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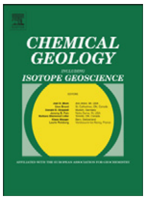

Development of in situ sulfur four-isotope analysis with multiple Faraday cup detectors by SIMS and application to pyrite grains in a Paleoproterozoic glaciogenic sandstone

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ABSTRACT

An in situ sulfur four-isotope analysis technique with multiple Faraday cup detectors by ion microprobe was developed and applied to detrital pyrite grains in ~2.4 Ga glaciogenic sandstone from the Meteorite Bore Member of the Turee Creek Group, Western Australia. Data are standardized with the UWPy-1 pyrite standard ($\delta^{34}S = 16.04 \pm 0.18‰$, $\Delta^{33}S = -0.003 \pm 0.009‰$, and $\Delta^{36}S = -0.21 \pm 0.24‰$, 2 SD) whose sulfur four isotopes were newly determined by gas-source mass spectrometry. Typical reproducibility at two standard deviations (2 SD) of spot-to-spot analyses of standard UWPy-1 pyrite with a primary beam size of ~20 μm were ±0.23, ±0.05, and ±0.86‰ for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$, respectively. The measured $^{36}S/^{32}S$ ratio [1 / (6641 ± 27)] is approximately 19‰ lower than the published ratio for VCDT, and we propose a revision of the ^{36}S abundance in VCDT.

Pyrite grains in ~2.4 Ga glaciogenic sandstone have wide ranging sulfur isotope ratios (−32.7 to 13.5 for $\delta^{34}S$, −3.03 to 11.66 for $\Delta^{33}S$, and −9.7 to 4.6 for $\Delta^{36}S$, respectively). Some pyrite grains are zoned in $\delta^{34}S$ values within a grain. Sulfur isotope ratios of most pyrite grains are distributed along a line with slope = −0.9 for $\Delta^{33}S$ vs. $\Delta^{36}S$, suggesting that pyrite grains mostly derived from a limited range of source rocks and near-surface sulfur reservoirs. One pyrite aggregate has a distinct texture from other pyrite grains in the same sandstone, and yields a significant mass-independent deficit in ^{36}S with a small excess in ^{33}S ($\Delta^{36}S/\Delta^{33}S \sim -4‰$). This is used to suggest that this grain authigenically formed by biological activity during or after sedimentation. This work demonstrates that the use of multiple Faraday cup detectors provides improved accuracy and precision for in situ sulfur four-isotope analysis with secondary ion mass spectrometry.

1. Introduction

Sulfur four-isotope systematics of sulfur-bearing minerals in sedimentary rocks provides constraints on the evolution of the Earth's atmosphere and biological activity. Sulfur mass-independent fractionation (S-MIF), or deviation from the mass-dependent fractionation trends in $^{33}S/^{32}S$ and $^{36}S/^{32}S$ vs. $^{34}S/^{32}S$ ($\Delta^{33}S$ and $\Delta^{36}S$, respectively; see Section 3.1.2 for definitions), recorded in sedimentary rocks before ~2.4 Ga is generally interpreted to result from photochemical dissociation of volcanogenic SO_2 by ultraviolet light in an anoxic atmosphere (Farquhar et al., 2000; Pavlov and Kasting, 2002; Zahnle et al., 2006; Lyon, 2007; Danielache et al., 2008; Masterson et al., 2011; Whitehill and Ono, 2012; Ono et al., 2013; Whitehill et al., 2013). Another way to produce mass independent signatures is by chemistry occurring in liquid phase (Watanabe et al., 2009; Oduro et al., 2011; Kopf and Ono, 2012), but it is not clear if such mechanisms can account for the observed relationships among $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$, or account for the abundance of S-MIF in the Archean record (e.g., Kopf and Ono, 2012). One feature of the record that needs to be explained by any model for the origin of S-MIF is the observation of a change in slope for values of the $\Delta^{33}S$ vs. $\Delta^{36}S$ from about −0.9 to approximately −1.7 (Ono et al., 2006a, 2009a; Farquhar et al., 2007b, 2013; Kaufman et al., 2007; Zerkle et al., 2012; Thomazo et al., 2013).

