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Paleoarchean sulfur cycle and biogeochemical surface conditions on the early Earth, Barberton, South Africa

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ABSTRACT

This study presents the first multiple sulfur isotope dataset on sulfides from the ca. 3.5–3.2 Ga Onverwacht Group in the Paleoarchean Barberton Greenstone Belt (BGB) of South Africa. In situ $\delta^{34}S_{CDT}$ and $\Delta^{33}S$ values of pyrite ($n = 568$) are reported from a wide range of hydrothermal, volcanic and sedimentary environments and are used to explore Mid-Archean biogeochemical sulfur cycling. Samples are from fresh drill core collected by the Barberton Scientific Drilling Project that intercepted cherts, metabasalts and sheared ultramafics of the ∼ 3.3–3.35 Ga Kromberg Formation; the sedimentary units of the ∼ 3.432 Ga Noisy *f*ormation; and the unconformably underlying metabasaltic pillow lavas of the ∼ 3.472 Ga Hooggenoeg Formation.

Pyrite in quartz-carbonate-veins in the lower diamictite of the Noisy sequence records the largest range and most negative $\delta^{34}S_{CDT}$ values so far reported from an Archean terrain ($\delta^{34}S_{CDT} = -55.04$ to $+27.46‰$). The Noisy sediments also contain detrital and diagenetic pyrites with a significant variation in $\Delta^{33}S$ of between -0.62 to $+1.4‰$ and $\delta^{34}S_{CDT}$ of between -7.00 and $+12.6‰$, interpreted to reflect tectonic exposure of these early sediments to atmospheric – shallow marine conditions. Early marine pyrites from the Kromberg Cherts also display strong positive $\Delta^{33}S$ values up to $+2.50‰$ with narrow range in $\delta^{34}S_{CDT}$ values (-6.00 to $+1.50‰$), whereas hydrothermal veins in the basal ultramafic shear zones preserve magmatic values (∼ 0‰). This study reveals a potential proto-tectonic control on atmospheric, geodynamic and hydrothermal environments available for early sulfate reducing and/or methanogenic microbes in the Paleoarchean.

No evidence for microbial sulfate reduction or disproportionation was identified in the Kromberg Cherts, despite previous morphological claims for microbial life. Highly variable and negative $\delta^{34}S_{CDT}$ values were found in the Noisy turbidites and Hooggenoeg pillow lava breccia supporting the presence of microbial sulfate reduction in early tectono-sedimentary basins and in the Paleoarchean sub-seafloor, respectively. In light of current controversies surrounding sulfur isotope studies in similar-aged rocks of the Pilbara Craton (West Australia), we argue that microbial elemental sulfur disproportionation was not a preferred metabolic pathway on the Paleoarchean earth.

1. Introduction

Multiple sulfur isotope analyses of sulfides from the early rock record enable us to investigate the nature of atmosphere–hydrosphere and volcanic processes in the Archean and to explore possible biological sulfur cycling (Farquhar et al., 2000, 2007; Farquhar and Wing, 2003; Kamber and Whitehouse, 2007; Ohmoto et al., 2006; Ono et al., 2003; Philippot et al., 2007; Papineau and Mojzsis, 2006; Shen et al., 2009; Ueno et al., 2008; Wacey et al., 2010; Whitehouse et al., 2005). Our understanding of the Archean sulfur cycle has been greatly advanced over the past decade by the application of high-resolution, in situ secondary ion mass spectrometry (SIMS) to study sulfides in petrographic context. Examples of such studies include the 3.8–3.77 Ga, Isua Supracrustal Belt of south–west Greenland (e.g. Papineau and Mojzsis, 2006; Whitehouse et al., 2005) and the black shales of the ca. 2.5–2.6 Ga late Archean Transvaal Supergroup (Kamber and Whitehouse, 2007; Whitehouse, 2013) to investigate early atmosphere–ocean sulfur chemistry. There has been much controversy surrounding sulfur isotope studies from the Pilbara Craton of West Australia proposing evidence for biologically-mediated sulfur cycling in the Mid-Archean focusing on pyrites from hydrothermal barite of the 3470–3490 Ma Dresser Formation at the North Pole locality (Philippot et al., 2007; Shen et al., 2009; Ueno et al., 2008) and conglomerates of the ca. 3430 Ma Strelley Pool Formation (Wacey et al., 2010). In the case of similar aged rocks from the Barberton Greenstone Belt (BGB) of South Africa however, only very sparse sulfur isotope data is available displaying a narrow $\delta^{34}S_{CDT}$ range (-2.9 to $+8.0‰$, mean value

