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Determination of Unbiased $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ Values by MC-ICP-MS Using Down to 30 nmol of Sulfur

Guillaume Paris *

CRPG UMR 7358 Université de Lorraine-CNRS, 54000 Nancy, France

* e-mail: guillaume.paris@univ-lorraine.fr

Abstract

The multi-collector inductively coupled plasma-mass spectrometer is an instrument suited to measuring sulfur isotopes in all types of samples, from ice cores and river waters to carbonates and Archaean rocks. Its main advantage is the more convenient method of sample preparation, as sulfate does not need to be reduced but purified from the sample through ion exchange. This method allows the measurement of unbiased and precise $\delta^{34}\text{S}$ values from samples as small as 10-nmol with a typical intermediate precision of 0.15‰ (2s) at 95% confidence. So far, no attempt has been made to understand at which levels of analytical precision and bias MC-ICP-MS could provide $\Delta^{33}\text{S}$ values. Here, the first standard addition experiment undertaken for $\Delta^{33}\text{S}$ evaluation shows that measurement results on a Neptune Plus MC-ICP-MS allows us to calculate $\Delta^{33}\text{S}$ values identical to those established by other measurement principles, for samples down to 30 nmol S, with an intermediate precision as good as 0.05‰ (2s). Though this precision is not as good as the analytical precision of data acquired by the SF_6 method, the advantages of small sample size and straightforward sample handling make it a very useful tool for investigating past and modern aspects of the sulfur cycle.

Keywords: MC-ICP-MS, sulfur isotopes, analytical protocols, $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$.

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Sulfur has four stable isotopes: ^{32}S (0.9504 mol mol⁻¹), ^{33}S (0.0075 mol mol⁻¹), ^{34}S

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(0.0420 mol mol⁻¹) and ³⁶S (0.0001 mol mol⁻¹) (Ding *et al.* 2001). Sulfur is abundant in the modern oxygenated ocean where it is present as sulfate and plays a key role as an electron acceptor in anaerobic metabolisms. It occurs on Earth under different redox states, from -2 in sulfides to +6 in sulfate, and the isotopic composition of sulfur in those species varies over a large range.

Isotopic ratios of sulfur are usually reported in ‰ using the δ^{3x}S notation (Equation 1):

$$\delta^{3x}\text{S} = \left[\frac{(^{3x}\text{S}/^{32}\text{S})_{\text{sample}}}{(^{3x}\text{S}/^{32}\text{S})_{\text{reference}}} - 1 \right] \quad (1)$$

where 3x = 33, 34 or 36. An additional notation exists, defined as Δ^{3x}S (Equation 2):

$$\Delta^{3x}\text{S} = \ln \left[\frac{(^{3x}\text{S}/^{32}\text{S})_{\text{sample}}}{(^{3x}\text{S}/^{32}\text{S})_{\text{reference}}} \right] \quad (2)$$

δ^{3x}S is reported in ‰ as well. The relationship between ³²S, ³³S, and ³⁴S is reported as Δ³³S (Equation 3):

$$\Delta^{33}\text{S} = \delta^{33}\text{S} - 0.515 \times \delta^{34}\text{S} \quad (3)$$

A similar equation exists for ³⁶S, though this isotope will not be discussed further in the current study. Sulfur isotopes were previously reported against the Canyon Diablo Troilite isotope standard (CDT). Because the CDT isotope standard turned out to be inhomogeneous and became unavailable, a new reference was defined at the 1993 Vienna Conference, the Vienna-CDT scale (Beaudoin *et al.* 1994, Gonfiantini *et al.* 1995, Robinson 1995). This new scale is based on the International Atomic Energy Agency (IAEA) S-1 isotope standard. In this scale, the ³⁴S/³²S is assigned a δ³⁴S value of -0.30‰ in the V-CDT scale (Coplen and Krouse 1998, Krouse and Coplen 1997) while the δ³³S of the IAEA-S-1 isotope standard has not been set. It has been measured at -0.047 ± 0.37‰ (Ding *et al.* 2001) -0.055‰ ± 0.16‰ (Ono *et al.* 2007); or -0.061‰ ± 0.03‰ (Wing and Farquhar 2015) against V-CDT (1s uncertainty). The V-CDT scale is thus a virtual scale as there is no isotope standard with δ³³S = δ³⁴S = 0‰ and slightly different δ³³S values are reported for the IAEA-S-1 reference material.

Many analytical advances have been made over the last 70 years since the first sulfur isotope measurements on a gas source mass spectrometer (GS-MS) as SO₂ (Thode *et al.* 1961, Wanless and Thode 1953). This initial work revealed the main structure that is still accepted today for the external sulfur cycle: sulfate in the ocean is isotopically positive, around +21‰, a value sustained by microbial sulfate reduction, which generates reduced sulfur and ultimately pyrite with lower and even negative δ³⁴S values. Documented δ³⁴S values in environmental samples range from at least -50‰ in pyrites to + 50‰ (e.g., Canfield 2004) and even up to +80‰ (e.g., Rennie and Turchyn 2014) in oceanic sediment pore waters. Because of this wide range in isotopic ratio, sulfur isotope abundance ratios can be very useful tracers of many environmental processes.

Following the SO₂ technique, the onset of SF₆-based measurements offered three new advantages (Hulston and Thode 1965). First, unlike oxygen, fluorine is mono-isotopic, limiting isotopologues. Second, there are no spectral interferences around the molecular mass of SF₅⁺ isotopologues, thus allowing unbiased and precise measurement of the three sulfur stable isotope abundance ratios (³³S/³²S, ³⁴S/³²S and ³⁶S/³²S). Finally, no memory effect is observed, as SF₆ is not a “sticky” gas. This method is widely used and allows great precision but requires extensive sample preparation. Sulfur needs first to be reduced to H₂S and then trapped as Ag₂S before being fluorinated. The SF₆ produced is then analysed using isotopic ratio mass spectrometry (IRMS). Significant progress has been made, allowing smaller and smaller sample test portions to be analysed, down to 150 nmol S (Ono *et al.* 2006b, Ueno *et al.* 2015) yet this decreased test portion size can be accompanied by a loss of precision on δ³⁴S measurement results. The SF₆ method allowed exploration of the processes generating non-zero Δ³³S and Δ³⁶S values (customarily referred to as mass-independent fractionation, MIF) in extra-terrestrial (meteorites) and terrestrial (Archaean sediments, sulfur aerosols trapped in ice cores) samples, contributing to improving the understanding of the evolution of Earth’s (and even Mars’s) atmosphere (Farquhar *et al.* 2000a, 2000b, Hulston and Thode 1965, Savarino *et al.* 2003, Thiemens 1999, Thode and Rees 1971). Progress also came from the measurement of oxygen isotopes in sulfate by IRMS, either as δ¹⁸O or Δ¹⁷O (Bao *et al.* 2000, Claypool *et al.* 1980). An ever-increasing variety of techniques are used to

measure S isotopes in various types of samples at different scales, such as thermal ionisation mass spectrometry (Paulsen and Kelly 1984), inductively coupled plasma-mass spectrometry (ICP-MS) (Mason *et al.* 1999, Menegario *et al.* 1998, Prohaska *et al.* 1999), Secondary Ion Mass spectrometry (SIMS) (Deloule *et al.* 1986, Pimlinger *et al.* 1984), and more recently laser spectroscopy (Christensen *et al.* 2007), ICP-MS/MS (Leyden *et al.* 2021) or orbitrap mass spectrometry (Neubauer *et al.* 2020), the latter allowing also 'clumped' sulfate isotopologue measurement.

