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Title: Intercomparison measurements of home-made sulfur isotope standards enriched in ^{33}S

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Abstract:

Despite widespread applications of sulfur isotope mass-independent fractionation (MIF) signals for probing terrestrial and extra-terrestrial environments, there has been no international sulfur isotope reference material available for normalization of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ data. International reference material to anchor isotope values is useful for interlaboratory data comparisons and needed to evaluate, e.g., whether issues exist associated with blanks and mass spectrometry when using different analytical approaches. We synthesized two sodium sulfate samples enriched in ^{33}S with different magnitudes, and termed them as S-MIF-1 and S-MIF-2, respectively. The sulfur isotopic compositions of these two samples were measured in five different laboratories using two distinct techniques to place them on the V-CDT scale for $\delta^{34}\text{S}$ and a provisional V-CDT scale for $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$. We obtained an average $\delta^{34}\text{S}$ of S-MIF-1 = 10.26 ± 0.22 ‰ and S-MIF-2 = 21.53 ± 0.26 ‰ (1 σ , versus V-CDT). The average $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values of S-MIF-1 were determined to be 9.54 ± 0.09 ‰ and -0.11 ± 0.25 ‰, respectively, while the average $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ of S-MIF-2 are 11.39 ± 0.08 ‰ and -0.33 ± 0.13 ‰ (1 σ , versus V-CDT). The lack of variation among the interlaboratory isotopic values suggests sufficient homogeneity of S-MIF-1 and S-MIF-2, especially for $\Delta^{33}\text{S}$. Although additional measurements may be needed to ensure the accuracy of the isotopic compositions of S-MIF-1 and S-MIF-2, they can serve as working standards for routine $\Delta^{33}\text{S}$ analysis to improve data consistency, and have the potential to serve as secondary sulfur isotope reference materials to address issues such as scale contraction/expansion and for normalization and reporting of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ between laboratories. For the same reasons as exposed for sulfur isotopes, the same standards were also artificially enriched in O-17. The calibration is still in progress but first estimations gave $\Delta^{17}\text{O} = 3.3 \pm 0.3$ ‰ with unassigned $\delta^{18}\text{O}$.

1. INTRODUCTION

Sulfur has four stable isotopes ^{32}S , ^{33}S , ^{34}S and ^{36}S with approximate abundances of 94.99 %, 0.75 %, 4.25 % and 0.01 %, respectively. The relative abundances of these isotopes in geologic materials (e.g., rocks, atmospheric aerosols, water, ice, meteorites, etc.) are affected by different geologic, atmospheric, biologic, and hydrologic processes. Therefore, variations in the relative abundances of sulfur isotopes in a variety of terrestrial and extra-terrestrial materials have the potential to serve as useful tracers of the source and transformation of sulfur in different environments, as well as provide information about their physical and/or chemical conditions. The relative abundances of sulfur isotopes are typically measured as the ratios of the rare isotopes (^{33}S , ^{34}S and ^{36}S) to the most abundant isotope, ^{32}S , and expressed as the delta notation which describes a deviation from a primary isotope reference material:

$$\delta^x\text{S} = \frac{xR_{spl}}{xR_{ref}} - 1 \quad (1)$$

where R represents $^x\text{S}/^{32}\text{S}$, and $x = 33, 34$ or 36 . The first principal reference material was troilite from the Canyon Diablo meteorite (Canyon Diablo Troilite - CDT). However, CDT was found to be variable in a prior study¹, and thus a V-CDT scale was established later by assigning a $\delta^{34}\text{S}$ value of -0.3 ‰ relative to V-CDT to an internationally distributed silver sulfide reference material IAEA-S-1². The assigned value of -0.3 ‰ was based on intercomparison measurements from fifteen individual laboratories.

A second historic aspect of sulfur isotope analyses has been a focus on $\delta^{34}\text{S}$. This occurred because of the difficulty of measuring ^{33}S and ^{36}S using standard combustion techniques, and a strong mass-dependent correlation between $\delta^{33}\text{S}$, $\delta^{34}\text{S}$ and $\delta^{36}\text{S}$ that led to the belief that independent information would not be obtained by measuring the two rarest sulfur isotopes. The recognition of mass-independent processes in meteoritic samples³⁻⁵, geologic samples⁶⁻⁹,

atmospheric and ice-core samples¹⁰⁻¹⁵, as well as the development of new techniques such as the MC-ICP-MS techniques for ³³S measurement^{16, 17} have made it of interest to have better calibrations over the full range of stable sulfur isotopes. In addition, mass-dependent fractionation processes in the biogeochemical sulfur cycle have also been measured and are known to produce small abundance deviations for ³³S and ³⁶S from mass-dependent relationships¹⁸⁻²⁰, and these variations have been shown to be useful in terms of obtaining additional information on the biogeochemical sulfur cycles in, for example, marine environments²¹⁻²³. The deviation from mass-dependent trends was commonly termed as mass-independent fractionation (MIF), although some was strictly related to mass-dependent processes, and expressed as the capital delta notation as follows:

$$\Delta^{33}\text{S} = \delta^{33}\text{S} - [(\delta^{34}\text{S} + 1)^{0.515} - 1] \quad (2)$$

$$\Delta^{36}\text{S} = \delta^{36}\text{S} - [(\delta^{34}\text{S} + 1)^{1.9} - 1] \quad (3)$$

These sulfur isotope anomalous signals, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, serve as unique proxies to track both mass dependent and mass independent fractionation processes.

