MC-ICP-MS measurement of $\delta^{34}S$ and $\Delta^{33}S$ in small amounts of dissolved sulfate

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**ABSTRACT**

Over the last decade, the use of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has significantly lowered the detection limit of sulfur isotope analyses, albeit typically with decreased precision. Moreover, the presence of isobaric interferences for sulfur prevented accurate analysis of the minor isotopes $^{33}S$ and $^{36}S$. In the present study, we report improved techniques for measuring sulfur isotopes on the MC-ICP-MS Neptune Plus (Thermo Fischer Scientific) using a heated spray chamber coupled to a desolvating membrane (Aridus, Cetac). Working at high mass resolution, we measured $\delta^{34}S$ values of natural samples with a typical reproducibility of 0.08–0.15‰ (2sd) on 5 to 40 nmol sulfur introduced into the instrument. We applied this method to two seawater profiles, using 25 µl of sample (700 nmol of sulfate). The average $\delta^{34}S_{\text{CDT}}$ value is $20.97 \pm 0.10$‰ (2sd, n = 25). We show that the amount of sulfate required for an analysis can be decreased to 5 nmol. Because the plasma is sustained by Ar, measurement of $^{36}S$ is impossible at the current mass resolution due to the presence of $^{36}Ar^+$, but a reproducibility of 0.1–0.3‰ (2sd) is achieved on the measurement of mass independent fractionations ($\Delta^{33}S$). This is the first time such precision has been achieved on samples of this size.© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Sulfur isotopes ($^{32}S$, $^{33}S$, $^{34}S$, $^{36}S$) are valuable tracers in many (paleo)environmental studies, but several analytical limitations remain that limit their utility. Sulfur isotopic compositions were originally measured on gas source isotope-ratio mass spectrometers (GS-IRMS) as $SO_2$ (Wanless and Thode, 1953; Thode et al., 1961) or $SF_6$ (Hulston and Thode, 1965). In the present study, we first measured on a quadrupole ICP-MS using masses 48 ($^{32}SO^+$) and 50 ($^{34}SO^+$) to get $^{34}S/^{32}S$ ratios. Precision on the ratios was better than 1‰ (1sd). Elemental S$^+$ ions were first analyzed directly using an RF-only hexapole ICP-MS where the collision cell was filled with a mixture of Xe and $H_2$ to decrease the $S^+/O^+$ ratio. This method resulted in precisions of better than 3‰ (1sd) for solutions containing between 300 and 1500 µmol S/l (Prohaska et al., 1999). Combining a double-focusing sector field mass spectrometer and a desolvating membrane to decrease (16O)$^2$ interference on mass 32, Prohaska et al. obtained $^{34}S/^{32}S$ ratios with precision of 0.4‰ (1sd) using less than 400 nmol S, and precision of 1‰ using 4 nmol S for one measurement (Prohaska et al., 1999). Multicollector ICP-MS (MC-ICP-MS) allows for simultaneous collection of $^{32}S^+$, $^{33}S^+$, $^{34}S^+$ and $^{36}S^+$, decreasing the effect of fluctuations in the plasma on the measured ratios (Clough et al., 2006). Isotopic compositions are usually reported using the δ notation (‰): $\delta^{34}S = 1000 \times \left(\frac{^{34}S}{^{32}S}_{\text{sample}} / \left(^{34}S/^{32}S\right)_{\text{standard}} - 1\right)$. More recently, Craddock et al. (2008) developed bulk and in-situ (by laser ablation) measurements of $\delta^{34}S$ on the MC-ICP-MS Neptune (Thermo
Fischer Scientific). Because of the $^{32}$S$^+$ interference at mass 33, they could not measure $\delta^{32}$S values with high precision however, and therefore did not report data for the mass-independent fractionation tracer $\Delta^{34}$S (Craddock et al., 2008). $\Delta^{34}$S is defined as $\delta^{34}$S - 0.515 $\times$ $\delta^{32}$S, where $\delta^{34}$S = 1000 $\times$ ln($^{34}$S/$^{32}$S)$_{sample}$/$^{34}$S/$^{32}$S)$_{standard}$ (Hulston and Thode, 1965). The use of MC-ICP-MS for S isotopes is becoming more widespread. Due to high useful ion yields (which combines ionization efficiency and sample usage) and low detection limits, sample sizes are order(s) of magnitude smaller than for SO$_2$ and SF$_6$ methods, down to 60 nmol with reproducibility of $\pm$ 0.3% for $\delta^{34}$S (Das et al., 2012). In many cases, the use of MC-ICP-MS allows higher throughput and requires less workup (e.g., no need for precipitation of dissolved sulfates or sulfides, no combustion to SO$_2$ or fluorination to SF$_6$). Working at a higher mass resolution can further reduce these interferences. In combination, these aspects of MC-ICP-MS provide much better accuracy than SO$_2$ measurements for both $^{33}$S/$^{32}$S and $^{34}$S/$^{32}$S ratios. $^{32}$S is not measureable by ICP-MS due to a severe interference by $^{32}$Ar.

Here we further push the limits of precision and sensitivity for sulfur isotope analysis on the MC-ICP-MS Neptune Plus (Thermo Fischer Scientific), and analyze the current limitations to our precision. Following the advent of GC–ICP-MS measurements of single organic compounds for their $\delta^{34}$S values at Caltech (Amrani et al., 2009), we present the development and application of trace sulfate analyses on the Neptune Plus and apply it to seawater profiles. Three points are assessed in this paper: purification of the samples, a decrease of isobaric interferences on the Neptune and measurement of $^{34}$S, and an increase of sensitivity and precision compared to previous MC-ICPMS studies. Because analysis of $^{33}$S on the Neptune is a new aspect of this work, we explore the limitations encountered by measuring this isotope abundance. The method developed in this paper is a novel and straightforward way to analyze $\delta^{32}$S, $\delta^{34}$S and $\Delta^{33}$S from carbonate-associated sulfate (CAS) or trace dissolved sulfate in waters down to $\pm$5 nmol S.

