



Determination of multiple sulfur isotopes in glasses: A reappraisal of the MORB $\delta^{34}\text{S}$

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ABSTRACT

We report on improvements to the sulfur extraction method out of silicate glasses by the use of HF + CrCl₂ solution for the precise determination of S multi-isotope compositions. This protocol has been designed to be sulfide specific and if needed, can be easily extended to oxidized sulfur. The complete method was validated on a synthetic powder and three laboratory mid-ocean ridge glassy internal standards (CH98 DR12, ED DR46 1-6 and ED DR26 type 1).

S extraction yields of the three basalt glass standards were $100 \pm 4\%$ (1σ , $n = 12$), $102 \pm 6\%$ (1σ , $n = 4$) and $97 \pm 6\%$ (1σ , $n = 4$) respectively. Their $\delta^{34}\text{S}$ show little variation, at $-1.20 \pm 0.08\%$, $-1.09 \pm 0.14\%$ and $-1.25 \pm 0.12\%$ (all 1σ) with respect to V-CDT. $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ are both negative with respect to our SF₆ tank, between -0.018 and -0.021% ($\pm 0.012\%$ maximum 1σ) for $\Delta^{33}\text{S}$ and between -0.216 and -0.282 (± 0.106 maximum 1σ) for $\Delta^{36}\text{S}$.

The method was then applied to sixteen additional glasses from worldwide mid-ocean ridges, including three samples for which $\delta^{34}\text{S}$ was reported previously. Our results show that previous data are affected by a systematic $\delta^{34}\text{S}$ shift toward positive values, of ≈ 0.4 to 1.5% . We infer that this shift originates from an incomplete S recovery when the Kiba extraction protocol is used. $\delta^{34}\text{S}$ values range between -1.80 and 0.02% with a mean value of $-0.91 \pm 0.50\%$ (1σ , $n = 19$). Such negative values contrast with the positive range previously reported leading us to suggest a revised mantle $\delta^{34}\text{S}$, mainly dominated by negative values. $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ are strikingly homogeneous with mean respective values of $-0.019 \pm 0.005\%$ and $-0.193 \pm 0.093\%$ (1σ , $n = 19$) versus our SF₆ tank. These estimates are indistinguishable from our CDT measurements and define the best present-day upper mantle estimate.

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1. Introduction

Together with H, C, N, and Cl, sulfur is one of the major volatile elements on Earth. It is released from volcanoes as SO₂ and H₂S, contributing to climate warming and acid rain (Lamb, 1970; McCormick et al., 1995; Scaillet et al., 1998). It occurs in at least four redox states, between fully oxidized (S⁶⁺) and reduced (S²⁻), in fluids, gas phases and various types of sulfur-bearing minerals. This makes sulfur an ubiquitous element involved in numerous geologic processes including hydrothermalism (e.g. Alt et al., 2007), ore deposit formation (e.g. Naldrett, 2004) or continental weathering (Calmels et al., 2007).

Sulfur isotope systematics have thus been extensively used in sedimentary and aqueous domains to characterize the surficial cycle of this element (see Johnston, 2011, for a review). Among important findings, the disappearance of non-zero $\Delta^{33}\text{S}$ values in Archean sediments at 2.4 Ga provides evidence for the oxygenation of the atmosphere (Farquhar et al., 2000). Comparatively, sulfur isotopes have been less used to decipher magma genesis and origin, most studies

being focused on plutonic or subaerial volcanic rocks (e.g. Schneider, 1970; Sasaki and Ishihara, 1979; Ueda and Sakai, 1984; Torssander, 1989; Marini et al., 1998; De Hoog et al., 2001; Mandeville et al., 2009).

Few analyses of sulfur stable isotopes have been carried out on fresh glassy submarine samples including mid ocean ridge basalts (MORB, $n = 18$, Kanehira et al., 1973; Sakai et al., 1984; Chaussidon et al., 1991), ocean island basalts (OIB, $n = 6$, Sakai et al., 1982) and back arc basin basalts (BABB, $n = 28$, Hochstaedter et al., 1990; Kusakabe et al., 1990; Alt et al., 1993). MORB data (strictly limited to ³⁴S/³²S measurements) show a consistent enrichment in ³⁴S compared to the Canyon Diablo Troilite (CDT) international standard (Kanehira et al., 1973; Sakai et al., 1984; Chaussidon et al., 1991), with values of $\delta^{34}\text{S}$ between -0.6 and $+1.6\%$ and a global mean value of $+0.5 \pm 0.6\%$ (1σ). For comparison, OIB data of Sakai et al. (1982) are between -0.6 and $+0.8\%$ with a mean value of $+0.5 \pm 0.5\%$ (1σ).

However, important concerns on previous S extraction techniques emerge given that two studies devoted to sulfur isotopes in BABB glasses from the same locations in Mariana Through show inconsistent results. $\delta^{34}\text{S}$ values reported in Kusakabe et al. (1990) are exclusively negative with a mean value of $-0.6 \pm 0.3\%$ (1σ , $n = 13$) whereas $\delta^{34}\text{S}$ values of Alt et al. (1993) are all positive with a mean value of $+1.1 \pm 0.5\%$ (1σ , $n = 10$). These measurements have been performed

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before those of [Beaudoin et al. \(1994\)](#) and [Ono et al. \(2006a\)](#) revealing a $\approx 0.5\%$ S isotope heterogeneity in the CDT international standard. However, the CDT overall heterogeneity encompasses a smaller range than the 1.8% S isotope discrepancy between the [Kusakabe et al. \(1990\)](#) and [Alt et al. \(1993\)](#) studies. Therefore, such a divergence cannot only be explained by a poorly defined reference. Moreover, there is no geochemical evidence that such an extreme dichotomy between these data can be explained by a sampling bias. This inconsistency may rather reveal an analytical artifact introduced during the chemical extraction of sulfur out of glass matrices. Yet both studies released sulfur using the same analytical procedure (i.e. the so called 'Kiba reagent', see [Section 2](#)) although designed for coarse silicate rocks ([Sasaki et al., 1979](#)). We argue in the present paper that this method is in fact not adapted to glasses.

