SHRIMP 4-S isotope systematics of two pyrite generations in the 3.49 Ga Dresser Formation

L. Liu*, T.R. Ireland¹, P. Holden¹

Abstract

The 3.49 Ga Dresser Formation has been considered to host evidence of the earliest microbes metabolising sulfur species on Earth. However, previous bulk analyses and in situ measurements conclude disparate metabolisms based on opposite $\Delta^{33}S$. This study first established the generations of pyrite growth, and then measured the multiple sulfur isotopes in situ using Sensitive High Resolution Ion Microprobe-Stable Isotope Analyses. Two main generations of pyrite were revealed based on core-rim textures and multiple sulfur isotopic compositions: $\Delta^{33}S$-positive Generation One (G1) and $\delta^{34}S$- and $\Delta^{33}S$-negative Generation Two (G2). In the chert-barite unit, the diluted $\Delta^{33}S$-positive and $\Delta^{33}S$-negative photochemical products were mainly sequestered in G1 and barite, respectively. G2 were formed via the sulfide pathway with sulfur derived from sulfate reduction and magmatic H$_2$S. The $\delta^{34}S$-$\Delta^{33}S$-$\Delta^{34}S$ systematics suggests an abiological origin for G1, and thermochemical and possible (minor) microbial sulfate reduction for G2.

Introduction

The 3.49 Ga Dresser Formation in the Pilbara Craton, Western Australia has been widely considered to preserve palaeontological and geochemical evidence of Earth’s earliest life (e.g., Buick et al., 1981; Ueno et al., 2006; Shen et al., 2009; Noffke et al., 2013). The multiple sulfur isotopes of sulfate and sulfide in the Dresser Formation have been measured by both bulk and in situ analytical methods. Results of bulk methods support microbial sulfate reduction (MSR; Ueno et al., 2008; Shen et al., 2009) while in situ measurements support elemental sulfur disproportionation (Philippot et al., 2007). The differences in these data sets are profound. Although recent in situ studies have confirmed separately the $\delta^{34}S$-$\Delta^{33}S$ positively correlated $\Delta^{33}S$-negative (Baumgartner et al., 2020) and $\Delta^{33}S$-positive (Wacey et al., 2015) pyrites, the relationship between the two groups remains unknown.

The chert-barite unit of Dresser Formation was generated by a complex hydrothermal system, thus the pyrites are likely to preserve multiple generations resulting from multiple stages of hydrothermal events (Van Kranendonk et al., 2008). This study established the generations of pyrite formation, and then measured the multiple sulfur isotopes in situ. We exploited the in situ capabilities of SHRIMP-SI allowing $\delta^{34}S$ measurements in pyrite with a precision at a similar level to conventional bulk methods. In this way, we uniquely identified the sulfur isotopic composition of each generation of pyrites, and provided constraints on their formation pathways.

Geological Setting

The 3.49 Ga (Tessalina et al., 2010) Dresser Formation crops out as a ring of the North Pole Dome in the Pilbara Craton. It consists of metabasalt interlayered with three chert horizons (Ueno et al., 2008). The lowermost chert hosts abundant barite, referred to as the chert-barite unit, and is composed of chert, barite, carbonate, sandstone and conglomerate. Below this unit are thousands of silica + sulfides (pyrite and sphalerite) ± organic matter veins and barite veins intruding and transecting the underlying komatiitic basalt. The chert-barite unit and the veins are generally considered to be formed in a volcanic caldera, with sedimentation accompanied by volcanism, hydrothermal circulation and precipitation, and tectonic activity (Van Kranendonk et al., 2008). The hydrothermal fluids ascended along growth faults and deposited as concordant layers in a feeder-deposit manner. Detailed geological setting is in Supplementary Information (SI).

Samples and Methods

The investigated samples are from two drill cores: PDP2b and PDP2c. Detailed sample descriptions are in Table S-1. The drill core sections were made into polished mounts, which were immersed in sodium hypochlorite solution (8–12.5 % NaOCl) to reveal the internal textures of pyrites. The principle of pyrite etching is in SI. Appropriate pyrites were selected for subsequent BSE (Back Scattered Electron) imaging, EDS (Energy Dispersive X-ray Spectroscopy) and Raman spectroscopy analyses. Then

1 Research School of Earth Sciences, The Australian National University, Canberra ACT 2601, Australia
* Corresponding author (email: emnalu1016@gmail.com)

$\Delta^{33}S$ and $\Delta^{34}S$ quantify the magnitudes of sulfur mass-independent fractionations (S-MIFs) during a reaction, which are the deviations of the $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{34}S$ isotopic ratios from those expected solely based on their mass differences (see section 3.2 in the Supplementary Information).
the pyrites were measured for multiple sulfur isotopes using SHRIMP-SI. Detailed methods are in SI.

## Results

Pyrites occur as tiny grains aligned in an array within barite (Py-i), pyrite laminae (Py-ii), individual grains (IG) or clusters associated with silica veinlets/beads in barite (within veinlet, Py-iii; adjacent to both barite and chert, Py-v), IG in barite with silica veinlets/beads (Py-vi), IG in chert with barite crystal fans (Py-vii), and IG in silica-barite-carbonate veins in hydrothermally altered komatiitic basalt (Py-viii) (Fig. S-2). Some pyrites show core-rim textures (portions of Py-i to vi and Py-viii) while the others are homogeneous (Figs. 1, S-3). The sulfur isotopic composition exhibits evident dependence on the internal texture and petrography of pyrite. The cores show a tendency towards positive $\delta^{34}S$ and $\Delta^{33}S$, whereas the rims have more negative $\delta^{34}S$ and $\Delta^{33}S$ (Fig. S-8). Py-ii are mostly core-rim textured and display both negative and positive $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$, whereas Py-iii to vi are characterised by negative $\delta^{34}S$ and $\Delta^{33}S$ and positive $\Delta^{36}S$, with only a few exceptions. Py-vii show characteristic positive $\delta^{34}S$ and $\Delta^{33}S$, and Py-viii exhibit negative $\Delta^{33}S$ and positive $\delta^{34}S$ (Table 1, Fig. S-9). Detailed petrography, internal texture, and sulfur isotopic compositions are in SI.

## Discussion

The core-rim relationship combined with sulfur isotopic composition reveals two main generations ($\Delta^{33}S$-positive, euhedral to subhedral, locally porous G1 and $\Delta^{33}S$-negative, anhedral G2) in the core-rim textured pyrites. The majority have $\Delta^{33}S$-positive cores and $\Delta^{33}S$-negative rims, indicating that $\Delta^{33}S$-positive pre-cede $\Delta^{33}S$-negative pyrites. $\Delta^{33}S$-0 (close to 0, considering uncertainties) pyrites are widespread, and can be formed via the sulfide pathway ($Fe^{2+} + S^2- = [FeS], [FeS] + H_2S = FeS_2 + H_2$; Rickard and Luther, 1997) with magmatic $H_2S$ abundant in the Dresser hydrothermal system throughout the multiple stages of hydrothermal events (Ueno et al., 2008 and references therein). $\Delta^{33}S$-0 pyrites can be synchronous with $\Delta^{33}S$-positive and $\Delta^{33}S$-negative pyrites, because both $\Delta^{33}S$-positive and $\Delta^{33}S$-negative pyrites show evident positive correlations between $\delta^{34}S$ and $\Delta^{33}S$ (Fig. 2b), indicating two separate mixing trends between two respective end members, with one being $\Delta^{33}S$-0. Minor pyrites show $\Delta^{33}S$-negative cores and rims, suggesting two stages of G2.

Some Py-ii show two additional growth zones prior to G1 and G2 (Fig. 2a). The earlier zones (G1') are tiny porous grains, the $\Delta^{32}S$ of which is beyond the resolution ability of SHRIMP spots. However, the textures of these pyrites are similar to the cores of core-rim textured Py-i (Fig. 1a) that have been shown to be $\Delta^{32}S$-positive (Philippot et al., 2007). The later zones...
Table 1 Classification and quadruple S isotopic compositions of pyrites.