2. Description of the method

2.1. Wet chemistry

Three types of sample have been analyzed; solid BaSO$_4$, dissolved sulfate in natural waters, and CAS. Each kind of sample is processed differently to the point of yielding dissolved aqueous SO$_4^{2-}$: from that point on, all are treated identically. Samples are typically split for measurement of both sulfate concentration by ion chromatography (IC) and sulfate isotopic composition by MC-ICP-MS (Fig. 1). Except if otherwise indicated, all acids are ultrapure ‘Baseline’ grade (Seastar Chemicals Inc.).

2.1.1. Barite

Barites are dissolved by sitting at room temperature for three days in a solution of 50 mmol/l of diethylene triamine pentaacetic acid (DTPA) and NaOH and manually shaking the vials regularly. Samples are left in the solution for three days and then purified according to the protocol described in Section 2.2. The final volume should not be greater than the volume of resin used for purification of the sample.

2.1.2. Aqueous sulfate

Water samples are aliquotted for measuring concentration and isotopic ratio. Ideally, 200 to 500 μl of sample with a sulfate concentration between 5 and 25 μmol/l are introduced on the IC. Sulfate extraction for isotopic measurement requires at least 5 nmol S. Samples are acidified with one drop of 10% HCl and one drop of 5% HNO$_3$, evaporated to dryness at 100 °C, and then rediluted in 0.25% HCl. Samples are then aliquotted and purified.

2.1.3. Carbonate samples

Carbonate samples are weighed, cleaned and ground to a fine powder. The deep-sea coral analyzed for this work is both physically

and chemically cleaned before dissolution. After removing the external part of the coral with a Dremel tool, it is ground and rinsed three times in MilliQ water. Corals are then left for 12 h in a 1:1 mixture of 30% H$_2$O$_2$ and 0.1 M NaOH solution, after which they were rinsed 3 times in MilliQ water.

After cleaning, the sample is dissolved in 5% HCl. An aliquot is sampled for concentration and another one for isotopic composition. They are independently dried down and the IC aliquot is rediluted in water while the isotopic composition aliquot is rediluted in 0.25% HCl.

2.2. Purification

Our first attempt to purify the samples consisted of running them through a Dionex Anion Self-Regenerating Suppressor membrane, in order to extract cations from the solutions. Quantitative sulfate recovery (>$95$%) and complete purification of the sample have never been achieved. A second attempt using the strong anionic resin AG1X8 (Bio-Rad) was also performed, however, its affinity for sulfate made its recovery difficult for low-concentration samples. Instead, samples are thus purified using the strong cationic resin AG50X8 (Bio-Rad). Active exchange sites are sulfonyl groups, potentially contributing to the sulfur blank, though this resin has been previously used for purification of sulfate minerals (Craddock et al., 2008). The resin is batch cleaned by rinsing it first in MilliQ H$_2$O three times to remove smaller particles. It is then rinsed in 8 N reagent grade HNO$_3$ and then alternatively rinsed in 10% HCl and MilliQ water, where each rinse is left for at least 3 h on a shaking table.

As the capacity of the resin is 1.7 meq/ml, varying cation/SO$_4^{2-}$ ratios in the samples require variable amounts of resin. The required amount of resin is introduced on columns made of shrink-wrap PTFE tubing (Small Parts, Inc.). The column is rinsed with MilliQ H$_2$O, acetone, MilliQ H$_2$O again and 10% HCl before loading the resin. Once
loaded, the resin is rinsed twice with 20 column volumes (CV) of MilliQ H2O and 20 CV of 10% HCl. The resin is conditioned with 3 x 5 CV of 0.25% HCl. The sample is introduced and the resin is rinsed with 3 x 1 CV of 0.25% HCl to ensure complete elution of sulfate. The final volume is then dried down and diluted in 5% HNO3 to reach a solution of known sulfate concentration. NaCl is added to the final solution to match the concentration of sodium in the sample to the bracketing standard. The sample is then ready to run on the Neptune. The yield of this procedure has been checked by measuring concentrations of seawater samples on the IC before and after purification. The measured yield is 103 ± 5%. The total procedural blank depends on the size of the column, but for the columns used in this study (20 μl of resin) the measured blank ranged from less than 0.1 to 0.3 nmol SO4 . This range is partially explained by the small amounts of sulfate, which are close to the detection limit of the IC.

Teflon vials used in this study are rinsed 5 times in MilliQ H2O, heated overnight in 8 N reagent grade HNO3, rinsed 5 times with MilliQ H2O. Vials have to be handled carefully because gloves have been found to be a source of sulfur contamination. Neptune autosampler vials are washed in 10% reagent grade HCl and rinsed with MilliQ H2O, rehydrated for 24 h in Seastar HNO3 and rinsed 5 times with MilliQ H2O. Vials have to be handled carefully because gloves have been found to be a source of sulfur contamination. Neptune autosampler vials are rinsed in 10% reagent grade HCl and rinsed five times in MilliQ H2O. The resin is not recycled and columns are stored in 10% reagent grade HCl.

2.3. Description of the IC

Sulfate concentrations are measured using a DX500 Ion Chromatograph ( Dionex). The system is comprised of an AS40 autosampler, an EG-40 eluent generator equipped with a KOH eluent generator cartridge EGG III KOH, an LC20 Analyzer equipped with an IonPac AS19 inorganic anion column and an ED40 electrochemical detector. Samples are introduced using 500 μl Dionex vials. They are injected via a 10 μl loop, mixed with in-situ generated KOH eluent and pushed through the guard column and then the analytical column that separates the anions. The sample flows through the Self Regenerating Suppressor to remove the eluent and enhance the detection of the analyte. Single injections are performed on each vial. Standards, and some samples, are analyzed in triplicate to evaluate reproducibility of the results.