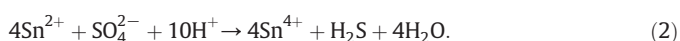
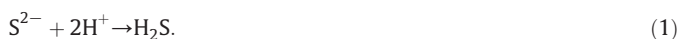
In the present study, we developed a reliable new procedure to chemically extract sulfur from glassy samples. We bypassed the analytical difficulties of the Kiba extraction method and applied the new method to MORB glasses. A special attention was paid to sulfide/sulfate specificity making this protocol suitable for BABB glasses where it is known that reduced and oxidized sulfur can coexist.

2. A review of previous S extraction methods

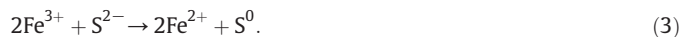
Two kinds of silicate matrices can be broadly recognized with respect to sulfur extraction: crystalline rocks and glasses. Within non glassy samples, sulfur is expressed in sulfide or sulfate minerals while in glassy samples it is dissolved in the silicate glass matrix. A wealth of papers describing S extraction procedure exist and the reader is referred to the review of [Mayer and Krouse \(2004\)](#) and references therein. In contrast, as mentioned earlier, the efficiency of these extraction methods for breaking the silicate network of glasses has not been demonstrated.

The most popular procedure for determining sulfur content in coarse crystalline rocks is pyrolysis, originally designed by [Gupta \(1963\)](#). This method has been extensively used to determine S contents of peridotite (e.g. [Lorand, 1989](#); [Lorand et al., 2003](#); [Luguet et al., 2003](#); [Lorand and Alard, 2010](#)). In the recent publication of [Gros et al. \(2005\)](#), this protocol has been improved and validated for sulfur extraction out of basaltic glasses. It was however not validated for $\delta^{34}\text{S}$ determination. It consists of oxidizing a powdered sample in an oxygen flow or with vanadium pentoxide as oxidizing agent. Produced SO_3 is converted to SO_2 by reaction with heated copper and is then quantified by chemical titration or with infrared spectroscopy. In [Gros et al. \(2005\)](#), the reported procedural blank is very low ($< 4.8 \mu\text{g} \cdot \text{g}^{-1}$) and extraction yields are $100\% \pm 3\%$ (1σ), in agreement with international recommendation for a coarse sample. When applied to glassy materials, this protocol allows complete S recovery, in agreement with the S content determined by electron microprobe on the same samples. Still, the main problem of this method resides in its non specificity with respect to sulfides or sulfates as all sulfur is converted into SO_2 during the extraction.

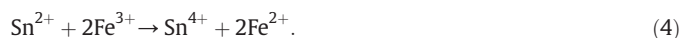
The usual technique used so far for $\delta^{34}\text{S}$ determination of silicate samples (glassy or not) employed the so called "Kiba reagent" method. Kiba reagent was originally designed to determine soluble sulfate contents by their reduction to hydrogen sulfide ([Kiba et al., 1955](#)). It is prepared by boiling a mixture of 20 to 80 g of pure SnCl_2 in 200 ml dehydrated orthophosphoric acid. The obtained reagent is then used for the acid digestion of the sample under N_2 or CO_2 flux at 280 °C. Both reduced and oxidized sulfur are extracted and converted to H_2S following the reactions (1) and (2):



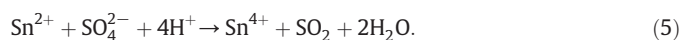
Of critical importance is the fact that in silicate rocks and especially basalts, the content of ferric iron can be high, up to 20% of the total iron ([Bézos and Humler, 2005](#); [Cottrell and Kelley, 2011](#)). However, a substantial part of the reduced sulfur reacts in solution with the ferric iron ([Pruden and Bloomfield, 1968](#); [Rice et al., 1993](#)), producing native sulfur as follows:



Here, in addition to its role in reaction (2), Sn(II) is used for the reduction of Fe(III) into Fe(II) through the reaction (4), inhibiting the formation of native sulfur.



As both sulfide and sulfate were recognized to occur in arc magmas and BABB, [Ueda and Sakai \(1983\)](#) proposed two further improvements to the protocol: Sn(II) concentration was reduced to one tenth that of the original amount, and reactions were carried out under vacuum. Thus, sulfate would only be reduced to SO_2 (i.e. not H_2S) via reaction (5) allowing its complete separation from sulfide (converted to H_2S).



According to the authors, vacuum is essential otherwise sulfates would be reduced to H_2S through reaction (2). However, as emphasized by the authors, up to 12% of the SO_4^{2-} pool is reduced to H_2S even under vacuum, requiring correction of isotope composition of both released SO_2 (i.e. from sulfate) and H_2S (i.e. from sulfide). [Ueda and Sakai \(1983\)](#) reported a high fractionation factor between these two species of +6.7% under their experimental conditions.