Measurement of sulfur isotopes by ICP-MS started only in the late 1990s because of the difficulties posed by major interferences on each isotope. To prevent such interferences, a first attempt to measure $^{34}\text{S}/^{32}\text{S}$ ratios came from measuring the ratio between m/z 48 ($^{32}\text{S}-^{16}\text{O}^+$) and 50 ($^{34}\text{S}-^{16}\text{O}^+$) (Menegario *et al.* 1998). For 1 ml of sample solutions with a sulfur concentration of 17 mg l⁻¹, the authors measured the 48/50 ratios using transient peaks and achieved an instrumental repeatability precision better than 10‰ (1s). Direct measurements at m/z 32 and 34 were first achieved using a mass spectrometer equipped with a radiofrequency-only hexapole as a reaction/collision cell in which a mixture of Xe and H₂ was introduced (Mason *et al.* 1999). Charge transfers occurring in the cell increased the S⁺/O₂⁺ ratio. This approach produced $\delta^{34}\text{S}$ values with a 1s intermediate instrumental repeatability between 2 and 3‰ for solutions with sulfur concentrations between 10 and 50 mg l⁻¹ (or 300 to 1500 $\mu\text{mol l}^{-1}$). Simultaneously, using a double focusing sector field mass spectrometer, Prohaska *et al.* (1999) obtained an intermediate instrumental repeatability of 0.4‰ 1s using 10 ng S or less for one individual measurement. Samples were measured for 2 min and replicated ten times. To decrease the $^{16}\text{O}_2^+$ interference at m/z 32, they used a microconcentric nebuliser and desolvation membrane. Craddock *et al.* (2008) first developed the measurement of $\delta^{34}\text{S}$ on a multi-collector ICP-MS (Neptune instrument) for both bulk and microanalysis. They demonstrated that since multi-collection allows the simultaneous collection of ^{34}S and ^{32}S isotopes, it decreases the risk of being sensitive to fluctuations in plasma conditions. They obtained a "long-term repeatability" (repeated independent measurements of independently purified samples over different sessions) of 0.2‰ (2s). Together with appropriate wet chemistry, the MC-ICP-MS approach has allowed increasingly smaller sample sizes to be measured (Das *et al.* 2012). In addition, the MC-ICP-MS can be used with liquid samples or be coupled to laser ablation or gas

chromatograph systems (Amrani *et al.* 2009, Craddock *et al.* 2008, Raven *et al.* 2015). Paris *et al.* (2013) further improved the liquid sample MC-ICP-MS method and first demonstrated the capacity of this instrument to measure unbiased $\Delta^{33}\text{S}$, though with an intermediate repeatability of 0.20‰ (2s). This is typically at least one order of magnitude higher than the best precisions reported with the SF_6 method based on repeated measurements, including the fluorination step, of a sample or of a material of reference ($2s < 0.02\text{‰}$; Izon *et al.* 2015, Sansjofre *et al.* 2016, Wing and Farquhar 2015). Here, I assess the uncertainty associated with both the MC-ICP-MS measurement itself (intermediate instrumental repeatability) and combined with the purification protocol (intermediate repeatability) on small samples ($< 300 \text{ nmol S}$).

Over the last decade, the decrease in sample size required to measure $^{34}\text{S}/^{32}\text{S}$ ratios permitted by MC-ICP-MS helped improve our knowledge of the sulfur cycle on land, in the ocean, in sediments, and back in time. Applications ranged from exploration of Archaean or recent atmospheric processes (Dasari *et al.* 2022a, McConnell *et al.* 2017, Paris *et al.* 2014a), air pollution (Dasari *et al.* 2023, 2022b), incorporation of sulfate in carbonates (Barkan *et al.* 2020, Paris *et al.* 2014b), weathering and past geological sulfur cycle (Burke *et al.* 2018, Crowe *et al.* 2014, Present *et al.* 2015, Rennie *et al.* 2018, Torres *et al.* 2016), to medical or microbiological studies (Albalat *et al.* 2016, Sim *et al.* 2017).

However, measurement results of sulfur isotope abundance ratios by MC-ICP-MS were not used to try to determine $\Delta^{33}\text{S}$ variations smaller than 0.15‰ (e.g., Laurent *et al.* 2021, Torres *et al.* 2017). Yet, small deviations from the reference mass fractionation law (i.e., $\Delta^{33}\text{S} < 0.20\text{‰}$) provide useful information on the sulfur cycle (e.g., Farquhar *et al.* 2003, Johnston *et al.* 2005, Ono *et al.* 2006a). The goal of the current publication is to document the ability of the MC-ICP-MS to provide unbiased and precise $\Delta^{33}\text{S}$ values from small samples (test portions). Thus, I document the first experiments using the standard addition technique for $\Delta^{33}\text{S}$ measurements, a hitherto unexploited approach for sulfur isotopes. By doing so, I demonstrate that MC-ICP-MS measurement results allow the calculation of unbiased $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values, with an intermediate precision close to that of the SF_6 method, for test portions containing 25–50 nmol S.

Measurement procedure

Sample preparation

Three kinds of samples were used: seawater, silver sulfide samples (IAEA-S-1, 2, 3 isotope standards), elemental sulfur (IAEA-S-4) and Na₂SO₄ salts. Acids were purified at the CRPG by sub-boiling distillation using a DST-1000 system (Savillex) and high purity water (HPW with 18.2 MΩ cm resistivity) was produced by an Elga system (Veolia). Unless otherwise stated, all acids used in the following protocols were purified. PFA vials (Savillex) used in this study were rinsed five times in HPW, heated overnight at 80 °C in ~ 8 mol l⁻¹ reagent grade HNO₃, rinsed five times with HPW, heated overnight at 80 °C in ~ 6 mol l⁻¹ reagent grade HCl, rinsed again five times with HPW. The interior of the vials was refluxed for 24 h at 160 °C using a drop of HNO₃ and rinsed five more times with HPW. Vials must be handled carefully because gloves commonly used in the laboratory have been found to be a source of sulfur contamination. The resin is not recycled, and columns are stored in ~ 1.1 mol l⁻¹ reagent grade HCl.

IAEA isotope standards: Roughly 0.5 mg of IAEA-S-1, 2, 3 (silver sulfide) and 4 (elemental sulfur) were weighed and poured into PFA vials. *Aqua regia*, made by mixing 2 ml of HNO₃ and 2 ml of distilled HCl, was added and the vials were placed on a hot plate for 24 h at 160 °C. After this oxidising step, the *aqua regia* was evaporated and the dry residue was diluted in 1 ml of HPW.

Synthetic solutions: Prior to sample analysis, 1 l of bracketing isotope standard (BIS) solution at 10 mmol l⁻¹ of Na₂SO₄ in 0.5 mol l⁻¹ HNO₃ was prepared, the same HNO₃ solution used as the introduction medium for MC-ICP-MS measurements (Paris *et al.* 2013). Three different solutions were then mixed in different proportions: the BIS solution, another solution made of Na₂SO₄ previously analysed for δ³⁴S and Δ³³S (S-MIF-1, Geng *et al.* 2019), provided by Joel Savarino, and Atlantic seawater (SW) also used as an long-term full repeatability isotope standard. All solutions intended for processing through column chemistry were prepared so that their sulfate concentration was as close to 1 mmol l⁻¹ as possible to facilitate the standard addition experiments. Solutions were mixed in various

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proportions, allowing a total sulfate amount of 300 nmol S to be loaded on each column. By doing so, this ensured an equal sample to chemistry blank ratio for all samples. One millilitre of bracketing isotope standard was evaporated and afterwards diluted again in 10 ml of HPW before mixing with other solutions. For S-MIF-1, 14.2 mg of salt were dissolved in 10 ml of HPW. S-MIF-1' was prepared by mixing 100 μl of BIS at 1 mmol l^{-1} and 900 μl of S-MIF-1 at 1 mmol l^{-1} . Finally, for Seawater, 100 μl of natural seawater solution were diluted in 2.7 ml of HPW. Then, three samples were prepared by standard addition of the bracketing isotope standard (BIS) and seawater solutions while five samples were prepared by standard addition of the BIS and S-MIF-1' solutions. All samples were then purified by column chemistry.