Prior community efforts have established a consensual value for the V-CDT scale on the basis of the $\delta^{34}\text{S}$ for IAEA-S-1 in order to normalize $\delta^{34}\text{S}$ measurements of different samples in different laboratories, for data comparability and consistency. Other sulfur reference materials, such as IAEA-S-2 and IAEA-S-3, are also routinely used with the same purpose. Provisional assignments of values for $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ have been assigned to V-CDT in various studies^{24, 25}, but a full assignment has yet to be made. Other studies have resorted to normalizations to IAEA-S-1¹⁹ or CDT for $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ ²⁶⁻²⁸. The number of studies reporting $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ of terrestrial and extra-terrestrial samples²⁹ has increased tremendously in the past two decades due to interest in the geological and/or environmental information embedded in $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ signals. Such

increase has brought forth a need for the establishment of working materials and interlaboratory comparisons that will lay the groundwork for establishing a consensus for the normalization of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ of V-CDT.

Appropriate data normalization, aside from precise and accurate measurements, is necessary to ensure proper interlaboratory data comparison and to reach consensual conclusions according to $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values measured from same or similar types of samples³⁰.

Appropriate data normalization is also important for interpretation of small $\Delta^{33}\text{S}$ and/or $\Delta^{36}\text{S}$ values (e.g., 0.03 ‰). The $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values are not directly measured, but calculated from the measured $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values as shown in the above equations. The $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values are typically measured with respect to a laboratory working reference gas (i.e., SF_6), and then need to be anchored to the V-CDT scale in order to ensure consistent comparison of data among different laboratories. Although consensual $\delta^{34}\text{S}_{\text{V-CDT}}$ values of international sulfur isotope reference materials have been established, currently there are no consensual $\delta^{33}\text{S}_{\text{V-CDT}}$ and $\delta^{36}\text{S}_{\text{V-CDT}}$ values. Here we use the provisional *Wing and Farquhar*²⁴ V-CDT calibration of IAEA-S-1 which assigns $\Delta^{33}\text{S} = 0.094$ ‰ and $\Delta^{36}\text{S} = -0.7$ ‰ as the values for IAEA-S-1 on the V-CDT scale. These values correspond to $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ of -0.061 ‰ and -1.27 ‰, respectively. These values along with the community-defined $\delta^{34}\text{S}$ value of IAEA-S-1 (-0.3 ‰) are used to normalize multiple sulfur isotope compositions of particular samples to the V-CDT scale, once the working reference gas is calibrated versus IAEA-S-1, or concurrent measurements of IAEA-S-1 are performed.

Given the small $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values measured in, e.g., stratospheric and tropospheric sulfate aerosols, marine S-bearing materials, meteorites and Proterozoic geological samples, small errors, scale contraction, or drift in one-point scale normalization can lead to significant

differences in the derived $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values for such samples. In addition, the mechanism behind the origin of S-MIF in atmospheric sulfate is still a subject of debate³¹⁻³⁴, and observations of small negative $\Delta^{36}\text{S}$ in atmospheric sulfate possibly associated with combustion processes^{14, 15} raise further questions on the photo-chemical origin of S-MIF. Accurate and precise measurements as well as consistent data normalization are also critical in distinguishing the difference between small non-zero $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values produced by mass-dependent fractionation processes in biogeochemical sulfur cycles and non-zero $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values produced by MIF processes, and in further discerning the contributions of different MIF processes. In principle, data normalization can be considerably improved by using two or more points to provide a normalization spanning a wide delta range. To enable proper data normalization and compatible data reporting from different laboratories, secondary reference materials of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ are necessary in addition to IAEA-S-1. The IAEA-S-1 material is used as a primary reference material to scale or anchor the measured data to the V-CDT scale, rather than a physically-real calibration standard.

To date, there is no international sulfur isotope reference material enriched in ^{33}S and/or ^{36}S available for the purpose of a global calibration. Individual laboratories generally report $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values normalized using concurrent IAEA-S-1 measurements, but consensus values of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ for IAEA-S-1 in the V-CDT scale have not been assigned. In this study, we report the sulfur isotopic compositions of two synthesized sodium sulfate samples artificially enriched in ^{33}S with different magnitudes. The data we report are from separate analyses by five different laboratories. We evaluate the interlaboratory variations in the reported values and use the data to assess the potential for further use of these samples as secondary reference materials for $\Delta^{33}\text{S}$ data normalization. Concomitantly, these samples are also enriched in ^{17}O for the same reasons

as exposed for sulfur. The calibration is still in progress and the preliminary result of $\Delta^{17}\text{O} = 3.3 \pm 0.3 \text{ ‰}$ (1σ) is reported only for information purposes. In the following we will not elaborate more on $\Delta^{17}\text{O}$.