This method has been used for routine analyses of oxidized and reduced sulfur isotope composition of various oceanic basalts ([Sakai et al., 1982, 1984](#); [Ueda and Sakai, 1984](#)). However, owing to the described analytical complexities, many authors prefer the original Kiba method to determine the isotope composition of bulk sulfur, even for samples with coexisting sulfate/sulfide ([Torsander, 1989](#); [Hochstaedter et al., 1990](#); [Kusakabe et al., 1990](#); [Chaussidon et al., 1991](#); [Alt et al., 1993](#); [Marini et al., 1994](#); [Mandeville et al., 1998](#); [Marini et al., 1998](#); [De Hoog et al., 2001](#); [Mandeville et al., 2009](#)).

Moreover, typical blanks, detection limits, external reproducibilities or extraction yields are usually scarcely given. The sulfate blank given in [Ueda and Sakai \(1983\)](#) is below 3 nmol and extraction yields reported for a single mid-ocean ridge glass varied between 68 and 80%. More importantly, [Sakai et al. \(1984\)](#) using the above protocol reported sulfur content despite the incomplete extraction. As a consequence, their reported S contents exhibit random variation when plotted against FeO contents ([Fig. 1](#)), in contrast to the high degree of correlation expected between these two elements in MORB ([Mathez, 1976](#); [Wallace and Carmichael, 1992](#)). Thus, in addition to the critical difficulty in obtaining redox specific data, the Kiba method seems to fail to produce complete extraction of bulk sulfur from glass matrices.

3. A new protocol for S extraction out of glasses

The method we have developed consists of an improved version of the method previously applied to sedimentary rocks. Our separation and recovery scheme comprise two separate extraction steps: the first for reduced sulfur (using CrCl_2 together with HF dissolution of silicate bonds) and the second for oxidized sulfur (using the sulfate reducing Thode-solution). For each of them, we paid special attention to the apparatus sealing and if necessary the connections were sealed with teflon ribbon. As there is no international glassy basalt standard, the extraction efficiency and specificity of our method are tested on natural MORB for yields and $\delta^{34}\text{S}$ reproducibility.

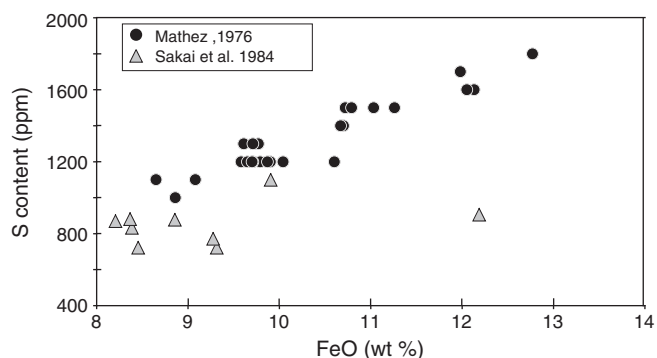


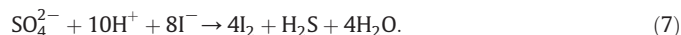
Fig. 1. Data compilation of Iron versus Sulfur contents in MORB (Mathez, 1976; Sakai et al. 1984). The positive trend reflects iron sulfide fractionation. In contrast, the S content data determined using the Kiba extraction (Sakai et al. 1984) are significantly shifted toward lower S content values, suggesting an incomplete S recovery.

S^{2-} is extracted from sediments in hot acidic conditions as it reacts spontaneously with H^+ to form H_2S . This extracted fraction is referred as the acid volatile sulfur (AVS). However, in the presence of Fe(III), some S^{2-} oxidizes to S^0 through reaction (3). In these conditions, the sub-boiling acidic $CrCl_2$ solution originally designed by Zhabina and Volkov (1978) and improved by Canfield et al. (1986) is widely used. Actually, Cr(II) prevents oxidation of sulfide through the reaction (6), imposing its reducing potential on sulfur itself:



With this protocol, reduced sulfur species are fully decomposed into H_2S even in the presence of Fe(III), then removed from the reaction flask with a stream of N_2 and precipitated as either ZnS , CdS or Ag_2S . The sulfur extracted during this step is referred as the chromium reducible sulfur (CRS). This protocol does not reduce sulfate, making it highly specific to only reduced sulfur (Canfield et al., 1986). The blank values are not specified in the original publications but this method is easy to use and enables routine analyses.

Sulfate extraction is then performed by adding a strongly reducing HI – H_3PO_2 – HCl solution (Thode et al., 1961) or “Thode-solution”, under sub-boiling conditions. At this step, sulfates react with HI and are reduced to form H_2S following the reaction (7):



Again, H_2S is removed from the reaction flask and precipitated as sulfide.

Most authors perform the CRS extraction after the removal of soluble sulfates from the reaction vessel (Mayer and Krouse, 2004), precipitated as $BaSO_4$ by addition of a $BaCl_2$ solution. The remaining sample is finally returned to the distillation apparatus and undergoes CRS extraction. It is unclear to us why this order of sequential extraction is commonly used. It may be justified by the fact that $CrCl_2$ batches at affordable prices are commonly associated with high blank levels of oxidized sulfur (e.g. 70 ppm SO_4^{2-} , Alfa AESAR).

3.1. Sample preparation

Centimeter size pieces of glassy basalts are sonicated in 99.9% ethanol in order to remove any aerosol or room dust from the sample. Glass pieces are handpicked under a binocular microscope, and if needed cleaned through a second sonication in weak acid solution (sulfate free HCl 0.6 N for 10 min at ambient temperature) in order to avoid any contamination by iron oxide or alteration materials. If samples contain a large proportion of phenocrysts (>5%), a Franz magnetic

separation is performed to select only glass shards. Sample crushing is then performed to obtain a grain size <63 μm .

