



## Measurement of sulfur isotope composition in two high-elevation snowpits by Multiple-Collector Thermal Ionization Mass Spectrometry (MC-TIMS) using a $^{33}\text{S}$ - $^{36}\text{S}$ Double Spike

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The variability of sulfur isotope ratios, caused by mass dependent fractionation during biogeochemical processing, is commonly used for tracing the various sources of sulfur and for understanding the sulfur cycle. A new analytical technique for the determination of  $\delta^{34}\text{S}$  and sulfur concentration that is both highly accurate and precise has been developed for the determination of sulfur isotope composition of low concentration samples. The technique is based on the production of singularly charged arsenic sulfide molecular ions ( $\text{AsS}^+$ ) by thermal ionization using silica gel as an emitter and combines multiple-collector thermal ionization mass spectrometry (MC-TIMS) with a  $^{33}\text{S}$ - $^{36}\text{S}$  double spike to correct instrumental fractionation. Because the technique is based on thermal ionization of  $\text{AsS}^+$ , and As is mononuclidic, corrections for interferences or for scale contraction/expansion are not required. The method has been applied to three international sulfur standards (IAEA-S-1, IAEA-S-2, and IAEA-S-3) and snow and firn samples collected from the Inilchek Glacier, Kyrgyzstan (42.16°N, 80.25°E, 5100 m) and Summit, Greenland (72.58°N, 38.53°W, 3238 m).

The standards were measured to evaluate the precision and accuracy of the new technique and to evaluate the consensus values for these standards. Two different double spike preparations were used. The  $\delta^{34}\text{S}$  values (reported relative to Vienna Canyon Diablo Troilite (VCDT), ( $\delta^{34}\text{S}$  (per mil) =  $[(^{34}\text{S}/^{32}\text{S})_{\text{sample}}/(^{34}\text{S}/^{32}\text{S})_{\text{VCDT}} - 1] \times 1000$ )),  $^{34}\text{S}/^{32}\text{S}_{\text{VCDT}} = 0.0441626$ ) determined were  $-0.32 \pm 0.04$  per mil (1s, n=4)

and  $-0.31 \pm 0.13$  per mil (1s, n=8) for IAEA-S-1,  $22.65 \pm 0.04$  per mil (1s, n=7) and  $22.60 \pm 0.06$  per mil (1s, n=5) for IAEA-S-2, and  $-32.47 \pm 0.07$  per mil (1s, n=8) for IAEA-S-3. The amount of natural sample used for these analyses ranged from 0.40 to 2.35  $\mu\text{mol}$ . Replicate determinations of each standard showed less than 0.5 per mil variability (IAEA-S-1 < 0.4 per mil, IAEA-S-2 < 0.2 per mil, and IAEA-S-3 < 0.2 per mil). The uncertainties reported are comparable to or better than those obtained by gas source isotope ratio mass spectrometers (IRMS). The  $\delta^{34}\text{S}$  measurements of the snow and firn samples were used to estimate seasonal sulfate sources contributing to precipitation in these regions.  $\delta^{34}\text{S}$  data from the Summit snowpit are the first continuous high-resolution ( $\approx 7$  samples/1 year) data for this site. The  $\delta^{34}\text{S}$  values for the Inilchek ranged from  $2.6 \pm 0.05$  per mil (1s) to  $7.6 \pm 0.06$  per mil (1s) on sample sizes ranging from 0.3 to 1.8  $\mu\text{mol S}$ .  $\delta^{34}\text{S}$  values for Greenland ranged from  $3.6 \pm 0.19$  per mil (1s) to  $13.3 \pm 2.51$  per mil (1s) for sample sizes ranging from 0.05 to 0.29  $\mu\text{mol S}$ . For both the Inilchek and Summit samples the uncertainties are dominated by blank corrections and not by measurement uncertainty. The  $\text{SO}_4^{2-}$  concentrations ranged from  $0.92 \pm 0.009 \mu\text{mol L}^{-1}$  to  $10.46 \pm 0.08 \mu\text{mol L}^{-1}$  (95% C.I.) for the Inilchek and from  $0.16 \pm 0.09 \mu\text{mol L}^{-1}$  to  $0.92 \pm 0.06 \mu\text{mol L}^{-1}$  (95% C.I.) for the Greenland snowpit. Although the Inilchek snowpit does not demonstrate the seasonality seen in the Greenland snowpit, the mass balance results show anthropogenic sulfate dominates ( $\approx 75\%$ ) throughout most of the year at both sites. Because of the reduction in sample size requirements of this technique, by as much as a factor of 10, accessing the higher-resolution sulfur isotope record of low concentration snow and ice is now possible.