Column chemistry: After mixing, each sample was purified using the anion-exchange resin AG1X8 (Bio-Rad, 100–200 mesh). In this procedure, the resin was batch cleaned by rinsing it first in HPW three times to remove smaller particles. It was then rinsed in 8-mol l^{-1} reagent grade HNO_3 and left overnight. After this step, the resin was rinsed again three times in HPW and was then ready for use. The protocol is very similar to one used previously (e.g., Burke *et al.* 2018, Paris *et al.* 2014a). As the capacity of the resin is 1.7 meq ml^{-1} , varying cation/ SO_4^{2-} ratios in the samples require variable amounts of resin. Except if stated otherwise, 600 μl of resin were introduced on disposable 10 ml Bio-Rad columns. Once loaded, the resin was rinsed twice with 2×10 column volumes (CV) of ~ 1.5 mol l^{-1} HNO_3 . This first step was designed to remove all traces of sulfate, following previous publications (e.g., Das *et al.* 2012, Paris *et al.* 2013, 2014). A strong concentration was used because NO_3^- has a lower affinity for the resin than sulfate and it is thus necessary to saturate the active sites of the resin with nitrate ions. The second step consisted of running 2×10 CV of ~ 3.5 mol l^{-1} HCl through the resin because Cl^- has a lower affinity for the resin than NO_3^- . The resin was then conditioned with 1×10 CV of $\sim 0.03\%$ mol l^{-1} HCl to remove excess Cl^- from the interstitial volume. The sample was introduced in a total volume of 1 ml and the resin was rinsed with 3×7.5 CV of HPW to remove major cations from the resin before elution with 3×2 CV of 0.45 mmol l^{-1} HNO_3 to ensure complete elution of sulfate (Paris *et al.* 2014). The final elution volume was evaporated to dryness. Doing so allowed the sample to be later diluted with the proper introduction medium before analysis on the Neptune instrument.

Isotope abundance ratio measurements

Sulfur isotope abundance ratios were measured on the Thermo Fischer Scientific MC-ICP-MS Neptune Plus installed at the CRPG in 2011. Samples were introduced in $\sim 0.5 \text{ mol l}^{-1} \text{ HNO}_3$ using an ESI PFA-50 nebuliser (with a measured uptake rate of about $60 \mu\text{l min}^{-1}$) and a Cetac Aridus II. The Aridus II comprised a PTFE spray chamber at $110 \text{ }^\circ\text{C}$ and a desolvating PTFE membrane heated at $160 \text{ }^\circ\text{C}$ to remove solvent vapour. The addition of a cation other than H^+ was necessary to ensure proper transmission through the Aridus. Here, Na^+ was used, following Paris *et al.* 2013, but NH_4^+ can also be used (Albalat *et al.* 2016). At the start of each run, the ion source was tuned using the BIS solution diluted to a final concentration of 20 or 40 $\mu\text{mol l}^{-1}$ depending on the session. The tuning aimed to optimise sensitivity, decrease isobaric interferences, increase the signal stability and improve the mass resolution as much as possible. After optimisation of the torch position, the best combination of the various gas flows was searched for through iterative tuning (sample gas and auxiliary gas on the Neptune MC-ICP-MS, sweep gas and additional gas on the Aridus). All three peaks at m/z of 32, 33 and 34 are affected by isobaric interferences mostly due to isotopologues of O_2 and SH with similar m/z ratios in addition to the $^{32}\text{S}^+$, $^{33}\text{S}^+$ and $^{34}\text{S}^+$ ions of interest (Craddock *et al.* 2008, Paris *et al.* 2013). The m/z peak 36 used to measure $^{36}\text{S}^+$ intensity is affected by a major $^{36}\text{Ar}^+$ interference, thus no attempt was made to measure this minor isotope. The m/z ratio of the interferences is heavier than that of the S^+ ions of interest, leaving an interference-free shoulder on the low-mass side of the peak. The signal for measuring ^{32}S abundance was measured in the central Faraday cup and heavy isotopes ^{33}S and ^{34}S in Faraday cups H1 and H3, respectively. The reference peak was m/z 34 because it is the least affected by interferences. The m/z position used to collect ^{32}S is slightly offset on the left of the sulfur plateau and ^{33}S even more (Paris *et al.* 2013). The relative position of the central cup was chosen such that the signal for each isotope was measured in the middle of the interference-free plateau, which sat on the left side on the peak. Special attention was given to the ^{33}S plateau, which was 4 mDa wide.

Once the respective positions of the peaks were chosen, raw signal intensity $^{34}\text{S}/^{32}\text{S}$ and $^{33}\text{S}/^{32}\text{S}$ ratios were collected to ensure that the raw $\Delta^{33}\text{S}$ value was 0.007‰ within $\pm 0.100\text{‰}$ and that no significant interferences affected the signals measured

on the collected masses. The 0.007‰ value is that determined for the BIS (Table S1). Intensity ratios were measured in high-resolution mode to allow optimal mass resolution. It was the typical aim to reach a $M/\Delta M$ value between 8000 and 10000 using the 5–95% valley definition (Weyer and Schwieters 2003) though most of the data here were acquired with an effective resolving power of 6000, due to a slightly worn entrance slit. The latter does not seem to have affected the results.

Intensity ratios were collected in fifty cycles of 4.194 s integration times each, following previous work on the topic, providing a mean ratio value (e.g., Paris *et al.* 2013). The standard error of the mean of the fifty cycles at the 95% confidence interval level (2SE) provides the “internal error”. Collection of a mean ratio thus lasted about four minutes, where the first minute corresponded to the solution uptake time. A sequence consisted of running the bracketing isotope standard between each sample, each intercalated with a wash and an instrumental measurement. Taking into account the time required to also measure the $^{34}\text{S}/^{32}\text{S}$ and $^{33}\text{S}/^{32}\text{S}$ ratios of the bracketing isotope standard and the instrumental blanks before and after the sample of interest, the complete cycle of data collection to provide a $\delta^{34}\text{S}$ value lasted ~ 25 min. For each sample, three to five individual measurement results were obtained. These were usually run at 20 $\mu\text{mol l}^{-1}$ following Paris *et al.* (2013). However, as the goal of the current study was to establish the precision that could be obtained for $\Delta^{33}\text{S}$ measurements by MC-ICP-MS, a sulfate concentration of 40 $\mu\text{mol l}^{-1}$ was used for the $\Delta^{33}\text{S}$ bias tests, which yielded a signal intensity of ~ 30 V for $^{32}\text{S}^+$.