2. EXPERIMENTAL

2.1. Synthetization of samples enriched in ^{33}S

Two sodium sulfate (Na_2SO_4) samples, namely, S-MIF-1 and S-MIF-2, with an enrichment in ^{33}S were prepared in the stable isotope laboratory at the University of California-San Diego. We chose Na_2SO_4 as it is chemically stable, nontoxic, does not hydrate, and is widely available and easy to manufacture. The samples were prepared from chemical conversions of a mixture of sulfur powder and sulfur-33 powder. Reagents used included sulfur powder (99.5%, Fisher ACS, Lot: 897542), sulfur-33 powder (99.8%, Isoflex, Lot: 07111L35969), H_2O_2 solution (30%, extra pure, Fisher Scientific, Lot: 110251), H_2SO_4 (95%, extra pure, Fisher Scientific, Lot: 49020), NaOH (99+%, extra pure, Fisher Scientific), and O_2 (99.999%, Matheson USA).

For S-MIF-1, 20 g of sulfur powder and 0.00445 g of sulfur-33 powder were weighed and mixed in an agate mortar. For S-MIF-2, 20 g of sulfur powder and 0.0015 g of sulfur-33 powder were weighed and mixed. The composition of the initial mixtures corresponded to $\Delta^{33}\text{S}_{\text{V-CDT}}$ values of $\sim 30 \text{ ‰}$ and 10 ‰ , respectively. The powder mixture was transferred into a crucible, and ignited with a flame. The crucible was then placed in a 4 L air-tight glass vessel followed by a flow of O_2 at a rate of 50 mL/min in order to purge the glass vessel. As a result, SO_2 was produced and carried by O_2 into a NaOH solution (made of 33 ml ^{17}O -enriched water ($\Delta^{17}\text{O} = 47 \text{ ‰}$), 33 ml NaOH (50 % w/w) and 133 ml of pure water (18.2 M Ω)), where SO_2 was trapped as Na_2SO_3 . The S(IV)-containing NaOH solution was placed in an ice-water bath during the collection process. After the combustion was complete, we suspended the flow of O_2 and

slowly added 80 mL 30% H₂O₂ (due to the exothermicity of the reaction) to the NaOH solution in order to oxidize the trapped SO₃²⁻ to SO₄²⁻. For S-MIF-1, 33 mL H₂SO₄ was added to dilute $\Delta^{33}\text{S}$ to ~ 10 ‰, and then a few drops of NaOH were added to adjust to neutral pH. For S-MIF-2, no dilution was made and only a few drops of H₂SO₄ were added to adjust neutral pH. The different treatments of S-MIF-1 and S-MIF-2 in this last step were intended to produce Na₂SO₄ with circa identical $\Delta^{33}\text{S}$ but different $\Delta^{17}\text{O}$. Both S-MIF-1 and S-MIF-2 were then dried and grounded, and the powder was collected and stored. In the end, we recovered ~136 g and ~ 55.6 g Na₂SO₄ for S-MIF-1 and S-MIF-2, respectively.

2.2. Isotopic analysis

After preparation, S-MIF-1 and S-MIF-2 were circulated to five laboratories, including the stable isotope laboratory at Ecole Normale Supérieure (ENS) de Lyon, the stable isotope laboratory at the Institut de Physique du Globe de Paris (IPGP), the stable isotope laboratory at the University of Maryland, College Park (UMD), the stable isotope Geo-biology laboratory of the Massachusetts Institute of Technology (MIT) and the stable isotope laboratory at Tokyo Institute of Technology (TIT). In these laboratories, the isotopic composition of S-MIF-1 and S-MIF-2 were characterized individually.

In the laboratories of IPGP, UMD, MIT and ITI, S-MIF-1 and S-MIF-2 were analyzed following the conventional SF₆ methods. In each laboratory, the Na₂SO₄ samples were first reduced to silver sulfide (Ag₂S), using the **STRIP** method³⁵ or the Kiba reagent³⁶ following the standard procedure described in Forrest and Newman³⁷. We note that in practice each laboratory uses slightly different reduction techniques for operational convenience. Briefly, the collected sulfide after sulfate reduction was converted to silver sulfide (Ag₂S). After purification, Ag₂S was dried,

weighed (1- 3 mg) and transferred into a small aluminum boat. The aluminum boats were folded and loaded into externally heated nickel reaction tubes. The reaction tubes were evacuated for 0.5-1 hours at ~ 100 °C until desired vacuum achieved. F_2 (in excess) was then introduced into the reaction tubes to produce SF_6 . The reaction tubes were heated to ~ 250 °C and held at this temperature overnight. The produced SF_6 gas was first purified using a series of cryogenic techniques and then by gas chromatography carried by a helium flow. The purified SF_6 was lastly trapped with liquid nitrogen and then expanded under vacuum to a gas-source isotope ratio mass spectrometer (Thermo Fisher MAT 253) where its sulfur isotopic composition was analyzed in dual-inlet mode.