3.2. Sulfide sulfur extraction

The powdered sample is introduced to a 120 ml digestion Teflon vessel (1 in Fig. 2). The digestion vessel includes three 1/8” ports (2, 3 and 4 on Fig. 2) enabling continuous flushing of pure nitrogen gas by the top port of the apparatus. Twenty millimeters of 2.1 M $CrCl_2$ solution and 5 ml of 29 N HF (48%, ultrapure) are then introduced in the digestion vessel with a plastic syringe (5 on Fig. 2) by one of the side ports to which a LUER stopcock (6 on Fig. 2) is connected.

Under these conditions, a large stoichiometric excess of reactants is insured during the acid digestion. The hot plate (7) maintains a sub-boiling temperature during the chemical extraction. The H_2S produced during acid attack is carried with N_2 gas into the first trap filled with distilled H_2O in order to remove the acid vapors from the gas. Finally, the H_2S is transported through the sulfide trap which is filled with $AgNO_3$ (0.3 M) where it reacts to precipitate Ag_2S . Approximately 3 h is needed until completion, as confirmed by the fact that no supplementary Ag_2S precipitates if the $AgNO_3$ trap is changed.

3.3. Sulfate sulfur extraction

When significant occurrence of oxidized sulfur in basalt glasses is suspected (e.g. from S-major element trends, see Jugo et al., 2010, and references therein), the whole S extraction follows a modified sequence. In contrast with the protocol described in Section 3.2 used when S occurs only under its reduced form, the S recovery is performed sequentially as follows.

The sample is first dissolved in 5 ml of 29 N HF using the previously described apparatus. If present, a significant amount of reduced sulfur is extracted as H_2S (i.e. acid volatile sulfur, or AVS). During this step, the sulfates present in the glassy structure of the sample are released in the solution. The solid residue (i.e. fluorides) and the reaction vessel are then thoroughly rinsed with hot distilled water and the resulting solution (i.e. containing the HF and the released sulfates) is removed from the digestion apparatus. Pure boric acid (1.5 g) is added to this solution, ensuring a complete complexation of the F^- ions and HF molecules into BF_4^- . The solution is finally transferred into a borosilicate distillation apparatus similar to that used by Tuttle et al. (1986) where it undergoes sulfate reduction to H_2S using 20 ml of preboiled and nitrogen purged HI – H_3PO_2 – HCl reducing solution (Thode et al., 1961).

Meanwhile, the solid residue undergoes a CRS extraction, using 10 ml of 99.9% ethanol, 20 ml of 2.1 $CrCl_2$ solution and 5 ml of 29 N HF. Under these conditions, any potential native sulfur produced during the AVS extraction step is efficiently solubilized and reduced into H_2S (Canfield et al., 1986). The AVS and CRS pools (≈ 90 and $\approx 10\%$

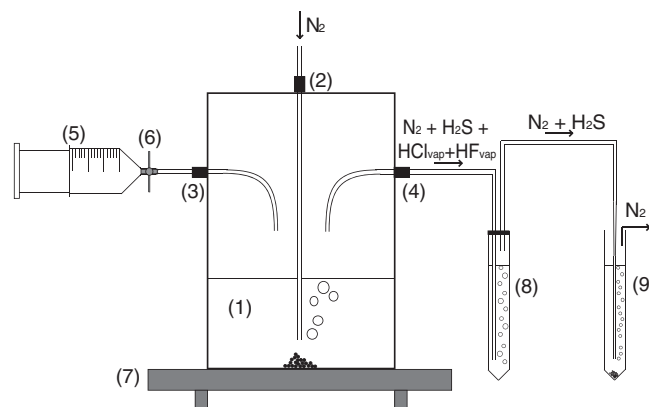


Fig. 2. Schematic illustration of the teflon digestion apparatus used in our study. See Sections 3.2 and 3.3 for details.

respectively, their respective amounts being related to the oxidized iron content according to reaction (3)) are then gathered together. The S content and isotope composition of this mixed pool reflect those of the bulk reduced S of the sample. All the performed blanks are below the detection limit, estimated to be $<0.1 \mu\text{mol S}$.

3.4. Determination of S content by external methods

S contents of MORB glasses are determined by electron microprobe (EMP) analyses on polished sections with a Cameca SX100 at the CAMPARIS facility (Pierre et Marie Curie University). The analytical conditions used are 15 kV accelerating voltage, 100 nA sample current, 20 μm beam size, and 60 s counting time for each point. Ten spots were analyzed on each polished section. The calculated mean value is taken as the sulfur content of the sample and the standard deviation of each series of measurements is taken as the 1σ uncertainty (≈ 25 ppm). A natural pyrite was used as a standard. In addition, results are systematically calibrated using two reference samples: the international reference natural glass JDF D2 and a Southwest Indian Ridge sample, ED DR11 1–9. Sample JDF D2 is taken as a high S content standard of 1420 ± 40 ppm (Wallace and Carmichael, 1992) and 1400 ± 40 ppm (Nilsson and Peach, 1993), both determined with EMP (all 1σ). The glass ED DR11 1–9 is a low S content standard, for which sulfur content has been determined by Bézou et al. (2005) using the pyrolysis method, yielding 731 ± 40 ppm. These two standards are alternatively analyzed every 3 or 4 samples. The correction on sulfur content is between -50 and $+50$ ppm for 90% of the samples and regardless of whether the high sulfur or low sulfur standard is used for the correction, the recalculated sulfur content is identical.

