GR Focus Review

Investigating sulfur pathways through the lithosphere by tracing mass independent fractionation of sulfur to the Lady Bountiful orogenic gold deposit, Yilgarn Craton

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ABSTRACT

As sulfur is the primary complexing ligand for gold transport in aqueous fluids, recent work has demonstrated that the Archean systems can preserve mass independent fractionation of sulfur (MIF-S) to yield near-zero values ($\Delta^{33}S_1 = 0 \pm 0.5‰$). In such cases, interpretation of the geological significance of such isotopic signatures may be compromised as it is known that mass dependent fractionation of sulfur (MDF-S) can yield small $\Delta^{33}S$ values (herein as $\Delta^{33}S_B$) often owing to geobiological reactions involving sulfur. In this study, we reassess the range of possible values of $\Delta^{33}S_B$ from the traditionally accepted value of $0 \pm 0.2‰$, to demonstrate that this range is not constant but rather directly linked to the degree of $\delta^{34}S$ fractionation. We present a multiple sulfur isotope dataset from the Neoarchean Lady Bountiful orogenic gold deposit from the Yilgarn Craton, Western Australia. This deposit contains pyrite with an isotopic composition of $\delta^{34}S = \sim +2.1 \pm 0.8‰$ and $\Delta^{33}S = +0.14 \pm 0.06‰$ (2SD on the mean). The analysis of these results, as well as of a data compilation from other ~2.65 Ga orogenic gold deposits of the Yilgarn Craton, indicates that $\Delta^{33}S_1$ values are too large to be the result of purely MDF-S processes. In addition, when compared to a compilation of >3400 $\Delta^{33}S_0$ measurements of Archean sedimentary rocks, which shows highly variable positive and negative signals, the remarkably constant positive MIF-S_1 signature of gold deposits from the Yilgarn Craton, with $\Delta^{33}S_1$ values between 0 and +0.6‰, is evidence that the source of the auriferous fluids equilibrated at depth by mixing with a non MIF-S_0-bearing sulfur reservoir. By enhancing the application of MIF-S_1 ($\Delta^{33}S_1$) as a powerful and indelible tracer to understand the source and emplacement pathways of gold-bearing fluids through the lithosphere, the outcomes from this study demonstrate the recorded $+\Delta^{33}S_1$ signature in the auriferous fluids reflects the presence of sulfur that was at least partially sourced from an Archean sediment reservoir.

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1. Introduction

Sulfur can act as a volatile component of many geochemical reservoirs on Earth. Consequently, the complex sulfur cycle plays a critical role in a variety of fundamental Earth processes such as regulating the global climate, the living cell, and ore deposit formation. As organic and inorganic sulfur molecules break to form new bonds, the isotopes of sulfur undergo mass dependent fractionation (MDF-S) during chemical exchange between different S-bearing reservoirs through its planetary cycle. For example, MDF-S, expressed as

$$\delta^{34}S = \left[\frac{\left(^{34}S/^{32}S\right)_{sample} - \left(^{34}S/^{32}S\right)_{reference}}{\left(^{34}S/^{32}S\right)_{reference}} \right] \times 1000,$$

has enabled understanding of the redox evolution of the oceans and atmosphere through the Precambrian (Kump, 2012 and references therein).

Prior to the Great Oxygenation Event (GOE) at ca. 2.4 Ga, sulfur also underwent mass independent fractionation (MIF-S) in the atmosphere by photodissociation of SO_2 (Farquhar et al., 2000a, 2000b, 2001). These molecules were transported to the surface and preserved as MIF-S_0 in the sedimentary rock record as sulfate and sulfide minerals (Farquhar and Wing, 2003). The discovery of MIF-S_0 in Archean supracrustal rocks has significantly improved our understanding of the early Earth's surface processes by, in particular, elucidating the link between the emergence of life and the development of an oxygenated atmosphere (Farquhar et al., 2007; Kaufman et al., 2007). MIF-S_0 is quantified as $\Delta^{33}S_0$ or $\Delta^{36}S_0$ to represent dispersion from normal MDF-S following the equation:

$$\Delta^{x}S = \delta^{x}S_{measured} - \left[\left(\frac{\delta^{34}S_{measured}}{1000} + 1 \right)^{x\lambda} - 1 \right] \times 1000,$$
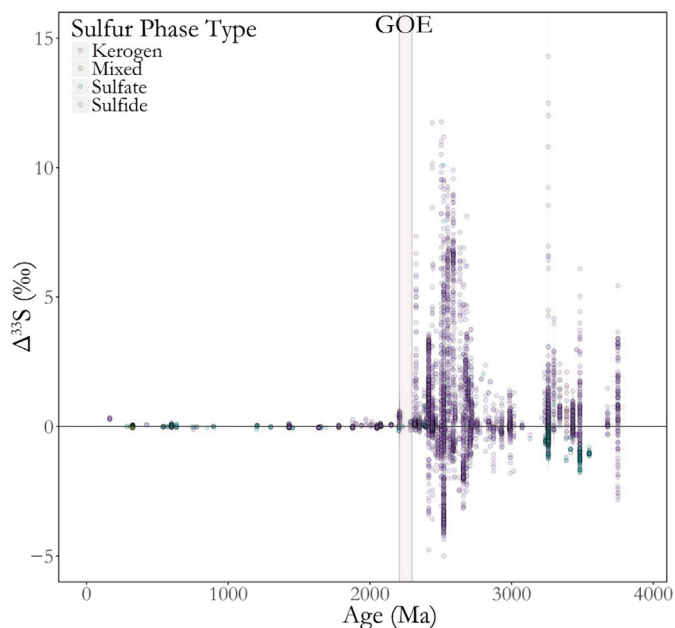

