Assessment of Sulfate Sources in High-Elevation Asian Precipitation Using Stable Sulfur Isotopes

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Stable sulfur isotope measurements (δ^{34}S) made on samples collected from a 2 m snowpit on the Inilchek Glacier, Tien Shan Mountains (42.16° N, 80.25° E, 5100 m) are used to estimate sources of sulfate (SO_4^{2-}) in high-elevation Central Asian precipitation. Comparison of snowpit oxygen isotope (δ^{18}O) data with previous work constrains the age of the snowpit samples to the summer season during which they were retrieved (1999). δ^{34}S measurements were made at 10 cm resolution (20 samples total), with δ^{34}S values ranging from 0.4‰ during background ([SO_4^{2-}] < 1 μequiv L^{-1}) periods to 19.4‰ during a single high [SO_4^{2-}] event. On the basis of the significant correlation ($r = 0.87$) between [SO_4^{2-}] and δ^{34}S values, coupled with major ion concentration time series and concentration ratios, we suggest a two-component mixing system consisting of evaporite dust and anthropogenic SO_4^{2-} to explain the observed δ^{34}S values. Using a regression model, we estimate that during the 1999 summer season 60% of the deposited SO_4^{2-} was from an evaporite dust source, while 40% of the SO_4^{2-} was from anthropogenic sources. Due to the potentially large and unconstrained range of δ^{34}S values for both evaporite and anthropogenic SO_4^{2-} sources in Asia, the error in our estimates is difficult to assess. However, the δ^{34}S data from the 1999 Tien Shan snowpit provide the first unambiguous identification of evaporite and anthropogenic SO_4^{2-} in high-elevation Asian precipitation, and future ice core studies using improved analysis techniques and source δ^{34}S values can provide detailed information on sulfur biogeochemistry and anthropogenic impacts in Asian alpine regions.

Introduction

Sulfate (SO_4^{2-}) aerosols in high-elevation and polar regions cause acidification of precipitation that can have adverse effects on ecosystems, influence geochemical cycling, and impact the radiative balance of the atmosphere. Understanding the relative contribution of natural versus anthropogenic SO_4^{2-} is critical for quantifying the physical and chemical effects of SO_4^{2-} aerosols in these regions. Studies

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in the Arctic, Antarctic, and alpine sites in Austria have used sulfur isotope ratios (δ^{34}S) as a powerful tool to explore SO_4^{2-} sources, transport pathways, and deposition in the remote atmosphere (4–6). For example, δ^{34}S measurements of aerosol samples from high-elevation alpine sites in Europe were used in combination with back trajectories to characterize anthropogenic emissions from different sources (6). Ice core studies in the Antarctic have used δ^{34}S measurements to determine the background source of SO_4^{2-} for a site near the South Pole (5) and in West Antarctica (7). Measurements of δ^{34}S from a Greenland ice core were used to assess changes in SO_4^{2-} production since the industrial revolution (4). There is some evidence of an anthropogenic influence on precipitation SO_4^{2-} (1, 8) at high-elevation sites in Central Asia; however, stable sulfur isotope data from the region may provide a more comprehensive assessment of anthropogenic impacts.

The Tien Shan region of Central Asia, located along the boundaries of eastern Kyrgyzstan and western China (Figure 1), is likely free from the influence of marine air masses and thus has only two potential sources of atmospheric SO_4^{2-}: anthropogenic and evaporite dusts (1, 8). Previous work in the Tien Shan has investigated the importance of evaporite dusts in precipitation chemistry using soluble major ion and trace element data (1, 9–15). The temporal variations of major ion concentrations are greater than spatial variations for an individual precipitation event, suggesting that the major control on ion concentrations is sporadic evaporite dust input (8, 16–18). However, elevated levels of SO_4^{2-} may only partially be accounted for by an influx of weathered soil materials. Anthropogenic emissions represent a potential additional SO_4^{2-} source, although the relative amount remains poorly understood, and soluble ion concentrations alone do not provide a quantitative estimate. A comparison of SO_4^{2-} levels from several central Asian glaciers revealed that SO_4^{2-} levels can vary greatly depending on location (from 1 to 50 μequiv L^{-1}), with a general enrichment in SO_4^{2-} to the east. Areas near urban locations in western China can have SO_4^{2-} levels that are five times as great as rural areas (8) and are attributed to anthropogenic emissions. A previous study of the δ^{34}S composition of central Asian precipitation found that a visible dust layer (with elevated SO_4^{2-} concentration) within a firn core had a δ^{34}S value of 15.0‰, whereas a visibly clean layer (with lower SO_4^{2-} concentration) had a δ^{34}S value of 5.4‰ (14). The δ^{34}S value from the dust layer suggests the presence of evaporitic material, whereas the δ^{34}S value of the clean layer may indicate SO_4^{2-} from an anthropogenic source. Here we present the first continuous snowpit δ^{34}S profile from Central Asia and attempt to quantitatively estimate the relative contribution of evaporite dust and anthropogenic sources to overall SO_4^{2-} deposition in the Tien Shan Mountains.

