Supporting Information

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SI Text

SI Methods. ***Background interferences from barium isotopes.*** When using solid $BaSO_4(s)$ for our optimization work, we discovered a number of issues that contribute to sample loss during chemical processing and high backgrounds that have not, to our knowledge, been previously reported. The most significant of these involves the background contributions from radiogenic barium, which appears to have a large variability that depends on the chemical source of barium used (0.86–559 $\mathrm{dpm\,mol^{-1}}$ of Ba). While the use of Ba to isolate SO_4 in samples is understandable, we have found that measurements of ^{35}S activity as SO_4 (aq.) completely avoid these difficulties.

Preparation efficiency. Until now, we have assumed that samples measured with LSS were prepared and collected with 100% efficiency, a reasonable assumption for laboratory standards. However, the preparation of natural samples, especially those prepared as aqueous samples, requires the use of resin columns for the removal of organics. Using the aqueous ^{35}S standard, we determined that the sample losses incurred from cleaning samples with HC-C18 and PVP (polyvinylpyrrilodone) were 10% and 12% ($\varepsilon_{\mathrm{prep}} \sim 0.90 \times 0.88 = 0.79$), respectively, for the natural samples reported in this study. A significant improvement in the sample preparation efficiency ($\varepsilon_{\mathrm{prep}} = 95\%$) was achieved by adding 1 ml of inactive 1 M Na_2SO_4 (aq.) to a sample before its passage through HC-C18 and/or PVP columns followed by a rinse of the columns with no less than 5 ml of Millipore H_2O (MQ-H_2O). Samples can subsequently be reconcentrated to smaller aqueous volumes to increase the counting efficiency of these samples as described earlier.

The counting of natural samples as Na_2SO_4 has additional benefits, including the minimizing of quenching due to self-absorption in $BaSO_4(s)$ particles, as well as the avoidance of variations in the count rate due to the gravimetric settling of $BaSO_4(s)$ samples during counting.

Natural sample collection and preparation.

Aerosol collection.

Aerosol samples were collected in La Jolla, California, and the San Fernando Valley, California, for short periods of time during 2007 and 2008. Ambient aerosol samples were collected on glass fiber filters using a high volume aerosol sampler with a four-stage cascade impactor to size select aerosols. The filters, representing 2,000 m^3 of air, were returned to the Stable Isotope Lab at the University of California, San Diego, for chemical and radiometric analysis. Soluble ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}, and NH_4^+) were extracted by soaking each filter in 50 mL of MQ H_2O and sonicating for 1 hr to effectively remove the particulates from the filters. Excess water was expelled from the filter with a recovery efficiency of 96%. The solution was then filtered using Steriflip 0.2 μm filters (Millipore) to remove any particulate matter or glass fibers from the solution. The concentrations of anions and cations in each stage (1–4 and backup filter) were measured using ion chromatography (IC).

Preparation of $BaSO_4$ for beta activity counting.

Equal volume aliquots of the filtrate for stages 1–3 and 4–5 were combined into two size fractions; fine (<1.5 μm) and coarse (>1.5 μm) aerosols. Each sample was spiked with 2 mL of dead (dpm = 0) 1 M Na_2SO_4 to minimize sample losses on the walls of the containers used. Next, each sample was passed through a 50-X8 hydrogen form resin, to remove cations such as K^+, and were rinsed with 5 mL of MQ H_2O and then subsequently passed through a polyvinylpyrrilodone (PVP) column and a premade high-capacity C18 (HC-C18) column to remove organic compounds.

Sample preparation for samples measured in 2007 was similar to the method used by Hong and Kim (1), Tanaka and Turekian (2), and Willis *et al.* (3). Excess reagent grade 1 M $BaCl_2$ (3 mL) was added to each sample to precipitate sulfate as solid $BaSO_4$ (4, 2, 1, 3). The samples were centrifuged and the supernatant was carefully decanted, taking care to minimize losses of $BaSO_4$. The $BaSO_4$ was quantitatively transferred to a preweighed aluminum boat and dried in an oven (29–32 °C) for a minimum of 12 hr. The dry samples were weighed to obtain the total amount of recovered $BaSO_4$ and were then transferred to scintillation vials using a pipette and 2 mL of MQ H_2O to suspend the $BaSO_4$. To each sample vial, 10 mL of Insta Gel Plus cocktail was added for a total volume of 15 mL (5 mL H_2O + 10 mL gel). The vial was vortexed for 2 min to mix the solution and to insure adequate suspension of the solid $BaSO_4$ in the scintillation gel. The samples were counted. Samples were counted again 20–30 d later and once again 90–100 d later to observe and verify the exponential decay of ^{35}S.