<table>
<thead>
<tr>
<th>Pyrite type</th>
<th>Description</th>
<th>δ34S (%)</th>
<th>Δ33S (%)</th>
<th>Δ36S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Py-i</td>
<td>Pyrites occur as tiny grains aligned in an array within barite.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Py-ii</td>
<td>Pyrite laminae.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Py-iii</td>
<td>Individual grains or clusters associated with silica veinlets/beads in barite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Py-iv</td>
<td>Individual grains in barite with silica veinlets/beads</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Py-v</td>
<td>Individual grains in barite with silica veinlets/beads</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Py-vi</td>
<td>Individual grains in chert with barite crystal fans</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Py-vii</td>
<td>Individual grains in silica-barite-carbonate vein in hydrothermally altered komatiitic basalt</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Photochemical reactions of gaseous sulfur species have been widely proposed to produce S-MIF, and the products are Δ34S-positive elemental sulfur and Δ36S-negative sulfate (Ono, 2017 and references therein). Δ33S-positive G1 and Δ33S-negative G2 yield a line of Δ36S = −0.98Δ33S + 0.05 (Fig. S-10a). The slope is close to that for products of SO2 photolysis under 193 nm UV (Farquhar et al., 2001). Thus the photochemical products sulfate and elemental sulfur are likely to have been mostly sequestered in barites and G1 pyrites via reactions with Ba2+-rich fluids and Fe2+-S2−-rich fluids, respectively, with the magnitudes diluted by magmatic and/or Δ33S-opposite sign sulfur species in the atmosphere/water mass (detailed explanation in SI).

G1 yield a line of Δ36S = −0.86Δ33S − 0.20 (Fig. S-10b) close to the Archean Reference Array (ARA). Some G1 show slight deviations from ARA, both upwards and downwards (one analysis exhibits a downward offset of >1‰), suggesting possible microbial elemental sulfur disproportionation or sulfate reduction, respectively (Johnston et al., 2007). However, neither is likely since microbial activities prefer 34S over 33S (i.e. negative δ34S) while G1 have positive δ34S.

(G2') are partly oscillatory zoned and porous, and these have been measured by Baumgartner et al. (2020) and are mostly Δ33S-negative. One Py-ii (Fig. S-3d) has a Δ33S-negative core (oscillatory zoned) and Δ33S-positive rim, confirming G2' precedes G1. Collectively, four generations are recorded in core-rim textured pyrites: Δ33S-positive G1', Δ33S-negative G2' (Baumgartner et al., 2020), Δ33S-positive G1 and Δ33S-negative G2 (this study). The multiple generations of pyrites in the same sample can be attributed to multiple pulses of hydrothermal fluids, with the later generation overgrown on the earlier generation.

The pyrites with no internal texture (Py-ii to vi) have the same petrography as the core-rim textured counterparts, and show similar multiple sulfur isotope systematics to the cores and rims, thus the homogeneous pyrites (Py-ii to vi) are also categorised into the four generations based on Δ33S and internal texture. The homogeneous Py-ii to vi lack the characteristic textures of G1' and G2', thus are all classified to G1 and G2. Δ33S-positive Py-vii are Ni-free and not porous, distinct from G1' while similar to G1. The negative Δ33S and positive δ34S of Py-viii are similar to some G2'.
The sulfide pathway, with S$_3$S$^\Delta$+$^\Delta$S$^\Delta$ lower (i.e., $^\Delta$S$^\Delta$+$^\Delta$S$^\Delta$), was observed in situ (Shen et al., 2009). Additionally, barites and G2 pyrites yield a line of $^\Delta$S$^\Delta$ = -0.94$^\Delta$S$^\Delta$ - 0.02 close to ARA while distinct from the Biological Fractionation Line (BFL; Fig. S-10c). Therefore, MSR signal in G2 is weak, although we do not exclude its presence because two data points of Shen et al. (2009) show negative ($^\Delta$S$^\Delta$ + $^\Delta$S$^\Delta$) even relative to the lowest ($^\Delta$S$^\Delta$ + $^\Delta$S$^\Delta$) value of in situ barite data.

Furthermore, some G2 show positive ($^\Delta$S$^\Delta$ + $^\Delta$S$^\Delta$) with larger magnitudes of positive shifts in $^\Delta$S$^\Delta$ than negative shifts in $^\Delta$S$^\Delta$, which has not been observed in MSR but has been discovered in TSR (Figs. 2c, 3). TSR can induce positive and negative ($^\Delta$S$^\Delta$ + $^\Delta$S$^\Delta$) depending on reductant and temperature (Oduro et al., 2011), in addition to significant depletions in $^\Delta$S$^\Delta$ relative to initial sulfate (Ohmoto and Goldhaber, 1997). Therefore, the $^\Delta$S$^\Delta$ of G2 can also be derived from TSR apart from MSR. TSR could be in operation 3.49 Ga ago in the Dresser hydrothermal system. This is consistent with the highest temperature of 110 °C where sulfate reducers (discovered so far) can live (Jorgensen et al., 1992) while the temperature of the hydrothermal fluids associated with the Dresser Formation ranges from 300 °C at depth to 120 °C near the paleosurface (Harris et al., 2009).

Conclusions

A combination of sodium hypochlorite etching, BSE imaging and multiple sulfur isotopes reveals two main generations of pyrites associated with the barites of the 3.49 Ga Dresser Formation: $^\Delta$S$^\Delta$-positive G1 and $^\Delta$S$^\Delta$- and $^\Delta$S$^\Delta$-negative G2. Diluted sulfate and elemental sulfur produced by photochemical reactions were sequestered in barites and G1, respectively. The positive $^\Delta$S$^\Delta$ of G1 indicates an abiological genesis. G2 were formed via the sulfide pathway, with the sulfur derived from magmatic H$_2$S and S$_3$S$^\Delta$ produced by thermochemical and possible microbially produced sulfate reduction.

Acknowledgements

We sincerely thank the Perth Core Library for approving the access to drill cores and publishing the results. This work was supported by the Australian Research Council DP140103393 to TRI. The constructive comments from Dr. Boswell Wing and two anonymous reviewers are sincerely appreciated, which have improved this manuscript significantly.

Editor: Karim Benzerara

Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2113.

© 2021 The Authors. This work is distributed under the Creative Commons Attribution-Non-Commercial No-Derivatives 4.0 License, which permits unrestricted distribution provided the original author and source are credited. The material may not be adapted (remixed, transformed or built upon) or used for commercial purposes without written permission from the author. Additional information is available at https://www.geochemicalperspectivesletters.org/copyright-and-permissions.

References


SHRIMP 4-S isotope systematics of two pyrite generations in the 3.49 Ga Dresser Formation

L. Liu, T.R. Ireland, P. Holden

Supplementary Information

The Supplementary Information includes:

- 1. Geological Setting
- 2. Samples
- 3. Methods
- 4. Results
- 5. The Dependence of Multiple Sulfur Isotopic Compositions on Pyrite Texture and Petrography
- 6. The Dilution of S-MIF in Original Photochemical Products
- 7. Pyrites with Positive $\Delta^{33}$S and Negative $\delta^{34}$S
- Tables S-1 to S-6
- Figures S-1 to S-11
- Supplementary Information References
1. Geological Setting

The Dresser Formation crops out as a ring (up to 14 km in diameter) of the North Pole Dome in the East Pilbara Terrane of Pilbara Craton (Van Kranendonk et al., 2008). Stratigraphically, it is a subunit of the Warrawoona Group, Pilbara Supergroup, and consists of metabasalt interlayered with three chert horizons (Ueno et al., 2008). The lowermost chert hosts abundant barite, and is referred to as the chert-barite unit, which is the focus of most studies on the Dresser Formation. The bedded chert-barite unit is composed mainly of chert in variable colours, coarse barite in the form of bedding-concordant or discordant layers, carbonate, conglomerate and sandstone comprising predominantly volcanic detritus, and interlayered sulfidised stratiform and domical stromatolites. Below the bedded chert-barite unit are quantities of silica ± sulfides (pyrite and sphalerite) ± organic matter veins and barite veins of variable width intruding and transecting the underlying komatiitic basalt, resulting in intense hydrothermal alterations around the veins (particularly chloritic alteration).