Experimental Section

Snow pit samples were collected from the Inilchek Glacier (5100 m; Figure 1) during the summer of 1999. The snow pit was 2 m deep, and 1 L samples were collected every 10 cm for δ^{34}S analysis. A separate depth profile was sampled at 5 cm resolution for major ion and δ^{18}O measurements. Samples were placed into precleaned containers and stored below −15 °C until melting and analysis. Major ion (Na$^+$, K$^+$, NH$_4^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, NO$_3^-$, SO$_4^{2-}$) measurements were made via ion chromatography at the University of Maine. Anions were analyzed on a Dionex DX-500 ion chromatograph with an AS-11 column using 6 mM NaOH eluent. Cations were analyzed on a Dionex DX-500 ion chromatograph with a
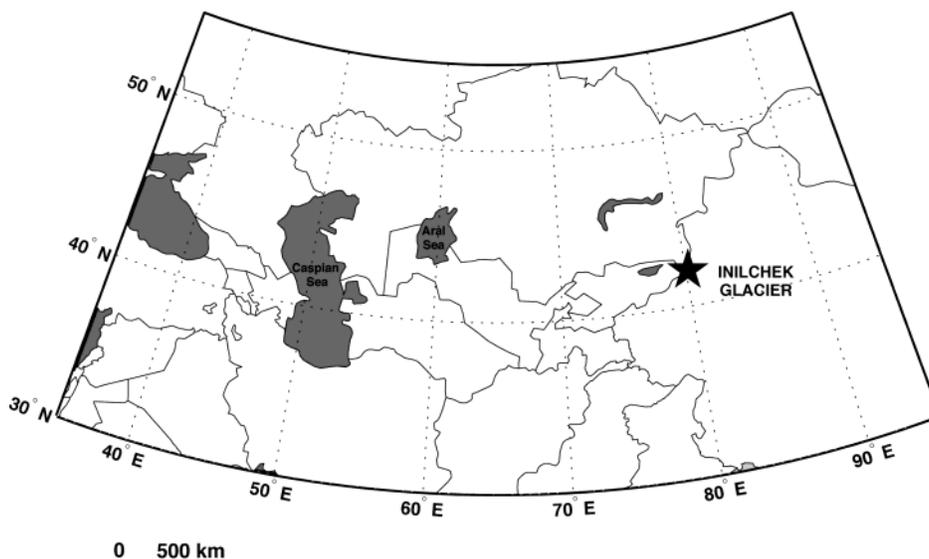
FIGURE 1. Location map for the Inilchek Glacier (star) snowpit sampled during 1999.

CS-12A column using 25 mM MSA eluent. Oxygen isotope ratios were measured at the University of Maine using standard CO_2 equilibration techniques (*19*) on a VG SIRAII mass spectrometer and have an analytical precision of ± 0.05‰ based on replicate analysis of samples and international standards. Data are reported in delta notation ($\delta^{18}O$) relative to the international water standard (SMOW).

Twenty samples, covering 0–2 m depth, were collected for $\delta^{34}S$ measurement at the Memorial University of Newfoundland. Sample aliquots used for sulfur isotopic analysis were transferred to acid washed "snap-cap" vials. Vials were placed on a hot plate in a positive-pressure, HEPA-filtered air fume hood, and the solutions were slowly evaporated until the volume was reduced to approximately 20 mL. The concentrated sample was then used to fill 10 × 10 × 10 mm tin capsules and evaporated to dryness. The process was repeated between 2 and 5 times according to the measured SO_4^{2-} concentration in order to obtain sufficient sample for isotopic analysis. After the final evaporation, the tin capsule was closed and placed in the autosampler of a Carlo Erba 1500 elemental analyzer interfaced by ConFlo II to a Finnigan MAT 252 stable isotope ratio mass spectrometer.