A gradient of KOH eluent concentration is applied. The concentration is 5 mmol/l for the first 5 min, then increases linearly from 5 to 45 mmol/l between 5 and 25 min at a constant pressure (2200 psi). The area of each peak is directly proportional to the concentration of the anion of interest. Data are manually processed to ensure that the baseline of each peak is accurate. Calibration standards are run during each session to ensure the validity of the calibration curve.

2.4. Description of the Neptune

Samples are analyzed for isotopic composition using a Thermo Fischer Scientific MC-ICPMS Neptune Plus equipped with nine faraday cups. Typical settings are shown in Table 1. Samples are introduced as the interference-free shoulders and con to the detection limit of the IC.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Neptune parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rf power</td>
<td>1200 W</td>
</tr>
<tr>
<td>Cool gas</td>
<td>15 l/min</td>
</tr>
<tr>
<td>Aux gas</td>
<td>0.8 l/min</td>
</tr>
<tr>
<td>Sample gas</td>
<td>0.8 l/min</td>
</tr>
<tr>
<td>N2 flow</td>
<td>0.02 l/min</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>PFA-50 (ESI)</td>
</tr>
<tr>
<td>Flow rate</td>
<td>60 μl/min</td>
</tr>
<tr>
<td>Cones</td>
<td>Al X-cones</td>
</tr>
<tr>
<td>Measurement parameters</td>
<td></td>
</tr>
<tr>
<td>Cup configuration</td>
<td>32S (C), 33S (H1), 34S (H3)</td>
</tr>
<tr>
<td>Resolution mode</td>
<td>High (15 μm entrance slit)</td>
</tr>
<tr>
<td>Acquisition</td>
<td>50 blocks</td>
</tr>
<tr>
<td>Integration time</td>
<td>4.194 s</td>
</tr>
<tr>
<td>Uptake time</td>
<td>60 s</td>
</tr>
<tr>
<td>Volume of sample</td>
<td>270 μl</td>
</tr>
<tr>
<td>Wash + background measurement</td>
<td>13 min</td>
</tr>
</tbody>
</table>

Instrumental background is measured after each sample or bracketing standard and is subtracted from the average signal measured on each cup. Each sample or bracketing standard is analyzed using a Matlab script that removes outliers and/or problematic portions of the 50 cycles. Typically, sections of a run are removed when the signal is not stable at the start of the run, and/or the sample runs out of solution before the 50 cycles are complete.

Mass drift is corrected using a bracketing standard made of dissolved reagent-grade Na2SO4. Both 34S/32S and the 33S/32S ratios are corrected independently assuming a linear variation between two consecutive bracketing standards. The measured ratio for sample j (Rmj) is drift corrected using Eq. (1):

\[
R_{corr} = R_{true} \left( \frac{R_{true} - R_{true}}{\alpha_i} \right)
\]

with \( \alpha_i = \frac{R_{true} - R_{true}}{R_{true}} \).
3. Experimental results

3.1. Peak shape

Fig. 2 shows the high-resolution peak shapes for 20 μmol/l of Na2SO4 introduced on the Neptune using either the Aridus or a Stable Introduction System (SIS). Measured ratios are affected by instrumental background and isobaric interferences (Table 2). Craddock et al. (2008) showed that the main interferences are 16O16O on mass 32 and 16O18O on mass 34. Isobars overlapping with 33S follow a more complicated pattern. The first interference on the right of the peak is 32S1H, characterized by a ΔM of about 8 mDa, which leaves a remaining 3-4 mDa flat shoulder to measure the interference free 33S signal. The second main interference (ΔM = 25.2 mDa), corresponds to 16O16O1H. The 16O17O interference is less than 4 mDa to the left of 1H16O16O and is not well resolved in Fig. 2. To prevent the risk of interferences due to Ni2+ on 32S and 34S we use Aluminum X-cones.

3.2. Matrix effects

All samples are run as Na2SO4 because ionization efficiency is related to the amount of Na+ in the solution (Fig. 3). Pure sulfuric acid solutions have very low ion yields (Fig. 3b). We know of no simple explanation for this dependence on the cation concentration. Such dependence has not been previously reported and might be related to the use of a desolvating membrane, which is the main difference between this study and Craddock et al. (2008). The sensitivity boost from Na addition is also independent of whether it comes as NaCl or as NaOH. Variations in the Na+/SO42− ratio also lead to variations in the measured isotopic ratios (Fig. 3a) and this effect is stronger at higher sulfate concentrations. Fig. 3 shows simultaneous intensity and ratio biases as a function of both the Na+/SO42− ratio and the sulfate concentration. However, for a same amount of Na+ (the one considered here is 40 μmol/l, similar to the bracketing standard, white dotted line in Fig. 3a) all of the measured ratios are the same, suggesting that the matrix effect depends on the amount of sodium more than on the Na+/SO42− ratio, as long as the amount of Na+ is more than twice the amount of sulfate. The average δ34S of the various concentrations of sulfate at 40 μmol/l of Na+ is −0.06 ± 0.14‰ (2sd), not including the most concentrated sulfate solution (50 μmol/l). Our Neptune based method is aided by first establishing the sulfate concentration for each solution and then matrix and intensity matching to the bracketing standards.