Initially, the chert-barite unit was interpreted as being deposited in a peritidal or sabkha environment based on sedimentary structures such as stromatolitic laminates, graded and crossed-bedding, ripples, desiccation cracks, and abundant carbonates and sulfates (e.g., Lambert et al., 1978; Groves et al., 1981; Buick and Dunlop, 1990). The veins were considered to be formed during a post-depositional stage along the fractures of the dome (Hickman, 1973, 1983). Nevertheless, later detailed mapping combined with sedimentological and structural analyses revealed that the bedding-conformable chert and barite are contemporaneous with the veins (Nijman et al., 1998; Van Kranendonk and Pirajno, 2004). Furthermore, X-ray computerised tomography provided evidence demonstrating that the barite is hydrothermal in origin (Runnegar et al., 2001) rather than replacement of gypsum (Lambert et al., 1978; Groves et al., 1981; Buick and Dunlop, 1990). The chert-barite unit is now generally considered to be formed in an active volcanic caldera with nearly contemporaneous volcanism, sedimentation, hydrothermal circulation, and tectonic activity (Van Kranendonk et al., 2008). Van Kranendonk et al. (2008) divided the chert-barite unit into six members (Fig. S-11), which represent three main sedimentation episodes. The first sedimentation is represented by carbonates and sandstone of Member 1 and sulfidised stromatolites of Member 2. The sedimentation of Member 1 was accompanied by volcanism and pyrite-barite-silica hydrothermal alteration and precipitation. The second sedimentation is indicated
by the volcaniclastic conglomerate of Member 3 (accompanied by growth faulting and precipitation of hydrothermal pyrite-barite-chert-sphalerite) and carbonates of Member 4 (followed by precipitation of hydrothermal barite and chert). The last sedimentation is represented by the sandstone and carbonates of Members 5 and 6. The hydrothermal fluids altering Members 5 and 6 are different from that of the lower members. The silica-, Ba\(^{2+}\)-rich and/or Fe\(^{2+}\)-rich hydrothermal fluids ascended through the growth faults and deposited as concordant layers in a feeder-deposit manner (Nijman et al., 1998; Ueno et al., 2001; Van Kranendonk et al., 2008). The sedimentary rocks of the main portions of the chert-barite unit have been altered to silica, barite, and pyrite (Van Kranendonk et al., 2008). Silica ± sulfides ± organic materials veins and barite veins are generally parallel, with around 1000-m and 100-m extension downwards into the underlying basalt, respectively, and terminate upwards into the chert unit (Ueno et al., 2008).

The age of the Dresser Formation has been constrained to around 3.49 Ga based on a Sm-Nd isochron age of 3.492 ± 0.1 Ga for the metabasalts, metakomatiites, barite and silicified carbonate of the chert-barite unit of Dresser Formation (Tessalina et al., 2010), a model Pb-Pb age of 3490 Ma for the galena from this unit (Thorpe et al., 1992a), and a zircon U-Pb age of 3.480 Ga for the volcanoclastic layer of this unit (Van Kranendonk et al., 2008). Additional age constraints are provided by zircon U-Pb ages of 3471 ± 5 Ma for felsic volcanics and 3465 ± 3 Ma for felsic schist of the overlying Duffer Formation (Thorpe et al., 1992b), and zircon U-Pb ages of 3515 ± 3 Ma for the rhyolite tuff (Buick et al., 1995) and 3498 ± 2 Ma for the rhyolite (Nelson, 2002) of the underlying Coonterunah Subgroup.

2. Samples

The drill core sections investigated in this study include PDP2c_97.17–97.20 m, PDP2b_90.94–90.97 m, PDP2b_94.69–94.74 m, and PDP2b_102.26–102.27 m. The selection of these samples was based on realistic availability of sampling and geological consideration.

The drill cores of PDP2c and PDP2b were collected at the Perth Core Library of the Geological Survey of Western Australia in 2016 and 2018, respectively, while the Pilbara Drilling Project (PDP) obtaining the drill cores of PDP2b and PDP2c was conducted in 2004. During this decade, the precious drill cores had been significantly sampled for
research. As such, only a very limited amount of drill cores were available for sampling, particularly PDP2c and the upper parts of PDP2b. Therefore, we selected the limited amount of available drill cores to cover different depths and pyrite occurrences (Fig. S-11).

The chert-barite unit of the Dresser Formation consists of six members (1, 2, 3, 4, 5, and 6 upwards), and below the chert-barite unit are quantities of silica veins and barite veins (Philippot et al., 2007; Ueno et al., 2008; Van Kranendonk et al., 2008; Muller et al., 2016). PDP2c intersects Members 1, 2, 3, 5, and 6, whereas PDP2b intersects Members 1, 2, 5, and 6. Since the entire PDP2c and the upper parts of PDP2b had been significantly sampled, thus our sampling focused on Member 1 and the veins below. PDP2c_97.17–97.20 m is a section representative of barite with pyrite laminae, PDP2b_90.94–90.97 m is a typical section of chert with barite crystal fans, PDP2b_94.69–94.74 m is a section representative of vein barite, and PDP2b_102.26–102.27 m is a section of hydrothermally altered komatiitic basalt with silica-barite-carbonate veins (Fig. S-1).

3. Methods

3.1. Etching and SEM analysis

Chips of barite with/without pyrite laminae/clusters were firstly cut from the drill cores and cast into the first batch of epoxy mounts. The mounts were polished and then immersed in sodium hypochlorite solution (8–12.5 % NaOCl) for about two to five minutes, revealing the internal textures of pyrites. The stained colour in the reflected light of optical microscope is attributed to the optical interference by a thin layer of elemental sulfur on pyrite surface (Fleet et al., 1993). The sulfur species on the surface of etched pyrite include elemental sulfur, disulfide, and sulfate. The proportion of elemental sulfur increases with the arsenic content of pyrite.

Subsequently, the mounts were observed under the reflected light of microscope for pyrite petrography, internal texture, and selection of appropriate pyrites for sulfur isotope analysis. Special attention was paid to the size of small pyrite grains associated with barite to ascertain that the selected grains were sufficiently large for small-spot analysis
(~18 × 15 μm) of SHRIMP-SI. The regions with targeted pyrites were cut from the mounts, and were assembled into the second batch of mounts together with the reference materials (Ruttan pyrite and Balmat pyrite) for sulfur isotope measurement. These polished mounts were immersed in the sodium hypochlorite solution again, rinsed, and dried, and were then re-photographed under reflected light. The photomicrographs were used subsequently to locate the SHRIMP-SI spots on pyrite grains with internal textures. The etched mounts were then polished with 1-μm diamond paste to remove the oxidised film on the surface, and to ensure the flatness of the mounts.

The mounts were then cleaned, dried, and coated with approximately 10 nm of gold or 15 nm of aluminium. Subsequently, they were analysed utilising a JEOL JSM-6610 SEM (Scanning Electron Microscope), revealing the internal textures of pyrites by BSE (Back Scattered Electron) imaging, semi-quantitatively identifying the mineral inclusions by EDS (Energy Dispersive X-ray Spectroscopy), and confirming that the minerals to be analysed were compositionally pyrite. The SEM analyses were conducted at the Research School of Earth Sciences (RSES), Australian National University (ANU). Operating conditions were acceleration voltage of 15 kV, beam current of 1 nA, and working distance of 10 mm. The supplementary BSE imaging and EDS analysis were conducted on a Carl Zeiss SUPRA55 SAPPHIR Field Emission-SEM, with the acceleration voltage being 20 kV and working distance being 8.2 to 8.5 mm. After SEM analysis, the gold or aluminium film was removed firstly by potassium iodide solution (for gold) or decon90 detergent (for aluminium) and then by polishing with 1-μm diamond paste. The Raman spectra were obtained using a Raman microscope WITec alpha300 R system equipped with a frequency doubled Nd:YAG laser emitting at 532 nm (fiber-coupled). The surface laser power was 11 mW, and each single spectrum was acquired by 5 to 10 accumulations of 1-second integration.

3.2. SHRIMP-SI analysis

Before sulfur isotope measurement, the mounts were again thoroughly cleaned in an ultrasonic bath successively using ethanol, RBS35 detergent, warm water, and deionised water. Subsequently, the mounts were dried and outgassed in a vacuum oven (60 °C, 1 kPa) for around five days, and were then coated with approximately 40 nm of gold or 45 nm of aluminium.
Pyrites were analysed on SHRIMP-SI at RSES, ANU following standard operating procedures (Ireland et al., 2014; Liu et al., 2020). A brief description of analytical conditions is provided below and further details are summarised in Table S-2.

A primary caesium ion beam was generated in a Kimbal Physics IGS5 ion gun with an internal acceleration potential of 5 kV. The ion beam was focused to a Kohler aperture that was used as the source for the immersion lens, which accelerated the beam through a further 10 keV to the sample potential. The incidence angle of the primary beam on the target was 45°, yielding elliptical spots on the sample surface. Due to the variable sizes of pyrite grains and growth zones, both big-spot (~27 × 20 μm) and small-spot (~18 × 15 μm) analyses were conducted. The spot size was changed by adjusting the Kohler aperture.

Negative sulfur ions were accelerated to real ground with resultant 10 keV energy, and were then focused through an ion extraction system to the source slit. The width of the source slit was 60 μm. The secondary sulfur ions were focused through the mass analyser to the collector. The four ion beams were focused to individual detector heads with their own collector slits, and the four sulfur isotope ions were collected and measured simultaneously in multiple collection mode. The mass resolution of 4000 M/ΔM (10 % peak height) achieved by a collector slit width of 150 μm was used for resolving $^{33}$S$^-$ from $^{32}$S$^-$. All four sulfur isotope ion beams were collected in Faraday cups; $^{32}$S$, ^{33}$S$^-$ and $^{34}$S$^-$ ions were measured using current mode with $10^{11}$ or $10^{12}$ Ω resistors whereas $^{36}$S$^-$ was measured using charge mode with a 22 pF capacitor (Ireland et al., 2014).