In the ENS laboratory, S-MIF-1 and S-MIF-2 were analyzed for sulfur isotopic compositions using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS)¹⁶. This method allows the measurements of ^{32}S , ^{33}S and ^{34}S at very low sulfur content (180 nmol, but can be as low as 10 nmole sulfur), with a typical reproducibility of $\pm 0.1\%$ for $\delta^{34}S$ and $\pm 0.15 \%$ for $\delta^{33}S$ (2σ) based on replicate measurements of the in-house Alfa Aesar (AA) standard solution. However, due to the interference of Ar-36 isotope, S-36 cannot be measured by this method. The chemistry procedure requires a first step of isolation and purification of sulfur (sulfate) from the sample matrix. In the ENS lab, after sulfate was isolated with anion exchange resin (200-400 mesh AG1-X8, in chloride form) and eluted in diluted HNO_3 media, sulfur isotopic compositions were measured on a Neptune Plus MC-ICP-MS with a Cetac Aridus II desolvator in the high-resolution mode. The isotopic values of $\delta^{33}S$ and $\delta^{34}S$ were measured with respect to the AA standard solution using standard-sample-standard bracketing technique. The $\delta^{34}S_{V\text{-CDT}}$ value of the AA standard solution, $4.86 \pm 0.14 \%$, was pre-calibrated using international reference materials IAEA-S-1, IAEA-S-2, IAEA-S-3 and IAEA-S-4. The $\delta^{33}S_{V\text{-CDT}}$

value of the AA standard solution was calculated using the mass-dependent fractionation law⁷. These values were then used to anchor the measured $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ values of S-MIF-1 and S-MIF-2 (with respect to AA) to the V-CDT scale.

In Table 1, we list important technical information of sample preparation and analysis in each laboratory. For the IR-MS method in laboratories other than ENS, IAEA-S-1 was measured repeatedly with S-MIF-1 and S-MIF-2. The measurement uncertainties of $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ in each laboratory as indicated by repeat measurements of IAEA-S-1 are listed in Table 2. The results of IAEA-S-1 in Table 2 were also used to anchor the sulfur isotopic composition of S-MIF-1 and S-MIF-2 into the V-CDT scale, given its known V-CDT values of $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$.

For information only, $\Delta^{17}\text{O}$ of these two samples was established based on the Ag_2SO_4 method³⁸⁻⁴⁰, and preliminary results indicate the two samples have an identical mean of $\Delta^{17}\text{O} = 3.3 \pm 0.3 \text{‰}$ (1σ), despite the efforts in sample preparation aiming to produce Na_2SO_4 with different $\Delta^{17}\text{O}$.

3. RESULTS AND DISCUSSION

3.1. Data reduction

The measured $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values of S-MIF-1 and S-MIF-2 with respect to individual laboratory working reference gas or standard solution are listed in Table 3 and Table 4, respectively. In these tables, the calculated $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values according to equations (2) and (3) are also listed. The means of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ for S-MIF-1 are $9.50 \pm 0.08 \text{‰}$ (1σ , $N = 33$) and $0.11 \pm 0.55 \text{‰}$ ($N = 26$), respectively, and that for S-MIF-2 are $11.36 \pm 0.08 \text{‰}$ ($N = 37$) and $-0.03 \pm 0.54 \text{‰}$ ($N = 23$), respectively. In order to compare the data from different laboratories and

to evaluate the isotopic variability of S-MIF-1 and S-MIF-2, these values need to be anchored in the same scale (i.e., the V-CDT scale).

For measurements done at IPGP, UMD, MIT and ITI, international reference material IAEA-S-1 was also measured at the same time with S-MIF-1 and S-MIF-2, and the results are reported with respect to laboratory working reference gases and listed in Table 2. IAEA-S-1 has a consensual $\delta^{34}\text{S}_{\text{V-CDT}}$ value of -0.3 ‰, but its $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values on the V-CDT scale have not been assigned. Wing and Farquhar²⁴ have compiled $\Delta^{33}\text{S}_{\text{V-CDT}}$ and $\Delta^{36}\text{S}_{\text{V-CDT}}$ data of IAEA-S-1 from the literature, and obtained provisional $\Delta^{33}\text{S}_{\text{V-CDT}}$ and $\Delta^{36}\text{S}_{\text{V-CDT}}$ values as 0.094 ± 0.004 ‰, and -0.7 ± 0.1 ‰, respectively. From there the $\delta^{33}\text{S}_{\text{V-CDT}}$ and $\delta^{36}\text{S}_{\text{V-CDT}}$ values of IAES-S-1 were also derived as -0.061‰ and -1.270‰, respectively. Hereafter, we refer to this scale as the V-CDT scale, but alert the reader to its provisional nature for the rarest isotopes. From the V-CDT values of IAEA-S-1 and its measured mean values with respect to the working gases, we obtained the isotopic values of the working reference gas in each laboratory with respect to V-CDT. Finally, the raw $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values of S-MIF-1 and S-MIF-2 with respect to working reference gases were converted into the V-CDT scale.

