

# 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 evolution<sup>1</sup>, its variable concentration in the oceans and atmosphere significantly affects  
9 the global climate<sup>2</sup>, and it is the most important carrier for precious metals accumulated in ore  
10 deposits<sup>3</sup>. 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*<sup>4,5</sup>. 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 signatures<sup>6-8</sup>. 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 atmosphere<sup>9</sup>, and where significant concentrations of precious metals are  
35 accumulated in sulfide-rich rocks<sup>5</sup>.

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<sup>10,11</sup>.  
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 atmosphere<sup>12</sup> and the generation of new continental crust<sup>13</sup> in  
42 environments akin to modern *arcs*<sup>12</sup>, where Archaean blocks collided and amalgamated into the  
43 supercontinent Columbia<sup>14</sup>. In these settings, significant amounts of volatiles and metals were  
44 circulated and focused to form some of the largest ore deposits on Earth<sup>5</sup>.

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 Terrane<sup>10</sup>. The deposit formed between 2.04 Ga and 1.99 Ga<sup>11</sup>, synchronous with subduction and  
48 *arc* magmatism<sup>10</sup>. 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 spectrometry<sup>15</sup>.

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 fluids<sup>16</sup>; and 2) the mass-independent fractionation of sulfur (MIF-S; defined as  $\Delta^{33}\text{S}$   
59 and  $\Delta^{36}\text{S}$ )<sup>6</sup>, which is a chemically conservative signature that fingerprints the source of sulfur  
60 through a wide range of geological processes<sup>17</sup>. Non-zero  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values, reflected in the  
61 fractionation of  $^{33}\text{S}$  and  $^{36}\text{S}$  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<sup>6,7,18</sup>. 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 sulfate<sup>8</sup>. 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 measurements<sup>7</sup>. 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 GOE<sup>7</sup>.

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  $\text{SO}_4^{2-}$  is reduced by  
80 amino acids to  $\text{H}_2\text{S}$ <sup>19</sup>. However, the experimental simulations of that process<sup>20</sup> 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  $\text{S}_8$  colloids exposed  
83 to a pre-2.45 Ga atmosphere, where they underwent high wavelength UV photochemical reactions<sup>6</sup>,  
84 <sup>8</sup>. In the Archaean eon, these  $\text{S}_8$  colloids were deposited as sediment-hosted pyrite at the bottom of  
85 the water column in iron- and carbon-rich shales<sup>8</sup>. 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 pyrite<sup>8</sup>.

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<sup>21,22</sup> 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  $0\text{‰}$ )<sup>23</sup>. 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 sediments<sup>4</sup>.

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 Craton<sup>24</sup>. 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 fluids<sup>25</sup> 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 magmas<sup>5</sup>, 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 rocks<sup>25</sup>. However, this hypothesis has never been conclusively tested. Given the insoluble nature of  
120 gold (Au) in H<sub>2</sub>O, it would have to be mobilised as an Au(HS)<sub>2</sub><sup>-</sup> complex in fluids at high  
121 temperatures and pressures, such as those in *arc* magmatic environments<sup>26</sup>. 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<sup>5, 26, 27, 28</sup>. 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  $\Delta^{33}\text{S} = 0\text{‰}$ <sup>29</sup> 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 wedge<sup>29</sup>.

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 preserved<sup>24</sup>. 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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153 **References**

- 154 1. Canfield, D. E., Habicht, K. S. & Thamdrup, B. The Archean Sulfur Cycle and the Early  
155 History of Atmospheric Oxygen. *Science* **288**, (2000).
- 156 2. Canfield, D. E. & Teske, A. Late Proterozoic rise in atmospheric oxygen concentration  
157 inferred from phylogenetic and sulphur-isotope studies. *Nature* **382**, 127–132 (1996).
- 158 3. Seo, J. H., Guillong, M. & Heinrich, C. A. The role of sulfur in the formation of magmatic-  
159 hydrothermal copper-gold deposits. *Earth Planet. Sci. Lett.* **282**, 323–328 (2009).
- 160 4. Tomkins, A. G. & Evans, K. A. Separate zones of sulfate and sulfide release from subducted  
161 mafic oceanic crust. *Earth Planet. Sci. Lett.* **428**, 73–83 (2015).
- 162 5. Richards, J. P. Magmatic to hydrothermal metal fluxes in convergent and collided margins.  
163 *Ore Geol. Rev.* **40**, 1–26 (2011).
- 164 6. Farquhar, J., Bao, H. & Thiemens, M. Atmospheric Influence of Earth's Earliest Sulfur  
165 Cycle. *Science* **289**, 756–758 (2000).
- 166 7. Johnston, D. T. Multiple sulfur isotopes and the evolution of Earth's surface sulfur cycle.  
167 *Earth-Science Rev.* **106**, 161–183 (2011).
- 168 8. Farquhar, J. *et al.* Pathways for NeoArchean pyrite formation constrained by mass-  
169 independent sulfur isotopes. *Proc. Natl. Acad. Sci.* **110**, 17638–17643 (2013).
- 170 9. Wallace, P. J. Volatiles in subduction zone magmas: Concentrations and fluxes based on  
171 melt inclusion and volcanic gas data. *J. Volcanol. Geotherm. Res.* **140**, 217–240 (2005).
- 172 10. Sheppard, S., Occhipinti, S. A. & Tyler, I. M. A 2005–1970 Ma Andean-type batholith in  
173 the southern Gascoyne Complex, Western Australia. *Precambrian Res.* **128**, 257–277  
174 (2004).
- 175 11. Roche, L. K. Unravelling the upper amphibolite to granulite facies hosted Glenburgh Au  
176 deposit- metamorphosed gold? Glenburgh Terrane, Gascoyne Province, Western Australia.  
177 (University of Western Australia, MSc Thesis, 2014).