Mass dependent fractionation of the more abundant sulfur isotopes ($\delta^{34}S$) by microbial sulfate reduction is suppressed to less than 6‰

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at sulfate concentrations less than 50 μmol, but it would increase at higher sulfate concentration and can be greater than 20‰ at sulfate concentrations higher than 200 μmol (Fig. 2(A) in Habicht et al., 2002). More recent observations of microbial sulfur isotope fractionation in a euxinic lake with sulfate concentrations of 100–350 μmol indicate that reservoir effects limit the degree to which larger (>20‰) kinetic fractionation effects are preserved in the rock record (Gomes and Hurtgen, 2013). Small variability in the δ^{34}S values of Archean sedimentary pyrite and expansion of variability in the δ^{34}S values of sedimentary pyrite after ~2.4 Ga are considered as the result of increasing concentration of seawater sulfate due to atmospheric oxygenation across the Great Oxygenation Event (GOE: Holland, 1984, 1994; Bekker et al., 2004; Canfield, 2005; Papineau et al., 2007; Partridge et al., 2008; Guo et al., 2009; Williford et al., 2011).

Sedimentary pyrite forms by multiple processes that are reflected in sulfur isotope signatures of individual pyrite grains. For example, Partridge et al. (2008) found that fine-grained pyrite in Neoarchean sedimentary rocks in the Hamersley Basin, Western Australia has positive Δ^{33}S values but that pyrite nodules in the same sedimentary rocks have negative Δ^{33}S values. Ono et al. (2009a) reported that Δ^{33}S and Δ^{36}S values of disseminated pyrite grains were distinct from those of pyrite nodules and layered pyrites in the same samples of 2.5 Ga Klein Naute Formation, South Africa. Furthermore, Williford et al. (2011) used a 3 μm diameter SIMS beam to show that many pyrite grains from glaciogenic mudstone and sandstone of the ~2.4 Ga Meteorite Bore Member of Western Australia are zoned with biogenic cores having low δ^{34}S values (<−20‰) and thin (≤10 μm) diagenetic or hydrothermal overgrowths with ~30‰ higher δ^{34}S values (4 to 7‰). This study showed that in situ sulfur isotope analyses with micrometer-scale spatial resolution provide additional information to investigate the signatures of multiple processes and multiple sulfur sources for pyrite formation, such as input of elemental sulfur aerosols, microbial sulfate reduction, and deposition by later hydrothermal activity (Williford et al., 2011; Philippot et al., 2012; Johnson et al., 2013).

In situ sulfur isotope analysis by the ion microprobe is a powerful technique to observe intra- and inter-grain sulfur isotope variability of a few to tens of μm-scale in sedimentary pyrite (Deloule et al., 1986; Graham and Valley, 1992; Farquhar et al., 2002, 2013; Mojzsis et al., 2003; Whitehouse et al., 2005; Kamber and Whitehouse, 2007; Papineau et al., 2007; Fayek, 2009; Kozdon et al., 2010; Williford et al., 2011; Roerdink et al., 2013; Whitehouse, 2013). Although it is recognized that sphalerite and galena exhibit crystal orientation effects which cause a significant change of the instrumental bias for the δ^{34}S value corresponding to crystal orientation (e.g., Kozdon et al., 2010; Kita et al., 2011), Kozdon et al. (2010) showed that using the same sulfur two-isotope technique as applied in this study, no significant crystal orientation effects exist for analysis of pyrite, chalcopyrite, and pyrrhotite beyond the reproducibility of spot-to-spot analyses of a single grain. Thus, no correction for crystal orientation effect is required for the sulfur isotope analysis of these three minerals.

In this study, we developed an ion microprobe technique for sulfur four-isotope analysis of pyrite with simultaneous detection by four Faraday cup (FC) detectors. In most other studies, in situ sulfur four-isotope analysis used an electron multiplier (EM) to measure the least abundant sulfur isotope, ^{36}S (Farquhar et al., 2013; Roerdink et al., 2013; Whitehouse, 2013). However, there are two important benefits to using a FC detector for the $^{36}\mathrm{S}^{-}$ signal. First, relative efficiency between two FC detectors is more stable than that between a FC detector and an EM detector. In particular, if an EM detector is used to measure ions whose count rate is higher than a few hundred thousand counts per second (cps), the aging effect (decrease of detection efficiency) of the EM detector is critical. The decrease of EM detector efficiency will change the measured isotope ratios and must be carefully monitored. Second, the upper limit of count rate for an EM (<several hundred thousands cps) prevents the use of a strong primary beam current and reduces the attainable analytical precision for the three other sulfur isotopes that are measured by FC detectors. Modification of a Faraday cup detection system (replacing a feedback resister with a capacitor, Ireland et al., 2014) provides further opportunity for improvement of precision of sulfur four-isotope analysis.