For measurements done in ENS, the $\delta^{34}\text{S}_{\text{V-CDT}}$ value of the working standard solution AA was 4.86 ± 0.14 ‰ as calibrated by international reference materials. According to the mass-dependent fractionation law, its $\delta^{33}\text{S}_{\text{V-CDT}}$ value was calculated as -2.52 ‰. These values were then used to convert the raw $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ data of S-MIF-1 and S-MIF-2 to the V-CDT scale.

3.2. Characterization of isotopic variability

The isotopic compositions of S-MIF-1 and S-MIF-2 in the V-CDT scale are listed in Table 5 and 6, respectively. The $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values were calculated using Equations (2) and (3), respectively. Taking into account all data from five laboratories, the uncertainty of $\delta^{34}\text{S}_{\text{V-CDT}}$ for

S-MIF-1 and S-MIF-2 is ± 0.22 and ± 0.26 ‰ (1σ), respectively, comparable to or better than that of international sulfur reference materials (e.g., ± 0.2 ‰ for IAEA-SO-6 and ± 0.4 ‰ for NBS-127). The uncertainty of $\Delta^{33}\text{S}_{\text{V-CDT}}$ for S-MIF-1 and S-MIF-2 is ± 0.09 and ± 0.08 ‰, respectively. For $\Delta^{36}\text{S}_{\text{V-CDT}}$, the uncertainties are ± 0.25 and ± 0.13 ‰ for S-MIF-1 and S-MIF-2, respectively. The relatively large uncertainties in $\Delta^{36}\text{S}_{\text{V-CDT}}$ are in part due to the extremely low abundance of ^{36}S , which leads to its accurate measurement more difficult, but maybe more likely come from an isobaric interference on the 131 peak during IRMS measurements (James Farquhar, personal communications). In addition, the uncertainties of the small delta values are larger than that of the capital delta values as always observed, and the best precision is for $\Delta^{33}\text{S}_{\text{V-CDT}}$. This is because the uncertainties of the small delta values are in part from sample preparation and conversion processes, but these processes would only induce mass-dependent fractionation and thus won't significantly affect the capital delta values.

It is noted that the V-CDT values of S-MIF-1 and S-MIF-2 derived from the measurement (one analysis available) done in MIT are slightly different from other labs, e.g., are at the low end for $\Delta^{33}\text{S}_{\text{V-CDT}}$ but the high end for $\Delta^{36}\text{S}_{\text{V-CDT}}$ among all data derived. However, this is only one measurement and its involvement in the global means did not affect the results (the means and standard deviations) much.

In all, S-MIF-1 was characterized with $\delta^{34}\text{S}_{\text{V-CDT}} = 10.26 \pm 0.22$ ‰ (1σ , $N = 32$), $\Delta^{33}\text{S}_{\text{V-CDT}} = 9.54 \pm 0.09$ ‰ ($N = 33$) and $\Delta^{36}\text{S}_{\text{V-CDT}} = -0.14 \pm 0.25$ ‰ ($N = 36$), and for S-MIF-2, its isotopic compositions were established as $\delta^{34}\text{S}_{\text{V-CDT}} = 21.52 \pm 0.26$ ‰ ($N = 37$), $\Delta^{33}\text{S}_{\text{V-CDT}} = 11.39 \pm 0.08$ ‰ ($N = 37$) and $\Delta^{36}\text{S}_{\text{V-CDT}} = -0.33 \pm 0.13$ ‰ ($N = 24$).

The mean $\delta^{34}\text{S}_{\text{V-CDT}}$, $\Delta^{33}\text{S}_{\text{V-CDT}}$ and $\Delta^{36}\text{S}_{\text{V-CDT}}$ values among all data and that of data from each laboratory including their one sigma standard deviations are plotted in Figure 1. Overall, the

