

## High-resolution $^{34}\text{S}$ spectra, and sulfur MIF due to $\text{SO}_2$ photolysis

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It is well known that photolysis of  $\text{SO}_2$  yields isotopic mass-independent fractionation of elemental sulfur [1]. Several mechanisms for photolytic MIF have been proposed including 1) self-shielding during photon absorption [2], 2) variations in band oscillator strengths, 3) hyperfine effects, and 4) resonant curve crossing. Here, we focus on the role of self-shielding in  $\text{SO}_2$ . Quantitative evaluation of  $\text{SO}_2$  self-shielding requires accurate and high-resolution absorption cross section data. We compare high resolution spectra with recently obtained low resolution data [3]. The low-resolution spectra produce sulfur MIF effects when included in photochemical models [4, 5], but not due to  $\text{SO}_2$  self-shielding. In addition the MIF is of opposite sign in  $\Delta^{33}\text{S}$  (SO) to the self-shielding case. Our goal here is to reconcile the different MIF signatures obtained for the high and low-resolution measured spectra.

Two cases can be considered. 1) The high optical depth case, and 2) the low optical depth case. The former is required for  $\text{SO}_2$  self-shielding [2], and is applies to recent laboratory experiments on  $\text{SO}_2$  [6]. The low-resolution spectra yield the wrong sign in  $\Delta^{33}\text{S}$  (SO) for this case. We are presently attempting to reduce systematic errors in the high-resolution spectra in order to address the low optical depth case.

[1] Farquhar *et al.* (2001) *JGR*. **106**, 32829–32840. [2] Lyons (2008) *Adv. Quant. Chem.* **55**, 57–74. [3] Danielache *et al.* (2008) *JGR* **113**, D17314. [4] Ueno *et al.* (2009) *PNAS*, art. #0903518106. [5] Lyons (2009) *Chem. Geol.* **267**, 164–174. [6] Pen & Clayton (2008) *EOS Trans. AGU* **89** (53) abstract V52B-02.

## Riverine chemical fluxes vs. long-term weathering, Central Panama

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Silicate mineral weathering is one of the most important geologic processes occurring on the earth's surface. Modern chemical weathering rates are usually determined by calculating solute fluxes in rivers/streams after atmospheric input is subtracted. Determining longer-term rates is problematic, in part, due to the difficulty in accurately dating soil profiles. Here we compare the present day chemical weathering yields determined from the Upper Rio Chagres, central Panama to longer-term rates derived from geochemical profiles of soil pits. Much of this watershed is underlain by mafic-intermediate lithologies (primarily gabbro, diorite, and granodiorite plus an altered andesite of regional extent). Our previous work has demonstrated high dissolved  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  fluxes in the river system. Longer-term weathering rates have been calculated using the soil profiles and two different methods reported in the literature. Open-system mass transport calculations yield high  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , plus  $\text{Na}^+$  loss from the soil derived from mafic rock. These longer-term cation loss values compare favourably with the present-day solute fluxes obtained through river water analysis. Differences in agreement between short and long-term yields could be attributed to both minor exposures of other lithologies in the watershed along with input from weathering of saprolite. Currently, the cation yields from this mafic-intermediate composition watershed in Panama are ~2x higher than from tropical rainforest watersheds underlain by more felsic terrain.