Each analysis commenced with rastering the primary beam over an area slightly larger than the spot for five (big-spot analyses) or two (small-spot analyses) minutes, removing the gold/aluminium coat and allowing the sample surface to become conditioned with Cs$^+$ ions. During this period, an in-line valve between the source chamber and the electrostatic analyser was closed and backgrounds for the electrometers were measured. This was followed by horizontal and vertical steering of the secondary ion beam to maximise the signal of sulfur ions and to further stabilise the secondary ion beam through the source slit. Each analysis consisted of four or five sets for big-spot analyses, and
two sets for small-spot analyses. Each set comprised ten scans, and each scan comprised ten subcounts of two-second integration. $^{32}\text{S}^-$, $^{33}\text{S}^-$, $^{34}\text{S}^-$ and $^{36}\text{S}^-$ were all measured in big-spot analyses whereas only $^{32}\text{S}^-$, $^{33}\text{S}^-$ and $^{34}\text{S}^-$ were measured for small-spot analyses due to low signal of $^{36}\text{S}^-$. The primary reference material was Ruttan pyrite and the secondary reference material was Balmat pyrite. Each analytical session generally commenced with analyses of Ruttan pyrite and Balmat pyrite, followed by unknowns, and then Ruttan pyrite and Balmat pyrite, and so forth. After SHRIMP-SI measurements, the pyrites analysed were etched again, confirming the locations of the spots.

The raw sulfur isotope data were reduced using the POXI-MC software developed at RSES, ANU. The measured $^x\text{S}^-/^{32}\text{S}^-$ ratios were firstly corrected by the primary reference material Ruttan pyrite for the Instrumental Mass Fractionation, and were then transformed to delta ($\delta$) notation as permil deviations relative to the standard ratios of Vienna Canyon Diablo Troilite (V-CDT) following $\delta^x\text{S}^-(\text{‰}) = [(x/^{32}\text{S}^\text{unknown}/x/^{32}\text{S}^\text{V-CDT}) - 1] \times 1000$, where $(x/^{32}\text{S}^\text{unknown})$ and $(x/^{32}\text{S}^\text{V-CDT})$ are the $x/^{32}\text{S}$ ratios of the unknown and V-CDT, respectively, and $x$ is the mass number of the S isotope (i.e. 33, 34, or 36). $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ were calculated following $\Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \times [(1 + \delta^{34}\text{S}/1000)^{0.515} - 1]$ and $\Delta^{36}\text{S} = \delta^{36}\text{S} - 1000 \times [(1 + \delta^{34}\text{S}/1000)^{1.90} - 1]$, respectively.

Although Ruttan pyrite has been measured by conventional methods only for $\delta^{34}\text{S} (1.2 \pm 0.1 \text{‰}, \text{Crowe and Vaughan, 1996})$, based on the post-Archaean age (ca. 1.88 Ga, Rayner and Corrigan, 2004), previous studies assumed $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ of 0 for Ruttan pyrite (e.g., Whitehouse, 2013). Williford et al. (2011) normalised Ruttan pyrite to Balmat pyrite that has been determined for $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ by conventional methods ($\Delta^{33}\text{S} = -0.003 \pm 0.009 \text{‰}, \Delta^{36}\text{S} = -0.21 \pm 0.24 \text{‰}, \text{Ushikubo et al., 2014}$), and the results show no significant S-MIF for Ruttan pyrite. Therefore, we assume the $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ of Ruttan pyrite to be 0, and the corresponding $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ of Ruttan pyrite are thus 0.618 ‰, and 2.281 ‰, respectively. $\delta^{34}\text{S}$ of Balmat pyrite has been measured by conventional methods to be 15.1 ± 0.2 ‰ (Crowe and Vaughan, 1996) or 16.04 ± 0.18 ‰ (Ushikubo et al., 2014). SIMS analyses have shown that the $\delta^{34}\text{S}$ of Balmat pyrite can be slightly variable between samples (Whitehouse, 2013; Muller et al., 2017).
4. Results

4.1. Petrography and internal texture of pyrites

In the drill core sections investigated in this study, pyrites occur as tiny grains aligned in an array within barite (Py-i), pyrite laminae (Py-ii), in the silica veinlet in barite (Py-iii), on the wall of silica veinlet in barite (Py-iv), adjacent to both barite and silica (Py-v), in barite with silica veinlets and beads (Py-vi), in chert with barite crystal fans (Py-vii), and in silica-barite-carbonate vein in hydrothermally altered komatiitic basalt (Py-viii) (Fig. S-2).

Tiny pyrite grains aligned in an array within barite (Py-i) are mostly less than 10 μm in size, and some show core-rim textures (Figs. 1 and S-3).

Pyrite laminae (Py-ii) are representative in PDP2c_97.17–97.20 m. They are contiguous to barite layers (Fig. S-2), and contain some barites as well. The barite crystals have been crosscut by silica veinlets, in which remain a small amount of barite residues. The pyrite laminae are approximately 1 to 1.5 mm-thick, and consist of mainly pyrite, subordinate barite and poorly crystallised silica, and minor other sulfides (mostly sphalerite). The size of pyrites varies from 5 to 120 μm. The pyrites closely associated with silica are generally recrystallised to coarser grains while those distant from silica are fine-grained. Pores, barite, poorly crystallised silica, and minor other sulfides are pervasive throughout the pyrite laminae, in the forms of residues, inclusions within pyrites, or intergranular filling. Pyrite overgrowth/rimming is widespread in both fine-grained and coarse-grained areas. For moderate to coarse pyrites adjacent to silica and barite, some display evident core-rim textures, while the others exhibit no internal texture. The cores are euhedral, generally less than 30 μm in size, and locally slightly to moderately porous, whereas the rims are anhedral and mostly homogeneous. Occasionally, inclusions are observed in cores and rims, including barite, other sulfides, carbonaceous materials, and anatase. The fine pyrites are porous and occur as cores. They are mantled by partly oscillatory-zoned pyrites, which are in turn overgrown by less porous and non-porous coarse pyrites (Fig. 1). It
is noteworthy that carbonaceous materials are not only observed in porous pyrites, but also in non-porous moderate to coarse pyrites (Fig. S-4).

Pyrites associated with silica veinlets in barite (Py-iii, iv, v) are widespread, and are observed in PDP2b_90.94–90.97 m, PDP2b_94.69–94.74 m, and PDP2c_97.17–97.20 m. Silica veinlets crosscut barite, and pyrites are located within or on the wall of silica veinlets as individual grains or clusters with/without sphalerite (Fig. S-2). The individual grains are euhedral to subhedral, 25 to 80 μm in size, with/without pores or inclusions (e.g., sphalerite, carbonaceous materials). Pyrites constituting clusters are homogeneous and of variable size, anhedral, and only porous locally, with the exception of a few grains that are intensely porous. The silica veinlets are discontinuous in some parts of barite, displaying silica beads or drops. In this case, pyrite occurs as individual grains adjacent to both barite and silica within barite (Fig. S-2). They are small (from 25 to 100 μm), euhedral to subhedral (mostly hexahedra), with/without inclusions (e.g., barite, carbonaceous materials). The majority are homogeneous, and only minor show core-rim textures, contain inclusions, or are locally porous. The cores are porous and small (less than 20 μm).

The pyrites in barite with silica veinlets and beads (Py-vi, Fig. S-2) are different from the tiny pyrites aligned in an array within barite mainly in size (20 to 50 μm, Fig. S-3). Some are homogeneous while others display euhedral hexahedron cores overgrown by anhedral rims (Fig. S-3), and are porous and/or contain inclusions (e.g., carbonaceous materials) locally.

Pyrite in chert with barite crystal fans (Py-vii) is observed in PDP2b_90.94–90.97 m. The chert is composed of poorly crystallised silica, minor silicates (two kinds, and one is barium-bearing), barite, pyrite, and pentlandite. The pyrites are sparsely disseminated within chert, mostly hexahedron in shape, 25 to 60 μm in size, and are predominantly homogeneous, with only a few grains containing pores locally (Fig. S-2).

Pyrite in silica-barite-carbonate vein in hydrothermally altered komatiitic basalt (Py-viii) is observed in PDP2b_102.26–102.27 m. The silica-barite-carbonate vein crosscut the komatiitic basalt, and consists of abundant
euhedral to subhedral coarse pyrites, poorly crystallised silica, barite, carbonate, and minor silicate (Fig. S-2). Some of these pyrites are homogeneous, while the others show oscillatory zoning, and a small proportion exhibit thin rims.