- 178 12. Kump, L. R. & Barley, M. E. Increased subaerial volcanism and the rise of atmospheric  
179 oxygen 2.5 billion years ago. *Nature* **448**, 1033–1036 (2007).
- 180 13. Cawood, P. A., Hawkesworth, C. J. & Dhuime, B. The continental record and the generation  
181 of continental crust. *Geol. Soc. Am. Bull.* **125**, 14–32 (2013).
- 182 14. Rogers, J. J. W. & Santosh, M. Configuration of Columbia, a Mesoproterozoic  
183 Supercontinent. *Gondwana Res.* **5**, 5–22 (2002).
- 184 15. Canfield, D. E., Raiswell, R., Westrich, J. T., Reaves, C. M. & Berner, R. A. The use of  
185 chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales.  
186 *Chem. Geol.* **54**, 149–155 (1986).
- 187 16. Ohmoto, H. Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. *Econ.*  
188 *Geol.* **67**, 551–578 (1972).
- 189 17. Bekker, A. *et al.* Atmospheric sulfur in Archaean komatiite-hosted nickel deposits. *Science*  
190 **326**, 1086–1089 (2009).
- 191 18. Farquhar, J. & Wing, B. A. Multiple sulfur isotopes and the evolution of the atmosphere.  
192 *Earth Planet. Sci. Lett.* **213**, 1–13 (2003).
- 193 19. Ohmoto, H., Watanabe, Y., Ikemi, H., Poulson, S. R. & Taylor, B. E. Sulfur isotope  
194 evidence for an oxic Archaean atmosphere. *Nature* **442**, 908–911 (2006).
- 195 20. Oduro, H. *et al.* Evidence of magnetic isotope effects during thermochemical sulfate  
196 reduction. *Proceedings of the National Academy of Sciences* **108**, 17635–17638 (2011).
- 197 21. Cawood, P. A. & Tyler, I. M. Assembling and reactivating the Proterozoic Capricorn  
198 Orogen: Lithotectonic elements, orogenies, and significance. *Precambrian Res.* **128**, 201–  
199 218 (2004).
- 200 22. Johnson, S. P. *et al.* Crustal architecture of the Capricorn Orogen, Western Australia and  
201 associated metallogeny. *Aust. J. Earth Sci.* **60**, 681–705 (2013).



- 202 23. Planavsky, N. J., Bekker, A., Hofmann, A., Owens, J. D. & Lyons, T. W. Sulfur record of  
203 rising and falling marine oxygen and sulfate levels during the Lomagundi event. *Proc. Natl.*  
204 *Acad. Sci.* 1–6 (2012). doi:10.1073/pnas.1120387109
- 205 24. Mole, D. R. *et al.* Crustal evolution, intra-cratonic architecture and the metallogeny of an  
206 Archaean craton. *Geol. Soc. London, Spec. Publ.* **393**, (2013).
- 207 25. Tomkins, A. G. Windows of metamorphic sulfur liberation in the crust: Implications for  
208 gold deposit genesis. *Geochim. Cosmochim. Acta* **74**, 3246–3259 (2010).
- 209 26. Goldfarb, R. J. & Groves, D. I. Orogenic gold: Common or evolving fluid and metal sources  
210 through time. *Lithos* (2015). doi:10.1016/j.lithos.2015.07.011
- 211 27. De Hoog, J. C. M., Taylor, B. E. & Van Bergen, M. J. Sulfur isotope systematics of basaltic  
212 lavas from Indonesia: Implications for the sulfur cycle in subduction zones. *Earth Planet.*  
213 *Sci. Lett.* **189**, 237–252 (2001).
- 214 28. Labidi, J., Cartigny, P. & Moreira, M. Non-chondritic sulphur isotope composition of the  
215 terrestrial mantle. *Nature* **501**, 208–11 (2013).
- 216 29. Saunders, J. E., Pearson, N. J., O’Reilly, S. Y. & Griffin, W. L. Gold in the mantle: The role  
217 of pyroxenites. *Lithos* **244**, 205–217 (2016).
- 218 30. Ding, T. *et al.* Calibrated sulfur isotope abundance ratios three IAEA sulfur isotope  
219 reference materials and V-CDT with a reassessment of the atomic weight of sulfur.  
220 *Geochim. Cosmochim. Acta* **65**, 2433–2437 (2001).

## 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.

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