

1 **Anomalous isotopes trace sulfur and gold pathways in magmatic arcs**

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6 **Abstract**

7 Sulfur plays a crucial role in numerous Earth processes: it is central to metabolic synthesis and
8 biological evolution¹, its variable concentration in the oceans and atmosphere significantly affects
9 the global climate², and it is the most important carrier for precious metals accumulated in ore
10 deposits³. Sulfur is transferred among different geochemical reservoirs in *arcs*, which are the
11 geological expression of subduction processes at convergent plate boundaries. However, a clear
12 understanding of the transport mechanism of sulfur has been obscured by a lack of distinct markers
13 to uniquely fingerprint this element and trace its pathway in *arcs*^{4,5}. These knowledge gaps are
14 addressed in this study by examining the indelible nature of the mass-independent fractionation of
15 sulfur (MIF-S) prior to 2.5 billion years ago, in the Archaean eon. This fractionation process led to
16 the formation of rocks with anomalous sulfur isotope signatures⁶⁻⁸. Just as radio-isotope dyes are
17 used in the medical sciences to map the intricate pathways of the inner human body, we have traced
18 the MIF-S anomalous signature to illuminate the pathway of sulfur through the Earth's upper
19 mantle and crust in the ca. 2 billion year old Glenburgh *arc* in Western Australia. Results from
20 high-precision sulfur isotope analysis indicate that the breakdown of MIF-S-bearing pyrite in
21 sediments from the Yilgarn Craton that subducted beneath the Glenburgh *arc* released sulfur that
22 mixed with sulfur derived from seawater sulfate minerals. The resulting MIF-S-bearing fluid
23 migrated through the mantle and crust, transporting the gold that is found in the Glenburgh gold
24 deposit. These findings revolutionise the current knowledge of the sulfur cycle on Earth and may
25 lead to a step change in the understanding of the planetary flux of volatiles and metals.

26 **Main Body**

27 The Earth's crust represents a complex and dynamically evolving chemical interface between two
28 convective fluid systems: the endosphere (linked core and mantle) and the exosphere (linked
29 hydrosphere and atmosphere). The nature of the physical and chemical processes that occur on the
30 surface of the planet are intimately linked by the energy available from sharp chemical and thermal
31 gradients that exist across this interface. The flux of volatiles and metals from the endosphere
32 through to the exosphere is best recorded in *arcs*, which are the *natural factories* where juvenile
33 continental crust is formed, where explosive volcanic eruptions emit large quantities of sulfur-
34 bearing gases into the atmosphere⁹, and where significant concentrations of precious metals are
35 accumulated in sulfide-rich rocks⁵.

36 This study focuses on the ca. 2 billion year old (Ga) Glenburgh sulfide-bearing gold deposit in
37 Western Australia, which formed when the Glenburgh Terrane collided with the Yilgarn Craton
38 resulting in a period of subduction and magmatism and in the progressive closure of an ocean^{10,11}.
39 This geodynamic scenario occurred in the Paleoproterozoic (2.5–1.6 billion years ago), when our
40 planet underwent profound and irreversible changes. These changes included the development of a
41 complex life-supporting oxygenated atmosphere¹² and the generation of new continental crust¹³ in
42 environments akin to modern *arcs*¹², where Archaean blocks collided and amalgamated into the
43 supercontinent Columbia¹⁴. In these settings, significant amounts of volatiles and metals were
44 circulated and focused to form some of the largest ore deposits on Earth⁵.

45 Our natural laboratory, the Glenburgh sulfide-bearing gold deposit, is hosted within <2.04 Ga
46 metasedimentary rafts in the ca. 2.0 Ga Dalgaringa Supersuite, which intrudes the Glenburgh
47 Terrane¹⁰. The deposit formed between 2.04 Ga and 1.99 Ga¹¹, synchronous with subduction and
48 *arc* magmatism¹⁰. In order to constrain the link between the sulfur cycle, precious metal transport,
49 and the geodynamic evolution of the Glenburgh *arc*, thirty-six samples were obtained from the
50 Glenburgh gold deposit and from nearby intercalated magmatic rocks of the Dalgaringa Supersuite
51 to investigate their multiple sulfur isotopic signatures. Analyses were performed at the Stable

52 Isotope Laboratory at McGill University, Canada. Sulfide-bearing samples were microdrilled to
53 generate a pure sulfide powder, whereas sulfide-free but sulfur-bearing whole rocks were milled
54 into a fine powder so as to facilitate extraction of the sulfur disseminated in the mineralogy of the
55 rocks. Both powder suites were dissolved and analysed by gas fluorination mass spectrometry¹⁵.