EDS results show that Py-i (cores and rims), Py-ii (fine porous pyrite, partly oscillatory-zoned porous mantles, and the majority of rims and homogeneous pyrites), Py-iii to vi (the majority), and Py-viii (portions) are Ni-bearing, while the rest (Py-vii and cores of Py-ii) are Ni-free. The semi-quantitative EDS composition of pyrite unknowns were corrected using Ruttan pyrite (FeS₂), which was measured simultaneously with the unknowns. The Ni contents are generally low (0.23 to 1.61 wt. %, mostly less than 1 wt. %), slightly higher in Py-i cores (1.62 to 3.66 wt. %). Nevertheless, the Ni concentrations are much lower than that of pentlandite ((Fe,Ni)₉S₈, 34.22 wt. %).

4.2. Multiple sulfur isotopic compositions

A total of 153 analyses were conducted on pyrites of the Dresser Formation, comprising 58 big-spot and 85 small-spot analyses, with 109 analyses on PDP2c and 44 analyses on PDP2b. A summarisation of these data is presented in Table S-3, and a full list of all sulfur isotope data is presented in Tables S-4 and S-5.

The CPS (counts per second) of $^{32}\text{S}^-, ^{33}\text{S}^-, ^{34}\text{S}^-, ^{36}\text{S}^-$ of unknowns, Ruttan pyrite, and Balmat pyrite is similar in each session, despite differences among sessions which can be attributed to different primary beam intensity. One spot analysis (1038-48_5) in Session 5 has lower CPS compared with the other unknowns and Ruttan and Balmat pyrites in this session; this is due to lower primary beam intensity (1.7 nA compared to 3.5–3.8 nA). The same cause goes for the spot analysis M-12_3 in Session 13. The CPS of $^{32}\text{S}^-, ^{33}\text{S}^-, ^{34}\text{S}^-$, and $^{36}\text{S}^-$ is 0.8–1 GHz, 6–10 MHz, 40–60 MHz, and 0.1–0.2 MHz, respectively, for big-spot analyses; 0.2–0.7 GHz ($^{32}\text{S}^-$), 1–5 MHz ($^{33}\text{S}^-$), and 8–30 MHz ($^{34}\text{S}^-$) for small-spot analyses.

Ruttan pyrite ($\delta^{34}\text{S} = 1.2 \%, \Delta^{33}\text{S} = 0$, and $\Delta^{36}\text{S} = 0$) was used as the primary reference material. In big-spot analyses, the weighted means of $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ of Ruttan pyrite are $1.11 \pm 0.36 \%$ to $1.34 \pm 0.88 \%$, $0.00 \pm 0.15 \%$ to
−0.01 ± 0.24 ‰, and 0.01 ± 0.36 ‰ to −0.03 ± 0.26 ‰ (2 s.d.), respectively. In small-spot analyses, the weighted means are 1.03 ± 1.09 ‰ to 1.25 ± 1.25 ‰ for δ34S, and 0.01 ± 0.25 ‰ to 0.06 ± 0.37 ‰ for Δ33S (2 s.d.).

Balmat pyrite was applied as the secondary reference material. In the fourteen sessions, δ34S of Balmat pyrite ranges from 14.42 ± 0.29 ‰ to 15.31 ± 1.01 ‰ for big-spot analyses and 14.12 ± 0.62 ‰ to 15.27 ± 1.40 ‰ (2 s.d.) for small-spot analyses, consistent with the previously reported value of 15.1 ± 0.2 ‰ obtained by conventional methods (Crowe and Vaughan, 1996), although several sessions show slightly lower values, which can be attributed to drifts of instrument or true heterogeneity of Balmat pyrite (Whitehouse, 2013). Δ33S and Δ36S of Balmat pyrite in both big-spot and small-spot analyses are close to 0, despite several sessions with slight deviations from 0. The discrepancies will be taken into account in data interpretation.

In plots of δ34S−δ33S and δ34S−δ36S, Rutten pyrite and Balmat pyrite are on the mass dependent fractionation lines (y = 0.515x and y = 1.90x, respectively), while the unknowns of Dresser pyrites deviate from the mass dependent fractionation lines to variable degrees (Fig. S-5).

As mentioned in the preceding section, the principle of pyrite etching to reveal the internal textures is based fundamentally on the different arsenic content. Although the difference in arsenic abundance in pyrite can potentially have slight matrix effects on the measurements of small deltas (δ33S, δ34S, δ36S), such matrix effects have been considered insignificant (at sub-per mil levels even with arsenic content up to 2.5 wt. %, Williford et al., 2011).

4.2.1. PDP2c. A single section contributed to the analyses of drill core PDP2c at a depth level of 97.17–97.20 m. Py-i to vi are observed in this section.

This sample shows an entire range from −13.3 to 2.1 ‰ in δ34S with a median of −5.2 ‰, −1.2 to 1.5 ‰ in Δ33S with a median of −0.4 ‰, and −2.1 to 1.1 ‰ in Δ36S with a median of 0.2 ‰. δ34S and Δ33S are tightly correlated (Fig. S-6).
The maximum range is represented in Py-ii, with $\delta^{34}\text{S}$ ranging from $-10.4$ to $2.1$ ‰, $\Delta^{33}\text{S}$ from $-1.2$ to $1.5$ ‰, and $\Delta^{36}\text{S}$ from $-2.1$ to $1.1$ ‰ (Figs. S-6, S-7). The most negative $\delta^{34}\text{S}$ of $-13.3$ ‰ is preserved in Py-v. Py-ii are characterised by core-rim textures. Twenty-three cores show a range in $\delta^{34}\text{S}$ from $-5.2$ to $2.1$ ‰ with a median of $0.8$ ‰, $\Delta^{33}\text{S}$ from $-0.4$ to $1.5$ ‰ with a median of $1.0$ ‰, $\Delta^{36}\text{S}$ from $-2.1$ to $-0.4$ ‰ with a median of $-1.0$ ‰. The associated rims, where sufficiently large for analysis, display $\delta^{34}\text{S}$ from $-10.4$ to $-0.7$ ‰ with a median of $-4.0$ ‰, $\Delta^{33}\text{S}$ from $-1.2$ to $0.6$ ‰ with a median of $-0.3$ ‰, $\Delta^{36}\text{S}$ from $0.3$ to $1.1$ ‰ with a median of $0.5$ ‰. Thus, while the ranges in cores and rims overlap to some degree, there is a distinct shift in the median values between these occurrences. The cores show a tendency towards positive $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$, whereas the rims exhibit more negative $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$. The rims appear to have compositions more relatable to Py iii to vi.

### 4.2.2. PDP2b.
Pyrites in three sections of this drill core (90.94–90.97 m, 94.69–94.74 m, 102.26–102.27 m) were analysed. The total range in $\delta^{34}\text{S}$ for the three sections is $-21.5$ to $5.1$ ‰ (median of $-13.0$ ‰), with $\Delta^{33}\text{S}$ from $-1.4$ to $3.6$ ‰ (median of $-1.0$ ‰) and $\Delta^{36}\text{S}$ from $-2.9$ to $1.9$ ‰ (median of $0.8$ ‰). The dependence on pyrite petrography is clear (Figs. S-9).

Py-vii from the section PDP2b_90.94–90.97 m are distinctive with the highest $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$, $3.7 \pm 1.7$ ‰ and $3.0 \pm 0.8$ ‰ (2 s.d.), respectively. Py-v in this section have been analysed. Six of seven analyses show a restricted range in multiple sulfur isotopic composition, with $\delta^{34}\text{S}$ of $-19.2 \pm 3.2$ ‰, $\Delta^{33}\text{S}$ of $-1.2 \pm 0.2$ ‰, and $\Delta^{36}\text{S}$ of $1.3 \pm 1.0$ ‰. An outlier in this section is a single core analysis that shows much lower $\delta^{34}\text{S}$ ($-3.9$ ‰) and distinctly positive $\Delta^{33}\text{S}$ ($1.5$ ‰). This $\delta^{34}\text{S}$ ($-3.9$ ‰) can be attributed to slight involvement of the $\delta^{34}\text{S}$-extremely negative ($-18$ ‰) rim, which is unavoidable due to the small size of the core.

