



Mass-dependent and Mass-independent Sulphur Isotope Fractionation Accompanying Thermal- and Photo-chemical Decomposition of Sulphur Bearing Organic Compounds

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The bimodal S-isotope record, specifically the transition from mass independent (MIF) to mass dependent fractionation (MDF), is perhaps the most widely cited line of evidence for an irreversible rise in atmospheric oxygen at ca. 2.4Ga. The production and preservation of S-MIF, manifested in both $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, within the geological record are linked to atmospheric O_2 via a number of arguments. However, to date, the only mechanism capable of generating S-MIF consistent with the Archaean sedimentary records involves gas-phase ultraviolet irradiation of SO_2 photolysis. More recently, $\Delta^{33}\text{S}$ S-MIF trends have been reported from en vitro thermochemical sulphate reduction (TSR) experiments, prompting authors to question the importance of S-MIF as a proxy for Earth oxidation². Importantly, whilst emerging TSR experiments^{3,4} affirm the reported $\Delta^{33}\text{S}$ trends², these experiments fail to identify correlated S-MIF between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values^{3,4}. Realization that S-MIF is confined to $\Delta^{33}\text{S}$ during TSR, precludes TSR as a mechanism responsible for the origin of the Archaean S-MIF record but strongly suggests the effect originating from a magnetic isotope effect (MIE) associated with ^{33}S nucleus^{3,4}.

Clearly, photochemical and thermochemical processes impart different $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ trends with significant variation in $\delta^{34}\text{S}$; however, a complete experimental elucidation of mechanisms responsible for the S-MIF and S-MIE signatures is lacking. Interestingly, a complete understanding of the S-isotope chemistry during thermal- and photo-chemical decomposition may reveal wavelength and thermal dependence archived in the sedimentary record. Here we extend the experimental database to explore the magnitude and sign of $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ produced during both photo- and thermochemical processes. Here the organic sulphur compounds (OSC) utilized in these experiments carries diagnostic $\Delta^{36}\text{S}/\Delta^{33}\text{S}$ patterns that differ from those reported from photolysis experiment SO_2 and from the Archaean sedimentary record. Further thermal decomposition of several sulphur containing compounds with; 1) an aliphatic-S (e.g., diphenyl disulphide), 2) tri-substituted aromatic-S (trithiane), and S-amino acids (e.g., cysteine, methionine, taurine, and glutathione) were tested for four S-isotope fractionation under vacuum. Among these, aromatic trithiane produced anomalous ^{33}S up to 1.3‰ indicating thermal decomposition through radical chemistry, producing S-MIE. While taurine with sulphonic acid ($\text{R-SO}_2\text{OH}$) functional groups yielded S-MDF up to 15‰ (between the AVS and the residual OSC), which is consistent with estimated zero-point energy shifts for thiol (R-SH), and thyl (R-S-CH_3) groups of cysteine and methionine, respectively. These results suggest that OSC might undergo either thermal or photochemical decomposition and the S-MIF, S-MDF, and S-MIE signatures may be archived in the geologic record. The emerging mechanisms responsible for these isotope signals and their implications will be discussed in more detail. Ultimately this work offers a framework where these signals can be used as a diagnostic marker to distinguish between thermo- and photochemical processes.

References:

1. Farquhar et al., Science 2000 2. Watanabe et al., Science 2010; 3. Oduro et al., PNAS 2011; 4. Kopf and Ono, GCA 2012.