56 We investigated two multiple sulfur isotope signatures: 1) the mass-dependent fractionation of
57 sulfur (defined as $\delta^{34}\text{S}$), which is sensitive to physical processes that occur during the hydrothermal
58 circulation of fluids¹⁶; and 2) the mass-independent fractionation of sulfur (MIF-S; defined as $\Delta^{33}\text{S}$
59 and $\Delta^{36}\text{S}$)⁶, which is a chemically conservative signature that fingerprints the source of sulfur
60 through a wide range of geological processes¹⁷. Non-zero $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values, reflected in the
61 fractionation of ^{33}S and ^{36}S away from the mass-dependent fractionation relationship, were
62 generated by the bombardment of S-bearing gases by short wavelength UV rays in the oxygen-poor
63 Archaean atmosphere, prior to the Great Oxygenation Event (GOE) at 2.45 Ga^{6,7,18}. The
64 photochemical products of these reactions led to positive $\Delta^{33}\text{S}$ values in sedimentary pyrite and
65 negative $\Delta^{33}\text{S}$ in reservoirs derived from oceanic sulfate⁸. Once formed in the Archaean, these non-
66 zero MIF-S signatures cannot be erased, only diluted in the terrestrial and marine geological record.

67 The analysed samples yielded $\Delta^{33}\text{S}$ values ranging from 0.22‰ to 0.82‰ (uncertainties on $\Delta^{33}\text{S}$
68 below $\pm 0.01\text{‰}$), $\Delta^{36}\text{S}$ values from -0.91‰ to 0.27‰ (uncertainties on $\Delta^{36}\text{S}$ below $\pm 0.1\text{‰}$) and
69 $\delta^{34}\text{S}$ values between 1.8‰ and 11.6‰ (uncertainties on $\delta^{34}\text{S}$ below $\pm 0.15\text{‰}$; Fig. 1). The Halfway
70 Gneiss, the ca. 2.5 Ga basement rock that hosts the Dalgaringa Supersuite and the Glenburgh gold
71 deposit, yielded sulfur contents below the extraction threshold (<50 parts per million). The linear
72 slope of the relationship between $\Delta^{36}\text{S}$ and $\Delta^{33}\text{S}$ in the sulfide-bearing samples and associated
73 magmatic rocks of the ca. 2.0 Ga Dalgaringa Supersuite is -1.361, which fits well within the
74 Archaean reference array of MIF-S measurements⁷. These results are unexpected as the Glenburgh
75 sulfide-bearing gold mineralisation and nearby magmatic rocks display MIF-S signatures that are
76 among the largest documented anomalies in rocks formed after the GOE⁷.

77 This opens up the question of how these anomalous MIF-S signatures were recorded and preserved
78 in a gold deposit that formed in a Proterozoic *arc*. It has been suggested that anomalous $\Delta^{33}\text{S}$
79 fractionation may be generated by thermochemical sulfate reduction, where SO_4^{2-} is reduced by
80 amino acids to H_2S ¹⁹. However, the experimental simulations of that process²⁰ are not able to
81 reproduce the large deviations in both $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ that are observed in this study. A more likely
82 mechanism to generate the positive $\Delta^{33}\text{S}$ anomaly is through the involvement of S_8 colloids exposed
83 to a pre-2.45 Ga atmosphere, where they underwent high wavelength UV photochemical reactions⁶,
84 ⁸. In the Archaean eon, these S_8 colloids were deposited as sediment-hosted pyrite at the bottom of
85 the water column in iron- and carbon-rich shales⁸. Thus, the $\Delta^{33}\text{S}$ values recorded in the ca. 2.0 Ga
86 Glenburgh gold deposit and surrounding Dalgaringa Supersuite are indicative of the input of
87 Archaean shale-derived sedimentary pyrite⁸.

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

97 This model is based upon the observation that multiple sulfur isotope data spread along a mixing
98 line between two end-member sulfur reservoirs in $\delta^{34}\text{S}$ - $\Delta^{33}\text{S}$ space (Fig. 1). The first end-member
99 reservoir is Archaean shale-derived sedimentary pyrite ($\delta^{34}\text{S} = \leq 0\text{‰}$; $\Delta^{33}\text{S} = \geq 1\text{‰}$), whereas the
100 second end-member is sulfur derived from seawater sulfate at ca. 2.0 Ga ($\delta^{34}\text{S} = 20\text{‰}$; $\Delta^{33}\text{S} =$
101 0‰)²³. We argue that the first end-member reservoir is likely to be derived from the metamorphic
102 devolatilisation of Archaean pyritic carbonaceous sedimentary rocks of the Yilgarn Craton during

103 subduction below the Glenburgh Terrane, generating *arc* magmatism and mineralising fluids (Fig.
104 2). The second end-member reservoir of seawater-sourced sulfur can be explained by
105 devolatilisation of Paleoproterozoic seawater-derived sulfate minerals contained in the subducted
106 sediments⁴.

