

Simultaneous Determination of Sulfur Isotopic Composition and Concentration in Two High-Elevation Snowpits Using a $^{33}\text{S}/^{36}\text{S}$ Double Spike Technique

The biogeochemical cycling of sulfur (S) and the formation of sulfate (SO_4^{2-}) aerosol particles in the atmosphere have important consequences for global climate that are not fully quantified. Sulfate aerosols interact “directly” with incoming solar and outgoing terrestrial radiation through scattering and absorption and “indirectly” function as cloud condensation nuclei (CCN) that influence the concentration and size of droplets as well as their surface reflectivity, and the radiative properties of clouds. Snow and ice cores provide archives of atmospheric SO_4^{2-} aerosols in many remote regions of the Earth including polar, temperate, and tropical environments. NIST has perfected a specialized high-accuracy mass spectrometric method to precisely measure the isotopic composition of sulfur simultaneously with its concentration. Sulfur isotope composition measurements of these aerosols provide information on the degree of influence anthropogenic contributions have on the natural sulfur cycle, and ultimately global climate.

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The variability of sulfur isotope ratios in nature, caused by mass-dependent fractionation during biogeochemical processing, provides a chemical tool for tracing the various sources of sulfur aerosols and a useful tool for understanding the sulfur cycle. Snow and ice cores provide archives of the sources, sinks, and processing of sulfur that reflect changes in this cycle through time. These archives can be used to assess the current and historical changes in sulfur source contributions to remote regions of the Earth including polar, temperate, and tropical regions. Typical concentrations of sulfate in these regions are 25 ng/g to 100 ng/g (ppb); thus, 300 g to 4000 g of sample is required to obtain enough material ($\approx 33 \mu\text{g S}$) for traditional isotope ratio mass spectrometric (IRMS) analysis. Global atmospheric sulfur cycling is a dynamic process that varies on short timescales, and these large quantities of sample can mask seasonal changes in sulfur sources. Consequently, an analytical technique that allows the reduction of sample needed for analysis is required to minimize masking and increase the resolution.

In this study we have focused on the use of multiple-collector thermal ionization mass spectrometry (MC-TIMS) combined with a $^{33}\text{S}/^{36}\text{S}$ internal standard for simultaneous determination of sulfur isotope composition $\delta^{34}\text{S}$ and concentration of small ($< 1 \mu\text{g}$) sulfate (SO_4^{2-}) samples. The fundamental limitation to accurate and precise isotopic ratio measurements by thermal ionization is that

the measured ratio differs from the true ratio in the source as a result of instrumental fractionation during vaporization of the sample from the filament. To address this changing ratio and to improve precision and accuracy in the $^{34}\text{S}/^{32}\text{S}$, a well-characterized $^{33}\text{S}/^{36}\text{S}$ internal standard was added to the samples and was used to calculate a fractionation factor (α) that corrects for this changing ratio (instrumental fractionation) to give the true ratio in the source. The $^{32}\text{S}/^{33}\text{S}$ ratio that has also been corrected for instrumental fractionation was used to calculate the sulfur concentration. This technique has a significant advantage over the IRMS technique that is limited to only isotope composition measurements.

The $\delta^{34}\text{S}$ results for the Inilchek and Greenland samples using the new double spike technique demonstrate it to be a superior method for the determination of sulfur isotope composition of snow samples with ng/g levels of sulfate. The new technique has reduced the sample size required for sulfur isotope analysis by as much as a factor of 10.

In the case of the Inilchek samples, because of the high measurement precision, low blank concentrations, and relatively precise determination of the blank composition, uncertainties of approximately $\pm 0.10\%$ (2σ) on the individual $\delta^{34}\text{S}$ measurements were obtainable. The isotopic ratios and associated uncertainties are stated in parts-per-thousand (‰) difference from the Vienna Canyon Diablo Troilite (VCDT) isotope-ratio standard, as defined by the formula $\delta^{34}\text{S} (\text{‰}) = [({}^{34}\text{S}/{}^{32}\text{S})_{\text{sample}}/({}^{34}\text{S}/{}^{32}\text{S})_{\text{VCDTstd}} - 1] \times 1000$. These precisions were determined using less meltwater, averaging 205 mL, and on smaller sample sizes, 0.26 μmol to 1.82 $\mu\text{mol S}$, than are typically used for gas source analysis and rival the precisions obtained by these techniques for larger sample sizes. The $\delta^{34}\text{S}$ measurements for Greenland are the first high-resolution measurements obtained for this location. The amount of meltwater used for sulfur isotope analysis in this portion of the study averaged 272 mL. This is considerably less than the 1 L to 2.5 L used in previous research. The uncertainties determined were quite large, averaging $\pm 1.5\%$ (2σ), due to the increased blank amount and the smaller sample size used

for analysis in this portion of the study. If the blank amount is lowered and the uncertainty in the blank composition reduced, estimates of the precisions obtainable, averaging $\pm 0.75\text{‰}$ (2σ), show that up to a factor of two to three improvement in the uncertainties on sample sizes ranging from $0.05 \mu\text{mol}$ to $0.29 \mu\text{mol S}$ is attainable with the double spike technique. In this case the precisions obtained would be similar to those of gas source techniques for snow samples but for much smaller sample sizes, $0.1 \mu\text{mol S}$ rather than $1 \mu\text{mol S}$.

Snowpit samples from the Inilchek Glacier in Kyrgyzstan and Summit, Greenland were analyzed. The elemental and sulfur isotope data obtained from these samples showed that the main sulfate contributors to the Inilchek Glacier in Kyrgyzstan were anthropogenic and evaporite dust, while at the Summit, Greenland site these were mostly anthropogenic and marine biogenic in origin. Overall, the results show that anthropogenic inputs tend to dominate, averaging almost 75%, for both sites. The anthropogenic contributor dominates throughout the year in the Inilchek region, while in Greenland the influence of anthropogenic sources wanes during the summer months when the marine biogenic contribution increases.

In addition to being able to measure smaller sample sizes, the double spike MC-TIMS method offers two additional advantages over gas source mass spectrometry. First, because it uses an internal standard rather than an external standard, it is intrinsically accurate because only isotope ratios need to be measured; therefore complete recovery of the sample is not required for unbiased results. Also, mass fractionation that may be caused by losses during drying and/or chemical reduction of the sample is accounted for by adding the spike prior to sample processing. This is a considerable advantage for small sample sizes ($< 1 \mu\text{mol S}$) where losses can result in potentially large biases without the use of an internal standard.

The second advantage it provides is a better evaluation of both the blank amount and composition. It is important to note that these are the first $\delta^{34}\text{S}$ measurements that include a correction for blank, and demonstrate that blanks must be measured to assess the accuracy of the $\delta^{34}\text{S}$ data. In all previous studies there is no mention of blanks and therefore this potentially significant bias and uncertainty has been ignored.

Impact and Future Plans: The significant reduction in sample size permitted by the double spike technique may provide the tool required to access the high-resolution temporal record contained in ice cores. Applying this technique to ice cores will extend the high-resolution temporal record back in time to establish a timeline of changes in the atmospheric sulfur cycle and allow for a more detailed reconstruction of the atmospheric sulfur cycle and the understanding of changes in sources, sinks, and processing through time. This becomes particularly important when examining periods in geologic history where abrupt changes (less than a decade) in climate occur. We also plan on applying the technique to an upcoming CCQM pilot study (CCQM P-75) to determine the $\delta^{34}\text{S}$ of the essential amino acid methionine.

