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Intercomparison measurements of two ^{33}S -enriched sulfur isotope standards

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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 materials to anchor isotope values are useful for interlaboratory data comparisons and are 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 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 average $\delta^{34}\text{S}$ values of S-MIF-1 = $10.26 \pm 0.22\text{‰}$ and S-MIF-2 = $21.53 \pm 0.26\text{‰}$ (1σ , versus V-CDT). The average $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values of S-MIF-1 were determined to be $9.54 \pm 0.09\text{‰}$ and $-0.11 \pm 0.25\text{‰}$, respectively, while the average $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values of S-MIF-2 are $11.39 \pm 0.08\text{‰}$ and $-0.33 \pm 0.13\text{‰}$ (1σ , 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 listed for sulfur isotopes, the same standards were also artificially enriched in ^{17}O . The calibration is still in progress but first estimations gave $\Delta^{17}\text{O} = 3.3 \pm 0.3\text{‰}$ with unassigned $\delta^{18}\text{O}$.

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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

geological materials (*e.g.*, rocks, atmospheric aerosols, water, ice, meteorites, *etc.*) are affected by different geological, atmospheric, biological, and hydrological 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:

$$\delta^x\text{S}(\text{‰}) = \left(\frac{^xR_{\text{spl}}}{^xR_{\text{ref}}} - 1 \right) \times 1000 \quad (1)$$

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 study,¹ and thus a V-CDT scale

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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-1.² The assigned value of -0.3‰ was based on intercomparison measurements from fifteen individual laboratories.

The second historic aspect of sulfur isotope analyses has been 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 could not be obtained by measuring the two rarest sulfur isotopes. The recognition of mass-independent processes in meteorite samples,³⁻⁵ geological samples,⁶⁻⁹ and atmospheric and ice-core samples,¹⁰⁻¹⁵ as well as the development of new techniques such as the MC-ICP-MS techniques for ^{33}S measurement^{16,17} has 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 ^{33}S and ^{36}S from mass-dependent relationships,¹⁸⁻²⁰ and these variations have been shown to be useful in terms of obtaining additional information on the biogeochemical sulfur cycles in, for example, marine environments.²¹⁻²³ The deviation from mass-dependent trends was commonly termed mass-independent fractionation (MIF), although some were strictly related to mass-dependent processes, and expressed as the capital delta notation as follows:

$$\Delta^{33}\text{S} (\text{‰}) = \delta^{33}\text{S} - [(\delta^{34}\text{S}/1000 + 1)^{0.515} - 1] \times 1000 \quad (2)$$

$$\Delta^{36}\text{S} (\text{‰}) = \delta^{36}\text{S} - [(\delta^{34}\text{S}/1000 + 1)^{1.9} - 1] \times 1000 \quad (3)$$

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 for 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 researchers have resorted to normalizations to IAEA-S-1 (ref. 19) 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 an increase has resulted in 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 inter-laboratory data comparison and to reach consensual

conclusions according to $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values measured from the same or similar types of samples.³⁰ 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 Farquhar²⁴ V-CDT calibration of IAEA-S-1 which assigns $\Delta^{33}\text{S} = 0.094\text{‰}$ and $\Delta^{36}\text{S} = -0.700\text{‰}$ 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 (-0.300‰) 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 debate,³¹⁻³⁷ and observations of small negative $\Delta^{36}\text{S}$ values in atmospheric sulfate possibly associated with combustion processes^{14,15} raise further questions on the photochemical 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 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 on 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 performed at 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 listed 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. Synthesis of samples enriched in ^{33}S

