



Laboratory measurements of SO₂ isotopologues for studies of the ancient Earth atmosphere, in particular for understanding the cause of Sulphur Mass Independent Fractionation.

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The timing of the rise of oxygen in the Earth's atmosphere is important for understanding Earth's paleoclimate. Our new laboratory study seeks understanding, through laboratory measurements and atmospheric modelling, of recent theories used in studies of atmospheric changes at the end of the era of low oxygen atmosphere approximately 2400 million years (2.4 Gyrs) ago.

The discovery [1] of mass-independent fractionation (MIF) in sulphur isotopes preserved in Archean and Paleoproterozoic rocks has led to new understanding of the rise of O₂ in the ancient Earth atmosphere. Possible causes for this S MIF have been studied, particularly photolysis of SO₂. Laboratory experiments have shown that S MIF signatures arise from SO₂ photolysis in closed reaction vessels [2] when UV radiation of particular wavelengths is used. In the modern Earth atmosphere oxygen and ozone absorb strongly in the UV, which is not the case in a low oxygen atmosphere, and so UV radiation would have penetrated the ancient Earth atmosphere in precisely the region of strong UV absorption bands of SO₂ (190-220nm), and indeed MIF is seen in the S deposited during those ancient times. Many conclusions on rise in oxygen, concentrations of O₂ and S, have been reached without an understanding of exactly

what the chemical mechanisms of sulphur MIF were in the ancient atmosphere.

Lyons (2007) proposed that the MIF signature arises from photolysis of SO₂ by utilizing radiative transfer methods and photo-chemical modelling in a low oxygen atmosphere to compute the effects of shifts in SO₂ vibronic bands with S isotope substitution. Lyons showed that a self shielding mechanism, and differences in photoabsorption cross sections with wavelength, and so differing photodissociation, for the main SO₂ isotopologues, would lead to S MIF signatures in a low O₂ atmosphere. While it is possible to make *estimates* [3] of vibronic band shifts based on standard molecular models, it is not presently possible to even roughly estimate the shift in rotational features, which comprise much of the SO₂ absorption spectrum. To investigate the contribution of photodissociation of SO₂ isotopologues to S MIF in the ancient Earth rock samples, accurate photoabsorption cross sections for SO₂ isotopologues are needed: laboratory measurements are necessary.

We are carrying out the first ever measurements of high resolution photo-absorption cross sections for several isotopologues of SO₂ including ³³SO₂, ³⁴SO₂ and ³⁶SO₂ from 180-220 nm, by high resolution Fourier Transform Spectrometry at Imperial College, complementing our previous ³²SO₂ results [4]. The measured cross-sections will be interpreted by radiative transfer calculations in atmospheric photochemical models to constrain the magnitude of the MIF signature associated with SO₂ photodissociation, and possibly sulphur concentration in the Archean atmosphere (collaboration with Lyons, UCLA). The cross section data will also be useful in existing photochemical models of the Archean atmosphere (eg Pavlov & Kasting 2002). These measurements can be expected to have far reaching implications for the use of S MIF as a tool for understanding the ancient Earth atmosphere.

[1] Farquhar, J., Bao, H. & Thiemens, M., Atmospheric influence of Earth's earliest sulfur cycle, *Science* 289, 756-758 (2000).

[2] Farquhar, J., Savarino, J., Airleau, S. & Thiemens, M. H, *J. Geophys. Res.* 106, 32829-32840 (2001).

[3] Lyons JR, Mass-independent fractionation of sulfur isotopes by isotope-selective photodissociation, *G Phys R L*, (34) L28811 (2007).

[4] Stark G., Smith P.L., Rufus J., Thorne A.P., Pickering J.C., & Cox G., "High-resolution photoabsorption cross section measurements of SO₂ at 295 K between 198 nm and 220 nm", *J. Geophys. Res.*, vol. 104, (1999), pp 16,585-16,590.

[5] Pavlov A & Kasting J, *Astrobiology* 2,27-41(2002).