material may have been more important for variations in $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ in Archean volcanic-hydrothermal deposits than previously considered, possibly complicating the interpretation of ancient biosignatures due to mixing of multiple atmospheric and microbial minor isotopic arrays. Here, we test this hypothesis using *in situ* quadrupole sulfur isotope analysis of pyrite from the 3.52 Ga Paleoproterozoic Londozi barite deposit in the Theespruit Formation of the Barberton Greenstone Belt, Swaziland. Radiogenic isotope data from metavolcanics in the same formation have been interpreted to reflect involvement of older crustal material in the magma source region (Kröner et al., 2013; Kröner et al., 1996; Van Kranendonk et al., 2009), whereas barite sulfur isotopic compositions suggest local microbial reduction of seawater sulfate (Roerdink et al., 2012). These unique features enable us to assess the roles of reworking versus microbial fractionation in determining S-MIF variability in one of the oldest hydrothermal systems preserved in the rock record.

2. Geological background

2.1. Barite deposit

The Londozi barite deposit occurs within a succession of metavolcanics belonging to the ca. 3.55–3.51 Ga Theespruit Formation (Kröner et al., 2013, 1996) of the Lower Onverwacht Group, on the eastern flank of the Steynsdorp anticline in the southernmost part of the Barberton Greenstone Belt (S26°11.359' E31°00.511', see inset in Fig. 1c). Mining operations in the area demonstrated the presence of a barite-bearing zone that is up to twelve meters thick and can be traced continuously over approximately 1.3 km along strike (Barton, 1982). The barite is finely crystalline and contains microcrystalline pyrite, sphalerite and rare chalcopyrite and galena (Reimer, 1980). The occurrence of the barite within a volcanic sequence and the presence of base metal sulfides has been interpreted to reflect a hydrothermal origin of the deposit (Barton, 1982; Reimer, 1980), which is substantiated by our field and isotopic data. Deformed pillow basalts (Fig. 1a) underlying the barite horizon provide direct evidence for subaqueous volcanic activity and indicate the presence of a magmatic heat source driving fluid convection. In addition, an alteration mineral assem-

blage with celsian, hyalophane, epidote, witherite and armenite that was found in metabasalts immediately below the barite (Fig. 1b) but not in the overlying felsic volcanic rocks suggests that barite precipitated as a primary deposit, since late-stage replacement reactions or precipitation during burial and metamorphism should alter rocks on both sides of the deposit (cf. Van Kranendonk and Pirajno, 2004). Sulfur isotopic compositions of the Londozi barite deposit have been interpreted to reflect a seawater source of the sulfate (Roerdink et al., 2012), consistent with barite formation as a submarine volcanic-hydrothermal deposit.

2.2. Host rocks

Metavolcanics underlying the barite horizon are of mafic to ultramafic composition and occur as pillowed and foliated massive beds, some of which are strongly silicified. Mineral assemblages consist of hornblende, plagioclase, quartz, biotite, ilmenite and garnet and are characteristic for the amphibolite facies metamorphism in the Steynsdorp region that reached temperatures of 640–660 °C at a pressure of 10–13 kbar (Lana et al., 2010). The barite deposit is overlain by strongly foliated mica schists with quartz, K-feldspar, plagioclase and biotite, that have been interpreted to reflect sheared felsic tuffs (Reimer, 1980). The contact between these felsic rocks and the barite is sharp, in contrast to the gradual transition from the metabasalts into altered metabasalts in which small-scale barite infiltrations occur below the main barite horizon. Lens- and sigmoidal-shaped fragments of metabasaltic host rocks and chert are also found within the barite, but intense deformation complicates the interpretation of original petrographic relations.

2.3. Age of the barite deposit

SIMS dating of zircon from felsic schists and metavolcanics in the lowermost part of the Theespruit Formation in the Londozi area yielded ages of 3552 ± 1 Ma (6 grains) and 3530 ± 4 Ma (12 grains), respectively (Kröner et al., 2013 and pers. comm.), suggesting an early Paleoproterozoic age for the deposit. To obtain a more specific age for the barite, we performed LA-ICP-MS analyses on prismatic and oscillatory zoned zircon grains from the felsic schists immediately overlying the main barite horizon at 0.5–1.0 m from the contact (see Supplementary Information for details of the sample preparation and analytical method). A total of 27 grains were analyzed, with 24 grains yielding ages at 95–105% concordance (Supporting Dataset S1). The age of the felsic tuffaceous schist was determined using the ISOPLOT TuffZirc algorithm (Ludwig, 2008), giving a $^{207}\text{Pb}/^{206}\text{Pb}$ deposition age of $3522 +13/-8$ Ma based on 20 concordant grains (Fig. 1c), compared to a concordia age of 3531 ± 19 Ma ($n = 27$, MSWD = 1.7). Interpretation of this result as the age of crystallization is consistent with Th/U ratios ranging from 0.42 to 0.72 (Hoskin and Schaltegger, 2003; Rubatto, 2002; Williams et al., 1996), as well as the oscillatory and lengthwise zoning in euhedral crystals (Supplementary Fig. S1) that is typical for zircon of magmatic origin (Corfu et al., 2003). Therefore, in this paper we adopt an age of 3.52 Ga as the minimum depositional age of the Londozi barite deposit.

3. Material and methods

3.1. Samples

Pyrite-bearing rock fragments were sampled from barite and immediate host rocks collected from surface outcrops of the Londozi deposit. Rock sample TR-03 consists of silicified barite, and the studied fragment of this sample contains 50–500 μm large

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