Two sodium sulfate (Na_2SO_4) samples, namely, S-MIF-1 and S-MIF-2, enriched 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, is nontoxic, does not become hydrated, and is widely available and easy to manufacture. The samples were prepared by 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 airtight glass vessel followed by purging of the glass vessel with a flow of O_2 at a rate of 50 mL min^{-1} . 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 the 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% H_2O_2 (due to the exothermicity of the reaction) to the NaOH solution in order to oxidize the trapped SO_3^{2-} to SO_4^{2-} . For S-MIF-1, 33 mL H_2SO_4 was added to dilute $\Delta^{33}\text{S}$ to $\sim 10\text{‰}$, 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 H_2SO_4 were added to adjust to neutral pH. The different treatments of S-MIF-1 and S-MIF-2 in this last step were intended to produce Na_2SO_4 with similar $\Delta^{33}\text{S}$ but

different $\Delta^{17}\text{O}$. Both S-MIF-1 and S-MIF-2 were then dried and ground, and the powder was collected and stored. In the end, we recovered $\sim 136 \text{ g}$ and $\sim 55.6 \text{ g}$ Na_2SO_4 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 the 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 at the Massachusetts Institute of Technology (MIT) and the stable isotope laboratory at the Tokyo Institute of Technology (TIT). In these laboratories, the isotopic compositions of S-MIF-1 and S-MIF-2 were characterized individually.

In the laboratories of IPGP, UMD, MIT and TIT, S-MIF-1 and S-MIF-2 were analyzed following the conventional SF_6 method. In each laboratory, the Na_2SO_4 samples were first reduced to silver sulfide (Ag_2S) using the Strongly Reducing hydriodic-hypoPhosphorous-hydrochloric acid (STRIP) method³⁸ or the Kiba reagent³⁹ method following the standard procedure described in Forrest and Newman.⁴⁰ 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 (Ag_2S). After purification, Ag_2S 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 hour at $\sim 100 \text{ °C}$ until the desired vacuum was achieved. F_2 (in excess) was then introduced into the reaction tubes to produce SF_6 . The reaction tubes were heated to $\sim 250 \text{ °C}$ and held at this temperature overnight. The produced SF_6 gas was purified first using a series of cryogenic techniques and then by gas chromatography using helium as the carrier gas. The purified SF_6 was then trapped with liquid nitrogen and transferred 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. Briefly, in each analysis, the sample and reference gas (SF_6) were measured one after another for masses of 127 ($^{32}\text{SF}_5^+$), 128 ($^{33}\text{SF}_5^+$), 129 ($^{34}\text{SF}_5^+$) and 131 ($^{36}\text{SF}_5^+$). In the end, the measured $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values of the sample were expressed in the delta notation with respect to the reference SF_6 gas.

In the ENS laboratory, S-MIF-1 and S-MIF-2 were analyzed for sulfur isotopic compositions using multi-collector inductively

Table 1 Sample preparation and analysis methods in each lab^a

Lab	IPGP	UMD	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 DI-IRMS VISC/O	MAT-253 DI-IRMS VISC/O	MAT-253 DI-IRMS VISC/O	MAT-253 DI-IRMS VISC/O	MC-ICP-MS

^a 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

	$\delta^{33}\text{S}$ (‰)	$\delta^{34}\text{S}$ (‰)	$\delta^{36}\text{S}$ (‰)	$\Delta^{33}\text{S}$ (‰)	$\Delta^{36}\text{S}$ (‰)	
IPGP	-8.734	-17.042	-32.506	0.079	-0.375	
	-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	
UMD	-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	
TIT	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	
	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