In section PDP2b_94.69–94.74 m, Py-iii to vi are observed. Py-vi show $\delta^{34}\text{S}$ of $-19.0$ to $-3.4$ ‰, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ of $-0.9 \pm 0.4$ ‰ and $0.6 \pm 0.7$ ‰, respectively. Py-iii to v exhibit $\delta^{34}\text{S}$ from $-16.0$ to $-2.5$ ‰, with the majority clustered from $-12$ to $-16$ ‰; $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ show restricted ranges, and are $-1.0 \pm 0.4$ ‰ and $1.0 \pm 0.5$ ‰, respectively.
In section PDP2b_102.26–102.27 m, Py-viii show positive δ34S (2 ‰) but negative Δ33S (~0.8 ‰), making it distinct from the disseminated pyrites in PDP2b_90.94-90.97 m.

Despite a range in δ34S, there is no strong correlation between δ34S and Δ33S (Fig. S-6). Py-vii in section PDP2b_90.94–90.97 m appear to represent a singular occurrence of a high δ34S and Δ33S composition, potentially on an extension to the array for PDP2c. The other data typically show a correlation between δ34S and Δ33S at a much lower slope than PDP2c. Py-vi tend to have higher δ34S than Py-iii to v, but the ranges overlap for sections PDP2b_90.94–90.97 m and PDP2b_94.69–94.74 m.

4.2.3. Quadruple sulfur isotope systematics. Larger pyrites from PDP2c and two sections of PDP2b (90.94–90.97 m and 94.69–96.74 m) were analysed for quadruple sulfur isotopes, while the other pyrites were analysed only for triple sulfur isotopes.

In the Δ33S-Δ36S plot, all the cores, rims and homogeneous pyrites of PDP2b and PDP2c are typically close to the Archaean Reference Array (ARA, Δ36S ≈ −Δ33S; Farquhar et al., 2001) with variable degrees of slight deviations (Fig. S-8). Only one analysis (M-12_36.1, a pyrite core) lies significantly (>1 ‰) off ARA. Similar to the δ34S-Δ33S plot, the data show distinct clusters that can be related to the petrography of pyrites (Fig. S-8).

5. The Dependence of Multiple Sulfur Isotopic Composition on Pyrite Internal Texture and Petrography

5.1. Dependence on pyrite internal texture

The core-rim textured pyrites are the most common in Py-ii of PDP2c_97.17–97.20 m, followed by Py-v and Py-vi of PDP2b_90.94–90.97 m and PDP2b_94.69–94.74 m. The cores show a tendency towards positive δ34S and Δ33S, whereas the rims show negative δ34S and Δ33S.
The majority of the core-rim textured pyrites show $\Delta^{33}\text{S}$-positive cores and $\Delta^{33}\text{S}$-negative rims (Table S-3, Fig. S-8). The cores show $\delta^{34}\text{S}$ of $-4$ to $2 \%$, $\Delta^{33}\text{S}$ of $0.8$ to $1.5 \%$, and $\Delta^{36}\text{S}$ of $-1.7$ to $-0.9 \%$, while the rims exhibit $\delta^{34}\text{S}$ of $-19$ to $-2 \%$, $\Delta^{33}\text{S}$ of $-1.4$ to $-0.3 \%$, and $\Delta^{36}\text{S}$ of $0.4$ to $1.9 \%$. Locally, some other combinations of cores and rims have also been observed, including (1) $\Delta^{33}\text{S}$-positive cores ($1$ to $1.5 \%$), rims with $\Delta^{33}\text{S}$ near $0$ ($-0.08$ to $0.2 \%$), (2) $\Delta^{33}\text{S}$-negative cores ($-1.2$ to $-0.4 \%$) and $\Delta^{33}\text{S}$-negative rims ($-1.2$ to $-0.6 \%$), (3) cores with $\Delta^{33}\text{S}$ near $0$ ($-0.04$ to $0.03 \%$) and $\Delta^{33}\text{S}$-negative rims ($-0.7$ to $-0.5 \%$), and (4) both cores and rims with $\Delta^{33}\text{S}$ near $0$ ($-0.2$ to $0.2 \%$).

Pyrites with no internal texture show three groups of multiple sulfur isotopic compositions (Table S-3, Fig. S-8). The majority exhibits negative $\delta^{34}\text{S}$ ($-22$ to $-3 \%$), negative $\Delta^{33}\text{S}$ ($-1.4$ to $-0.3 \%$) and positive $\Delta^{36}\text{S}$ ($0.04$ to $1.3 \%$). A minority shows $\Delta^{33}\text{S}$ close to $0$ ($-0.3$ to $0.3 \%$), with corresponding small magnitudes of $\Delta^{36}\text{S}$ ($-0.3$ to $0.1 \%$) and $\delta^{34}\text{S}$ ($-7$ to $-0.8 \%$). Homogeneous pyrites with positive $\Delta^{33}\text{S}$ ($0.4$ to $3.6 \%$) have also been observed, with negative $\Delta^{36}\text{S}$ of $-2.9$ to $-0.8 \%$ and $\delta^{34}\text{S}$ of $-8$ to $5 \%$.

5.2. Dependence on pyrite petrography

Py-ii show variable multiple sulfur isotopic compositions mostly via the core-rim textures. They have $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ of positive, negative, and near $0$ (Table S-3, Fig. S-9).

In contrast, Py-iii to vi are characterised by negative $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ and positive $\Delta^{36}\text{S}$, with only a few exceptions; Py-vii display characteristic higher positive $\Delta^{33}\text{S}$, with corresponding positive $\delta^{34}\text{S}$ and negative $\Delta^{36}\text{S}$ (Table S-3, Fig. S-9).

Py-viii in hydrothermally altered komatiitic basalt (PDP2b_102.26–102.27 m) exhibit negative $\Delta^{33}\text{S}$ with positive $\delta^{34}\text{S}$ (Table S-3, Fig. S-9).
6. The Dilution of S-MIF in Original Photochemical Products

The magnitudes of sequestered Δ³³S in barite and G1 pyrite are significantly smaller than those in the original photochemical products, particularly positive Δ³³S compared to other locations and Archaean periods where and when Δ³³S of up to 14 ‰ has been recorded (Philippot et al., 2012; Williford et al., 2016). The negative Δ³³S of barite can have been diluted in the atmosphere and/or water mass by sulfate derived from disproportionation of (1) SO₂ erupted during submarine and subaerial volcanisms (Bao et al., 2007; Ueno et al., 2008; Ohmoto, 2020), and (2) Δ³³S-positive elemental sulfur produced by photochemical reactions of gaseous sulfur species (Ono et al., 2003). The dilution of positive Δ³³S is mainly caused by S₈ produced by photo-oxidation of H₂S erupted during volcanism (Halevy, 2013).

The processes of pyrite formation can also contribute to the dilution of S-MIF. Pyrites with negative Δ³³S are more likely to be formed via the sulfide pathway (Fe²⁺ + S²⁻ = [FeS], [FeS] + H₂S = FeS₂ + H₂; Rickard and Luther, 1997). S²⁻/H₂S are derived directly from magmatic H₂S (abundant in the Dresser hydrothermal system, Ueno et al., 2008 and references therein) or reduction of Δ³³S-negative/0 sulfate, thus the negative Δ³³S can be diluted by magmatic H₂S. Additionally, the process of sulfate reduction, be it thermochemical or microbial, can induce slightly positive Δ³³S (Johnston et al., 2007; Oduro et al., 2011), which thus dilute the negative Δ³³S to some extent. The pyrites carrying positive Δ³³S are most likely to be formed via the polysulfide pathway FeS + S⁻ⁿ⁺ = FeS₂ + S⁻ⁿ⁻ (n ≥ 5; Rickard, 1975; Luther, 1990). The sulfur of polysulfide pathway-formed pyrite is derived entirely from polysulfide (Sn²⁻; Butler et al., 2004). The S⁻² combined with elemental sulfur forming polysulfide (Sn⁻¹ + S²⁻ = Sn⁻₂⁻) can be derived from magmatic H₂S or sulfate (Δ³³S-negative/0) reduction. As such, the original positive Δ³³S in elemental sulfur are diluted by magmatic H₂S and/or S²⁻ derived from reduction of Δ³³S-negative sulfate during the sequestration in G1 pyrites. Furthermore, G1 pyrites are mostly euhedral, and larger in size compared with the adjacent fine grains (Fig. S-2), suggesting possible recrystallisation. The process of recrystallisation can homogenise, and to some degree, dilute Δ³³S (Halevy, 2013 and references therein).

