

## MIF of sulfur isotopes induced by UV laser: A kinetic approach

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The finding of mass-independent fractionation of sulfur (MIF-S) isotopes in Archaean sedimentary rocks has been used to imply very low concentrations of free oxygen in the Archaean atmosphere. This is due to the experimental finding that MIF-S anomalies can be produced by UV photolysis of atmospheric SO<sub>2</sub> in the absence of ozone, which implies very low atmospheric oxygen concentrations. It is known that the extent of MIF-S is strongly dependent on the UV wavelength used during SO<sub>2</sub> photolysis. Recently, we measured the UV absorption spectra for the four sulfur isotopomers of SO<sub>2</sub> (<sup>32</sup>SO<sub>2</sub>, <sup>33</sup>SO<sub>2</sub>, <sup>34</sup>SO<sub>2</sub> and <sup>36</sup>SO<sub>2</sub>), demonstrating an isotope-dependent spectral shift at UV wavelengths. In this study, we investigate the importance of the spectral shift of SO<sub>2</sub> isotopomers to the MIF-S produced during SO<sub>2</sub> photolysis using a 193 nm laser (Farquhar et al., 2001).

UV photolysis of SO<sub>2</sub> is a first-order reaction, such that  $-d[\text{SO}_2]/dt=k[\text{SO}_2]$ , where  $k$  is the rate constant. If  $k$  is proportional to the absorption cross section ( $A$ ) of SO<sub>2</sub>, then  $[\text{SO}_2]_t=[\text{SO}_2]_0\exp(-kAt)$ , where  $[\text{SO}_2]_0$  is the initial concentration of SO<sub>2</sub>. Application of this equation for each isotopomer of SO<sub>2</sub> yields the isotope relationships  $d^{33}\text{S}=\{\exp(-k(A_{33}-A_{32})t)-1\} \times 1000$  (per mil),  $d^{34}\text{S}=\{\exp(-k(A_{34}-A_{32})t)-1\} \times 1000$  (per mil) and  $d^{36}\text{S}=\{\exp(-k(A_{36}-A_{32})t)-1\} \times 1000$  (per mil), where  $A_{32}$ ,  $A_{33}$ ,  $A_{34}$ , and  $A_{36}$  are the absorption cross sections of <sup>32</sup>SO<sub>2</sub>, <sup>33</sup>SO<sub>2</sub>, <sup>34</sup>SO<sub>2</sub> and <sup>36</sup>SO<sub>2</sub>, respectively. The absorption cross sections are determined from the UV spectral measurements at 193 nm. Using  $d^{33}\text{S}$  values of residual SO<sub>2</sub> after UV photolysis by 193 nm ArF laser (Farquhar et al., 2001), we can then calculate  $d^{34}\text{S}$  and  $d^{36}\text{S}$  values. Calculated  $d^{34}\text{S}$  and  $d^{36}\text{S}$  values show good agreement with the measured values.

These results suggest that the large MIF-S produced by the photolysis of SO<sub>2</sub> using UV lasers or resonance lamps is a result of the interaction of the narrowly-defined UV wavelengths emitted by these light sources with the isotope-dependent UV spectra of the SO<sub>2</sub> isotopomers. Furthermore, this suggests that broadband solar radiation may produce MIF-S results that are very different than the UV laser experiments.