Finally, as noted by Wallace and Carmichael (1992) and Nilsson and Peach (1993), increase in the S^{6+}/S_{tot} ratio shifts the SK_{α} X-ray peak, leading to a systematic underestimation of the total S content if a sulfide standard is used. However, oxidized S in MORB does not represent more than 5% of the total sulfur (Métrich et al., 2009; Jugo et al., 2010). In these conditions, the SK_{α} shift has an insignificant effect on the S content measurement and the EMP obtained value represents the total sulfur content of the sample.

3.5. Isotope analysis

The sulfur isotope measurements are done according to Farquhar et al. (2007): Weighed aliquots of silver sulfide are wrapped in Al-foil and placed into Ni-reaction bombs for fluorination with purified F_2 at 250°C overnight. The produced SF_6 is then purified first by cryogenic separation and secondly by gas chromatography (1/8 in. diameter column of a 6 ft 5A molecular sieve followed by a 8 ft Haysep Q column as in Ono et al., 2006b). Purified SF_6 is then quantified and analyzed using a dual inlet ThermoFinnigan MAT 253 mass spectrometer where $m/z = 127^+$, 128^+ , 129^+ and 131^+ ion beams are monitored. The $\delta^{34}\text{S}$ values are determined after calibration of our in-house SF_6 tank using the IAEA-S1 recommended value of Robinson (1993). As this reference material is anchored to V-CDT, the $\delta^{34}\text{S}$ values of the present contribution are all given with respect to V-CDT. In contrast, raw $\Delta^{33-36}\text{S}$ values are reported with respect to our SF_6 tank, and are calculated as follows (see Farquhar and Wing, 2003):

$$\Delta^{33}\text{S} = \left(\delta^{33}\text{S} - 1000 \left(\left(\frac{\delta^{34}\text{S}}{1000} + 1 \right)^{0.515} - 1 \right) \right) \quad (8)$$

and

$$\Delta^{36}\text{S} = \left(\delta^{36}\text{S} - 1000 \left(\left(\frac{\delta^{34}\text{S}}{1000} + 1 \right)^{1.889} - 1 \right) \right) \quad (9)$$

The quality of these measurements is estimated on the basis of the long-term reproducibility of IAEA reference materials. Repeated analyses give $\delta^{34}\text{S} = -0.29 \pm 0.04\%$, $\Delta^{33}\text{S} = +0.082 \pm 0.004\%$, $\Delta^{36}\text{S} = -0.91 \pm 0.11\%$ for IAEA S1 (all 1σ , $n = 43$) and $\delta^{34}\text{S} = +22.33 \pm 0.06\%$, $\Delta^{33}\text{S} = +0.030 \pm 0.006\%$, $\Delta^{36}\text{S} = -0.17 \pm 0.07\%$ for IAEA S2 (all 1σ , $n = 20$).

These values are statistically indistinguishable from those given in Farquhar and Wing (2005), Ono et al. (2006a) and Johnston et al. (2008), showing that our reference gas lies, within error, on the same fractionation curve as the Maryland University and Geophysical Laboratory SF_6 tanks. We also determined the $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ of two CDT samples, yielding mean values of $\delta^{34}\text{S} = -0.08 \pm 0.15\%$, $\Delta^{33}\text{S} = -0.025 \pm 0.004\%$, $\Delta^{36}\text{S} = -0.11 \pm 0.05\%$ (all 1σ , $n = 2$), indistinguishable from the results on CDT reported in Ono et al. (2006a).

4. Results and discussion

In order to demonstrate that no isotope fractionation is caused by the use of the teflon apparatus itself, we performed extraction from synthetic FeS in both the teflon apparatus with HF + CrCl_2 ($n = 8$) and in the borosilicate apparatus with HCl + CrCl_2 ($n = 4$). The extraction yields and isotope compositions obtained in the two experiments are given in Table 1 and are indistinguishable. This strong accordance between the classical extraction technique and the extraction performed with HF in our teflon apparatus shows that no isotopic shift occurs using our apparatus.

4.1. Reduced sulfur recovery out of natural glasses

Three sub-marine glasses were selected as internal standards and analyzed for their S content: CH98 DR12, from the Mid-Atlantic Ridge, ED DR46 1-6 and ED DR26 type-1, from the Southwest Indian Ridge. Our S content determination for ED DR26 type-1 is identical within error with the value reported by Bézou et al. (2005) (see Table 2).

Results for replicate extractions of the three reference samples are presented in Table 3. Extraction experiments of sulfide sulfur in CH98 DR12 gave S yields between 90 and 105% ($n = 12$) with a mean of $100 \pm 4\%$ (1σ). The four extractions on ED DR46 1–6 show yields between 99 and 111% with a mean of $102 \pm 6\%$ (1σ) whereas extraction

Table 1

Replicate analyses of S isotope compositions of our synthetic FeS internal standard. The standard deviation (1σ) is given as indication of precision. The multiple extractions ($n = 8$) performed in the teflon apparatus show good agreement with the extraction processed in the borosilicate apparatus ($n = 4$). (a): versus V-CDT. (b): versus our SF_6 tank.