107 Mixing between the two distinct sulfur isotope reservoirs occurred during subduction of dense
108 mafic crust located at the margin of the Archaean Yilgarn Craton²⁴. Dehydration metamorphic
109 reactions drove the breakdown of Archaean pyrite, hosted in the shale sediments overlying the
110 subducting mafic crust, contemporaneously with the breakdown of ca. 2.0 Ga seawater-derived
111 sulfate minerals. The resulting sulfur-rich hydrothermal fluids²⁵ metasomatised the mantle wedge,
112 driving partial melting of the sub-continental mantle lithosphere. Subsequently, mantle-derived
113 melts containing the mixed isotopic signature ascended diapirically through the crust, undergoing
114 crustal assimilation and fractional crystallization to form the buoyant andesitic magmas⁵, which
115 crystallised as the large batholiths of the Dalgaringa Supersuite.

116 By constraining the source of sulfur, it is possible to also identify the source and transfer
117 mechanisms of gold that operated in the Glenburgh *arc*. It has been suggested that the ultimate
118 source of gold in continental *arc*-hosted gold deposits is from subducted carbon-rich sedimentary
119 rocks²⁵. However, this hypothesis has never been conclusively tested. Given the insoluble nature of
120 gold (Au) in H₂O, it would have to be mobilised as an Au(HS)₂⁻ complex in fluids at high
121 temperatures and pressures, such as those in *arc* magmatic environments²⁶. Following this line of
122 evidence, the ultimate source of gold should be the same as the source of sulfur, and the isotopic
123 composition of sulfide in the deposit should reflect the isotopic signature of the subducted carbon-
124 rich sedimentary rocks, consistent with the dataset presented in this study. Thus, it is argued that
125 sulfide complexes were responsible for the transfer of sulfur and gold from the subducted crust into
126 the mantle wedge, and from there to the large batholiths of the Dalgaringa Supersuite, from which
127 mineralising fluids exsolved to form the Glenburgh gold deposit.

128 The data from this study provide new insights into the heavily debated topic of the mass balance
129 problem between the known concentrations of sulfur and gold in the mantle wedge below *arcs* and
130 the observed concentrations in *arc* magmas and associated mineralisation^{5, 26, 27, 28}. Isotope data
131 indicate that the contribution of sulfur from the mantle wedge is minimal. In fact, if a hypothetical
132 third isotopic reservoir for the depleted mantle displaying $\delta^{34}\text{S} = -1.3\text{‰}$ and $\Delta^{33}\text{S} = 0\text{‰}$ ²⁹ was
133 added, it would be apparent that the observed mixing line between the Archaean MIF-S-bearing
134 reservoir and the Proterozoic seawater sulfate is not deflected towards the depleted mantle end
135 member. By inference, it is possible to argue that the gold of the Glenburgh deposit is largely
136 derived from the Archaean carbon-rich sedimentary rocks subducted underneath the Proterozoic
137 Glenburgh *arc*, and not directly from the sulfides hosted in the mantle wedge²⁹.

138 The application of chemically conservative isotopic tracers such as $\Delta^{33}\text{S}$ is critical for a better
139 understanding of magmatic and tectonic processes that drive fluid and metal transfer from Archaean
140 cratons into their reworked margins, where some of the largest ore deposits on Earth formed and are
141 currently preserved²⁴. At the Glenburgh deposit, multiple sulfur isotope data show that mixing
142 between Archaean shale-derived pyrite sulfur with sulfur from Paleoproterozoic seawater-derived
143 sulfate records the onset of continent-continent collision between the Glenburgh Terrane and the
144 Yilgarn Craton. Hence, multiple sulfur isotope data are able to image a process that is cryptic to
145 most other currently available datasets, showing that sulfur and metal cycling in *arc* settings occurs
146 on very large scales, from the atmosphere-hydrosphere through to the lithosphere during crustal
147 generation.

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221 **End Notes**

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232 **Author Contributions**

233 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
234 B.A.W. conceived the project. V.S. performed field work to obtain the samples and sample
235 preparation. V.S and T.H.B. performed the S-isotope analyses on all samples. All authors
236 participated in the discussion and interpretation of results, and preparation of the manuscript.

237 **Author Information**

238 The authors declare no competing financial interests. Readers are welcome to comment on the
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