Reproducibility of the sulfur four-isotope analyses (δ^{34}S, Δ^{33}S, and Δ^{36}S) was evaluated using the pyrite standards, UWPy-1 (Kozdon et al., 2010) and Ruttan pyrite (Crowe and Vaughan, 1996; Cabral et al., 2013). This technique was also applied to measure sulfur four-isotope ratios of detrital pyrite grains in the glaciogenic sandstone, MB190583, from Williford et al. (2011). Williford et al. (2011) performed sulfur three-isotope analyses of sedimentary pyrite grains from multiple layers in exposures of the uppermost Hamersley Group and the lowermost Turee Creek Group at the Boundary Ridge and Deepdale localities, Western Australia (~2.4 Ga; Martin, 1999; Van Kranendonk, 2010). Williford et al. (2011) recognized that the glaciogenic sandstone (MB190583) layer contained abundant detrital pyrite grains with a wide range of Δ^{33}S values (−3.6 to 11.7‰), which were more variable than the authigenic pyrite grains of neighboring beds (typically −1 to 1‰). Results of sulfur four-isotope analyses of the same detrital pyrite grains analyzed for sulfur 3-isotope ratios by Williford et al. (2011) will be presented. Repeated measurements with a new analytical protocol for sulfur four-isotopes provide an opportunity to evaluate reproducibility of results by different analytical conditions and place further constraints on the origin of pre-GOE detrital pyrite grains in this glaciogenic sandstone.

2. Samples

2.1. Pyrite standards

The UWPy-1 pyrite standard (Kozdon et al., 2010) is coarse grained and homogeneous due to upper amphibolite facies recrystallization of the Mesoproterozoic Balmat massive sulfide deposit. UWPy-1 was used as a running standard for all sulfur isotope analysis sessions in this study. Sulfur four-isotope ratios of UWPy-1 have been determined using bulk analysis techniques that converted them to SF_6, which was measured using gas-source mass spectrometry at the University of Maryland and Harvard University (Table 1). Individual analysis data are provided in Table S1 in Electronic Annex. In this study, the newly determined sulfur isotope ratios of UWPy-1 were used. Sulfur isotope ratios of Ruttan pyrite (~1.88 Ga, $\delta^{34}\mathrm{S} = 1.2$ to 1.4‰, Crowe and Vaughan, 1996; Barrie and Taylor, 2001; Cabral et al., 2013) were also measured by ion microprobe. Although we did not determine sulfur four-isotope ratios of Ruttan pyrite by gas-source mass spectrometry in this study, no detectable S-MIF signature in Ruttan pyrite was reported ($\Delta^{33}\mathrm{S} = -0.003 \pm 0.012$, 2σ, Cabral et al., 2013) and its formation age is at least 400 Ma younger than GOE. For these reasons, we assume that the Ruttan pyrite we used does not have S-MIF signature larger than reproducibility by ion microprobe analyses.

2.2. Detrital Paleoproterozoic pyrite grains in glaciogenic sandstone

Sample MB190583 (sample 5 in Williford et al., 2011) is a glaciogenic sandstone with abundant detrital quartz and pyrite grains from the Meteorite Bore Member of the Turee Creek Group at the Boundary Ridge locality, Western Australia (Van Kranendonk, 2010; Williford et al., 2011). Two rock chips (~1 cm in size) of the sandstone were mounted in a 2.5 cm diameter epoxy disk with the pyrite standard UWPy-1 near the center. Most pyrite grains measured in this study were analyzed for sulfur three-isotope ratios by Williford et al. (2011). The sample mount was lightly ground and repolished to remove previous analysis pits (~1 μm in depth) and the new surface of each grain was checked by SEM before sulfur four-isotope analysis.

Most pyrite grains in MB190583 are 10 to 200 μm in size and have either rounded or irregular anhedral shapes (Fig. 1a–d). Pyrite grains with subhedral shape are rare (Fig. 1e). A single pyrite aggregate, g9,