$n_s(\mu\text{mol})$	yield (%)	$\delta^{34}\text{S}^a$ (‰)	$\Delta^{33}\text{S}^b$ (‰)	$\Delta^{36}\text{S}^b$ (‰)
S extractions from FeS (AVS + CRS) performed in the borosilicate distillation apparatus with HCl				
10.1	103	15.67	0.025	-0.271
7.8	99	15.51	0.023	-0.243
10.5	92	15.47	0.023	-
12.3	95	15.93	0.022	-0.152
Averaged values				
-	97 ± 5	15.64 ± 0.21	0.023 ± 0.001	-0.222 ± 0.062
S extractions from FeS (AVS + CRS) performed in the teflon distillation apparatus with HF				
18.4	101	15.91	0.020	-0.262
28.9	98	15.68	0.028	-0.239
10.1	100	15.45	0.019	-0.268
16.5	102	15.63	0.022	-0.226
17	97	15.39	0.030	-0.124
12.4	99	15.54	0.016	-0.158
35.4	89	15.75	0.023	-0.200
12.9	95	15.46	0.033	-0.217
Averaged values				
-	98 ± 4	15.60 ± 0.17	0.024 ± 0.006	-0.212 ± 0.050

Table 2

Localization and S content for in-house basalt glass standards and samples from Chaussidon et al. (1991). (a) Data from Bézou et al. (2005). (b) Data from Chaussidon et al. (1991).

Name	Locality	Reported S (ppm)	Determined S (ppm)
<i>Internal standards</i>			
CH98 DR12	Mid-Atlantic Ridge	–	1039 ± 40
ED DR46 1–6	South-West Indian Ridge	–	914 ± 48
ED DR26 type 1	South-West Indian Ridge	722 ± 40 ^a	711 ± 46
<i>Samples analyzed in Chaussidon et al. (1991)</i>			
CL DR01-5	East-Pacific Ridge	957 ^b	–
CY82-29-03	East-Pacific Ridge	1011 ^b	–
CY82-27-01	East-Pacific Ridge	1104 ^b	1086 ± 48

of sulfur out of ED DR26 1–2 gives recoveries between 90 and 103% with an average of 97 ± 6% (1σ).

The abundance of exsolved sulfides in natural MORB is however too low (<0.5% of the S, Czamanske and Moore, 1977) to account for any “nugget” effect and hence the precision on extraction yields rather reflects the numerous uncertainties propagated during weighing the powdered sample and the obtained Ag₂S.

We did perform the sulfate extraction step for these glasses but never recovered any Ag₂S. Combining this observation with the ≈100% yield of sulfide extraction suggests that if present at all, sulfates in these samples may represent <1% of the total sulfur.

We analyzed six glasses from the EPR 12.5°N including three samples of Chaussidon et al. (1991): two aliquots of the original powders of CLDR01-5 and CY82 29-03 and a newly-made CY82 27-01 powder.

For CLDR01-5 and CY82 29-3 powders, the S amount could not be remeasured by EMP and hence we calculated our yields of sulfur extraction using the S contents reported by Chaussidon et al. (1991). For CY82 27-01, reduced sulfur (n=2) gave mean yields of 100 ± 2% (1σ). In contrast, yields were lower, ≈93 ± 2% for CLDR01-5 (1σ, n=5) and ≈76 ± 4% for CY82 29-03 (1σ, n=2). In these three samples, sulfate extraction has been attempted without success. The lowered yields might reflect either an over-estimated S content by Chaussidon et al. (1991) or insufficient removal of phenocrysts before the crushing step, leading in both cases to lowered extraction yields. Both of these suggestions are consistent with the observed very reproducible yields. We applied our method to additional samples from the North Atlantic, South-West Indian and East Pacific Ridges (see Table 6) bringing the total number of samples to nineteen. Extraction yields of reduced sulfur fall always within a narrow range of 96–105% showing that sulfur is likely to be exclusively under its reduced form, consistent with XANES spectroscopic results (Métrich et al., 2009; Jugo et al., 2010).

δ³⁴S and Δ^{33–36}S results determined on MORB internal standards are reported in Table 3. All the analyzed reference samples have δ³⁴S between –0.03 and –1.25‰ with respect to V-CDT, Δ³³S between –0.018 and –0.031‰ and Δ³⁶S between –0.196 and –0.282‰ both with respect to our SF₆ tank. The external reproducibility for δ³⁴S, Δ³³S and Δ³⁶S are respectively 0.08, 0.007 and 0.106‰ for CH98 DR12 (n=12) and systematically lower than 0.2, 0.015 and 0.140‰ when considering all internal standards.

As the whole S blank of the extraction protocol is too low to be directly determined (likely <0.1 μmol), its δ^{33–34–36}S was estimated indirectly: various masses of CH98 DR12 (equivalent to 2 to 15 μmol S) have been processed. Fig. 3 shows that no significant deviation of

Table 3

Replicate analyses for laboratory standards and for Chaussidon et al. (1991) samples. The standard deviation (all 1σ) is taken as the precision on the measurement. (a): versus V-CDT. (b): versus our rmSF₆ tank. (c): values determined in Chaussidon et al. (1991).