Before introduction into the MC-ICP-MS, the solutions that were run on the columns were evaporated to dryness and then diluted in 0.6 mol l^{-1} HNO_3 , usually in 1 ml, depending on the amount of sulfur in the purified sample. Care was taken to ensure that solutions were run with a known sulfate concentration, equal to or lower than that of the bracketing isotope standard and a sodium concentration equal to that of the bracketing isotope standard solution (Paris *et al.* 2013). Here, depending on the run and the amount of sulfur available, the Na_2SO_4 molarity of the bracketing isotope standard solution was 20 or 40 $\mu\text{mol l}^{-1}$. The proper amount of sample was taken and transferred to a 4 ml PTFE vial for isotopic measurement. In the vial, Na^+ was added as NaOH from a 2.3 mmol l^{-1} stock solution. The amount added was calculated so that the final solution matched the sodium molarity of the sample with that of the

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bracketing isotope standard (40 or 80 $\mu\text{mol l}^{-1}$ Na, depending on the bracketing isotope standard used for the run). Finally, 0.6 mol l^{-1} HNO_3 was added to reach the required final volume as well as the appropriate Na^+ and SO_4^{2+} concentrations. By doing so, this ensured that the solvent composition (HNO_3 and Na^+ concentration) of the bracketing isotope standard and that of the “samples” were the same.

The minimum amount required for one run on the Neptune instrument was 0.35 ml. Depending on the samples, the final volume varied from 0.5 to 4 ml. Instrumental background was measured in the same 0.6 mol l^{-1} HNO_3 solution as used for the dilutions, with the same Na^+ concentration as the bracketing isotope standard and the samples.

Data processing

The data processing was done offline. Each sample or bracketing isotope standard was processed using a Matlab script that removed outliers within the fifty cycles. The script also allowed the manual truncation of the beginning or the end of the fifty cycles, should a problem have occurred, such as a sample running out of solution or a longer uptake time. The script is available on demand, and is based on one initially developed at Caltech for uranium isotope ratio measurements. Using an offline spreadsheet, both $^{34}\text{S}/^{32}\text{S}$ and $^{33}\text{S}/^{32}\text{S}$ ratios were first independently corrected for the instrument background using the mean of the background measured before and after the isotopic ratio considered (bracketing isotope standard or sample). Finally, the mass drift was corrected using the isotopic ratios determined for the bracketing isotope standard and assuming a linear variation between two consecutive bracketing isotope standards, following Paris *et al.* (2013). Once each individual $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ mean values were calculated, a mean value (and standard deviation) of the instrument replicate population was calculated for each sample. The 2s value was used to estimate the instrumental intermediate repeatability. When the same sample has been purified independently a repeated number of times indicated in the different tables, and the result of the purification measured as an individual sample, the uncertainty provided is a “full” intermediate repeatability where the uncertainty accounts for purification and instrumental repeatability and will represent the precision at which the values are obtained. All processed values are provided relative to the V-CDT scale (data associated with this study).

Experimental results

Bias

The stock solution of bracketing isotope standard used was a 10 mmol l⁻¹ solution of Na₂SO₄ diluted in a 0.6 mol l⁻¹ HNO₃ solution. To establish the value of the Na₂SO₄ bracketing isotope standard the solution was run against the IAEA-S-1 isotope standard, which defines the V-CDT scale. The δ³⁴S value of the S-1 isotope standard is defined as being -0.300‰ exactly (Coplen and Krouse 1998) and its Δ³³S value is 0.094 ± 0.004‰, following Geng *et al.* (2019). Numerically, this translates into ³⁴S/³²S and ³³S/³²S ratios of 0.0441493 and 0.0078768 respectively for IAEA-S-1, using a numerical value for the ³⁴S/³²S and ³³S/³²S ratio values of the virtual V-CDT isotope standard of exactly 0.0441626 (³²S/³⁴S = 22.6436 ± 0.0020, *k* = 1) and 0.0078772 (³²S/³⁴S = 126.948 ± 0.047, *k* = 1), respectively (Ding *et al.* 2001). Here, in order to compare only the uncertainty produced by the protocol described (purification and measurement), I followed Farquhar and Wing (2015) and Geng *et al.* (2019) and did not propagate the uncertainty associated with the determination of the sulfur isotope abundance ratios of the IAEA-S-1 standard. As a result, full expanded uncertainties cannot be discussed here, only the uncertainty of the measurement result. These values were used to establish the isotopic ratios of the bracketing isotope standard. To do so, three aliquots of the IAEA-S-1 isotope standard were processed as described above; each independently-purified aliquot was run as a bracketing isotope standard, and the in-house bracketing isotope standard (BIS) was used as a sample, six successive times on the Neptune instrument for each purified IAEA-S-1 solution. Results are presented in Table S1, where also shown is the value of our ³³S/³²S ratio using a reference value for δ³³S of -0.055‰ of the IAEA-S-1 isotope standard (Ono *et al.* 2012). Once the bracketing isotope standard was calibrated, the purified international isotope standards IAEA-S-2, 3 and 4 were run, and the results were compared with published values. Results are presented in Table S2 and compared with published values for the different isotope standards, showing that the MC-ICP-MS allows measurement of sulfur isotopic ratios in full agreement with other methods. Results for the synthetic solutions and comparison standards are presented in Tables 1 and S3, and Figure 1.

Concentration tests

To evaluate the measurement precision for smaller samples, the first step was to run the bracketing isotope standard diluted with the blank solution (0.6 mol l⁻¹ HNO₃ with 80 μmol l⁻¹ NaOH) against the BIS itself at 40 μmol l⁻¹. A purified sample seawater and isotope standard IAEA-S-3 at different sulfate concentrations were also run on the Neptune instrument as they provide high and low ends of the δ³⁴S scale, using a bracketing isotope standard concentration of 20 μmol l⁻¹. In each case, NaOH concentration matching that of the bracketing isotope standard was used (in this case, 80 μmol l⁻¹ of Na⁺ as the bracketing isotope standard concentration is 40 μmol l⁻¹). The last test consisted of ensuring that purification of smaller samples would not generate any concentration bias. To do so, 100 μl of diluted seawater (each containing initially 28 nmol S) were run on smaller, hand-made, PFA columns, containing 50 μl of resin each. Results are presented in Table S2 and Figure 2. Values are reported as a function of relative intensity, which is the intensity obtained for ³²S of the sample over that of the bracketing isotope standard. In each case, there was no significant variation of the δ³⁴S or Δ³³S values and the instrumental intermediate mean value remained identical within uncertainty (2s - full intermediate repeatability). The uncertainty however remained roughly constant for relative intensities down to 0.5 (2s lower than 0.3‰) and increased only for the lowest relative concentrations (2s up to 0.9‰).

Discussion

Potential bias of δ³⁴S measurements

The mean δ³⁴S values obtained here for IAEA-S-2 and IAEA-S-3 are 22.21 ± 0.10‰ and -32.41 ± 0.15‰ (2s), respectively. Uncertainties are provided as a full intermediate repeatability of three independent purification of each standard analysed independently five times each on the MC-ICP-MS. “Full” and instrument intermediate repeatability are identical, suggesting no additional contribution of the purification step to the uncertainty. Thus, instrument and “full” intermediate repeatability can be used to assess the level of precision. The ability to obtain unbiased isotopic ratios by MC-ICP-MS is shown through the comparison of the data generated with previously

published values and the values assigned by the International Atomic Energy Agency, hereafter reference values (IAEA 2020). The assigned reference values are $22.62 \pm 0.16\text{‰}$ and $-32.49 \pm 0.16\text{‰}$ (2s, IAEA 2020). Uncertainties are provided as the 95% confidence interval expanded uncertainty of the mean $\delta^{34}\text{S}$ value calculated from independent measurements performed in different laboratories using either gas source IRMS or a double-spike TIMS techniques (IAEA 2020, Mann *et al.* 2009). However, as no uncertainty is attached to the value of IAEA-S-1, the expanded uncertainty here is only determined by the standard deviation of the population of individual values from the chosen techniques. Standard IAEA-S-1 was used as the reference value against which our bracketing isotope standard is anchored. IAEA-S-1 has an assigned $\delta^{34}\text{S}$ value of -0.30‰ and its uncertainty is zero by definition (IAEA 2020). For intercomparison purposes however, an uncertainty of 0.06‰ (2s) is attributed to the $\delta^{34}\text{S}$ value of the isotope standard (IAEA 2020). However, regardless of the nature of the uncertainty provided in the literature, the uncertainty of the IAEA-S-1 standard is not considered, and neither is that of the in-house reference isotope standard of the laboratories, as this uncertainty is considered to not affect instrumental repeatability. Only instrumental (and here with the contribution of the chemical purification) uncertainty is provided. This must be kept in mind in the comparison discussed below.