coupled plasma mass spectrometry (MC-ICP-MS).¹⁶ This method allows the measurement of ³²S, ³³S and ³⁴S at very low sulfur content (180 nmol, but can be as low as 10 nmol sulfur), with a typical reproducibility of $\pm 0.1\%$ for $\delta^{34}\text{S}$ and $\pm 0.15\%$ for $\delta^{33}\text{S}$ (2σ) based on replicate measurements of the in-house Alfa Aesar (AA) standard solution. However, due to the interference of the Ar-36 isotope, ³⁶S 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 an anion exchange resin (200–400 mesh AG1-X8, in chloride form) and eluted in dilute HNO₃ media, the sulfur isotopic compositions were measured on a Neptune Plus MC-ICP-MS with a Cetac Aridus II desolvator in high-resolution mode. The isotopic values of $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ were measured with respect to the AA standard solution using the standard-sample-standard bracketing technique. The $\delta^{34}\text{S}_{\text{V-CDT}}$ value of the AA standard solution, $4.86 \pm 0.14\%$, was pre-calibrated using the international reference materials IAEA-S-1, IAEA-S-2, IAEA-S-3 and IAEA-S-4. The $\delta^{33}\text{S}_{\text{V-CDT}}$ value of the AA standard solution was calculated using the mass-dependent fractionation law.⁷ 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 about 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 repeated 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 to 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 Ag₂SO₄ method,^{41–43} and preliminary results indicate that the two samples have an identical mean of $\Delta^{17}\text{O} = 3.3 \pm 0.3\%$ (1σ), despite the efforts taken during sample preparation aiming to produce Na₂SO₄ 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 Tables 3 and 4, respectively. These $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values are raw values, and were calculated relative to the measured $^{x}\text{S}/^{32}\text{S}$ ($x = 33, 34$ or 36) ratio of the working reference gas (*i.e.*, $^{x}\text{S}/^{32}\text{S} = ^{x}R_{\text{ref}}$ in eqn (1)). The working reference gas (*i.e.*, SF₆) used in each laboratory possesses different sulfur isotopic compositions, *i.e.*, $^{x}\text{S}/^{32}\text{S}$

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	
	UMD	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

	$\delta^{33}\text{S}$ (‰)	$\delta^{34}\text{S}$ (‰)	$\delta^{36}\text{S}$ (‰)	$\Delta^{33}\text{S}$ (‰)	$\Delta^{36}\text{S}$ (‰)
IPGP	13.531	4.306	7.746	11.316	-0.451
	13.529	4.260	7.662	11.337	-0.448
	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
UMD	19.991	16.771	31.484	11.388	-0.622
	19.924	16.640	31.283	11.389	-0.571
	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
TIT	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
	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
ENS ^a	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	
	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	

^a Values relative to Alfa Aesar standard solution.

values are different. This means the raw $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values of S-MIF-1 and S-MIF-2 from different laboratories are on different scales ($^xR_{\text{ref}}$ is different), and thus they are very different as shown in Tables 3 and 4.

In Tables 3 and 4, the calculated $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values from raw $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ data according to eqn (2) and (3) are also listed. Despite the difference in raw $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values among different laboratories, the $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values of the same sample from different laboratories are almost identical. This is because $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ are relative values reflecting the deviations from the mass-dependent lines, and are not much affected by the scale differences. But when small differences are focused on, they still need to be on the same scale. 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 those 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 better 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 on the same scale (*i.e.*, the V-CDT scale). For measurements done at IPGP, UMD, MIT and TIT, the 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 -0.300‰ , 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 of $0.094 \pm 0.004\text{‰}$ and $-0.700 \pm 0.100\text{‰}$, respectively. From this the $\delta^{33}\text{S}_{\text{V-CDT}}$ and $\delta^{36}\text{S}_{\text{V-CDT}}$ values of IAEA-S-1 were also derived to be -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 (Table 2), 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 at the ENS, the $\delta^{34}\text{S}_{\text{V-CDT}}$ value of the working standard solution AA was $4.86 \pm 0.14\text{‰}$ as calibrated using international reference materials. According to the mass-dependent fractionation law, its $\delta^{33}\text{S}_{\text{V-CDT}}$ value was calculated to be -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.

The above processes placed all $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values on the same scale, *i.e.*, the V-CDT scale with the same $^xR_{\text{ref}}$. After all raw $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values were anchored on the V-CDT scale, the $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values were re-calculated using eqns (2) and (3).