The sulfur isotopic ratio is expressed in delta notation with respect to the international standard Vienna Canyon Diablo Troilite (VDCT):

$$\delta^{34}S(‰) = \{[(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{VDCT}] - 1\} \times 1000 \tag{1}$$

Calibration to VCDT was performed using two National Institute of Standards and Technology reference materials, IAEA S-1 and IAEA S-2, with reported values of -0.30 ± 0.3‰ and $+21.0 \pm 0.3$‰, respectively. The overall error on isotopic analysis based on duplicates and internal standards is ± 0.5‰.

Results and Discussion

Oxygen isotope ratio ($\delta^{18}O$) values in the 1999 snowpit samples range from -8.0‰ to -18.4‰ (Figure 2). A 14.4 m firn core previously collected and analyzed from the same location on the Inilchek Glacier shows a clear seasonal $\delta^{18}O$ trend (Figure 2), with summer values generally higher than -20‰ and winter values reaching as low as -35‰ (*1*). The 2 m snow pit samples were collected in the summer of 1999 (July–August), and the lowest $\delta^{18}O$ value is -17.8‰. Because this value is not low enough to represent snowfall from the previous winter season, the snow pit data likely record
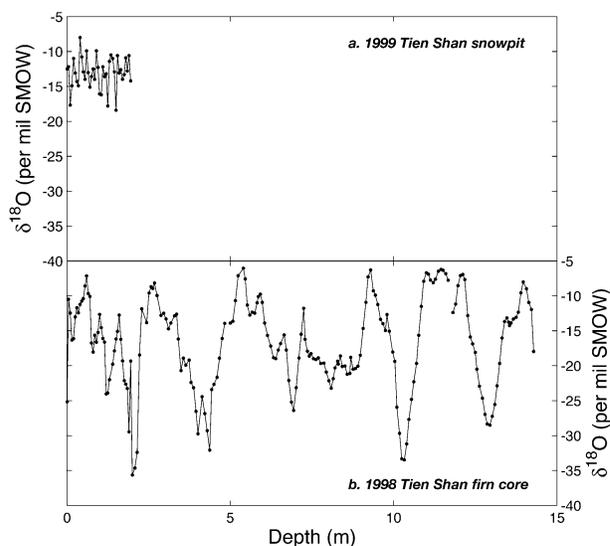

FIGURE 2. (a) $\delta^{18}O$ profile of the 2 m snowpit collected in 1999 on the Inilchek Glacier. (b) $\delta^{18}O$ profile of the 15 m firn core collected in 1998 at the same location on the Inilchek Glacier(*1*).

precipitation events that occurred only during the summer of 1999 or possibly the spring/summer season. The samples taken for sulfur isotopic analysis, therefore, provide continuous high-resolution $\delta^{34}S$ data of the 1999 summer season. The range of snowpit $\delta^{18}O$ values is comparable to other summer seasons in the firn core, and thus we assume that for the present study the 1999 snowpit is representative of previous summer conditions. This assumption will need to be tested in future ice core studies, particularly if new analysis methods can reduce the sample volume needed for $\delta^{34}S$ measurement.

Concentration data for all soluble major ion species measured in the 1999 snowpit are presented in Figure 3 and are comparable to mean concentrations found in the 1998 Tien Shan firn core (*1*). All major ion species show similar trends, with concentration peaks just below 0 m, a concentration peak above and below 0.5 m and a concentration peak above 1.5 m. The concentrations of all major ions except NH_4^+ and NO_3^- are <1 μequiv L^{-1} in certain portions of the snowpit, which we define as being background intervals. A snowpit chemistry dataset from Glacier Number 1 in the eastern Tien Shan has similar concentrations for SO_4^{2-}, Cl$^-$,
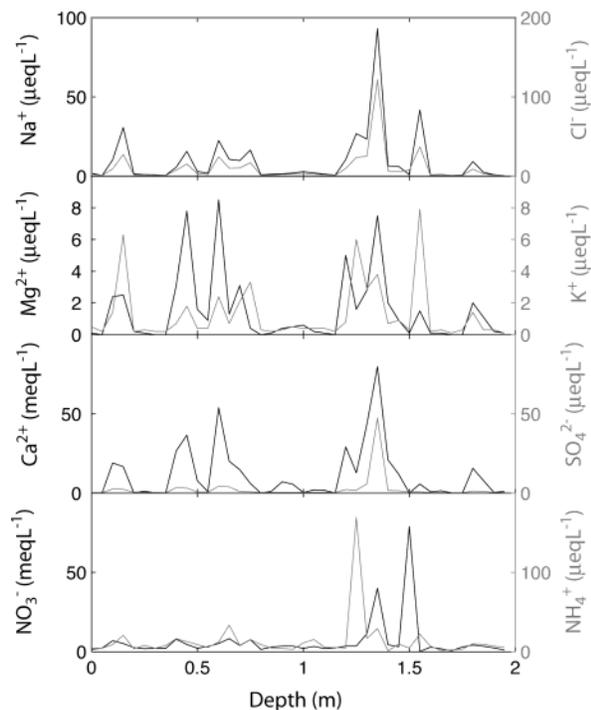
FIGURE 3. Soluble major ion concentrations vs depth in the 2 m Inilchek Glacier snowpit sampled in 1999.