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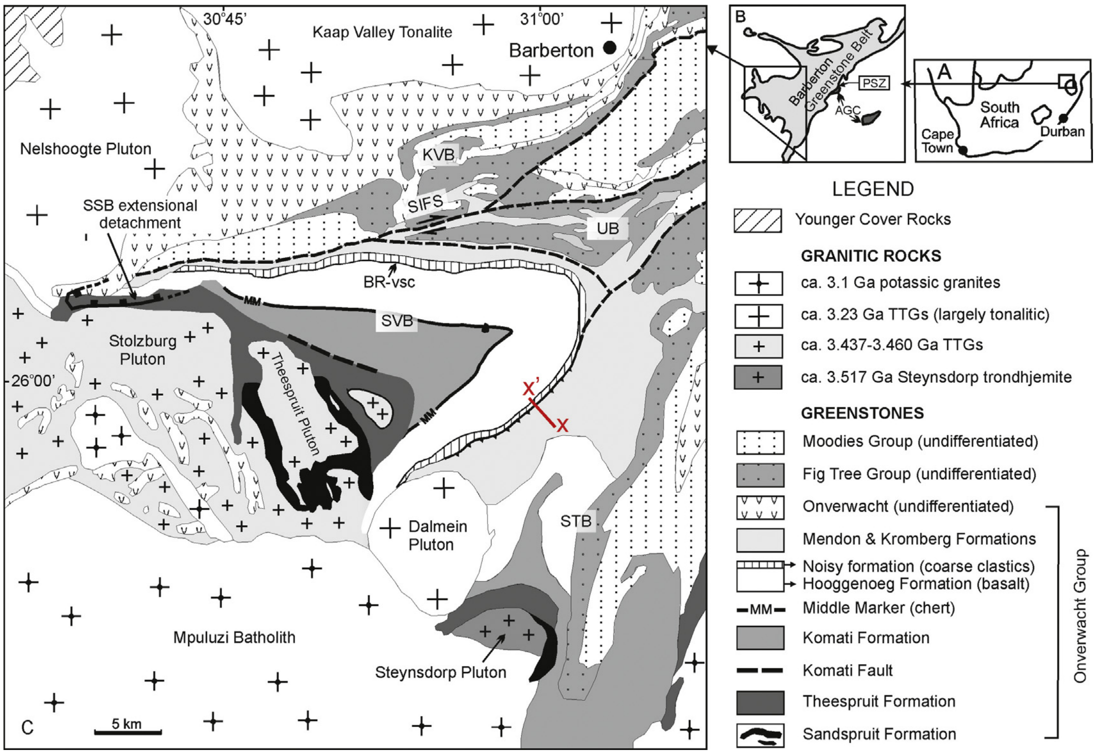

Fig. 1. Regional geology and drill core locations in the Paleoarchean Barberton Greenstone Belt (modified after Anhaeusser, 1984 and Grosch et al., 2009a, 2011). (A)–(C) Location and simplified geological map of the southwestern part of the Paleoarchean Barberton Greenstone Belt, South Africa. AGC = Ancient Gneiss Complex. The profile marked X–X′ in the simplified map in (C) marks drill site area and corresponds to the geological profile shown Fig. 2 and the simplified geological block diagram in Supplementary appendix A.