For IAEA-S-2, roughly two sets of values exist in the literature. Values between 22.50‰ and 22.70‰ all come from IRMS, either through SF_6 or SO_2 measurements, while values between 22.20 and 22.45‰ are based on IRMS or MC-ICP-MS methods. The spread is similar for IAEA-S-3, though, for the latter, part of the spread might be related to the isotopic heterogeneity of the standard (Mann *et al.* 2009). IAEA-S-4 (Qi and Coplen 2003) is less extensively used and fewer published values are available.

The results obtained here mostly agree with existing data, both in terms of $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ (see Table 1), though the MC-ICP-MS $\delta^{34}\text{S}$ value for IAEA-S-2 ($22.21 \pm 0.10\text{‰}$) obtained here is slightly lower than the reference value ($22.62 \pm 0.16\text{‰}$, IAEA 2020). There is a minor, statistically significant spread observed between the values obtained by different studies, and the method employed in the present study does not particularly differ from any other approach. The $\delta^{34}\text{S}$ value obtained here is in full

agreement with other MC-ICP-MS published results and with IRMS values reported from MIT (e.g., $22.24 \pm 0.27\text{‰}$ ($2s$); Ono *et al.* (2012) – uncertainty is given as the 95% confidence interval from eight replicate measurements).

This minor discrepancy is not related to laboratory contamination or instrument background correction. Indeed, the total procedural blank (TPB) of the process employed in this study is lower than 0.5 nmol S. The TPB thus represents about $\sim 0.1\text{‰}$ of the total sulfur introduced on the columns. Because the $\delta^{34}\text{S}$ of the blank comprises between 0 and 5‰ it would affect the value of IAEA-S-3 more than the value of IAEA-S-2, and our IAEA-S-3 value is in full agreement with published values. The offset is also not due to the instrumental background signal on the instrument employed. Indeed, the concentration tests show that as soon as enough sulfur is introduced into the MC-ICP-MS, the mean value remains unbiased. IAEA-S-2 was run in the same conditions as the other materials, thus suggesting that the instrumental background correction does not come into play. Because these two isotope standards bracket most of the values found on Earth, it is confirmed here that MC-ICP-MS allows us to measure unbiased $\delta^{34}\text{S}$ values, at least for $\delta^{34}\text{S}$ values between -32 and $+22\text{‰}$.

The results for seawater ($21.14 \pm 0.08\text{‰}$) fall within the range of values published since the V-CDT scale has existed (Table 2). The $\delta^{34}\text{S}$ value for seawater in this study slightly differs from that obtained in previous work on the MC-ICP-MS by about 0.15‰ (Paris *et al.* 2013), though the values agree within uncertainty ($2s$ – full intermediate repeatability). It should be also noted that for both studies, the calibrations were made independently and that each is anchored in the V-CDT scale independently and that each bracketing isotope standard has a roughly 0.10‰ uncertainty ($2s$ - full intermediate repeatability) associated (0.15‰ and 0.08‰ for the 2013 and this study, respectively). Taking into account the 0.06‰ ($k = 2$) uncertainty on IAEA-S-1, the expanded uncertainties are 0.16 and 0.05‰ ($k = 2$). In addition, our previous value was the mean of thirty-five measurement results of individual natural samples while the current value is the mean of different measurements from the same standard seawater bottle. For all the reasons above, it can be considered that this offset is extremely small and indicates that the two independent calibrations (at Caltech and at CRPG) are robust.

Limits of quantification of $\Delta^{33}\text{S}$ values in small samples

Most processes on Earth's surface generate sulfur isotope fractionations according to mass-dependent processes where $\delta^{33}\text{S} = \lambda^{33} \times \delta^{34}\text{S}$. In this equation $\lambda^{33}_{\text{ref}} = 0.515$, the equilibrium reference fractionation coefficient at room temperature (Johnston 2011). There are however different types of situations where $\Delta^{33}\text{S}$, the deviation from this fractionation line, can be non-zero: true mass-independent fractionation (MIF) processes, or mass-dependent processes where the fractionation law factor λ^{33} slightly deviates from the reference value $\lambda^{33}_{\text{ref}}$, for instance because of biological processes, or during mixing or distillation processes (e.g., Farquhar *et al.* 2003, Johnston *et al.* 2005, Ono *et al.* 2006a). Though the latter processes are mass-dependent, they generate non-zero $\Delta^{33}\text{S}$ values and are thus usually grouped with the MIF generating processes.

As the end goal is to compare the ability of the MC-ICP-MS to provide $\Delta^{33}\text{S}$ values with an uncertainty comparable to the SF_6 method, the uncertainty provided here as full intermediate repeatability is compared with the precision provided for $\delta^{33}\text{S}$ calculated from SF_6 measurements results as the 2s value of repeated measurements of the same samples. The MC-ICP-MS used here is sufficiently sensitive to distinguish the subtle $\Delta^{33}\text{S}$ variations created by such processes. First, MC-ICP-MS data fully agree with published values of $\Delta^{33}\text{S}$ values for seawater and S-MIF-1. The lack of bias in the standard addition experiments shown in Figure 1 is the first assessment of $\Delta^{33}\text{S}$ bias on any instrument. All the values fall on the theoretical mixing trend. As a result, despite 2s values than can vary by a factor of 3, the mean value is not biased. Importantly, comparison of the Na_2SO_4 solution, the seawater and standard addition experiment 2 shows that the Neptune MC-ICP-MS is able to resolve $\Delta^{33}\text{S}$ differences down to 0.05‰, since the smallest uncertainty achieved is 0.03‰ (2s, full intermediate repeatability). As a result, uncertainty associated to $\Delta^{33}\text{S}$ calculations could probably be estimated as the 95% confidence interval of the standard error of the mean from the population of mean values (2SE) and thus overlap with precision achieved from SF_6 measurement results, using 300 nmol S.

Limits of quantification of $\Delta^{33}\text{S}$ values in small samples

In order to assess how precise the calculation of $\Delta^{33}\text{S}$ can be, we will explore the samples with the lowest concentrations (Figure 2). Doing so is of importance for at least two reasons: (1) the "internal error" (the standard error of the mean of the fifty cycles at the 95% confidence interval level, 2SE), directly depends on the amount of sulfur determined, up to a certain point where plasma flicker dominates. The nature of the relationship depends on the magnitude of the Johnson noise of the detectors (e.g., John and Adkins 2010, Paris *et al.* 2013). When evaluating intermediate reproducibility (thus taking into account the effect of bracketing and instrument background correction), the direct correlation with concentration is less strong for sulfur isotope ratio measurement results. Thus, the relationship between intermediate precision and sample concentration must be assessed. (2) Correlations between individual measurements $^{34}\text{S}/^{32}\text{S}$ and $^{33}\text{S}/^{32}\text{S}$ during SF_6 measurements reveals a correlation that induces a more precise $\Delta^{33}\text{S}$ compared with $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ while this is not the case on the MC-ICP-MS (Paris *et al.* 2013). Thus, developing a way to calculate more precise $\Delta^{33}\text{S}$ values is required.