and K^+; higher concentrations of Na^+, Ca^{2+} and Mg^{2+}; and lower concentrations for NO_3^- and NH_4^+ (8). A comparison of aerosol measurements with snow samples at Glacier 1 found that the snow chemistry was a good reflection of air chemistry because ion concentrations from aerosol measurements were similar in proportion to Glacier 1 precipitation data (20). Overall, the pattern of low (or background) concentration periods punctuated by abrupt increases in ion concentrations appears to be typical of both aerosol and

snowpit chemistry records from the Tien Shan region. This pattern, coupled with ion ratio data, suggests that a significant source of major ion chemistry (including SO_4^{2-}) in the Tien Shan is evaporite dusts (1, 14). Major ion ratios, the long distance from a significant marine (i.e., high salinity) source, and the general synoptic meteorology of the region do not support a contribution from sea salt for any of the major ion species including SO_4^{2-} (1, 8, 13). Another possible SO_4^{2-} source in Central Asian snow is volcanic activity, but there are no known active volcanic centers in the region, nor is there evidence for global-scale explosive volcanic activity during 1999. No convincing evidence exists for a discernible impact of volcanic SO_4^{2-} in Asian ice core records, even during major global volcanic events (e.g., Agung, Krakatau, Tambora; ref 18). Therefore, we assume that there is no significant volcanic impact on the 1999 Tien Shan snowpit SO_4^{2-} record.

In addition to the well-established evaporite dust source for SO_4^{2-} in Central Asia, previous work has indicated a possible contribution of anthropogenic SO_4^{2-} in certain mountain regions. This idea was developed based on increased snow SO_4^{2-} concentrations and decreased cation:anion ratios downwind of a major Chinese industrial center in the eastern Tien Shan (8). Because the Tien Shan Mountains in Kyrgyzstan lie downwind of several large-scale industrial centers, anthropogenic SO_4^{2-} may have a potential impact on aerosol and snow chemistry in the region. Sulfate concentration and ion ratios alone, however, cannot be used to unambiguously determine an anthropogenic SO_4^{2-} source in Central Asia, as changing dust SO_4^{2-} concentrations may be driven by a combination of meteorological and land-use factors. However, the sulfur isotope ratio ($\delta^{34}S$) of the precipitation SO_4^{2-} may hold source-specific information that can be used to determine the presence of anthropogenic SO_4^{2-} and possibly to also assess the relative proportions of evaporite dust SO_4^{2-} and anthropogenic SO_4^{2-}.