7. Pyrites with Positive Δ³³S and Negative δ³⁴S

...
A small proportion of Py-ii to vi are characterised by positive $\Delta^{33}\text{S}$ and negative $\delta^{34}\text{S}$. Such multiple sulfur isotope systematics have been reported in Philippot et al. (2007) and Philippot et al. (2012) for the 3.49 Ga Dresser Formation and the 3.24 to 3.26 Ga Mapepe Formation. The slightly to moderately positive $\Delta^{33}\text{S}$ and negative $\delta^{34}\text{S}$ measured in macroscopic pyrites of Dresser Formation are interpreted to be formed via reduction or disproportionation of elemental sulfur, and the considerably positive $\Delta^{33}\text{S}$ and negative $\delta^{34}\text{S}$ of microscopic pyrites in Dresser Formation are thought to be generated by microbial elemental sulfur disproportionation (Philippot et al., 2007). The slightly to extremely positive $\Delta^{33}\text{S}$ and negative $\delta^{34}\text{S}$ values discovered in the ash layer of Mapepe Formation are explained as a single S-MIF source with most sulfur species products as sulfate and minor as elemental sulfur and no further reequilibration with a non-atmospheric, mass-dependent chemical process (Philippot et al., 2012). However, the magnitudes of the positive $\Delta^{33}\text{S}$ and negative $\delta^{34}\text{S}$ in this study are significantly smaller. Taking the uncertainties (both internal error and reproducibility of the primary reference material Ruttan pyrite in associated analytical session) into account, the majority are close to 0 ($\delta^{34}\text{S} [\%o], \Delta^{33}\text{S} [%o]$): $(-0.22 \pm 0.50, 0.86 \pm 0.21)$, $(-1.76 \pm 1.23, 0.53 \pm 0.29)$, $(-1.48 \pm 1.14, 0.42 \pm 0.29)$, $(-1.51 \pm 1.12, 0.33 \pm 0.31)$, $(-2.35 \pm 1.23, 0.19 \pm 0.30)$, $(-2.17 \pm 1.28, 0.15 \pm 0.33)$, $(-1.21 \pm 0.45, 0.24 \pm 0.44)$, $(-1.51 \pm 1.12, 0.33 \pm 0.31)$, $(-2.50 \pm 0.61, 0.20 \pm 0.26)$, $(-1.98 \pm 0.41, 0.10 \pm 0.11)$, $(-2.98 \pm 0.73, 0.12 \pm 0.25)$, $(-2.80 \pm 0.73, 0.11 \pm 0.25)$, $(-4.01 \pm 1.13, 0.26 \pm 0.29)$, $(-0.79 \pm 1.10, 0.22 \pm 0.32)$, $(-1.54 \pm 0.60, 0.10 \pm 0.26)$, $(-1.31 \pm 0.59, 0.20 \pm 0.27)$, $(-8.38 \pm 1.56, 0.47 \pm 0.52)$. The two data points of ($-0.72 \pm 1.11 \%o$, $0.56 \pm 0.29 \%o$) and ($-3.85 \pm 1.47 \%o$, $1.50 \pm 0.38 \%o$) are noticed to have unavoidably involved slightly of the core ($1.55 \pm 1.12 \%o$, $1.46 \pm 0.30 \%o$) and the rim ($-17.94 \pm 0.97 \%o$, $-1.22 \pm 0.31 \%o$), respectively, during analyses. Based on the positive correlation between $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ for G1 ($\Delta^{33}\text{S}$-positive generation of pyrites) indicative of mixing between S-MIF end member ($\Delta^{33}\text{S}$-positive elemental sulfur) and magmatic sulfur end member, the slightly positive $\Delta^{33}\text{S}$ in these $\Delta^{33}\text{S}$-positive and $\delta^{34}\text{S}$-negative pyrites in this study is more likely to be derived from mixing between minor $\Delta^{33}\text{S}$-positive sulfur and major magmatic sulfur, and the slightly negative $\delta^{34}\text{S}$ can be of erupted H$_2$S mixed with H$_2$S derived from disproportionation of erupted SO$_2$. 
## Supplementary Tables

### Table S-1  Descriptions of the drill core sections investigated in this study.

<table>
<thead>
<tr>
<th>Drill core section</th>
<th>Drill core&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Location</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDP2c_97.17–97.20 m</td>
<td>PDP2c 21°10'34.5''S, 119°25'51''E</td>
<td>Grey prismatic barite with irregular sulfide (mainly pyrite, minor sphalerite) laminae and silica veinlets. Barite is partly transected by silica veinlets of variable width. Pyrite occurs as (1) tiny grains aligned in an array within barite (Py-i), (2) pyrite laminae (Py-ii), (3) individual grains or clusters in or on the wall of silica veinlets (Py-iii, iv), (4) individual grains adjacent to both barite and silica (Py-v), and (5) individual grains in barite (larger than the tiny grains) (Py-vi).</td>
<td></td>
</tr>
<tr>
<td>PDP2b_90.94–90.97 m</td>
<td>PDP2b 21°10'34''S, 119°25'50.9''E</td>
<td>Chert with barite crystal fans. Pyrite occurs as (1) disseminated grains in chert (Py-vii), (2) clusters or individual grains in or on the wall of silica veinlets (Py-iii, iv), (3) individual grains within barite (Py-vi), and (4) individual grains adjacent to both barite and silica (Py-v).</td>
<td></td>
</tr>
<tr>
<td>PDP2b_94.69–94.74 m</td>
<td>PDP2b 21°10'34''S, 119°25'50.9''E</td>
<td>Vein barite. Relatively pure grey prismatic barite with minor silica veinlets. Only a small amount of pyrite grains occur. They are associated with the silica veinlets, in or on the wall of veinlets (Py-iii, iv), adjacent to both barite and silica (Py-v), and within barite (Py-vi).</td>
<td></td>
</tr>
<tr>
<td>PDP2b_102.26–102.27 m</td>
<td>PDP2b 21°10'34''S, 119°25'50.9''E</td>
<td>Hydrothermally altered komatiitic basalt with silica-barite-carbonate veins. Pyrite occurs as euhedral coarse grains in the veins (Py-viii).</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Detailed drill core descriptions are available in Van Kranendonk et al. (2008).
Table S-2  Acquisition conditions of SHRIMP-SI.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Big-spot analyses</th>
<th>Small-spot analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot size</td>
<td>ca. 27 × 20 μm</td>
<td>ca. 18 × 15 μm</td>
</tr>
<tr>
<td>Sets</td>
<td>4 or 5</td>
<td>2</td>
</tr>
<tr>
<td>Scans</td>
<td>40 or 50</td>
<td>20</td>
</tr>
<tr>
<td>Total analytical time</td>
<td>ca. 21 or 26 min</td>
<td>ca. 13 min</td>
</tr>
<tr>
<td>Source slit width</td>
<td>60 μm</td>
<td>60 μm</td>
</tr>
<tr>
<td>Collector slit width for $^{32}$S$^-$</td>
<td>300 μm</td>
<td>300 μm</td>
</tr>
<tr>
<td>Collector slit width for $^{33}$S$^-$</td>
<td>150 μm</td>
<td>150 μm</td>
</tr>
<tr>
<td>Collector slit width for $^{34}$S$^-$</td>
<td>200 μm</td>
<td>200 μm</td>
</tr>
<tr>
<td>Collector slit width for $^{36}$S$^-$</td>
<td>300 μm</td>
<td>300 μm</td>
</tr>
<tr>
<td>Mass resolution (at 10 % peak height)</td>
<td>4000 M/ΔM</td>
<td>4000 M/ΔM</td>
</tr>
<tr>
<td>Primary beam ion species</td>
<td>Cs$^+$</td>
<td>Cs$^+$</td>
</tr>
<tr>
<td>Primary beam energy</td>
<td>15 keV</td>
<td>15 keV</td>
</tr>
<tr>
<td>Primary beam intensity</td>
<td>ca. 7 nA</td>
<td>ca. 2 nA</td>
</tr>
<tr>
<td>Total acceleration voltage for the extraction of secondary ions</td>
<td>10 kV</td>
<td>10 kV</td>
</tr>
<tr>
<td>Amplifier and V-F Converter range for $^{32}$S$^-$</td>
<td>Electrometer current mode, 10$^{11}$ Ω, 0–50 V</td>
<td>Electrometer current mode, 10$^{11}$ Ω, 0–50 V</td>
</tr>
<tr>
<td>Amplifier and V-F Converter range for $^{33}$S$^-$</td>
<td>Electrometer current mode, 10$^{11}$ or 10$^{12}$ Ω, 0–50 V</td>
<td>Electrometer current mode, 10$^{11}$ or 10$^{12}$ Ω, 0–50 V</td>
</tr>
<tr>
<td>Amplifier and V-F Converter range for $^{34}$S$^-$</td>
<td>Electrometer current mode, 10$^{11}$ or 10$^{12}$ Ω, 0–50 V</td>
<td>Electrometer current mode, 10$^{11}$ or 10$^{12}$ Ω, 0–50 V</td>
</tr>
<tr>
<td>Amplifier and V-F Converter range for $^{36}$S$^-$</td>
<td>Electrometer charge mode, 22 pF, 0–50 V</td>
<td>Electrometer charge mode, 22 pF, 0–50 V</td>
</tr>
</tbody>
</table>
Table S-3  Summarised quadruple and triple sulfur isotopic compositions of pyrites in the Dresser Formation.