Decreasing the sample size from 300 nmol S to 30 nmol S does not alter the precision of the $\Delta^{33}\text{S}$ calculations. A triplicate measurement of seawater samples representing 28 nmol S each yielded a $\Delta^{33}\text{S}$ value of $0.05 \pm 0.06\text{‰}$ (2s – full intermediate repeatability, Table S3). Both the mean and the precision are thus identical to the measurement results using samples of 300 nmol S. However, decreasing the amount of sulfur introduced to a relative intensity of 0.18, which corresponds to 4 nmol of sulfur introduced into the instrument, has a clear effect on the uncertainty (2s – full intermediate repeatability). The mean values nonetheless agree within uncertainty. Overall, the ability to resolve small $\Delta^{33}\text{S}$ variations is lost, as the instrument intermediate repeatability becomes larger than 0.2‰ . In order to resolve $\Delta^{33}\text{S}$ variations smaller than 0.2‰ , at least 16 nmol must be introduced in the instrument. Routinely, measurement results of 30 nmol S samples result in unbiased $\Delta^{33}\text{S}$ values with an uncertainty around 0.05‰ (2s). Altogether, these results show that the values determined by MC-ICP-MS can allow us not only to determine true mass-independent processes (schematically, $\Delta^{33}\text{S} > 0.2\text{‰}$) but also to distinguish minor isotope effects ($\Delta^{33}\text{S} < 0.2\text{‰}$) arising from mixing, distillation, or minor changes in the mass fractionation law.

Intercomparison with previously published values

When it comes to such a level of analytical precision, two aspects become critical. First, the method of calculating $\Delta^{33}\text{S}$ must be considered. $\Delta^{33}\text{S}$ is calculated here using Equation (3). As explained in the introduction, different definitions exist. For instance, Ono *et al.* (2012) use the same equation as Equation (3), while Geng *et al.* (2019) calculate $\Delta^{33}\text{S}$ following Equation (4):

$$\Delta^{33}\text{S} = \delta^{33}\text{S} - [(\delta^{34}\text{S}/1000+1)^{0.515} - 1] \times 1000 \quad (4)$$

In most cases, the different expressions round up to extremely close values. However, when it comes to strong deviations from $\Delta^{33}\text{S} = 0$, the difference can be perceptible. For instance, in the case of the proposed isotope standard S-MIF-1, using Equation (3) produces a value of $9.44 \pm 0.09\text{‰}$, while using Equation (4) results in a $\Delta^{33}\text{S}$ value of $9.54 \pm 0.09\text{‰}$, as published in Geng *et al.* (2019). This source of uncertainty is not taken into account in the articles cited here. In order to ensure proper comparison, and to be influenced only by analytical precision, I have used Equation (3) and recalculated previously published $\Delta^{33}\text{S}$ values when necessary (see all the tables).

The second sensitive aspect is the choice of the $\Delta^{33}\text{S}$ value assigned to IAEA-S-1 as difference choices of this value exist. In all the references listed here, the $\delta^{34}\text{S}$ of IAEA-S-1 is set at -0.30‰ , in agreement with the definition of the V-CDT scale. However, $\Delta^{33}\text{S}$ values ranging from 0.094‰ to 0.107‰ can be found for IAEA-S-1, which corresponds to $\delta^{33}\text{S}$ ranging from -0.061‰ to -0.047‰ , respectively (Ding *et al.* 2001, Ono *et al.* 2012, Wing and Farquhar 2015). It is necessary to agree on what this value is as the IRMS SF_6 routinely yields values with precisions better than 0.02‰ (2s). Defining an unbiased $\Delta^{33}\text{S}$ value of seawater is a goal of different publications and is a good example of why the values chosen for IAEA-S-1 matter (Ono *et al.* 2012, Paris *et al.* 2013, Tostevin *et al.* 2014). All the published values for modern seawater agree and indicate that seawater has a non-zero $\Delta^{33}\text{S}$ value that is slightly positive ($\sim 0.05\text{‰}$). Yet, the IAEA-S-1 normalisation is different in each of these publications (Table 1). Tostevin *et al.* (2014) assumed that the $\Delta^{33}\text{S}$ value of the international reference material was 0.107‰ , Ono *et al.* (2012) used 0.100‰ and Paris *et al.* (2013) used 0.094‰ . When renormalising using 0.094‰ for the $\Delta^{33}\text{S}$

value of IAEA-S-1 as assumed here, the $\Delta^{33}\text{S}$ values measured for seawater become $0.036 \pm 0.014\text{‰}$, $0.044 \pm 0.007\text{‰}$ to $0.050 \pm 0.030\text{‰}$ (2s) instead of having identical mean values. Similarly, if a value of 0.100‰ is assumed for IAEA-S-1, the respective mean values would become 0.042‰ , 0.050‰ and 0.056‰ . As $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ are independently anchored in the V-CDT scale, it is necessary to converge towards a common definition of $\delta^{33}\text{S}$ to allow comparisons of data from different laboratories and establish a proper budget of ^{32}S , ^{33}S and ^{34}S in the external reservoirs of the Earth. In any case, the results yield consistently positive values, but the differences are sufficient to affect interpretations of the sulfur cycle interpretations.

Conclusions

This paper documents the first standard addition experiments demonstrating that MC-ICP-MS allows us to calculate unbiased $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values. The results show that $\Delta^{33}\text{S}$ values obtained from MC-ICP-MS measurement results are and with a satisfactory precision for samples as small as 20 nmol S introduced into the instrument. When taking the full 'intermediate repeatability' into account, thus including the purification step, a precision of 0.05‰ (2s) can be obtained from 30 nmol of sulfur. This makes the MC-ICP-MS a useful instrument to estimate small $\Delta^{33}\text{S}$ deviations. Though producing results not as precise as those obtained from SF_6 measurements, the approach described here is ideal for the analysis of natural waters or carbonate samples for trace sulfate, making both techniques complementary to each other.

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Data availability statement

Data available in article supplementary material and online (<https://doi.org/10.24396/ORDAR-132>).

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Supporting information

The following supporting information may be found in the online version of this article:

Table S1. Calibration of the Na₂SO₄ stock solution using a concentration of 40 μmol l⁻¹.

Table S2. Concentration tests for different samples.