Sulfur isotope ratio ($\delta^{34}S$) and SO_4^{2-} concentration data in time (depth) series from the Tien Shan 1999 snowpit samples are plotted in Figure 4. There is a significant positive
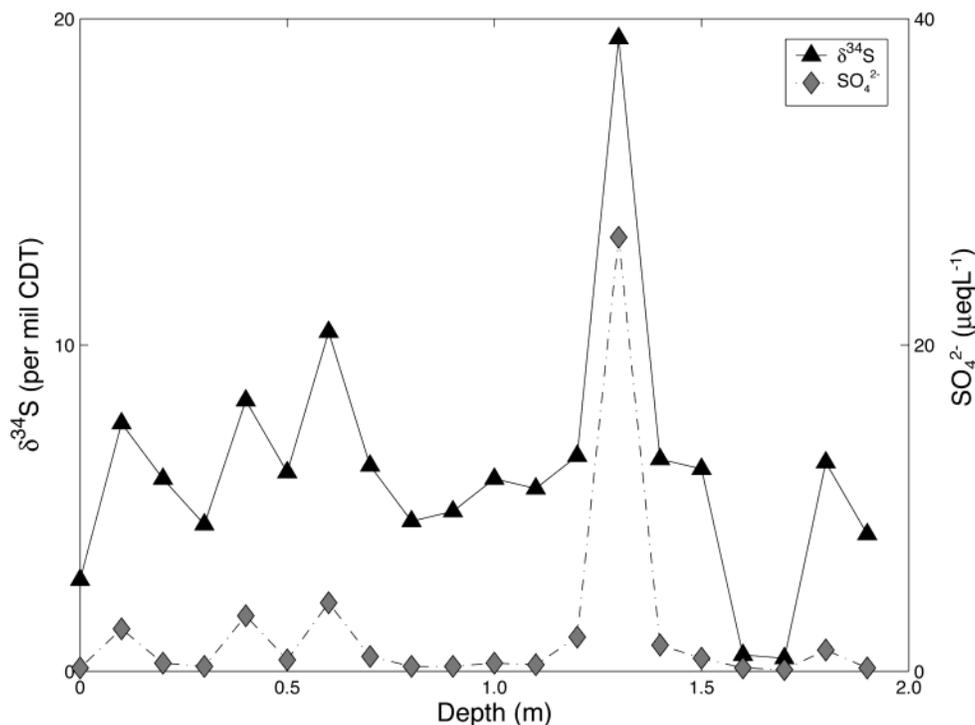

FIGURE 4. SO_4^{2-} concentration and $\delta^{34}S$ ratios plotted against depth in the 2 m Inilchek Glacier snowpit sampled in 1999. SO_4^{2-} concentration was measured at 5 cm resolution however because $\delta^{34}S$ ratios were measured at 10 cm resolution. The average of two SO_4^{2-} concentration values is plotted for each isotope ratio value.
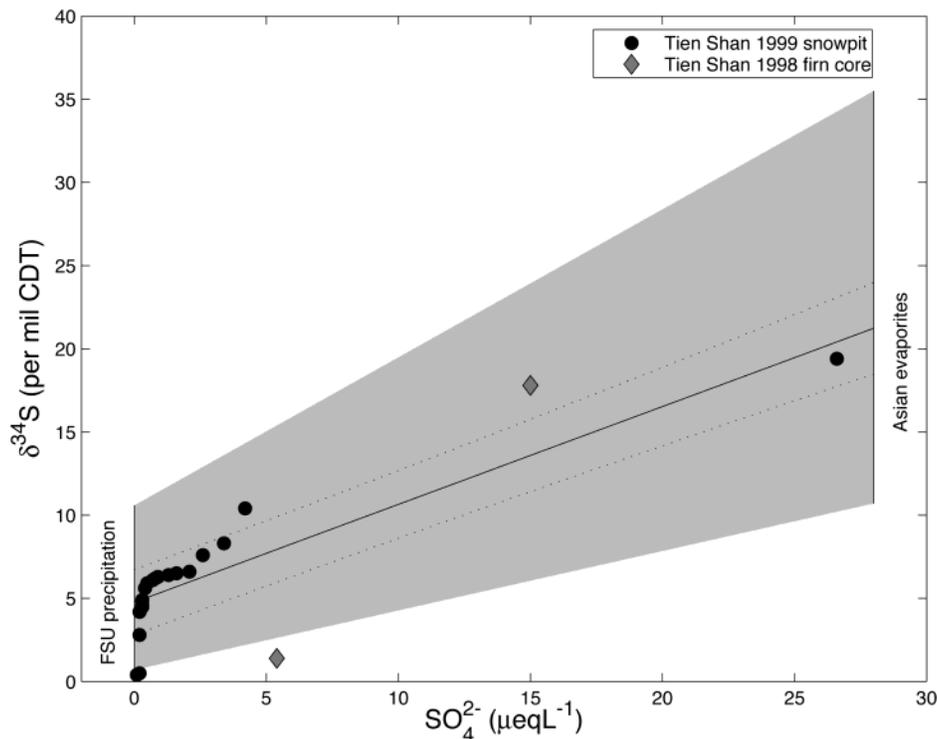
FIGURE 5. $\delta^{34}S$ ratios vs SO_4^{2-} concentration in the 1999 Inilchek snowpit and 1998 Inilchek firn core. The $\delta^{34}S$ range of Former Soviet Union (FSU) precipitation values is from Chukhrov et al. (*2*), and the $\delta^{34}S$ range of Asian evaporates is from Krouse and Grinenko (*3*).