Sample	Mass (mg)	S (ppm)	Yield (%)	δ ³⁴ S ^a (‰)	Δ ³³ S ^b (‰)	Δ ³⁶ S ^b (‰)
<i>Internal reference standards</i>						
CH98 DR12	86	1039	90	–1.28	–0.037	–
	90		105	–1.25	–0.016	–
	140		103	–1.28	–0.022	–
	186		105	–1.13	–0.018	–
	340		103	–1.13	–0.023	–0.333
	342		105	–1.27	–0.020	–0.095
	345		97	–1.13	–0.029	–0.315
	350		102	–1.22	–0.017	–
	350		103	–1.05	–0.018	–0.149
	360		99	–1.24	–0.017	–0.079
	362		96	–1.19	–0.022	–0.284
	395		99	–1.29	–0.010	–0.260
				–1.20 ± 0.08	–0.021 ± 0.007	–0.216 ± 0.106
	ED DR46 1–6		315	914	99	–0.91
311		111	–1.25		–0.036	–0.334
370		99	–1.08		–0.013	–0.240
271		100	–1.13		–0.025	–0.150
			–1.09 ± 0.14		–0.021 ± 0.012	–0.241 ± 0.092
ED DR26 type 1	324	711	90	–1.26	–0.026	–0.386
	450		95	–1.28	–0.017	–0.282
	442		103	–1.08	–0.007	–0.314
	367		99	–1.39	–0.023	–0.144
				–1.25 ± 0.12	–0.018 ± 0.009	–0.282 ± 0.102
<i>Chaussidon et al. (1991) samples</i>						
CL DR01-5	410	957 ^c	96	–0.32	–0.027	–0.167
	390		91	–0.31	–0.013	–0.175
	358		92	–0.27	–0.018	–0.134
	367		92	–0.47	–0.023	–0.309
				–0.35 ± 0.09	–0.020 ± 0.006	–0.196 ± 0.077
CY82 29-3	334	1011 ^c	78	0.14	–0.023	–0.296
	332		74	–0.21	–0.39	–0.179
				–0.03 ± 0.18	–0.031 ± 0.008	–0.238 ± 0.059
CY82 27-1	339	1221	98	–0.77	–0.017	–0.373
	338		102	–0.60	–0.018	–0.176
				–0.69 ± 0.12	–0.018 ± 0.001	–0.275 ± 0.139

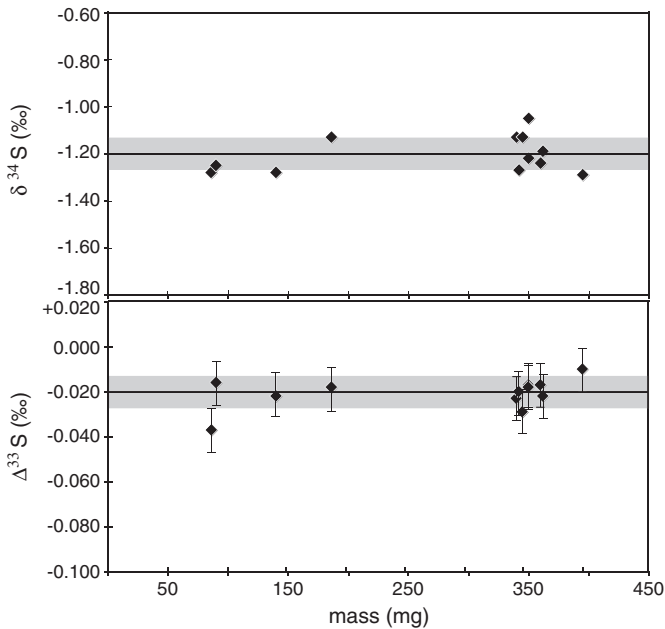


Fig. 3. Replicate analyses of CH98 DR12 internal standard glass. (a) $\delta^{34}\text{S}$ and (b) $\Delta^{33}\text{S}$ versus mass of sample powder.

the measured $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ is observed regardless of the amount of sample analyzed. This confirms the previous observation (see Section 3.1) that blanks may be negligible. A parallel observation cannot be made however for the $\Delta^{36}\text{S}$ for the lowest amount of S ($<4 \mu\text{mol}$), the intensity on the $m/z = 131$ being below 400 mV resulting in an increased standard deviation (typically $>0.25\%$).

4.2. Evaluating the redox specificity of the method

In MORB, S occurs predominantly or exclusively under reduced form whereas both sulfide and sulfate are known to occur in arc magmas and back-arc basin related-melts (e.g. Mandeville et al., 2009). In order to evaluate the degree of specificity of our protocol, we performed two sets of experiments, where artificial mixtures of basalts (i.e. carrying the reduced sulfur pool) and sulfates have been processed.

Table 4

Replicate analyses of S isotope compositions for seawater sulfate. Extractions have been undertaken in the classical borosilicate apparatus, either directly or after the whole HF- H_3BO_3 method. (a): versus V-CDT. (b): versus our SF_6 tank.

$n_{\text{S}}(\mu\text{mol})$	$\text{S}^{2-}/\text{S}_{\text{total}}$ mole ratio	yield (%)	$\delta^{34}\text{S}^{\text{a}}$ (‰)	$\Delta^{33}\text{S}^{\text{b}}$ (‰)	$\Delta^{36}\text{S}^{\text{b}}$ (‰)
S extractions from seawater performed directly in the borosilicate distillation apparatus with the Thode solution					
31.0	0	96	21.03	0.034	-0.255
31.0	0	103	20.71	0.046	-0.271
31.0	0	104	21.45	0.037	-0.152
31.0	0	103	21.04	0.040	-0.254
Averaged values					
-	-	102 ± 4	21.06 ± 0.30	0.040 ± 0.005	-0.254 ± 0.077
S extractions from seawater performed in the borosilicate apparatus after the whole HF- H_3BO_3 proceeding					
31.0	0	98	20.87	0.047	-0.378
31.0	0	98	21.27	0.039	-0.457
15.5	0	104	21.03	0.039	-0.278
15.5	0	100	21.15	0.039	-0.183
Averaged values					
-	-	101 ± 3	21.10 ± 0.13	0.041 ± 0.004	-0.324 ± 0.119