3.2. Characterization of isotopic variability

The isotopic compositions of S-MIF-1 and S-MIF-2 on the V-CDT scale are listed in Tables 5 and 6, respectively. As shown in these tables, the $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ V-CDT values of S-MIF-1 (or S-MIF-2) from different laboratories are identical. This is as expected because now they are all on the same scale (*i.e.*, $^xR_{\text{ref}}$ is the same in eqn (1)), and the small or negligible difference is due to measurement uncertainties. Considering all data from the five laboratories, the uncertainties of $\delta^{34}\text{S}_{\text{V-CDT}}$ for S-MIF-1 and S-MIF-2 are ± 0.22 and $\pm 0.26\text{‰}$ (1σ), respectively, comparable to or better than those of international sulfur reference materials (*e.g.*, $\pm 0.2\text{‰}$ for IAEA-SO-6 and $\pm 0.4\text{‰}$ for NBS-127). Regarding the $\Delta^{33}\text{S}_{\text{V-CDT}}$ and $\Delta^{36}\text{S}_{\text{V-CDT}}$, it can be noted that they are slightly different from those calculated from the raw $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ data (Tables 3 and 4). These small differences may be considered to be negligible regardless of the scale when the capital delta values are large, *e.g.*, in the case of $\Delta^{33}\text{S}$ of S-MIF-1, it is $9.50 \pm 0.08\text{‰}$ and $9.54 \pm 0.09\text{‰}$ before and after



anchoring on the V-CDT scale. But when small capital values are the subject of interest, the difference becomes important, *e.g.*, in the case of $\Delta^{36}\text{S}$ of S-MIF-1, it is $0.11 \pm 0.55\text{‰}$ and $-0.14 \pm 0.25\text{‰}$ before and after anchoring on the V-CDT scale. Overall, the uncertainties of $\Delta^{33}\text{S}_{\text{V-CDT}}$ for S-MIF-1 and S-MIF-2 are ± 0.09 and $\pm 0.08\text{‰}$, respectively. For $\Delta^{36}\text{S}_{\text{V-CDT}}$, the uncertainties are ± 0.25 and $\pm 0.13\text{‰}$ 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 makes its accurate measurement more difficult, but maybe more likely come from an isobaric interference on the 131 peak during IRMS measurements probably due to C_3F_5^+ .⁴⁴ In addition, the uncertainties of the small delta values are larger than those of the capital delta values as always observed, and the best precision is obtained 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 can be noted that the V-CDT values of S-MIF-1 and S-MIF-2 derived from the measurement (one analysis available) done at MIT are slightly different from those done at other labs, *i.e.*, they 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

Table 5 Sulfur isotopic composition of S-MIF-1 on 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	
	UMD	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	
MIT	14.885	10.416	19.799	9.534	-0.084	
	14.888	10.420	19.763	9.535	-0.127	
	ENS	14.393	10.246	19.879	9.130	0.323
		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 on 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	22.387	21.392	40.581	11.427	-0.455	
	22.385	21.345	40.494	11.449	-0.451	
	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	
	UMD	22.613	21.836	41.379	11.426	-0.516
		22.546	21.704	41.176	11.426	-0.464
		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
TIT		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	
	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	
MIT	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	
	ENS	21.696	20.934	39.977	10.969	-0.173
		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		
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	

and its involvement in the global means did not affect the results (the means and standard deviations) much.

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

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 the data and those data from each laboratory including their one sigma standard deviations are plotted in Fig. 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 at 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 at IPGP, UMD, TIT and ENS, respectively. In comparison, the $\Delta^{33}\text{S}_{\text{V-CDT}}$ values of