correlation ($r = 0.87$) between SO_4^{2-} concentration and $\delta^{34}S$ (Figures 4 and 5), with low (background) SO_4^{2-} concentration periods corresponding to low $\delta^{34}S$ values. The continuous time (depth) series isotope/concentration data from the 1999 snowpit agree with a previous study from the 1998 Tien Shan firn core, where two samples (one with high SO_4^{2-} concentration, and one with low SO_4^{2-} concentration) had distinctly different $\delta^{34}S$ values (*14*) (Figure 5). The majority of the 1999 snowpit samples have $\delta^{34}S$ values <10‰, which overall corresponds to SO_4^{2-} from an anthropogenic source. For typical sulfur-bearing materials used in industrial and consumer processes (e.g., petroleum, natural gas, coal, sulfide ores) and likely to generate atmospheric SO_4^{2-}, $\delta^{34}S$ ranges of different geological ages generally have the following ranges: petroleum natural gas, -20 to 30‰; coal, -35 to 30‰; and sulfide ores, -18 to 28‰ (*3*, *21*). While the overall $\delta^{34}S$ ranges are large, specific individual large pools and large pools of genetically related deposits are exceedingly uniform in isotopic content (*22*). For example, oil deposits in the USSR are typically below 10‰, regardless of geologic age (*21*). Likewise, measured USSR coal deposits have $\delta^{34}S$ values <0‰ (*21*), and the vast majority of sulfide ore deposits range between -3 and 5‰ (*3*). There are few precipitation $\delta^{34}S$ values available for the USSR and FSU countries, but published values range between 0.7 and 21.6‰, and mean values are all <10‰ (*2*, *23*) (Figure 5). As most of these measurements were made near industrialized areas, it was assumed that the precipitation $\delta^{34}S$ values primarily represent SO_4^{2-} from anthropogenic sources. Therefore, while there is a broad range of $\delta^{34}S$ values from anthropogenic materials, precipitation SO_4^{2-} in the Former Soviet region (including the Tien Shan) is somewhat better constrained and likely ranges between 0 and 10‰. Because the only other typical SO_4^{2-} source with low $\delta^{34}S$ values (<10‰) is volcanic, we conclude that the background SO_4^{2-} deposition on the Inilchek Glacier has a component of anthropogenic SO_4^{2-}.

Several previous studies have suggested that evaporite dust makes a significant contribution to snow and ice SO_4^{2-} concentrations in Central Asia (*1*, *12*, *14*); therefore, the $\delta^{34}S$ of evaporite material may be responsible for the observed high SO_4^{2-} concentration and high $\delta^{34}S$ value of one of the 1999 snowpit samples (Figures 4 and 5). On the basis of trace element and major ion data, gypsum ($CaSO_4 \cdot 2H_2O$) has been identified as a major source of SO_4^{2-}-rich dust in the Inilchek Glacier, with lesser amounts of magnesium sulfates (*14*). Soil modeling indicates that the largest source of soil gypsum in the world is to the west of the Inilchek Glacier surrounding the Caspian and Aral Seas (*24*), and prevailing synoptic meteorological conditions favor atmospheric transport to the Inilchek Glacier. To our knowledge, there are no $\delta^{34}S$ data available from these specific Asian evaporite deposits; however, examination of other Asian evaporates reveals a $\delta^{34}S$ range of 10.8–35.5‰ (*3*). This range is consistent with the modern seawater sulfate $\delta^{34}S$ value (21‰) and the range of marine sulfate $\delta^{34}S$ through geologic time (12–32‰; ref *25*). In limited regions where more intensive study has occurred, the range of evaporite $\delta^{34}S$ values is better constrained (e.g., 14–21‰ for Australian gypsum; ref *26*). We therefore assume that the 1999 snowpit sample with high SO_4^{2-} concentration and high $\delta^{34}S$ (Figures 4 and 5) has a significant evaporite SO_4^{2-} component.