Table S3. Composition and results for the synthetic solutions resulting of the mixing between the “in-house” bracketing standard and seawater on the one hand (NS samples) and S-MIF-1’ on the other hand (NM samples)

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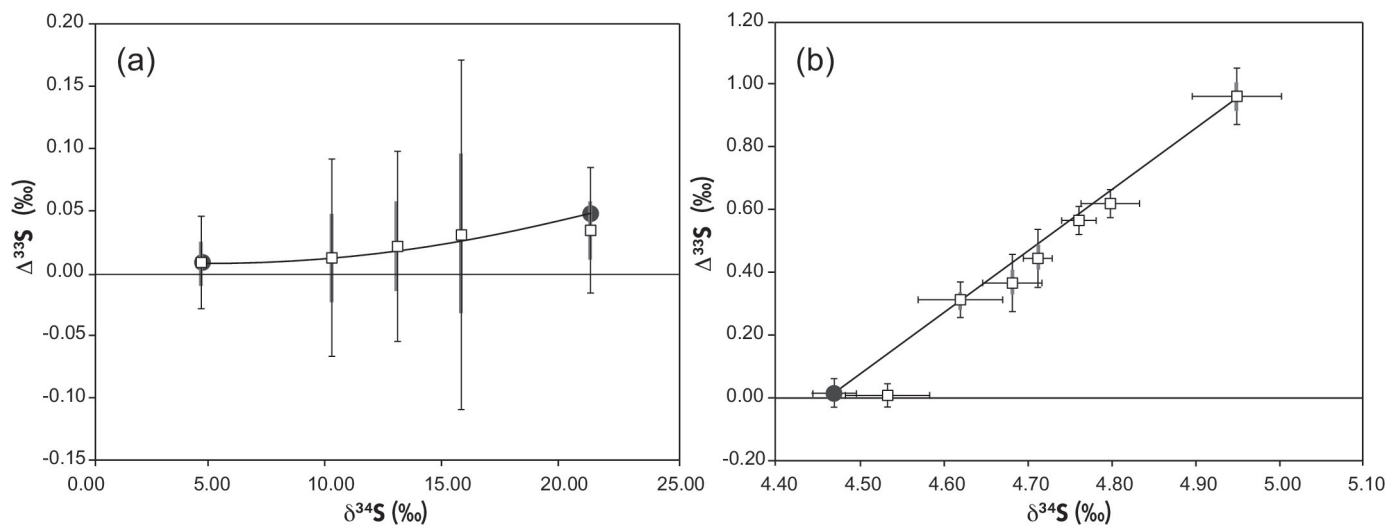
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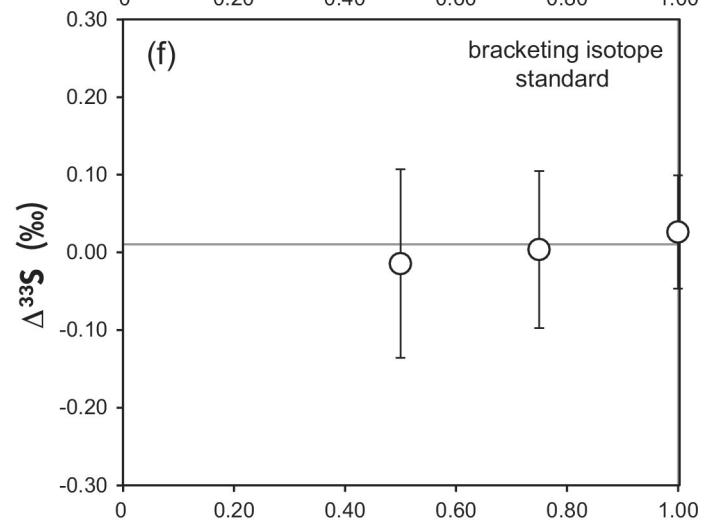
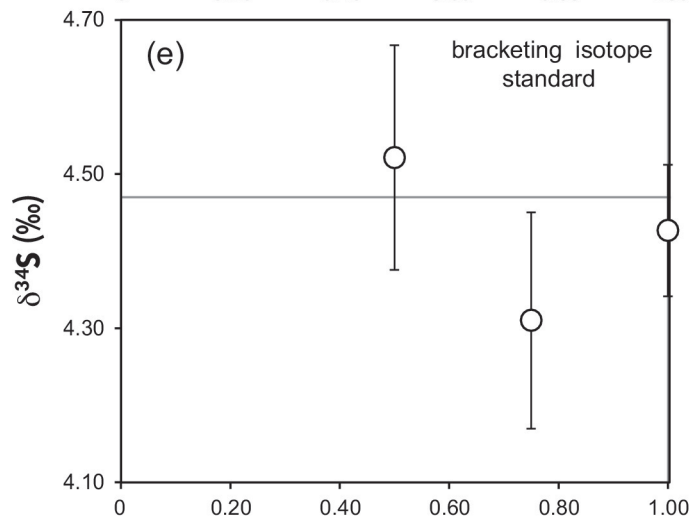
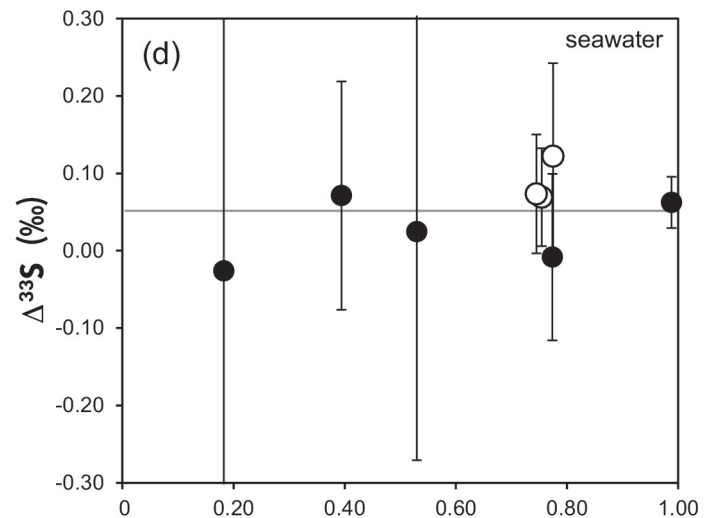
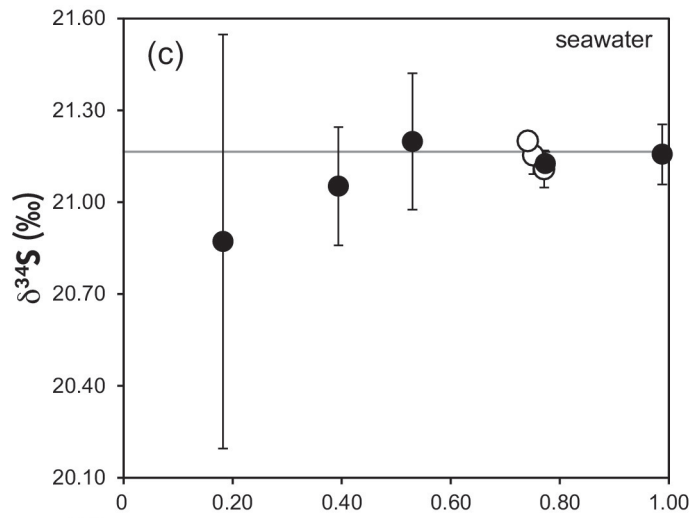
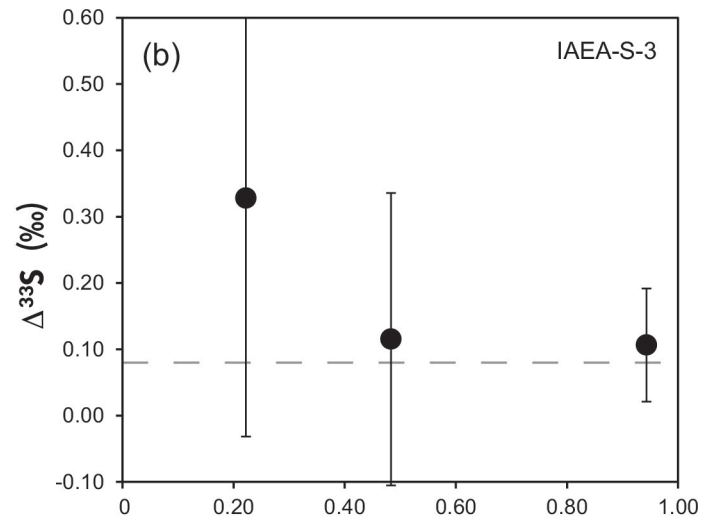
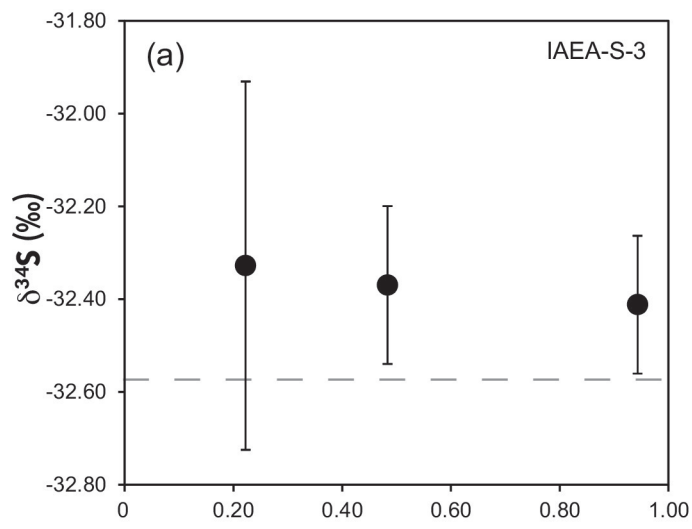
Figure 1. Measurement results for the standard additions between the bracketing isotope standard and (a) S-MIF-1 and (b) seawater. Intermediate instrument repeatability is plotted as the standard deviation at the 95% confidence interval (2s) of the instrumental mean value determination replicates. The thicker grey lines indicate the standard error of the mean at the 95% confidence interval level (2SE) for $\Delta^{33}\text{S}$ values. The end-members of the mixing lines (grey circles) are the mean of