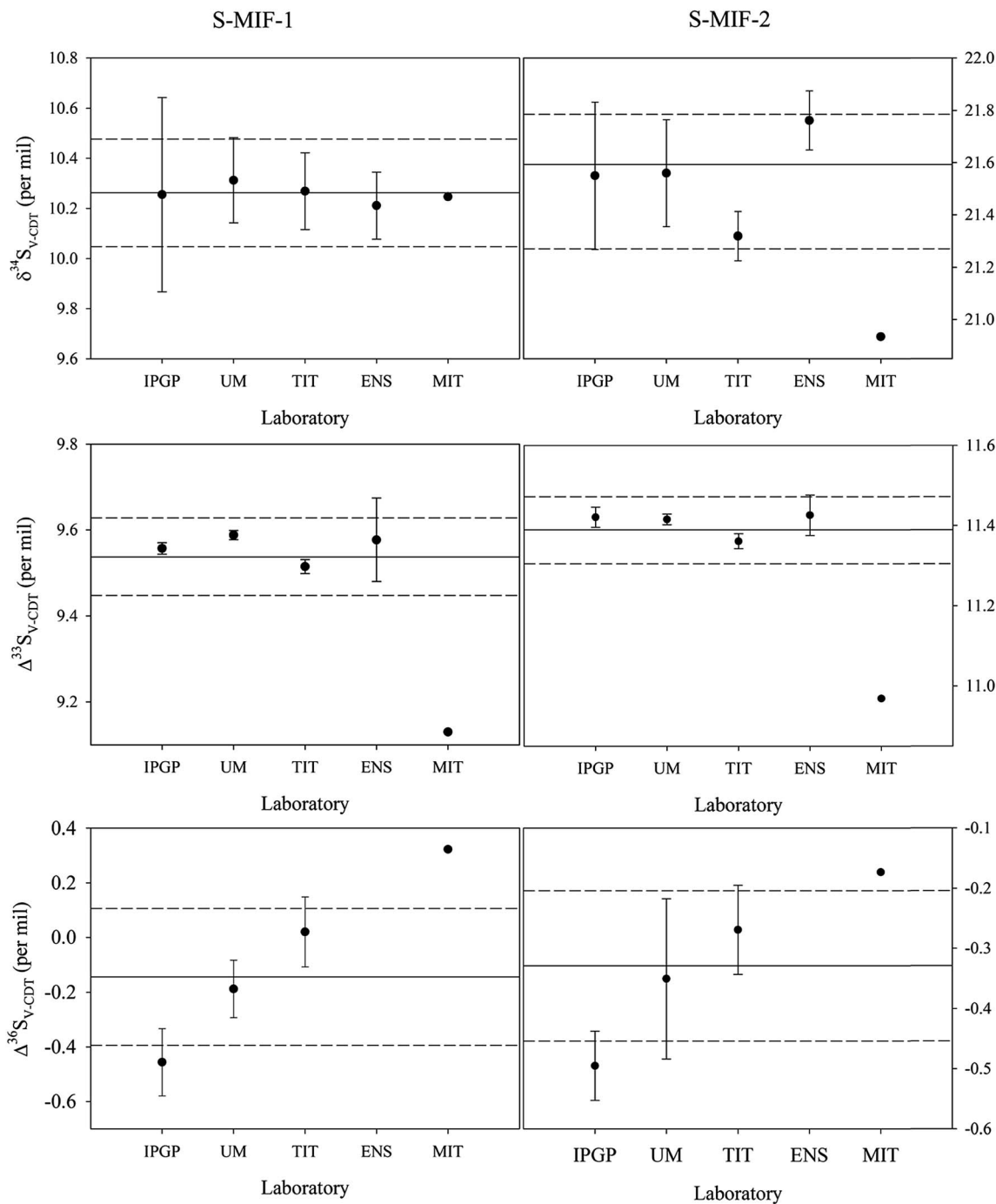


Fig. 1 The individual laboratory results of S-MIF-1 and S-MIF-2. The error bars for the individual laboratory results are 1σ ; the solid and dashed lines represent the interlaboratory averages and $\pm 1\sigma$, respectively.

S-MIF-1 and S-MIF-2 derived at 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 differentiation 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 scale,²⁴ 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 ^{33}S and ^{17}O . 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 at five different laboratories using two distinct methods, the conventional IR-MS method and the newly developed MC-ICP-MS method.¹⁶ Except for one data point from the MIT laboratory, results from the other four laboratories are in good consistency. The good precision of these isotopic values indicates isotopic homogeneity of S-MIF-1 and S-MIF-2. Although further calibration efforts may be needed 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 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, 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 from Joel Savarino.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 G. Beaudoin, B. E. Taylor, D. Rumble and M. Thiemens, *Geochim. Cosmochim. Acta*, 1994, **58**, 4253–4255.
- 2 T. B. Coplen and H. R. Krouse, *Nature*, 1998, **392**, 32.