3.3. Accuracy and sample size

The true δ34S value of the bracketing standard has been evaluated by running this solution against the IAEA S1 standard, which defines the VCDT scale. The value of the S1 standard is defined as being −0.3‰ exactly (Coplen and Krouse, 1998). A known weight of standard (about 1.5 mg) has been dissolved in concentrated Seastar HNO3, dried down, dissolved again in 10% HCl + 5% HNO3, dried down again and then purified. This procedure has been repeated twice. Each sulfate solution has been purified three independent times and the Na2SO4 has been run against each of these solutions at least 3 times. The mean δ34S/
\[ \delta^{34}S = \delta^{34} \text{VCDT} + (0.15) \] and \( \Delta^{33}S \) values for the three standards run, without and with background subtraction. This table shows that if all of the data are background subtracted, the measured values are accurate. This is true for concentration as low as 5 \( \mu \text{mol/l} \), with no significant loss of precision on the measured \( \delta^{34}S \) value, which means that only 3 nmol of S is sufficient to accurately and precisely measure the isotopic composition of sulfur. To explore the possibility of running small samples, we ran diluted seawater on the columns so that only 5 and 10 nmol of sulfate were purified and run on the Neptune. The measured \( \delta^{34}S \) values were

<table>
<thead>
<tr>
<th>Concentration</th>
<th>NBS 127</th>
<th>( \delta^{34} \text{VCDT} ) (( \Delta^{34}S ))</th>
<th>2sd</th>
<th>SO(_5)</th>
<th>( \delta^{34} \text{VCDT} ) (( \Delta^{34}S ))</th>
<th>2sd</th>
<th>SO(_6)</th>
<th>( \delta^{34} \text{VCDT} ) (( \Delta^{33}S ))</th>
<th>2sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 ( \mu \text{mol/l} )</td>
<td>1</td>
<td>21.14% (0.05%)</td>
<td>0.07</td>
<td>1</td>
<td>0.59%</td>
<td>0.07</td>
<td>1</td>
<td>-33.99%</td>
<td>0.07</td>
</tr>
<tr>
<td>2</td>
<td>21.23% (0.22%)</td>
<td>0.03</td>
<td>2</td>
<td>0.97%</td>
<td>0.08</td>
<td>2</td>
<td>1-34.04%</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>21.08% (0.12%)</td>
<td>0.12</td>
<td>3</td>
<td>0.47%</td>
<td>0.03</td>
<td>3</td>
<td>-34.06%</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>21.07% (0.30%)</td>
<td>0.30</td>
<td>4</td>
<td>0.43%</td>
<td>0.09</td>
<td>4</td>
<td>-34.12%</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Mean of the population</td>
<td>21.12% (0.05%)</td>
<td>(0.14)</td>
<td>n = 14</td>
<td>0.51% (0.09%)</td>
<td>(0.34)</td>
<td>n = 14</td>
<td>-34.05% (0.09%)</td>
<td>(0.24)</td>
<td></td>
</tr>
<tr>
<td>5 ( \mu \text{mol/l} )</td>
<td>21.09% (0.22%)</td>
<td>0.09</td>
<td>3</td>
<td>0.75%</td>
<td>0.10</td>
<td>3</td>
<td>-34.04%</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>10 ( \mu \text{mol/l} )</td>
<td>21.09% (0.22%)</td>
<td>0.07</td>
<td>3</td>
<td>0.60%</td>
<td>0.08</td>
<td>3</td>
<td>-34.06%</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Mean of the population</td>
<td>20.93% (0.24)</td>
<td>0.24</td>
<td>3</td>
<td>0.58%</td>
<td>0.17</td>
<td>3</td>
<td>-33.74%</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>5 ( \mu \text{mol/l} )</td>
<td>20.48% (0.09)</td>
<td>0.09</td>
<td>3</td>
<td>0.58%</td>
<td>0.1</td>
<td>3</td>
<td>-32.95%</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>10 ( \mu \text{mol/l} )</td>
<td>20.77% (0.07)</td>
<td>0.07</td>
<td>3</td>
<td>0.55%</td>
<td>0.08</td>
<td>3</td>
<td>-33.45%</td>
<td>0.08</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) Values measured using the SF\(_6\) method.

\( b \) Values measured using the SO\(_2\) method.
20.7 ± 0.15‰ and 20.6 ± 0.15‰ respectively. The measured δ34S value for the blank being −2.2 ± 0.8‰, the measured seawater isotopic compositions suggest a blank contamination of 0.05 to 0.15 mmol S due to the purification process, in agreement with the amount of sulfate from the blank measured using the IC.

4. Discussion

4.1. Errors and statistics

Following the approach of John and Adkins (2010) on iron isotopes, we describe the processes affecting the precision of our measurements by dividing them into three categories; internal, intermediate and external errors. Internal error is the standard error of the 50 cycles measured for each sample. Intermediate error is the reproducibility of different measurements of the same solution post-purification and matrix matching. External error is the reproducibility of separate aliquots of the original sample processed separately through all of the chemistry. The step from internal to intermediate errors is the largest of the progression from a single measurement to true external reproducibility so we discuss it last in this section.

4.1.1. Internal error

Estimation of the internal standard error has been described previously (Albarède and Beard, 2004; John and Adkins, 2010). Ion beam collection is expected to follow a Poisson distribution (or ‘counting statistics’, Eq. (2)) for its uncertainty:

\[ \sigma = \sqrt{n} \quad (2) \]

where \( n \) is the number of ions collected at a given mass.

For a measured ratio \( R_m \) of two ion beams

\[ R_m = \frac{X}{Y} \quad (3) \]

The error on the ratio is:

\[ \sigma_{R_m} = \frac{\sigma_X}{R_m} = \sqrt{\frac{n_X + n_Y}{n_X n_Y}} \quad (4) \]

with \( n_X = 4.194 \times 50 \times 62.5 \times 10^6 \times V_i \) (the measured voltage on 1011 Ω resistors). Using Eq. (1), Eq. (4) can be rewritten as following:

\[ \sigma_{\text{counting statistics}} = \sqrt{\frac{n_X + n_Y}{n_X n_Y}} \quad (5) \]

John and Adkins (2010) defined a quantity \( N_{\text{eff}} \) (Eq. (6)) representing the effective number of counts to be used in estimating counting statistics (Eq. (7)):

\[ N_{\text{eff}} = \frac{n_X n_Y}{n_X + n_Y} \quad (6) \]

\[ \sigma_{\text{counting statistics}} = \sqrt{\frac{1}{N_{\text{eff}}}} \quad (7) \]

This relationship is represented in a log-log plot of measured variability versus signal strength by a linear trend with a −0.5 slope (Fig. 4).