derived $\delta^{34}\text{S}_{\text{V-CDT}}$, $\Delta^{33}\text{S}_{\text{V-CDT}}$ and $\Delta^{36}\text{S}_{\text{V-CDT}}$ values of S-MIF-1 and S-MIF-2 from the laboratories except for MIT are in good agreement, especially for the $\Delta^{33}\text{S}_{\text{V-CDT}}$ values, which are $9.56 \pm 0.01 \text{ ‰}$ ($N = 7$), $9.59 \pm 0.01 \text{ ‰}$ ($N = 6$), $9.52 \pm 0.02 \text{ ‰}$ ($N = 12$) and $9.58 \pm 0.09 \text{ ‰}$ ($N = 6$) for S-MIF-1, and $11.42 \pm 0.03 \text{ ‰}$ ($N = 5$), $11.42 \pm 0.01 \text{ ‰}$ ($N = 5$), $11.36 \pm 0.02 \text{ ‰}$ ($N = 12$), and $11.43 \pm 0.05 \text{ ‰}$ ($N = 13$) for S-MIF-2 from IPGP, UM, TIT and ENS, respectively. In comparison, the $\Delta^{33}\text{S}_{\text{V-CDT}}$ values of S-MIF-1 and S-MIF-2 derived from MIT are 9.13 and 10.97 ‰, respectively.

4. SUMMARY

There is a compelling need to have international sulfur and oxygen isotope reference materials enriched in ^{33}S , ^{36}S and ^{17}O , respectively, to calibrate the $\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$ and $\Delta^{17}\text{O}$ values measured from a variety of atmospheric and geological samples. This is important not only in terms of data comparisons within a laboratory and/or among different laboratories, but also regarding the differentiations of small $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values from mass-dependent and mass independent fractionation processes. Currently there is only one international sulfur reference material, IAEA-S-1, with established $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values ($0.094 \pm 0.004 \text{ ‰}$, and $-0.7 \pm 0.1 \text{ ‰}$, respectively) reported on the V-CDT scale²⁴, but IAEA-S-1 can be regarded more as a primary reference material. There are no reference materials with apparently large anomalies in $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$.

In this report, we synthesized two sodium sulfate samples, S-MIF-1 and S-MIF-2, artificially enriched in S-33 and O-17. The preliminary assessments of their oxygen isotopic compositions yielded $\Delta^{17}\text{O} = 3.3 \pm 0.3 \text{ ‰}$. The sulfur isotopic compositions of these two samples were characterized by five different laboratories using two distinct methods, the conventional IR-MS method and the newly developed MC-ICP-MS method¹⁶. Except for one data point from the

MIT laboratory, results from other four laboratories are in good consistence. The good precisions of these isotopic values indicate isotopic homogeneity of S-MIF-1 and S-MIF-2. Although further calibration efforts may need to improve the accuracy of $\Delta^{33}\text{S}_{\text{V-CDT}}$ assessments of S-MIF-1 and S-MIF-2, their current values can be adopted to calibrate $\Delta^{33}\text{S}$ measurements. In particular, mixing of them with other sulfur reference materials with zero $\Delta^{33}\text{S}$ such as IAEA-SO-5 and IAEA-SO-6 should generate working standards with different $\Delta^{33}\text{S}$ values, and which can be used to establish a calibration curve spanning a large $\Delta^{33}\text{S}$ range (e.g., 0 to 11 ‰) for better data normalization. These standards are available for the community and can be requested on demand to Joel Savarino.

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Table 1. Sample preparation and analysis methods in each lab.

Lab	IPGP	UMP	TIT	MIT	ENS
Preparation	STRIP/SF ₆	STRIP/SF ₆	Kiba/SF ₆	STRIP/SF ₆	Solution/SO ₄ ²⁻
Purification	GC	GC	GC	GC	Resin
Mass Spectrometry	MAT-253	MAT-253	MAT-253	MAT-253	MC-ICP-MS
	DI-IRMS VISC/O	DI-IRMS VISC/O	DI-IRMS VISC/O	DI-IRMS VISC/O	

VISC/O: Variable Ion Source Conductance (sulfur window) open.

Table 2. Sulfur isotopic composition of IAEA-S-1. Values are reported relative to individual laboratory working SF₆ gas.

	$\delta^{33}\text{S}$ (‰)	$\delta^{34}\text{S}$ (‰)	$\delta^{36}\text{S}$ (‰)	$\Delta^{33}\text{S}$ (‰)	$\Delta^{36}\text{S}$ (‰)
	-8.734	-17.042	-32.506	0.079	-0.375
IPGP	-8.727	-17.004	-32.079	0.066	-0.019
	-8.764	-17.096	-32.643	0.077	-0.411
mean	-8.742	-17.047	-32.409	0.074	-0.268
σ	0.020	0.046	0.294	0.007	0.217
UM	-2.581	-5.177	-10.701	0.088	-0.888
	-2.668	-5.333	-10.818	0.083	-0.709
mean	-2.624	-5.255	-10.760	0.086	-0.799
σ	0.061	0.111	0.083	0.004	0.126
	3.888	7.510	14.23	0.028	-0.083
	3.907	7.514	14.29	0.045	-0.036
	3.896	7.514	14.30	0.033	-0.025
	3.893	7.510	14.26	0.032	-0.062
	3.906	7.510	14.29	0.045	-0.024
TIT	3.907	7.506	14.27	0.048	-0.035
	3.968	7.638	14.479	0.041	-0.083
	3.972	7.626	14.482	0.051	-0.058
	3.964	7.631	14.415	0.042	-0.133
	3.963	7.629	14.434	0.042	-0.111
	3.964	7.629	14.487	0.042	-0.058
	3.967	7.630	14.389	0.044	-0.158
mean	3.933	7.571	14.361	0.041	-0.072
σ	0.035	0.063	0.096	0.007	0.043
MIT	-0.492	-1.021	-2.47	0.034	-0.531

Table 3. Sulfur isotopic composition of S-MIF-1. Values are reported relative to individual laboratory working SF₆ gas.