- 3 G. W. Cooper, M. H. Thiemens, T. L. Jackson and S. Chang, *Science*, 1997, **277**, 1072–1074.
- 4 H. B. Franz, S. T. Kim, J. Farquhar, J. M. D. Day, R. C. Economos, K. D. McKeegan, A. K. Schmitt, A. J. Irving, J. Hoek and J. Dottin, *Nature*, 2014, **508**, 364–368.
- 5 J. Farquhar, J. Savarino, T. L. Jackson and M. H. Thiemens, *Nature*, 2000, **404**, 50–52.
- 6 S. Ono, J. L. Eigenbrode, A. A. Pavlov, P. Kharecha, D. Rumble, J. F. Kasting and K. H. Freeman, *Earth Planet. Sci. Lett.*, 2003, **213**, 15–30.
- 7 J. Farquhar, H. M. Bao and M. Thiemens, *Science*, 2000, **289**, 756–758.
- 8 H. Ohmoto, Y. Watanabe, H. Ikemi, S. R. Poulson and B. E. Taylor, *Nature*, 2006, **442**, 908–911.
- 9 J. Farquhar, M. Peters, D. T. Johnston, H. Strauss, A. Masterson, U. Wiechert and A. J. Kaufman, *Nature*, 2007, **449**, 706–709.
- 10 M. Baroni, J. Savarino, J. H. Cole-Dai, V. K. Rai and M. H. Thiemens, *J. Geophys. Res.*, 2008, **113**, D20112.
- 11 J. Cole-Dai, D. Ferris, A. Lanciki, J. Savarino, M. Baroni and M. H. Thiemens, *Geophys. Res. Lett.*, 2009, **36**, L22703.
- 12 J. Savarino, A. Romero, J. Cole-Dai, S. Bekki and M. H. Thiemens, *Geophys. Res. Lett.*, 2003, **30**, 2131.
- 13 A. B. Romero and M. H. Thiemens, *J. Geophys. Res.*, 2003, **108**, 4524.
- 14 M. Lin, X. L. Zhang, M. H. Li, Y. L. Xu, Z. S. Zhang, J. Tao, B. B. Su, L. Z. Liu, Y. A. Shen and M. H. Thiemens, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **115**, 8541–8546.
- 15 R. Shaheen, M. M. Abaunza, T. L. Jackson, J. McCabe, J. Savarino and M. H. Thiemens, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 11979–11983.
- 16 E. Albalat, P. Telouk, V. Balter, T. Fujii, V. P. Bondanese, M. L. Plissonnier, V. Vlaeminck-Guillem, J. Baccheta, N. Thiam, P. Miossec, F. Zoulim, A. Puisieux and F. Albarede, *J. Anal. At. Spectrom.*, 2016, **31**, 1002–1011.
- 17 G. Paris, A. L. Sessions, A. V. Subhas and J. F. Adkins, *Chem. Geol.*, 2013, **345**, 50–61.
- 18 S. Ono, *Space Sci. Rev.*, 2008, **135**, 203–220.
- 19 S. Ono, B. Wing, D. Johnston, J. Farquhar and D. Rumble, *Geochim. Cosmochim. Acta*, 2006, **70**, 2238–2252.
- 20 D. T. Johnston, J. Farquhar, B. A. Wing, A. Kaufman, D. E. Canfield and K. S. Habicht, *Am. J. Sci.*, 2005, **305**, 645–660.
- 21 G. M. Luo, S. Richoz, B. van de Schootbrugge, T. J. Algeo, S. C. Xie, S. Ono and R. E. Summons, *Geochim. Cosmochim. Acta*, 2018, **231**, 73–87.
- 22 D. T. Johnston, S. W. Poulton, P. W. Fralick, B. A. Wing, D. E. Canfield and J. Farquhar, *Geochim. Cosmochim. Acta*, 2006, **70**, 5723–5739.
- 23 Y. A. Shen, J. Farquhar, H. Zhang, A. Masterson, T. G. Zhang and B. A. Wing, *Nat. Commun.*, 2011, **2**, 210.
- 24 B. A. Wing and J. Farquhar, *Geochim. Cosmochim. Acta*, 2015, **170**, 266–280.
- 25 S. Ono, W. C. Shanks, O. J. Rouxel and D. Rumble, *Geochim. Cosmochim. Acta*, 2007, **71**, 1170–1182.