At low concentrations however, the measured isotope ratio variance will be dominated by Johnson noise, the fluctuation of the background signal due to thermal noise in feedback resistors of the amplifier circuit. This translates into (John and Adkins, 2010):

\[ V_{\text{measured}} = V_{\text{signal}} + V_{\text{Johnson noise}} \quad (8) \]

where \( V_{\text{measured}} \) is the recorded voltage, \( V_{\text{signal}} \) is the voltage due to the ion beam captured in the Faraday cup, and \( V_{\text{Johnson noise}} \) is the magnitude of the baseline Johnson noise.

The error can then be calculated as

\[ \log(R_{\text{JN}}) = -\log(N_{\text{eff}}) + \log\left(\frac{R}{R + 1}\right) \sqrt{n_{\text{noise} a}^2 + n_{\text{noise} b}^2} \quad (9) \]

with \( n_{\text{noise}} \) the number of ions corresponding to the Johnson noise mean intensity and \( R \) the measured isotopic ratio. This corresponds to a linear trend with a −1 slope in the Neff plot. We evaluate Johnson noise by measuring the standard deviation of the intensity of a thousand cycles of 4.194 s with the Neptune analyzer gate closed. The noise is 40 μV on the central cup and 17 μV on cups C1 and H3. The intercept in Eq. (9) is 4.48 for 34S/32S and 4.49 for 33S/32S ratios, respectively. As seen in Fig. 4, S isotope measurements follow the same trends, showing little or no deviation from theory in terms of internal error. It also shows that the transition from Johnson noise to counting statistics is ~20 μmol/l for 33S/32S and ~2.5 μmol/l for 34S/32S.

4.1.2. Background subtraction

One of the issues affecting sulfur isotope measurements on the Neptune is the instrumental background signal. As seen in Table 3, background subtraction is necessary to get accurate measurements of δ34S and Δ33S. This background usually represents 0.1 to 1% of the measured intensity on cups C, H1 and H3. The ratios measured in the blank for H1/C and H3/C are close to 33S/32S and 34S/32S suggesting that the background signal is mostly due to sulfur. This constant background might be explained by the presence of sulfate in the solutions or a memory effect in the Aridus. For each measured ratio, the intensity measured in the blank solution before and after a given standard or sample is averaged and subtracted from the respective signal. The background variance is larger than the internal errors and ultimately limits the
precision of our measurements. In the following, we evaluate the influence of the background correction on the error of the measured ratio.

\( R_{blk} \) is the ratio measured on the Neptune and \( R_{blk} \) is the ratio of the blank.

\[
\frac{X_{blk}}{Y_{blk}} \quad (10)
\]

To adjust the measured intensities of \( X \) and \( Y \), a blank intensity is subtracted, respectively \( X_{blk} \) and \( Y_{blk} \). The blank corrected ratio is

\[
R_{blk \, corr} = \frac{X - X_{blk}}{Y - Y_{blk}} \quad (11)
\]

Eq. (11) can be rewritten using ratios.

\[
R_{blk \, corr} = \frac{R_{m}Y - R_{f}Y_{blk}}{Y - Y_{blk}} \quad (12)
\]

The error on blank corrected ratios can be calculated by propagating errors through the different terms in Eq. (12), including their covariances. However, the calculation can be somewhat simplified as there is no covariance between \( R_{m} \) and \( Y_{blk} \), \( R_{m} \) and \( r_{f} \), \( r_{f} \) and \( Y \), or \( Y \) and \( y_{blk} \). The propagated error on the blank corrected ratios can then be written as Eq. (13):

\[
\sigma_{R_{f}Y}^{2} = \sigma_{Y}^{2} \left( \frac{\partial R_{f}Y_{blk}}{\partial Y} \right)^{2} + \sigma_{Y_{blk}}^{2} \left( \frac{\partial R_{f}Y_{blk}}{\partial Y_{blk}} \right)^{2} + \sigma_{r_{f}}^{2} \left( \frac{\partial R_{f}Y_{blk}}{\partial r_{f}} \right)^{2} + 2 \sigma_{r_{f}} \sigma_{Y_{blk}} \left( \frac{\partial R_{f}Y_{blk}}{\partial r_{f}} \right) \left( \frac{\partial R_{f}Y_{blk}}{\partial Y_{blk}} \right)
\]

where the terms in the first row are the variances of the signals and the blanks, and the two terms in the bottom row are the covariances between the measured ratios and the intensities in both the signal and blank. The covariance \( \sigma_{R_{f}Y} \) is defined as:

\[
\sigma_{R_{f}Y} = \frac{n_{cycles}}{(n_{cycles} - 1)} \sum_{i=1}^{n_{cycles}} (R_{m,Y} - \bar{R}_{m,Y}) (Y_{i} - \bar{Y}) \quad (14)
\]

where \( n_{cycles} \) is the number of 4.194 s integrations that are combined into a single ratio measurement (typically 25 or 50). However, this formulation of the covariance does not let us do the calculation after we have processed the raw data into averaged ratios. To solve this problem, we follow (Rae, 2011) and start by reformulating Eq. (14):

\[
\sigma_{R_{f}Y} = \frac{1}{(n_{cycles} - 1)} \sum_{i=1}^{n_{cycles}} (X_{i} - \bar{R}_{m,Y}) (Y_{i} - \bar{Y})
\]

The next step is to use the linearity of the sum:

\[
\sigma_{R_{f}Y} = \frac{1}{(n_{cycles} - 1)} \left[ \sum_{i=1}^{n_{cycles}} X_{i} - \sum_{i=1}^{n_{cycles}} R_{m,Y} Y_{i} + \sum_{i=1}^{n_{cycles}} R_{m,Y} \bar{Y} + \sum_{i=1}^{n_{cycles}} \bar{R}_{m,Y} Y_{i} \right]
\]

The covariance can now be written as:

\[
\sigma_{R_{f}Y} = \frac{1}{(n_{cycles} - 1)} \left[ n_{cycles} \bar{X} - n_{cycles} \bar{R}_{m,Y} \bar{Y} \right] 
\]

because \( \bar{X} = \frac{1}{n_{cycles}} \sum_{i=1}^{n_{cycles}} X_{i} \).