To estimate the relative contribution of anthropogenic and evaporite SO_4^{2-} in the 1999 Tien Shan snowpit samples, we apply a regression model to the SO_4^{2-} and $\delta^{34}S$ data (Figure 5). Our assumption is that the system is a two-component mixing situation that behaves linearly through the 1999 season. The *y*-intercept of the regression is 4.77‰, which is within the $\delta^{34}S$ range of FSU precipitation assumed to be from anthropogenic emissions (*3*). Likewise, the upper bound of the regression is consistent with $\delta^{34}S$ data from Asian evaporates (*3*). We acknowledge that this simple model does not account for the possible range of $\delta^{34}S$ values from both anthropogenic and evaporite sources (as noted by the gray polygon in Figure 5) or any changes in source strength and transport through time. Nonetheless, the model provides the first estimates of the relative contributions of the two
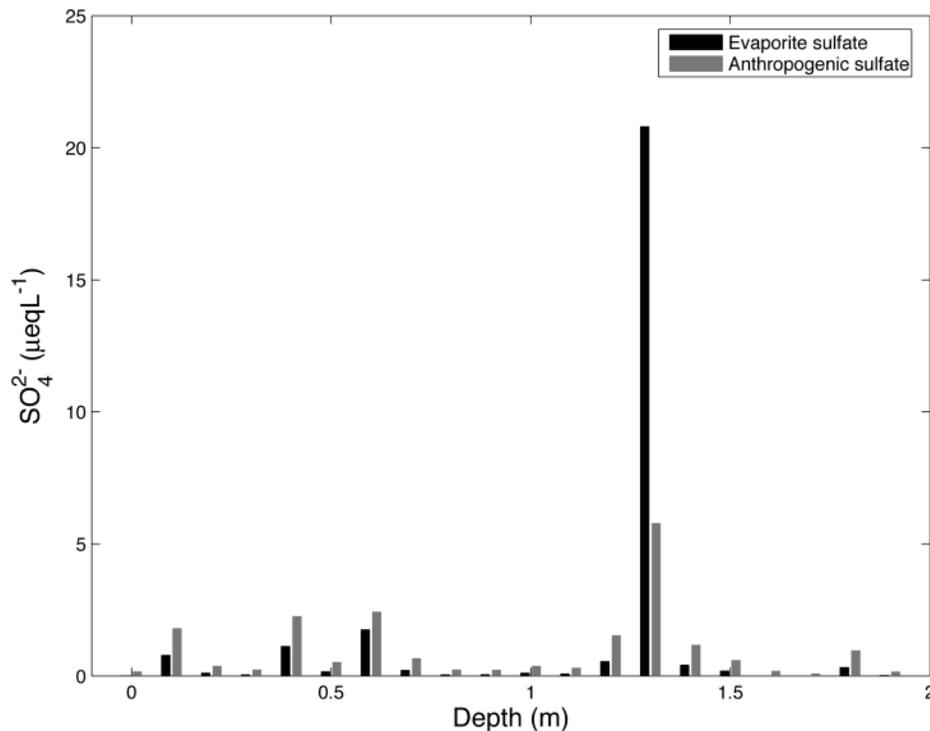
FIGURE 6. a. Estimates of the contribution of evaporite dust and anthropogenic SO$_4^{2-}$ to the total SO$_4^{2-}$ concentration in each snowpit sample.

SO_4^{2-} sources in Central Asia. The measured $\delta^{34}S$ for SO_4^{2-} in the 1999 Tien Shan snowpit samples can be resolved in the following way:

$$\delta_{measd} = f_{dust}\delta_{dust} + f_{anth}\delta_{anth} \qquad (2)$$

δ_{dust} is set at 20‰, which is consistent with the modern seawater value and the mean Asian evaporite value. The regression model provides an estimate of the δ_{anth} value (5‰). Thus, it is possible to partition the SO_4^{2-} concentration for each of the 20 samples into two parts. If f_{dust} is equal to x and f_{anth} is therefore $1 - x$, then eq 2 can be rewritten as

$$(\delta_{measd} - 5)/15 = x \qquad (3)$$

Once this has been calculated for each sample, it is possible to look at changes in SO_4^{2-} source contribution over time (Figure 6). We have not placed error bars on the estimates in Figure 6 due to our lack of knowledge of the exact end member $\delta^{34}S$ values. However, we note that this technique with uncertainties is a common method for estimating SO_4^{2-} source contributions in other regions (27).

