

## Experimental constraints on the mechanism of S isotope mass-independent fractionation during SO<sub>2</sub> dissociation

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The discovery of mass-independent fractionation (MIF) in Archean and Paleoproterozoic sedimentary sulfides and sulfates (Farquhar et al. 2000) offers the possibility of a quantitative proxy for atmospheric O<sub>2</sub> levels through time. Laboratory photolysis experiments on pure-SO<sub>2</sub> and mixtures of SO<sub>2</sub> and other gases show that photolysis at wavelengths < the dissociation wavelength for SO<sub>2</sub> (220 nm) can produce MIF similar (in sign) to that observed in ancient rocks. In the laboratory experiments, product elemental sulfur has  $\Delta^{33}\text{S} > 0$ , and product sulfate (presumably produced from SO<sub>3</sub> when an H<sub>2</sub>O extraction is performed) has  $\Delta^{33}\text{S} < 0$ . This is consistent with the geochemical observation of  $\Delta^{33}\text{S} > 0$  for pyrites and  $\Delta^{33}\text{S} < 0$  for sulfates. However, the chemical mechanism producing MIF during photolysis of SO<sub>2</sub> is not understood, and is sure to be necessary for a complete understanding of sulfur isotope chemistry in the atmosphere.

Several processes can produce MIF: 1) symmetry-dependent non-equilibrium effects, such as those proposed for MIF during the O<sub>3</sub> association reaction (Gao and Marcus 2001); in the case of sulfur, the isovalent S<sub>3</sub> association reaction (S + S<sub>2</sub> → S<sub>3</sub>) is an obvious candidate, but other such reactions are possible. 2) Because SO<sub>2</sub> undergoes at least partial predissociation at wavelengths < 220 nm, self-shielding during photolysis may also contribute to overall MIF in product sulfur and sulfate 3) Non-symmetry dependent MIF is also known to occur (e.g., CO + OH → CO<sub>2</sub> + H), and may play a role in sulfur dissociation chemistry. 4) Isotope substitution causes changes in absorption coefficients that yield measurable MIF and potentially large mass-dependent fractionations.

In the context of these mechanisms we will consider the available SO<sub>2</sub> photolysis data, and report results from recent spark discharge experiments on SO<sub>2</sub>, in an attempt to elucidate the cause of MIF during SO<sub>2</sub> dissociation.

### References

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## Covarying molybdenum and organic carbon distributions in organic-rich sediments and sedimentary rocks

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The positive covariation between concentrations of Mo and organic C (OC) in black shales and the sediments of modern, oxygen-deficient marine basins is well known. While some of this correlation may be an artifact of dilution effects, such as in the modern Black Sea, Mo/Al ratios and Mo mass accumulation rates suggest true mechanistic linkages between the delivery/burial fluxes of the two components at many locations. This relationship is generally coherent over the Phanerozoic, but it is clear that no universal linear relationship exists for the covariation. In ancient sediments, shifts in the slope and scatter in the data can reflect selective loss of OC or Mo remobilization during burial and weathering. Our work in modern settings, however, reveals that primary differences can occur over comparatively short time intervals even within a single anoxic setting, such as the Cariaco Basin.

Ultimately, we agree with past workers that the availability of dissolved sulfide is central in Mo sequestration, and parallel OC concentrations may simply drive the hydrogen-sulfide-generating capacity of the system. A number of workers have suggested, however, that the requisite high levels of sulfide can occur in both pore waters and the water column—thus limiting the utility of Mo as an unambiguous indicator of euxinic. Recognizing that persistent availability of dissolved sulfide is a function of bacterial production as well as loss through reaction, supplies of reactive Fe become an essential control in Mo enrichment. In addition to sulfide production, there is likely a more direct coupling between OC and Mo burial through reactions with the organic matter. If so, the type of organic matter may be critical—giving rise to regional variations in Mo (vs. OC) distributions in, for example, Carboniferous shales. Despite these and other complications and the potential for scatter in patterns of Mo versus OC burial, Mo-OC ratios show similarities among many temporally and spatially diverse organic-rich sediments, particularly for our Devonian and Carboniferous data. In general, the correlation is strongest where sulfide concentrations and/or organic matter type are most favorable to Mo accumulation.