In the end, the covariance is:

\[
\sigma_{R_{f}Y} = \frac{n_{cycles}}{(n_{cycles} - 1)} \left( \sum_{i=1}^{n_{cycles}} (R_{m,Y} - \bar{R}_{m,Y}) (Y_{i} - \bar{Y}) \right) \quad (15)
\]

Now all of the parameters required to calculate \( \sigma_{R_{f}Y} \) are available after averaging the 25 or 50 cycles, making it less cumbersome to estimate the covariance. The same calculation can be applied to \( \sigma_{r_{f}Y_{blk}} \). It is thus possible to combine the internal error with the propagation of the background subtraction to get a final estimate of the instrument blank corrected uncertainty on a measured ratio.

4.1.3. External error

To evaluate external variability, a sample of surface seawater from the Pacific Ocean (Catalina Island) is purified three times on separate columns, using 50 µl of seawater for each replicate. The average \( \Delta^{34}S_{\text{VCDT}} \) value is 20.94 ± 0.08‰ (2 sd of the three averaged measured \( \Delta^{34}S_{\text{VCDT}} \) values) and the average \( \Delta^{33}S \) value is 0.12 ± 0.09‰ (2 sd, \( n = 3 \)). The same process is applied to aliquots of 5 mg of cleaned powder of the deep-sea coral Desmophyllum diantus collected off Tasmania during the Southern Surveyor cruise (SS0108 STA011 1/13/2008). The measured \( \Delta^{34}S_{\text{VCDT}} \) value is 22.06 ± 0.17‰ and \( \Delta^{33}S \) value is 0.12 ± 0.13‰ (2 sd, \( n = 3 \)). This variability is significantly higher than the internal error. We thus want to understand if the increased variance is due to the purification or to the mass spectrometry, which can be done by investigating intermediate errors (where replicates are duplicate measurements of the same sample solution, not separate chemical processing of the sample CAS or water sample).

4.1.4. Intermediate error

In the course of a Neptune run, the difference between two measured ratios of the same solution is larger than what would be expected based on the internal errors. John and Adkins (2010) use the END (Error Normalized Deviates, normalized to the expected variance from internal statistics alone) statistic to quantify this extra variability and defined as:

\[
END = \frac{R_{2} - R_{1}}{\sqrt{\sigma_{1}^{2} + \sigma_{2}^{2}}} \quad (16)
\]

If the internal errors completely describe the variability between replicates, then a large number of END values will describe a histogram with a mean of 0 and a standard deviation of 1. For the seawater samples that were run in this study, the standard deviation of the END for the \( 34S/32S \) ratios is 2.34 and the mean is −0.89 (Table 4). While the internal errors follow the predictions of Johnson noise.

### Table 4

<table>
<thead>
<tr>
<th>Run 1</th>
<th>Run 2</th>
<th>Seawater run</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
<td>Average sd</td>
<td>Time (min)</td>
</tr>
<tr>
<td>34/12</td>
<td>30</td>
<td>0.01</td>
</tr>
<tr>
<td>30</td>
<td>0.12</td>
<td>1.94</td>
</tr>
<tr>
<td>60</td>
<td>0.01</td>
<td>2.53</td>
</tr>
<tr>
<td>33/32</td>
<td>30</td>
<td>0.09</td>
</tr>
<tr>
<td>30</td>
<td>1.04</td>
<td>30</td>
</tr>
<tr>
<td>60</td>
<td>0.02</td>
<td>1.3</td>
</tr>
</tbody>
</table>
and Poisson statistics, replicates run over many hours show much more variability.

We designed two different experiments to explore the source of this variability. Run 1 is a continuous aspiration of a single sample where data are averaged every 25 cycles. The autosampler tube was simply left in a large volume of solution (Fig. 5). Run 2 uses the same solution but the autosampler tube moved up and down every 25 cycles to inject air into the sample stream (Fig. 6). Means and standard deviations of the different END populations are reported in Table 4, which shows that END standard deviations increase with time between bracketing standards and with injecting air every 25 cycles. Overall, the standard deviation of the END is larger for the $\delta^{34}S/\delta^{32}S$ ratio than for the $\delta^{33}S/\delta^{32}S$ ratio. By comparing Run 2 with data collected on seawater samples, we find that introducing the same solution again and again induces the same intermediate reproducibility as a run with standard-sample-standard bracketing and washes. As the highest variability of these runs overlaps with the true external sample replicates reported above, it is clear that the origin of our extra variance (after drift correction) is not due to problems with sample matrix, machine memory, or poorly matched standards. Instead, the problem seems to be within the mass spectrometry itself.

One possibility for the extra variability in intermediate replicates is that we have not properly accounted for mass bias drift over the course of the run. Allan variance plots are a good test of this hypothesis. First introduced to estimate the stability of atomic clocks, this statistic provides an evaluation of the drift for any given system. Considering three evenly spaced measured ratios during a run, $x_n$, $x_{n+1}$, and $x_{n+2}$, spaced by a measurement interval $\tau$, the difference between ratios normalized for the sampling interval is given by $y_n = (x_{n+1} - x_n) / \tau$. The instability in the system may be represented by the change in this difference across the whole run (for a given time interval): $\Delta y_n = y_{n+1} - y_n = \Delta$. The Allan variance $\sigma^2(\tau)$ is then:

$$\sigma^2(\tau) = \frac{1}{2(N-1)} \sum_{i=1}^{N-1} (y_{i+1} - y_i)^2 = \frac{1}{2(N-1)} \sum_{i=1}^{N-1} (x_{i+2} - 2x_{i+1} + x_i)^2.$$

where $N$ is the total number of measured ratios used to calculate the sum. For a system with no drift in the ratios, the Allan variance will drop as $\tau$ increases. We evaluate the Allan variance for two different runs where the sample was continuously introduced into the instrument, Run 1 (same run as previously described) and Run 1b. The integration time is 4.194 s in each case but Run 1 had an idle time of 3 s between each time step while 1b did not, explaining the slightly different starting points for the two runs in Fig. 7. The solid lines indicate the theoretical evolution of the variance in the case of no drift. An unchanging Allan variance with $\tau$ indicates linear drift in the mass bias of our measured ratios. Data are calculated from the integration time to 20,000 s (~5 h30), which is half the total duration of a run.