values obtained from replicates (the same original sample purified independently more than once and ran during different sessions) as shown in Tables 2 and S1. The white squares represent the mean value of five measurement results for a single purification (Table S3). Black lines are theoretical mixing curves between the end-members.

Figure 2. Influence of the amount of sulfur determined on measurement bias for the isotope standard IAEA-S-3 (a, b, bracketing isotope standard at $20 \mu\text{mol l}^{-1}$), seawater (c, d bracketing isotope standard at $20 \mu\text{mol l}^{-1}$ – closed circles ; only 28 nmol S of purified seawater against a bracketing isotope standard at $40 \mu\text{mol l}^{-1}$ – open circles) and the unpurified diluted bracketing isotope standard as a sample (e, f bracketing isotope standard at $40 \mu\text{mol l}^{-1}$). Intermediate repeatability precisions are given at the 95% confidence interval (2s).



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Relative intensity

Relative intensity

Table 1.

Published and new values for IAEA-S-2, S-3 and S-4 with errors as provided in the cited studies

	IAEA-S-2				IAEA-S-3				IAEA-S-4			
	$\delta^{34}\text{S}$	2s	$\Delta^{33}\text{S}$	2s	$\delta^{34}\text{S}$	2s	$\Delta^{33}\text{S}$	2s	$\delta^{34}\text{S}$	2s	$\Delta^{33}\text{S}$	2s
This study ($n = 3$) ¹	22.21	0.10	-0.010	0.13	-32.41	0.15	0.11	0.08	16.45	0.2	0.03	0.11
Craddock <i>et al.</i> (2008) ¹	22.44	0.43							16.55	0.29		
Das <i>et al.</i> (2012) ¹	22.26	0.42			-32.29	0.45						
Albalat <i>et al.</i> (2016) ¹	22.23	0.11			-32.1	0.31			16.7	0.23		
Ref. value (IAEA)	22.62	0.16			-32.49	0.16			16.9	0.16		
Ding <i>et al.</i> (2001)	Geel	22.64	0.22	0.038	n.a.	-32.06	0.22	0.081	n.a.			
	Beijing	22.67	0.3	-0.132	n.a.	-32.55	0.24	0.248	n.a.			
Hu <i>et al.</i> (2003)		22.5	0.8			-32.1	0.2					
Wu <i>et al.</i> (2010)		22.23	0.16	0.038*	0.018							
Ono <i>et al.</i> (2012)		22.24	0.27	0.038*	0.01	-32.58	0.2	0.077*	0.01			
Wing and Farquhar (2015)		22.67	0.16	0.043	0.012	-32.49	0.14	0.067	0.014			
Ueno <i>et al.</i> (2015)		22.14	0.74	0.045*	0.012	-33.02	0.28	0.068*	0.05			

For this study, the 2s is calculated comes from four repeated measurements of a standard purified independently three times. It thus represents a full intermediate repeatability. Reference values are those provided on the IAEA website (IAEA 2020) and come from Mann *et al.* (2009).

* $\Delta^{33}\text{S}$ values are recalculated assuming that IAEA-S-1 $\delta^{33}\text{S}$ is -0.061‰, hence the differences that can appear with the data seen in the cited studies.

¹ Data obtained by MC-ICP-MS

Table 2.
New and published values for seawater and S-MIF-1 (Geng *et al.* 2019)

	Seawater				S-MIF-1			
	$\delta^{34}\text{S}$	2s	$\Delta^{33}\text{S}$	2s	$\delta^{34}\text{S}$	2s	$\Delta^{33}\text{S}$	2s
Tostevin <i>et al.</i> (2014)	21.24	0.88	0.036*	0.014				
Ono <i>et al.</i> (2012)	21.34	0.13	0.044*	0.007				
Paris <i>et al.</i> (2013)	20.97	0.10	0.07*	0.16				
Geng <i>et al.</i> (2019)					10.26	0.43 ^a	9.44*	0.18 ^a
Dasari <i>et al.</i> (2022)	21.14	0.09	0.05	0.06	10.06	0.14	9.46	0.14
<i>This study (replicates of the same seawater)</i>								
<i>Replicate 1</i>	<i>21.14</i>	<i>0.05</i>	<i>0.07</i>	<i>0.12</i>	<i>10.1</i>	<i>0.01</i>	<i>9.47</i>	<i>0.06</i>
<i>Replicate 2</i>	<i>21.11</i>	<i>0.1</i>	<i>0.04</i>	<i>0.10</i>				
<i>Replicate 3</i>	<i>21.19</i>	<i>0.04</i>	<i>0.03</i>	<i>0.05</i>				
<i>Replicate 4</i>	<i>21.12</i>	<i>0.06</i>	<i>0.05</i>	<i>0.05</i>				
<i>Mean value</i>	<i>21.14</i>	<i>0.08^b</i>	<i>0.05</i>	<i>0.03^b</i>				

All $\Delta^{33}\text{S}$ are recalculated using Equation (3), which is why for Geng *et al.* (2019) the $\Delta^{33}\text{S}$ value for S-MIF-1 value appears here as 9.44 instead of the published value of 9.54.

For the first three publications, the 2s values provided for seawater are the standard deviations of mean values from different natural samples.

^a the 2s value is calculated from different mean values produced in different laboratories and thus represent external reproducibility

* $\Delta^{33}\text{S}$ values are recalculated assuming that IAEA-S-1 $\delta^{33}\text{S}$ is -0.061‰, hence the differences that can appear with the data published in the cited studies.

For this study, each independently purified replicate (four for seawater, but only one for S-MIF-1) was measured five times against a bracketing standard at 40 $\mu\text{mol l}^{-1}$, providing the 2s value used here that documents the instrumental intermediate repeatability. The value of S-MIF-1 from Dasari *et al.* (2022) was measured using the method described here, thus providing a full external replicate.

^b the 2s value is calculated from the four replicates above. Each replicate represents an independent purification. Thus, 2s here represents full intermediate repeatability.