- 26 M. A. Antonelli, S. T. Kim, M. Peters, J. Labidi, P. Cartigny, R. J. Walker, J. R. Lyons, J. Hoek and J. Farquhar, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 17749–17754.
- 27 J. W. Dottin, J. Farquhar and J. Labidi, *Geochim. Cosmochim. Acta*, 2018, **224**, 276–281.
- 28 J. Labidi, P. Cartigny and M. G. Jackson, *Earth Planet. Sci. Lett.*, 2015, **417**, 28–39.
- 29 J. M. Eiler, B. Bergquist, I. Bourg, P. Cartigny, J. Farquhar, A. Gagnon, W. F. Guo, I. Halevy, A. Hofmann, T. E. Larson, N. Levin, E. A. Schauble and D. Stolper, *Chem. Geol.*, 2014, **372**, 119–143.
- 30 J. Kaiser and T. Röckmann, *Rapid Commun. Mass Spectrom.*, 2008, **22**, 3997–4008.
- 31 S. Hattori, J. A. Schmidt, M. S. Johnson, S. O. Danielache, A. Yamada, Y. Ueno and N. Yoshida, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 17656–17661.
- 32 J. R. Lyons, *Geophys. Res. Lett.*, 2007, **34**, L22811.
- 33 A. R. Whitehill, B. Jiang, H. Guo and S. Ono, *Atmos. Chem. Phys.*, 2015, **15**, 1843–1864.
- 34 A. R. Whitehill, C. J. Xie, X. X. Hu, D. Q. Xie, H. Guo and S. H. Ono, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 17697–17702.
- 35 A. L. Buchachenko, *J. Phys. Chem. B*, 2013, **117**, 2231–2238.
- 36 S. Kopf and S. Ono, *Geochim. Cosmochim. Acta*, 2010, **74**, A531.
- 37 J. R. Lyons, *Chem. Geol.*, 2009, **267**, 164–167.
- 38 H. G. Thode, J. Monster and H. B. Dunford, *Geochim. Cosmochim. Acta*, 1961, **25**, 159–174.
- 39 T. Kiba, T. Tagaki, Y. Yoshimura and I. Kisha, *Bull. Chem. Soc. Jpn.*, 1955, **28**, 641–644.
- 40 J. Forrest and L. Newman, *Anal. Chem.*, 1977, **49**, 1579–1584.
- 41 L. Geng, A. J. Schauer, S. A. Kunasek, E. D. Sofen, J. Erbland, J. Savarino, D. J. Allman, R. S. Sletten and B. Alexander, *Rapid Commun. Mass Spectrom.*, 2013, **27**, 2411–2419.
- 42 J. Savarino, B. Alexander, V. Darmohusodo and M. H. Thiemens, *Anal. Chem.*, 2001, **73**, 4457–4462.
- 43 A. J. Schauer, S. A. Kunasek, E. D. Sofen, J. Erbland, J. Savarino, B. W. Johnson, H. M. Amos, R. Shaheen, M. Abaunza, T. L. Jackson, M. H. Thiemens and B. Alexander, *Rapid Commun. Mass Spectrom.*, 2012, **26**, 2151–2157.
- 44 D. Rumble, T. C. Hoering and J. M. Palin, *Geochim. Cosmochim. Acta*, 1993, **57**, 4499–4512.