Preparation of Na_2SO_4/H_2SO_4 for counting.

Because of concerns about the inconsistent recovery of $Ba^{35}SO_4$, possible contributions to the background from radiogenic barium isotopes, and problems maintaining solids suspended in the scintillation gel, the measurement of $^{35}SO_4^{2-}$ in solution was explored. Sample preparation was the same as in the previous section up to the addition of $BaCl_2$. Instead, these samples were passed through an IC-Ag resin to remove Cl^- from the solution. The sample solutions were then evaporated to solid Na_2SO_4 and then quantitatively transferred to a scintillation vial with 5 mL MP H_2O. Ten mL of Insta Gel Plus was added to the scintillation vial. The samples were mixed, placed in the scintillation counter, and counted for 10 min to 4 hr. These samples were recounted 20–30 d later and again 90–100 d later to observe the exponential decay of ^{35}S for optimal activity determination.

SO_2 collection.

Sulfur dioxide was collected simultaneously with ambient aerosols in San Fernando Valley, California, and La Jolla, California, in 2008. Atmospheric SO_2 was collected by placing a KOH impregnated filter after the backup filter on the four-stage cascade impactor (5). The KOH filter samples were processed and prepared for radiogenic analysis as described above for aerosol SO_4^{2-}.

1. Hong YL and Kim G (2005) Measurement of cosmogenic ^{35}S activity in rainwater and lake water. *Anal Chem* 77(10):3390–3393.
2. Tanaka N, Turekian KK (1991) Use of cosmogenic ^{35}S to determine the rates of removal of atmospheric SO_2. *Nature* 352(6332):226–228.
3. Willis CP, Olson DG, and Sill CW (1970) Radiochemical determination of sulfur-35 in large samples of vegetation. *Anal Chem* 42(1):124–126.
4. Tanaka N and Turekian KK (1995) Determination of the dry deposition flux of SO_2 using cosmogenic ^{35}S and ^7Be measurements. *J Geophys Res-Atmos* 100(D2):2841–2848.
5. Forrest J and Newman L (1973) Sampling and analysis of atmospheric sulfur-compounds for isotope ratio studies. *Atmos Environ* 7(5):561–573.

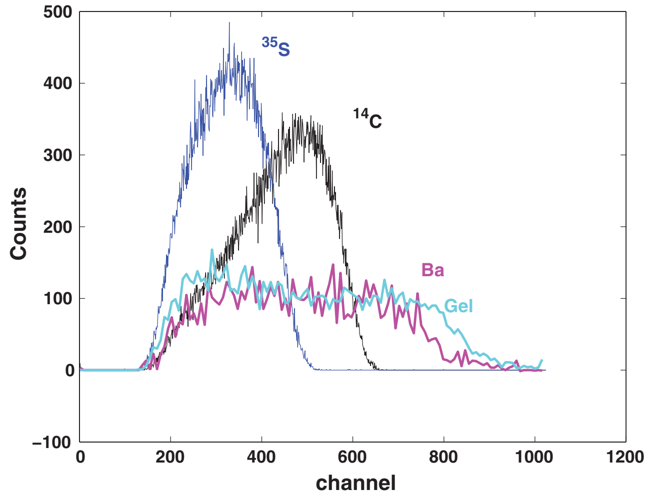

Fig. S1. Energy spectra of ^{35}S, ^{14}C, Ba, and gel vs. channel number. These spectra were used to optimize the integration of ^{35}S activity.

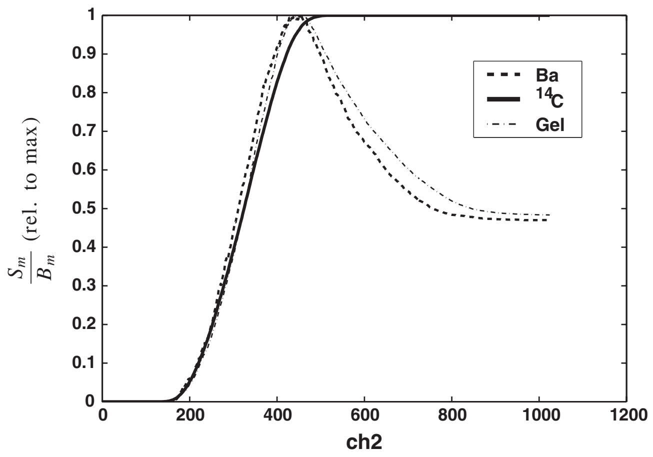

Fig. S2. Ratio of integrated ^{35}S counts vs. Ba, ^{14}C, and gel backgrounds as a function of ch2 (see Eq. **1**).