Anomalous isotopes trace sulfur and gold pathways in magmatic arcs

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Abstract

Sulfur plays a crucial role in numerous Earth processes: it is central to metabolic synthesis and biological evolution\textsuperscript{1}, its variable concentration in the oceans and atmosphere significantly affects the global climate\textsuperscript{2}, and it is the most important carrier for precious metals accumulated in ore deposits\textsuperscript{3}. Sulfur is transferred among different geochemical reservoirs in arcs, which are the geological expression of subduction processes at convergent plate boundaries. However, a clear understanding of the transport mechanism of sulfur has been obscured by a lack of distinct markers to uniquely fingerprint this element and trace its pathway in arcs\textsuperscript{4,5}. These knowledge gaps are addressed in this study by examining the indelible nature of the mass-independent fractionation of sulfur (MIF-S) prior to 2.5 billion years ago, in the Archaean eon. This fractionation process led to the formation of rocks with anomalous sulfur isotope signatures\textsuperscript{6-8}. Just as radio-isotope dyes are used in the medical sciences to map the intricate pathways of the inner human body, we have traced the MIF-S anomalous signature to illuminate the pathway of sulfur through the Earth’s upper mantle and crust in the ca. 2 billion year old Glenburgh arc in Western Australia. Results from high-precision sulfur isotope analysis indicate that the breakdown of MIF-S-bearing pyrite in sediments from the Yilgarn Craton that subducted beneath the Glenburgh arc released sulfur that mixed with sulfur derived from seawater sulfate minerals. The resulting MIF-S-bearing fluid migrated through the mantle and crust, transporting the gold that is found in the Glenburgh gold deposit. These findings revolutionise the current knowledge of the sulfur cycle on Earth and may lead to a step change in the understanding of the planetary flux of volatiles and metals.
Main Body

The Earth’s crust represents a complex and dynamically evolving chemical interface between two convective fluid systems: the endosphere (linked core and mantle) and the exosphere (linked hydrosphere and atmosphere). The nature of the physical and chemical processes that occur on the surface of the planet are intimately linked by the energy available from sharp chemical and thermal gradients that exist across this interface. The flux of volatiles and metals from the endosphere through to the exosphere is best recorded in *arcs*, which are the *natural factories* where juvenile continental crust is formed, where explosive volcanic eruptions emit large quantities of sulfur-bearing gases into the atmosphere\(^9\), and where significant concentrations of precious metals are accumulated in sulfide-rich rocks\(^5\).

This study focuses on the ca. 2 billion year old (Ga) Glenburgh sulfide-bearing gold deposit in Western Australia, which formed when the Glenburgh Terrane collided with the Yilgarn Craton resulting in a period of subduction and magmatism and in the progressive closure of an ocean\(^{10,11}\). This geodynamic scenario occurred in the Paleoproterozoic (2.5–1.6 billion years ago), when our planet underwent profound and irreversible changes. These changes included the development of a complex life-supporting oxygenated atmosphere\(^{12}\) and the generation of new continental crust\(^{13}\) in environments akin to modern *arcs*\(^{12}\), where Archaean blocks collided and amalgamated into the supercontinent Columbia\(^ {14}\). In these settings, significant amounts of volatiles and metals were circulated and focused to form some of the largest ore deposits on Earth\(^5\).

Our natural laboratory, the Glenburgh sulfide-bearing gold deposit, is hosted within <2.04 Ga metasedimentary rafts in the ca. 2.0 Ga Dalgaringa Supersuite, which intrudes the Glenburgh Terrane\(^ {10}\). The deposit formed between 2.04 Ga and 1.99 Ga\(^ {11}\), synchronous with subduction and *arc* magmatism\(^ {10}\). In order to constrain the link between the sulfur cycle, precious metal transport, and the geodynamic evolution of the Glenburgh *arc*, thirty-six samples were obtained from the Glenburgh gold deposit and from nearby intercalated magmatic rocks of the Dalgaringa Supersuite to investigate their multiple sulfur isotopic signatures. Analyses were performed at the Stable
Isotope Laboratory at McGill University, Canada. Sulfide-bearing samples were microdrilled to generate a pure sulfide powder, whereas sulfide-free but sulfur-bearing whole rocks were milled into a fine powder so as to facilitate extraction of the sulfur disseminated in the mineralogy of the rocks. Both powder suites were dissolved and analysed by gas fluorination mass spectrometry\(^{15}\).