Previous research in the Swiss Alps identified seasonal anthropogenic emissions changes at high elevations with increased SO_4^{2-} concentrations in precipitation in the summer due to an increase in atmospheric vertical convective transport (28). Wagenbach et al. (29) identified a relationship between a summer SO_4^{2-} peak and high $\delta^{18}O$ values in a shallow snow pit in the Swiss Alps, which was also attributed to increased vertical convection during summer. The same mechanism may apply in the Tien Shan (14). The amount of anthropogenic SO_4^{2-} deposited during the high dust period is significantly higher than during background periods, even though anthropogenic SO_4^{2-} dominates during background periods. During times of negligible dust deposition (for example, 0.3 m depth), the quantity of anthropogenic deposition is low but accounts for nearly all (83%) of the SO_4^{2-} deposition. The high dust period (1.3 m) is characterized by a dominance of evaporite material (78% of the SO_4^{2-}) as well as an increase in the anthropogenic SO_4^{2-} concentration.

Overall, on the basis of the partitioning described above, 60% of the SO_4^{2-} that accumulated in the snowpack during the 1999 summer season was from an evaporite dust source, while 40% was anthropogenic in origin. A similar study of $\delta^{34}S$ was carried out in Japan in order to assess changes in anthropogenic input to rural and urban areas with samples taken in 1960 and throughout the 1970s (30). The dominant source of SO_4^{2-} in rural areas was marine aerosols, whereas anthropogenic emissions dominated urban areas. The rural $\delta^{34}S$ values ranged from 12.3 to 14.7‰, while urban values ranged from 4.5 to 6.8‰. These urban values are similar to those measured during the anthropogenically dominant periods ($SO_4^{2-} < 1 \mu$equiv L^{-1}) in the Tien Shan (0.4–6.3‰).

As mentioned previously, key assumptions in our model are the $\delta^{34}S$ values for the two composition end members. While the $\delta^{34}S$ and SO_4^{2-} depth profiles match each other closely (Figure 4), two samples (1.6 and 1.7 m depth) have anomalously low $\delta^{34}S$ values (i.e., there is not a proportional drop in SO_4^{2-} concentration). One potential explanation for the lower $\delta^{34}S$ values of these two samples is the uncertainty of the anthropogenic end member $\delta^{34}S$ value. A $\delta^{34}S$ change of roughly 4‰ in SO_4^{2-} source could explain the $\delta^{34}S$ values of the two low data points. A similar explanation can be invoked for the 1998 firn core sample (Figure 5; at 5.5 μequiv L^{-1}) that lies well below the 1999 snowpit regression line. The required 4‰ change in source $\delta^{34}S$ value is within the range of available materials. For example, Russian coal has $\delta^{34}S$ values between 3‰ and 5‰, while coal from Bohemia has been measured at −1.4‰ to 0.1‰ (3). Therefore, differences in source strength, and/or the efficiency of transport of one constituent versus another may play a significant role in determining the snow (precipitation) $\delta^{34}S$ value. In future studies, combination of co-registered snowpit or ice core $\delta^{34}S$, water isotope, major ion, and trace element data may provide a more complete method for resolving potential changes in SO_4^{2-} source and transport.

While the $\delta^{34}S$ data presented here demonstrate the potential value of this technique for resolving SO_4^{2-} sources in high-elevation precipitation, the lack of a detailed dataset

on source $\delta^{34}S$ is limiting. The method does hold promise for using snow and ice core chemistry for determining contributions from overall groups (e.g., anthropogenic vs evaporite dust) and possibly also for examining changing anthropogenic contributions through time (e.g., changes in coal vs petroleum usage in FSU countries and subsequent ecosystem impacts). A further limitation of the technique is the sample size currently required for $\delta^{34}S$ analysis via gas source mass spectrometry ($\sim$1 L). The large sample size precludes a detailed, high-resolution ice core record of the industrial period from being produced and also for testing how representative the seasonal snowpit data presented here are. However, new analysis techniques such as inductively coupled plasma-mass spectrometry (ICP-MS) hold the promise of precise $\delta^{34}S$ measurement on samples with SO_4^{2-} concentration as low as 100 ppb (*31*). If these two limitations can be satisfied, $\delta^{34}S$ measurement in Central Asian snow and ice cores represents a powerful tool for examining sulfur biogeochemistry and climate impacts in the region.

Acknowledgments

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