	$\delta^{33}\text{S}$ (‰)	$\delta^{34}\text{S}$ (‰)	$\delta^{36}\text{S}$ (‰)	$\Delta^{33}\text{S}$ (‰)	$\Delta^{36}\text{S}$ (‰)
IPGP	6.116	-6.445	-12.748	9.440	-0.538
	6.069	-6.584	-13.050	9.465	-0.577
	6.087	-6.521	-12.685	9.451	-0.331
	6.083	-6.549	-12.873	9.461	-0.467
	6.060	-6.620	-13.126	9.475	-0.585
	5.619	-7.479	-14.475	9.478	-0.313
	6.209	-6.317	-12.320	9.467	-0.352
UM	12.304	5.362	9.972	9.546	-0.241
	12.276	5.280	9.591	9.560	-0.465
	12.237	5.199	9.539	9.563	-0.361
	12.239	5.200	9.673	9.564	-0.230
	12.428	5.618	10.420	9.539	-0.282
	12.217	5.167	9.660	9.559	-0.180
TIT	18.756	18.076	35.365	9.488	0.742
	18.750	18.075	35.485	9.482	0.864
	18.768	18.074	35.402	9.500	0.782
	18.745	18.066	35.422	9.481	0.816
	18.756	18.069	35.406	9.491	0.796
	18.747	18.085	35.398	9.474	0.756
	18.938	18.372	35.728	9.518	0.534
	18.918	18.366	35.761	9.501	0.577
	18.936	18.371	35.760	9.516	0.566
	18.923	18.369	35.736	9.504	0.547
	18.938	18.371	35.760	9.519	0.566
18.941	18.375	35.723	9.520	0.522	
MIT	14.051	9.517	17.940	9.161	-0.220
ENS ^a	12.322	5.139		9.679	
	12.209	5.283		9.492	
	12.174	5.135		9.533	
	12.330	5.370		9.569	
	12.433	5.441		9.635	
	12.192	5.404		9.412	
mean			9.501	0.113	
σ			0.083	0.545	

a. Values relative to Alfa Aesar standard solution.

Table 4. Sulfur isotopic composition of S-MIF-2. Values are reported relative to individual laboratory working SF₆ gas.

	$\delta^{33}\text{S}$ (‰)	$\delta^{34}\text{S}$ (‰)	$\delta^{36}\text{S}$ (‰)	$\Delta^{33}\text{S}$ (‰)	$\Delta^{36}\text{S}$ (‰)
	13.531	4.306	7.746	11.316	-0.451
	13.529	4.260	7.662	11.337	-0.448
IPGP	13.506	4.236	7.498	11.327	-0.566
	13.790	4.860	8.720	11.290	-0.534
	13.666	4.644	8.391	11.277	-0.451
	19.991	16.771	31.484	11.388	-0.622
	19.924	16.640	31.283	11.389	-0.571
UM	19.786	16.432	31.097	11.357	-0.355
	19.726	16.280	30.745	11.375	-0.413
	19.770	16.358	30.984	11.379	-0.324
	26.404	29.433	57.109	11.353	0.446
	26.422	29.434	57.016	11.370	0.351
	26.412	29.445	57.004	11.354	0.317
	26.404	29.447	56.942	11.346	0.253
	26.409	29.450	56.985	11.349	0.289
	26.417	29.448	57.035	11.357	0.342
TIT	26.316	29.256	56.751	11.354	0.433
	26.315	29.262	56.809	11.350	0.480
	26.305	29.265	56.710	11.339	0.376
	26.307	29.269	56.790	11.339	0.449
	26.300	29.261	56.788	11.336	0.461
	26.298	29.259	56.795	11.335	0.472
MIT	21.351	20.198	38.000	10.999	-0.725
	20.026	16.812		11.403	
	20.165	16.886		11.504	
	19.988	16.835		11.353	
	20.102	16.926		11.421	
	19.990	16.782		11.382	
	20.040	16.886		11.379	
ENS ^a	20.084	16.737		11.499	
	20.015	16.903		11.345	
	20.001	16.813		11.377	
	19.947	16.725		11.368	
	19.871	16.575		11.369	
	20.013	16.805		11.394	
	19.970	16.687		11.410	
Mean				11.356	-0.034

σ	0.076	0.463
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a. Values relative to Alfa Aesar standard solution.