The influence of mass bias drift on $\delta^{34}S/\delta^{32}S$ and $\delta^{33}S/\delta^{32}S$ ratios is different between the two runs, but no drift affects the $\Delta^{33}S$ values, implicating true mass dependent mass bias drift as the source for variability between measured ratios. Fig. 7a shows that different runs have different timescales of variability. Run 1 has an oscillation of ~10–30 min but with no long term change in the mean value of the ratios, while Run 1b is characteristic of a linear drift in the uncorrected ratios. $\delta^{33}S/\delta^{32}S$ ratios appear to drift at a longer timescale, but this is due to the smaller size of the $^{33}S$ beam being inherently more variable (Fig. 7b). In a linearly drifting system with more noise between the individual points, deviations from the ideal line first show up at longer periods. In each Run the drift is mass dependent because it does not affect the calculated $\Delta^{33}S$ value (Fig. 7c).

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**Fig. 5.** $\delta^{34}S$ vs. $\delta^{32}S$ and $\delta^{33}S$ vs. $\delta^{32}S$ for raw data and drift corrected data during a run where the autosampler probe remained in the same solution the entire time. MDF line is the Mass Dependent Fractionation line.
This is confirmed when we make Allan variance plots with the corrected ratios (not shown). Allan variance analysis demonstrates that there is mass bias drift within the 50 cycles we use to average for a single ratio, and that we might improve the overall $\delta^{34}$S and $\delta^{33}$S ratios with fewer cycles per measurement. However, shorter acquisition would clearly adversely affect the uncertainty in the $\Delta^{33}$S value. This analysis also explains why points in Fig. 4 lie slightly above the counting statistics and Johnson noise lines.

4.2. Discussion on the source of variability

In this section we unpack the sources of variability that can give rise to an END standard deviation of 2–4 over and above that due to internal errors. Fig. 5 shows the relationships between $\delta^{33}$S, $\delta^{34}$S, and $\Delta^{33}$S for the data in Run 1. Each point in the left hand column (a and c) is a non-drift corrected, and non-normalized, value of the Na$_2$SO$_4$ solution for a 25 cycle integration. The right column (b and d) are the same data but now using every other 25 cycle block to drift correct and normalize the data between blocks. A trend between the scatter in the $\delta^{34}$S and $\delta^{32}$S data is presented in Fig. 5a, but Fig. 5b shows that drift correction shrinks the $\delta^{34}$S data much more than the $\delta^{33}$S data (the ranges on the x and y-axes are the same in a and b). Calculating the mass independent $\Delta^{33}$S variance for each sample shows that this value is dominated by scatter in the $\delta^{32}$S data (Fig. 5c). The $\Delta^{33}$S and $\delta^{34}$S data do not correlate (not shown). Drift correction shrinks the $\delta^{33}$S vs. $\Delta^{33}$S trend to a relatively tight 1:1 relationship. Fig. 5d is the signature of an isobaric interference on $\delta^{35}$S but not $\delta^{36}$S or $\delta^{32}$S.

From the peak shape data in Fig. 2, the $^{32}$S–$^1$H hydride species is the most likely candidate for this interference on $\delta^{33}$S and $\Delta^{33}$S. The hydride of $^{16}$O dimer might also contribute, but it is almost an order of magnitude smaller and much easier to mass resolve. With only a <4 mDa interference free plateau, small changes in the absolute mass stability could change the relative intensity of the hydride interference. The combined high voltage and magnetic field stability of the Neptune is about 1 part in $10^5$, which corresponds to 3 mDa over a 300 Da full mass range. The peak shapes in Fig. 2 also show that oxygen dimer interferences are the most likely cause of extra variance at masses 32 and 34. However, these interferences are very hard to detect, because they affect the 34/32 ratio with a slope close to the regular mass dependent drift in the ratio ($^{32}$S/$^{32}$S = 0.007877, $^{34}$S/$^{32}$S = 0.044163, $^{33}$O$_2$/$^{32}$O$_2$ = 0.00038 and $^{34}$O$_2$/$^{32}$O$_2$ = 0.00205).

When air is injected to the plasma in between measurements (Run 2), the overall range of variability nearly doubles (Fig. 6) and the competing effects of oxygen interferences and mass bias drift can be seen. In the non-drift corrected $\delta^{34}$S vs. $\delta^{33}$S data (Fig. 6a) the larger range compared to Run 1 comes from the increased mass bias effect of changing the plasma conditions by injecting air rather than from increasing the O$_2$ interferences, as the source of oxygen for the interference is the water aspirated with the sample. This drift can be normalized by sample-standard bracketing (Fig. 6b), but again it does not change the $\delta^{33}$S data substantially. The predominance of the $^{32}$S–$^1$H interference is still visible when plotting $\delta^{32}$S vs. $\Delta^{32}$S (Fig. 6c), but a larger scatter appears, due to mass dependent fractionation. When the data is mass bias corrected (Fig. 6d), the strong 1:1 relationship returns.