We investigated two multiple sulfur isotope signatures: 1) the mass-dependent fractionation of sulfur (defined as \(\delta^{34}\)S), which is sensitive to physical processes that occur during the hydrothermal circulation of fluids\(^{16}\); and 2) the mass-independent fractionation of sulfur (MIF-S; defined as \(\Delta^{33}\)S and \(\Delta^{36}\)S)\(^{6}\), which is a chemically conservative signature that fingerprints the source of sulfur through a wide range of geological processes\(^{17}\). Non-zero \(\Delta^{33}\)S and \(\Delta^{36}\)S values, reflected in the fractionation of \(^{33}\)S and \(^{36}\)S away from the mass-dependent fractionation relationship, were generated by the bombardment of S-bearing gases by short wavelength UV rays in the oxygen-poor Archaean atmosphere, prior to the Great Oxygenation Event (GOE) at 2.45 Ga\(^{6,7,18}\). The photochemical products of these reactions led to positive \(\Delta^{33}\)S values in sedimentary pyrite and negative \(\Delta^{33}\)S in reservoirs derived from oceanic sulfate\(^{8}\). Once formed in the Archaean, these non-zero MIF-S signatures cannot be erased, only diluted in the terrestrial and marine geological record.

The analysed samples yielded \(\Delta^{33}\)S values ranging from 0.22\(\%\) to 0.82\(\%\) (uncertainties on \(\Delta^{33}\)S below \(\pm\) 0.01\(\%\)), \(\Delta^{36}\)S values from -0.91\(\%\) to 0.27\(\%\) (uncertainties on \(\Delta^{36}\)S below \(\pm\) 0.1\(\%\)) and \(\delta^{34}\)S values between 1.8\(\%\) and 11.6\(\%\) (uncertainties on \(\delta^{34}\)S below \(\pm\) 0.15\(\%\); Fig. 1). The Halfway Gneiss, the ca. 2.5 Ga basement rock that hosts the Dalgaringa Supersuite and the Glenburgh gold deposit, yielded sulfur contents below the extraction threshold (<50 parts per million). The linear slope of the relationship between \(\Delta^{36}\)S and \(\Delta^{33}\)S in the sulfide-bearing samples and associated magmatic rocks of the ca. 2.0 Ga Dalgaringa Supersuite is -1.361, which fits well within the Archaean reference array of MIF-S measurements\(^{7}\). These results are unexpected as the Glenburgh sulfide-bearing gold mineralisation and nearby magmatic rocks display MIF-S signatures that are among the largest documented anomalies in rocks formed after the GOE\(^{7}\).
This opens up the question of how these anomalous MIF-S signatures were recorded and preserved in a gold deposit that formed in a Proterozoic arc. It has been suggested that anomalous $\Delta^{33}S$ fractionation may be generated by thermochemical sulfate reduction, where $SO_4^{2-}$ is reduced by amino acids to $H_2S$\textsuperscript{19}. However, the experimental simulations of that process\textsuperscript{20} are not able to reproduce the large deviations in both $\Delta^{33}S$ and $\Delta^{36}S$ that are observed in this study. A more likely mechanism to generate the positive $\Delta^{33}S$ anomaly is through the involvement of $S_8$ colloids exposed to a pre-2.45 Ga atmosphere, where they underwent high wavelength UV photochemical reactions\textsuperscript{6}. In the Archaean eon, these $S_8$ colloids were deposited as sediment-hosted pyrite at the bottom of the water column in iron- and carbon-rich shales\textsuperscript{8}. Thus, the $\Delta^{33}S$ values recorded in the ca. 2.0 Ga Glenburgh gold deposit and surrounding Dalgaringa Supersuite are indicative of the input of Archaean shale-derived sedimentary pyrite\textsuperscript{8}.

The conundrum lies in the fact that the rocks that host the Glenburgh gold deposit are largely Proterozoic in age, and hence are not likely the original sources of MIF-S. The only Archaean unit in the observed stratigraphy is the ca. 2.5 Ga Halfway Gneiss, which comprises the regional country rocks that host the Dalgaringa Supersuite and the Glenburgh gold deposit. However, it is improbable that the Halfway Gneiss contributed to the sulfur isotope signature recorded in the Glenburgh gold deposit for two reasons: 1) it has a very low sulfur content (<50 parts per million), and 2) it is an orthogneiss with a granitic protolith\textsuperscript{21,22} and as such it is unlikely to contain any Archaean surface-derived sulfur. We present here a compelling model to explain the observed large MIF-S signatures in the Proterozoic Glenburgh gold deposit.

This model is based upon the observation that multiple sulfur isotope data spread along a mixing line between two end-member sulfur reservoirs in $\delta^{34}S$-$\Delta^{33}S$ space (Fig. 1). The first end-member reservoir is Archaean shale-derived sedimentary pyrite ($\delta^{34}S = \leq 0\%o; \Delta^{33}S = \geq 1\%o$), whereas the second end-member is sulfur derived from seawater sulfate at ca. 2.0 Ga ($\delta^{34}S = 20\%o; \Delta^{33}S = 0\%o$)\textsuperscript{23}. We argue that the first end-member reservoir is likely to be derived from the metamorphic devolatilisation of Archaean pyritic carbonaceous sedimentary rocks of the Yilgarn Craton during
subduction below the Glenburgh Terrane, generating *arc* magmatism and mineralising fluids (Fig. 2). The second end-member reservoir of seawater-sourced sulfur can be explained by devolatilisation of Paleoproterozoic seawater-derived sulfate minerals contained in the subducted sediments\(^4\).