about +2.0‰) and is limited to the uppermost parts of the Onverwacht Group stratigraphy (e.g. Kakegawa and Ohmoto, 1999; Ohmoto et al., 1993). The Barberton Greenstone Belt is remarkable in that it comprises one of the best preserved sequences of Paleoarchean volcanic, volcaniclastic and sedimentary rocks in the world, with deformation and high-grade metamorphism localized in gneiss terrains and along shear-zones bounding well-protected internal crustal blocks (e.g. de Wit et al., 2011; Furnes et al., 2011; Grosch et al., 2009b; 2012; López-Martinez et al., 1992; Schoene et al., 2008). For example, López-Martinez et al. (1992) provided Ar–Ar geochronologic age constraints on low-temperature greenschist facies metamorphism, that preserved evidence for early 3482 Ma subseafloor hydrothermal alteration in the southwestern part of the BGB. Yet, despite the high degree of preservation in parts of the BGB, there is currently no in situ multiple sulfur isotope data (SIMS) available on sulfides from the oldest parts of this greenstone belt.

This study presents an extensive multiple sulfur isotope (^{32}S, ^{33}S, ^{34}S) dataset from a wide range of samples from various geological settings in the ca. 3472 to 3334 Ma mid-upper Onverwacht Group (Figs. 1 and 2). These include in situ microprobe analyses of fresh, pyrite-bearing drill core samples collected in stratigraphic context and spanning a geological period of ~150 Ma across the Paleoarchean eon (see Figs. 1 and 2, Grosch et al. 2009a, 2009b). The sulfide-bearing samples include detrital, diagenetic and hydrothermal vein pyrite from three major formations of the mid-upper Onverwacht Group in the BGB, including the Hooggenoeg, Noisy and Kromberg Formations (Figs. 1 and 2). The pyrite analyses are used to test for the possible existence of microbial metabolic pathways, such as sulfate reduction and/or elemental sulfur disproportionation in various Paleoarchean environments and also to investigate the possible contribution of early plate tectonic-type processes to the Paleoarchean sulfur cycle. The dataset reported herein greatly expands the available Paleoarchean sulfur isotope dataset, especially on the Kaapvaal Craton and provides a new window for studying atmospheric, crustal, hydrothermal and biogeochemical surface conditions on the early Earth.

2. Geological background

The Barberton Greenstone Belt (BGB) forms part of the easternmost margin of the Kaapvaal Craton as a NE–SW trending tectono-metamorphic belt on the border between South Africa and Swaziland (Fig. 1(A), (B)). The belt is structurally sub-divided into two parts, namely a TTG (tonalite–trondhjemite–granitoid) gneiss terrain and a supracrustal greenstone sequence of mafic–ultramafic and clastic-volcaniclastic rocks (e.g. Brandl et al., 2006; see Fig. 1(C)). Although tectonic activity in the BGB between ca. at 3227–3223 Ma is well characterized (e.g. Lowe and Byerly 1999, 2007; Moyen et al., 2006), the possibility of an earlier tectonic or proto-tectonic event at 3432 Ma has also been proposed (e.g. Grosch et al., 2011). Traditionally, the low-grade supracrustal greenstone sequence is referred to as the Barberton Supergroup and consists of 3 groups (Figs. 1 and 2): the dominantly mafic–ultramafic (ca. 3530–3334 Ma) Onverwacht Group which is the focus of this study; the predominantly argillaceous (ca. 3258–3226 Ma) Fig Tree Group; and the arenaceous (ca. 3230–3110 Ma) Moodies Group (e.g. Brandl et al., 2006; Lowe and Byerly 1999, 2007; Viljoen and Viljoen, 1969a).

This study presents new data on fresh drill core retrieved during the Barberton Scientific Drilling Project (BSDP) that focused on the oldest 3.530–3.334 Onverwacht Group (Figs. 1 and 2) of the BGB (Grosch et al. 2009a, 2009b). A detailed overview of the BSDP drilling project objectives, drill core logs and the regional geological context with regard to the drill site locations are provided in Grosch et al. (2009a, 2009b). Fig. 1 shows the drill site locations in the southwestern region of the BGB with a simplified geological block diagram provided in Supplementary appendix A. A detailed geological section of the study area in the Onverwacht Group is