<table>
<thead>
<tr>
<th>Pyrite</th>
<th>N</th>
<th>( \delta^{34}S ) (‰)</th>
<th>( \Delta^{33}S ) (‰)</th>
<th>( \Delta^{36}S ) (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite internal texture-specific</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cores</td>
<td>30</td>
<td>0.77</td>
<td>2.12</td>
<td>16</td>
</tr>
<tr>
<td>Rims</td>
<td>24</td>
<td>-5.15</td>
<td>-0.22</td>
<td>14</td>
</tr>
<tr>
<td>Homogeneous</td>
<td>99</td>
<td>-18.86</td>
<td>-0.72</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.39</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-21.45</td>
<td>-0.79</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.70</td>
<td>5.09</td>
<td>9</td>
</tr>
<tr>
<td>Pyrite petrography-specific</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite laminae (Py-ii)</td>
<td>65</td>
<td>-10.40</td>
<td>-0.22</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.70</td>
<td>2.12</td>
<td>18</td>
</tr>
<tr>
<td>Pyrite associated with silica veinlets (Py-iii, iv, v)</td>
<td>70</td>
<td>-21.45</td>
<td>-0.79</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite in barite (Py-vi)</td>
<td>9</td>
<td>-18.99</td>
<td>-1.54</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite in chert with barite crystal fans (Py-vii)</td>
<td>6</td>
<td>2.81</td>
<td>5.09</td>
<td>6</td>
</tr>
<tr>
<td>Pyrite in silica-barite-carbonate vein in hydrothermally altered komatitic basalt (Py-viii)</td>
<td>2</td>
<td>1.67</td>
<td>2.39</td>
<td>2</td>
</tr>
</tbody>
</table>

\(a\) Pyrite in silica-barite-carbonate vein in hydrothermally altered komatitic basalt.

\(b\) One rim analysis shows \(\Delta^{33}S\) of 0.56 was due to slight involvement of \(\Delta^{33}S\)-positive core (this analysis was abandoned).

Table S-4  All multiple sulfur isotope data obtained by SHRIMP-SI (all combined).

The data table is available for download (Excel file) at https://www.geochemicalperspectivesletters.org/article2113.

Table S-5  All multiple sulfur isotope data obtained by SHRIMP-SI (each session).

The data table is available for download (Excel file) at https://www.geochemicalperspectivesletters.org/article2113.

Table S-6  All the data in literature compiled in the figures of main text and Supplementary Information.

The data table is available for download (Excel file) at https://www.geochemicalperspectivesletters.org/article2113.
Supplementary Figures

Figure S-1  Photographs of drill core sections investigated in this study.
**Figure S-2**  BSE images ((f) is SE image) and photomicrographs (insets in (a, b)) showing pyrites Py-i to viii. Py-i: tiny pyrite grains aligned in an array within barite; Py-ii: pyrite lamina; Py-iii: pyrite in the silica veinlet in barite; Py-iv: pyrite on the wall of silica veinlet in barite; Py-v: pyrite adjacent to barite and silica; Py-vi: pyrite in barite with silica veinlets and beads; Py-vii: pyrite in chert with barite crystal fans; Py-viii: pyrite in silica-barite-carbonate vein in hydrothermally altered komatiitic basalt. Py: pyrite; Ba: barite; Si: silica; C: carbonate; S: silicate; Ba-s: barium-bearing silicate.
Figure S-3  Photomicrographs and BSE images showing the internal textures of pyrites. (a) Core-rim textured tiny pyrite grains aligned in an array within barite (PDP2c_97.17–97.20 m). (b–e) BSE images and (g–i) reflected-light photomicrographs of NaOCl-etched pyrites showing core-rim textured pyrites in pyrite laminae (PDP2c_97.17–97.20 m). (f) Photomicrograph in reflected light (NaOCl-etched) of core-rim textured pyrites within barite (PDP2b_94.69–94.74 m). Note that the colour of etched pyrites can be variable, depending on the duration of etching and the NaOCl concentration of sodium hypochlorite solution. The objective of etching is to reveal the internal texture of pyrite, i.e. the relative differences in colour of individual pyrites, thus the specific etching colour does not matter as long as the internal textures can be revealed.
Figure S-4  (a–d) Raman spectra of carbonaceous material inclusions in pyrites (Py-ii, iv, vi, G2’, G1, G2).  (g–k) EDS spectra of Ni-bearing Δ33S-negative (porous core, the first mantle, and non-porous rim of Py-ii) and Ni-free Δ33S-positive (Py-vii, and the second mantle of Py-ii) pyrites indicated in (e, f).
Figure S-5  Plots of $\delta^{34}S$–$\delta^{33}S$ and $\delta^{34}S$–$\delta^{36}S$, along with their respective mass dependent fractionation lines of $y = 0.515x$ and $y = 1.90x$. 
Figure S-6  $\delta^{34}\text{S}-\Delta^{33}\text{S}$ plots of pyrites from PDP2b (three sections) and PDP2c (one section). Error bars are the average $1\sigma$ of the plotted spots. $1\sigma$ for each spot is calculated following $[(\text{SE})^2 + (\text{SD})^2]^{0.5}$, where SE is standard error of each spot, and SD is standard deviation of Ruttan pyrite analyses in the associated session.
Figure S-7  $\Delta^{33}S$-$\Delta^{36}S$ plots of pyrites from PDP2b (two sections) and PDP2c (one section). Error bars are the average 1σ of the plotted spots. Archaean Reference Array: $\Delta^{36}S \approx -\Delta^{33}S$ (Farquhar et al., 2001). Biological Fractionation Line: $\Delta^{36}S \approx -7\Delta^{33}S$ (Ono et al., 2006).
Figure S-8  δ^{34}S-Δ^{33}S and Δ^{33}S-Δ^{36}S plots of the data for cores and rims of core-rim textured pyrites and pyrites with no internal texture. The data include the results of both big-spot and small-spot analyses. Error bars are the average 1σ of the plotted spots. Compiled data of previous studies (Philippot et al., 2007, 2012; Ueno et al., 2008; Shen et al., 2009; Wacey et al., 2015; Muller et al., 2016; Baumgartner et al., 2020) on the Dresser Formation are also plotted for comparison. Bulk data of barite are from Ueno et al. (2008) and Shen et al. (2009); in situ data of barite are from Muller et al. (2016).
Figure S-9  \( \delta^{34}S - \Delta^{33}S \) and \( \Delta^{33}S - \Delta^{36}S \) plots of the data for pyrites of different petrography in the Dresser Formation. The data include the results of both big-spot and small-spot analyses. Error bars are the average 1σ of the plotted spots.
Figure S-10  $\Delta^{33}S$-$\Delta^{36}S$ plots for (a) barites and G1 pyrites, (b) G1 pyrites, (c) barites and G2 pyrites. The data of barites are from Ueno et al. (2008), Shen et al. (2009) and Muller et al. (2016). Error bars are the average 1σ of the plotted spots.
Figure S-11  A compilation of δ^{34}S, Δ^{33}S, and Δ^{36}S of pyrite and barite from the drill cores PDP2b and PDP2c in literature (open symbols; Philippot et al., 2007, 2012; Muller et al., 2016; Baumgartner et al., 2020) and this study (filled symbols). The stratigraphic columns are modified from Van Kranendonk et al. (2008). Micro-Py: microscopic pyrite; Macro-Py: macroscopic pyrite; VS-Py: pyrite in volcaniclastic sandstone; BCV-Py: pyrite in black chert vein; BCar-Py: pyrite in bedded carbonate; KB-Py: pyrite in komatiitic basalt; NaP-Py: nano-porous pyrite; NonP-Py: non-porous pyrite; inbarite-Py: pyrite within barite. Py-ii: pyrite lamina; Py-iii: pyrite in the silica veinlet in barite; Py-iv:
pyrite on the wall of silica veinlet in barite; Py-v: pyrite adjacent to both barite and silica; Py-vi: pyrite in barite with silica veinlets and beads; Py-vii: pyrite in chert with barite crystal fans; Py-viii: pyrite in silica-barite-carbonate veins in hydrothermally altered komatiitic basalt. Note the absence of Members 3 and 4 in PDP2b and Member 4 in PDP2c.
Supplementary Information References