Mixing between the two distinct sulfur isotope reservoirs occurred during subduction of dense mafic crust located at the margin of the Archaean Yilgarn Craton\(^24\). Dehydration metamorphic reactions drove the breakdown of Archaean pyrite, hosted in the shale sediments overlying the subducting mafic crust, contemporaneously with the breakdown of ca. 2.0 Ga seawater-derived sulfate minerals. The resulting sulfur-rich hydrothermal fluids\(^25\) metasomatised the mantle wedge, driving partial melting of the sub-continental mantle lithosphere. Subsequently, mantle-derived melts containing the mixed isotopic signature ascended diapirically through the crust, undergoing crustal assimilation and fractional crystallization to form the buoyant andesitic magmas\(^5\), which crystallised as the large batholiths of the Dalgaringa Supersuite.

By constraining the source of sulfur, it is possible to also identify the source and transfer mechanisms of gold that operated in the Glenburgh *arc*. It has been suggested that the ultimate source of gold in continental *arc*-hosted gold deposits is from subducted carbon-rich sedimentary rocks\(^25\). However, this hypothesis has never been conclusively tested. Given the insoluble nature of gold (Au) in H\(_2\)O, it would have to be mobilised as an Au(HS)\(^2\) complex in fluids at high temperatures and pressures, such as those in *arc* magmatic environments\(^26\). Following this line of evidence, the ultimate source of gold should be the same as the source of sulfur, and the isotopic composition of sulfide in the deposit should reflect the isotopic signature of the subducted carbon-rich sedimentary rocks, consistent with the dataset presented in this study. Thus, it is argued that sulfide complexes were responsible for the transfer of sulfur and gold from the subducted crust into the mantle wedge, and from there to the large batholiths of the Dalgaringa Supersuite, from which mineralising fluids exsolved to form the Glenburgh gold deposit.
The data from this study provide new insights into the heavily debated topic of the mass balance problem between the known concentrations of sulfur and gold in the mantle wedge below arcs and the observed concentrations in arc magmas and associated mineralisation\textsuperscript{5, 26, 27, 28}. Isotope data indicate that the contribution of sulfur from the mantle wedge is minimal. In fact, if a hypothetical third isotopic reservoir for the depleted mantle displaying $\delta^{34}S = -1.3\%o$ and $\Delta^{33}S = 0\%o$\textsuperscript{29} was added, it would be apparent that the observed mixing line between the Archaean MIF-S-bearing reservoir and the Proterozoic seawater sulfate is not deflected towards the depleted mantle end member. By inference, it is possible to argue that the gold of the Glenburgh deposit is largely derived from the Archaean carbon-rich sedimentary rocks subducted underneath the Proterozoic Glenburgh arc, and not directly from the sulfides hosted in the mantle wedge\textsuperscript{29}.

The application of chemically conservative isotopic tracers such as $\Delta^{33}S$ is critical for a better understanding of magmatic and tectonic processes that drive fluid and metal transfer from Archaean cratons into their reworked margins, where some of the largest ore deposits on Earth formed and are currently preserved\textsuperscript{24}. At the Glenburgh deposit, multiple sulfur isotope data show that mixing between Archaean shale-derived pyrite sulfur with sulfur from Paleoproterozoic seawater-derived sulfate records the onset of continent-continent collision between the Glenburgh Terrane and the Yilgarn Craton. Hence, multiple sulfur isotope data are able to image a process that is cryptic to most other currently available datasets, showing that sulfur and metal cycling in arc settings occurs on very large scales, from the atmosphere-hydrosphere through to the lithosphere during crustal generation.
References


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End Notes

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Author Contributions

V.S, C.K.L. and M.L.F. wrote the paper and V.S. prepared the figures and tables. V.S, M.L.F and B.A.W. conceived the project. V.S. performed field work to obtain the samples and sample preparation. V.S and T.H.B. performed the S-isotope analyses on all samples. All authors participated in the discussion and interpretation of results, and preparation of the manuscript.

Author Information

The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to M.L.F (marco.fiorentini@uwa.edu.au)
Figure 1. $\Delta^{33}$S versus $\delta^{34}$S from the Glenburgh continental arc system (this study) compared to known S-isotope reservoirs\textsuperscript{7,18,23,29}. Error bars are smaller than the size of the point in all cases.
Figure 2. Schematic cross-section model (not to scale) of the gold mineralising process in the Glenburgh continental arc, which formed upon collision between the Glenburgh Terrane and Yilgarn Craton. Mixing of the two major sources of sulfur occurs in the partial melting zone. The mafic crust is thought to be similar to that reported on the eastern margin of the Yilgarn Craton.

24