Overall, it is clear that much, but not all, of the mass bias drift and O$_2$ interferences on $\delta^{35}$S can be normalized with sample-standard bracketing. Unfortunately this technique has little effect on the short term variability of $^{32}$S–$^1$H interference on $\delta^{32}$S. The END standard deviation is smaller for the $\delta^{32}$S data because the internal errors are larger, not because there is inherently less extra variability on this ratio. The absolute variance of $\delta^{34}$S can be reduced, but the internal errors are so small (~20 ppm on normal sized samples) that the END standard deviation is still large. A longer duration between bracketing standards leads to larger END standard deviations for
δ³⁴S because non-linear changes in both mass biasing and the oxygen interferences are more likely to occur.

To improve our reproducibility on the measured Δ³³S, we need to better separate the ³²S¹H interference. We could achieve this goal using an entrance slit thinner than 25 μm thus increasing the mass resolution. END standard deviations for δ³⁴S will have higher standard deviations than internal errors as long as the sample-standard bracketing interval is longer than the variability in the water induced O₂ interference on masses 32 and 34.

5. Seawater profiles

The method described in this paper has been applied to a collection of two seawater profiles from the San Pedro basin (Pacific Ocean, 10 samples, (John et al., 2012)) and the Atlantic ocean (US Geotraces Atlantic, station 9, 24 samples). The first profile goes down to 895 m and the second one down to 3000 m water depth.

Since the development of the sulfur isotopic measurement, seawater has been stated to have a constant isotopic composition of ~20‰. The first published systematic study of seawater δ³⁴S suggested a value of 20.12 ± 0.74‰, n = 17 (Thode et al., 1961) followed by 20.99 ± 0.17‰, n = 25 (Rees et al., 1978), 20.88 ± 0.95‰, n = 39 (Kampschulte et al., 2001), and values ranging from 18.8 to 20.3‰ (Krouse and Coplen, 1997; Coplen and Krouse, 1998; Ding et al., 2001). All of these numbers are an average over different locations and depth. Rees et al. (1978) are the first ones who systematically explored potential variations of seawater δ³⁴S values with depth in the open ocean, followed by a joint study of oxygen and sulfur isotopes of seawater (Longinelli, 1989) with values ranging from 18.8 to 20‰. A depth transect of sulfur isotopes has also been established for the North Sea (Böttcher et al., 2007) with very similar mean values for seawater samples collected over springtime (δ³⁴S = 20.1 ± 0.13‰; n = 131) and summertime (δ³⁴S = 21.1 ± 0.13‰; n = 59). Unfortunately, studies prior to 1995 cannot be accurately compared with data more recent than 1995. The δ³⁴S scale was previously reported using the Canyon Diablo Troilite standard (CDT). The supply of the standard was eventually depleted and a new scale was defined at the 1993 Vienna Conference, the Vienna-CDT scale. Because the CDT standard turned out to be slightly inhomogeneous, this new scale is based on the International Atomic Energy Agency (IAEA) S1 standard, defined as being

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**Fig. 7.** Square root of the Allan variance vs. time in a log–log space for Run 1 (open circles) and Run 1 bis (gray circles). The line represents the ideal time-dependant variation following a Poisson law with time. Integration times are the same for both runs but each cycle of 4.194 s is separated by a 3 s idle time in Run 1 and not in Run 1 bis. The solid line (50 cycles) indicates the duration of one measurement (~210 s). The dashed line indicates the time span between two successive bracketing standards (~35 min).
—0.3‰ in the VCDT scale (Krouse and Coplen, 1997; Coplen and Krouse, 1998; Ding et al., 2001). Here we investigated two depth transects, on a total of 34 samples that place seawater data on the VCDT scale. Results are presented in Fig. 8. They display a constant δ34S value with depth. The average on the two sites is 20.96 ± 0.12‰ and 20.99 ± 0.10‰ respectively (2sd). These two values are indistinguishable from one another. They appear however slightly lower than the value measured for the standard NBS 127, which is barite precipitated from seawater, or compared to the value measured for modern barites (21.10 ± 0.20‰, 2sd) (Paytan et al., 1998). The standard deviation of the END for these runs is shown in Table 4. These profiles exhibit δ34Svcdt values that are constant with depth within error bars, in agreement with the conclusion that the open ocean has an homogeneous isotopic composition (Rees et al., 1978; Longinelli, 1989). The δ34S values are in agreement with recent studies showing values for standard IAPSO seawater by MC-ICPMS after column purification of 21.11 ± 0.40‰ (Das et al., 2012) and 21.18 ± 0.27‰ (Cradock et al., 2008), or as SF6 by IRM after extraction from four natural samples as BaSO4 (21.34 ± 0.13‰, Ono et al., 2012). Average Δ33S for San Pedro Basin 0.08 ± 0.10 (n = 10) and the Atlantic Ocean (0.07 ± 0.07‰; n = 24) agree well with the value of 0.050 ± 0.03‰ (2sd, n = 6 samples) measured by gas source isotope-ratio-monitoring MS (Ono et al., 2012).

6. Conclusions

The method described in this paper allows for the first time a measurement of the triple isotopic composition of sulfur isotopes on samples of a few nmol of sulfate. Although, significant progress had already been achieved in measurement of S isotopes on the MC-ICP-MS Neptune (Cradock et al., 2008; Das et al., 2012), we are able to work on samples one order of magnitude smaller using a method than can be applied to a broad range of samples such as waters, carbonates, sulfides or samples available in limited amount such as foraminiferae. As an example, 20–50 mg of carbonates with less a 100 ppm of sulfate or a few ml of waters (such a rivers or rainwaters) containing less than 100 μmol S/l carry enough sulfate to be measured by this method. Applying this method to seawater yields a δ34Svcdt value of 20.97 ± 0.10‰ (2sd, n = 34).

Precision on the measured Δ33S could be improved by working at a higher resolution than achieved by the slits available for the Neptune. Such improvement will allow exploration of fine mass independent fractionation in modern samples with a simple method than does not require specific fluorination line and requires very small amount of sulfate.

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