Table 5. Sulfur isotopic composition of S-MIF-1 in the V-CDT scale.

	$\delta^{33}\text{S}$ (‰)	$\delta^{34}\text{S}$ (‰)	$\delta^{36}\text{S}$ (‰)	$\Delta^{33}\text{S}$ (‰)	$\Delta^{36}\text{S}$ (‰)
IPGP	14.907	10.458	19.419	9.535	-0.545
	14.860	10.317	19.107	9.560	-0.586
	14.878	10.381	19.484	9.545	-0.332
	14.874	10.352	19.290	9.556	-0.471
	14.851	10.280	19.029	9.570	-0.594
	14.406	9.407	17.636	9.573	-0.312
	15.001	10.588	19.861	9.562	-0.353
UM	14.906	10.370	19.661	9.579	-0.134
	14.878	10.288	19.276	9.593	-0.361
	14.839	10.206	19.224	9.596	-0.257
	14.841	10.207	19.359	9.597	-0.124
	15.031	10.627	20.113	9.571	-0.175
	14.819	10.174	19.346	9.592	-0.073
TIT	14.704	10.123	19.410	9.503	0.089
	14.698	10.122	19.529	9.498	0.210
	14.715	10.122	19.447	9.515	0.128
	14.693	10.114	19.466	9.497	0.162
	14.703	10.116	19.450	9.506	0.142
	14.695	10.133	19.443	9.489	0.103
	14.884	10.417	19.768	9.533	-0.116
	14.865	10.411	19.801	9.517	-0.073
	14.883	10.416	19.800	9.532	-0.084
	14.870	10.414	19.776	9.520	-0.103
	14.885	10.416	19.799	9.534	-0.084
	14.888	10.420	19.763	9.535	-0.127
MIT	<i>14.393</i>	<i>10.246</i>	<i>19.879</i>	<i>9.130</i>	<i>0.323</i>
ENS	14.869	10.054		9.703	
	14.755	10.199		9.516	
	14.720	10.050		9.557	
	14.877	10.286		9.593	
	14.980	10.357		9.659	
	14.738	10.320		9.436	
Mean	14.810	10.262	19.467	9.538	-0.144
σ	0.141	0.215	0.457	0.090	0.250

Table 6. Sulfur isotopic composition of S-MIF-2 in the V-CDT scale.

	$\delta^{33}\text{S}$ (‰)	$\delta^{34}\text{S}$ (‰)	$\delta^{36}\text{S}$ (‰)	$\Delta^{33}\text{S}$ (‰)	$\Delta^{36}\text{S}$ (‰)
	22.387	21.392	40.581	11.427	-0.455
	22.385	21.345	40.494	11.449	-0.451
IPGP	22.362	21.321	40.325	11.438	-0.573
	22.649	21.956	41.587	11.401	-0.541
	22.523	21.736	41.247	11.388	-0.455
	22.613	21.836	41.379	11.426	-0.516
	22.546	21.704	41.176	11.426	-0.464
UM	22.407	21.495	40.989	11.395	-0.247
	22.347	21.343	40.633	11.412	-0.307
	22.391	21.421	40.874	11.416	-0.217
	22.321	21.392	40.819	11.361	-0.216
	22.339	21.393	40.728	11.378	-0.310
	22.329	21.404	40.716	11.363	-0.343
	22.321	21.405	40.655	11.354	-0.406
	22.326	21.409	40.697	11.357	-0.371
	22.334	21.407	40.746	11.366	-0.319
TIT	22.234	21.216	40.467	11.363	-0.229
	22.232	21.222	40.524	11.359	-0.183
	22.223	21.225	40.427	11.348	-0.285
	22.225	21.228	40.506	11.348	-0.213
	22.217	21.221	40.503	11.344	-0.201
	22.215	21.219	40.510	11.343	-0.191
	22.381	21.406	40.832	11.413	-0.232
MIT	<i>21.696</i>	<i>20.934</i>	<i>39.977</i>	<i>10.969</i>	<i>-0.173</i>
	22.592	21.785		11.432	
	22.731	21.859		11.533	
	22.553	21.808		11.381	
	22.668	21.899		11.449	
	22.555	21.754		11.410	
	22.606	21.858		11.407	
ENS	22.650	21.709		11.528	
	22.580	21.875		11.374	
	22.567	21.786		11.406	
	22.513	21.697		11.397	
	22.437	21.546		11.398	
	22.579	21.777		11.422	
	22.437	21.546		11.398	
Mean	22.418	21.528	40.725	11.389	-0.329

σ	0.192	0.257	0.356	0.083	0.125
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Figure 1. The individual laboratory results of S-MIF-1 and S-MIF-2. The error bars for the individual laboratory results are 1σ ; The Solid and dashed lines represent the interlaboratory averages and $\pm 1 \sigma$, respectively.