Fig. 1. The evolution of the global sedimentary $\Delta^{33}S$ record through time produced from the sulfur isotope through time database1. GOE – Great Oxygenation Event.

where x equals 33 or 36. The distinct process is a highly effective tracer of a specific reservoir because it is chemically conservative and mostly indelible. Large $\Delta^{33}S_0$ (and $\Delta^{36}S_0$) dispersions were created prior to ca. 2.4 Ga (Fig. 1). Once formed, these signatures were preserved during subsequent normal equilibrium and kinetic reactions.

However, small $\Delta^{33}S$ values can also be generated by MDF-S. With the improved ability to precisely measure ^{33}S and ^{36}S, the paleomicrobiology community demonstrated that kinetic reactions involving mostly organic compounds can impart small $\Delta^{33}S$ and $\Delta^{36}S$ values (Farquhar et al., 2003; Johnston et al., 2005). This allowed for a greater understanding of interaction of biotic sulfur reactions through time (Johnston et al., 2007) and their importance in oxygenation of the hydrosphere.

The sulfur cycle is and has been, however, not only part of Earth's surface processes. In addition to tracking sulfur cycling in the surface environment, atmospheric MIF-S_0 signatures can also be used to track sulfur sources and mobility between surface and subsurface reservoirs. For example, non-zero MIF-S_0 signatures, which uniquely fingerprints Archean supracrustal rocks (Farquhar et al., 2013), were recently identified in Cenozoic plume lavas (Cabral et al., 2013; Delavault et al., 2016). The preservation of this signal indicates that MIF-S can be stored in the mantle for prolonged periods of time.

In this contribution, we focus on ore deposits which are locations of sulfur enrichment, to better understand how sulfur is transported through the lithosphere. In fact, ore deposits, leaving aside their economic significance, are loci where mass and energy concentrative processes take place and are, therefore, the ideal natural laboratories to study the cycling of sulfur. In mineralised systems, sulfur acts as a primary complexing ligand for metal transportation and/or deposition (e.g., Loucks and Mavrogenes, 1999). However, the source of sulfur, is often difficult to fingerprint using $\delta^{34}S$ for two reasons: different sulfur reservoirs can have the same $\delta^{34}S$ and, more importantly, fluids/magmas travel great distances and record changes in their thermochemistry that modify the isotopic composition of the fluid. Conversely, the MIF-S_0 that is inherited as MIF-S_1 cannot be modified, other than by dilution (and consequently its amplitude diminished) by mixing with non MIF-S_0-bearing sulfur reservoirs (e.g., Wacey et al., 2015; Selvaraja et al., 2017b).

By applying the study of MIF-S_1 to ore deposits, it has been demonstrated that Precambrian mineral systems may source sulfur from Archean supracrustal reservoirs in magmatic ore deposits associated with komatiites (Bekker et al., 2009; Fiorentini et al., 2012a; LaFlamme et al., 2016; Caruso et al., 2017) and mafic intrusions (Sharman et al., 2013; Penninston-Dorland et al., 2012; Fiorentini et al., 2012b), and/or hydrothermal systems associated with volcanic-hosted massive sulfides (Jamieson et al., 2006, 2013; Sharman et al., 2015) and orogenic gold deposits (Agangi et al., 2016; Selvaraja et al., 2017a, 2017b, 2017c; LaFlamme et al., 2018; Thébaud et al., in press). Specific mineral systems are the geological expression of distinct tectonic regimes (McCuaig et al., 2010) and, therefore, by understanding the source of sulfur in their formation, we can infer geological processes that control sulfur exchange pathways in the surface and subsurface environment, as depicted schematically in Fig. 2.

Here, we focus on a better understanding of the transfer mechanism of sulfur among different lithospheric reservoirs by identifying the occurrence of MIF-S_1 in orogenic gold systems. To do so, we present a publicly available database of over 5000 compiled multiple sulfur isotope measurements of sediments through time.[1] Further, we redefine the magnitude of $\Delta^{33}S$ values possible from purely MDF-S processes that

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[1] http://www.cet.edu.au/research-projects/special-projects/gssid-global-sedimentary-sulfur-isotope-database.