In the absence of basalt glass standard containing both sulfide and sulfate, a solution of seawater sampled in the southeast Indian ocean around 32°S – 84°E during the MD175 cruise has been used as a standard for oxidized sulfur. Its sulfate content of 2978 mg/kg has been determined using ion chromatography. Table 4 presents the S multi-isotope composition results for five aliquots of this batch, determined after sulfate reduction in the conventional glass vessel. The mean $\delta^{34}\text{S}$ of our seawater standard is $21.06 \pm 0.30\%$ with respect to V-CDT, and the $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ are $0.040 \pm 0.005\%$ and $-0.254 \pm 0.077\%$ respectively (all 1σ), both with respect to our SF_6 tank. These values are similar to published results obtained on Atlantic and Pacific seawater aliquots (Ono et al., 2006a, 2007; Peters et al., 2010). Seawater standards have also been analyzed with our new S extraction protocol (see Table 4). The S recovery during the oxidized sulfur step is $100 \pm 3\%$ and mean $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ are $21.10 \pm 0.13\%$, $0.041 \pm 0.004\%$ and $-0.324 \pm 0.119\%$ (all 1σ), respectively. These isotope composition are indistinguishable from those determined previously, thereby validating our protocol as an efficient method to extract and determine the isotope composition of sulfate S.

Although the specificity of the CrCl_2 for reduced forms of S has already been demonstrated (see Table 1 in Canfield et al., 1986), we performed the following tests to ensure the redox specificity of the method with HF. Between 0.1 and 2 ml of seawater ($n=8$) were processed alone with HF + CrCl_2 in the teflon apparatus. As expected, these experiments did not lead to any noticeable reduction of sulfate into H_2S . In addition, the protocol for reduced sulfur extraction has been applied to artificial mixtures of CH98 DR12 and seawater ($n=4$) (labeled “exp. 1” in Table 5). In these experiments, the mole ratios of reduced S over total S are around 0.4 such that any contamination of the reduced S pool by our standard sulfates (having a relatively high $\delta^{34}\text{S}$) would result in a significant deviation of the sulfide $\delta^{34}\text{S}$. For the reduced sulfur extraction, the mean recovery yield is $101 \pm 1\%$ (1σ), and the mean $\delta^{34}\text{S}$ is -1.19 ± 0.10 (1σ), indistinguishable from the value determined previously for this basalt (i.e. when the sample was processed alone). This confirms that sulfate, whether naturally occurring or present as a contaminant, does not interfere with the extraction of the reduced sulfur when our protocol is used.

Table 5

Replicate analyses of S isotope compositions from artificial mixtures. Seawater sulfate and CH98 DR12 have been mixed and respectively used as oxidized and reduced S pool. (a): bulk S amount denotes for total sulfur, regardless of its speciation. (b): versus V-CDT. (c): versus our SF_6 tank.

$n_{\text{S}}(\mu\text{mol})^{\text{a}}$	$\text{S}^{2-}/\text{S}_{\text{total}}$ mole ratio	yield (%)	$\delta^{34}\text{S}^{\text{b}}$ (‰)	$\Delta^{33}\text{S}^{\text{c}}$ (‰)	$\Delta^{36}\text{S}^{\text{c}}$ (‰)
Exp. 1: Reduced S extracted in one step from artificial mixture of CH98DR12 + seawater					
43.0	0.28	102	-1.24	-0.024	-
42.0	0.27	100	-1.05	-0.019	-0.125
43.0	0.28	101	-1.20	-0.020	-0.169
43.0	0.26	100	-1.27	0.024	-0.210
Averaged values					
-	-	101 ± 1	-1.19 ± 0.10	-0.022 ± 0.003	-0.168 ± 0.042
Exp. 2: Reduced S extracted in two steps (AVS then CRS) from artificial mixture of CH98DR12 + seawater					
25.2	0.38	97	-1.18	-0.018	-0.169
24.6	0.37	95	-0.97	0.000	-
30.0	0.48	99	-1.02	-0.020	-
Averaged values					
-	-	97 ± 2	-1.06 ± 0.11	-0.013 ± 0.011	-0.169
Exp. 2: Oxidized S extracted from artificial mixture of CH98DR12 + seawater					
25.2	0.38	107	19.04	0.031	-0.433
24.6	0.37	103	19.2	0.036	-0.246
30.0	0.48	101	19.8	0.040	-0.354
Averaged values					
-	-	104 ± 3	19.35 ± 0.41	0.040 ± 0.004	-0.344 ± 0.094

Finally, similar artificial mixtures have been processed to achieve both reduced and oxidized S extraction (labeledized “exp. 2” in Table 5). Three aliquots of CH98 DR12 have been mixed with seawater sulfates (sulfide/total S molar ratio around 0.4). In this case, the sulfide extraction was performed in two steps (i.e. AVS and then CRS extraction, see Section 3.3). For this, the mean extraction yield is $97 \pm 2\%$ (1σ) and the mean $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ are -1.06 ± 0.11 , -0.013 ± 0.011 and -0.169% , respectively (all 1σ). Although the extraction yields are slightly lower than 100%, the S isotope values are within error identical to those obtained when sulfide S is extracted in a single step.

The mean sulfate extraction yield is $104 \pm 3\%$ (1σ), showing that our chemical protocol of S extraction is accurate enough to determine the sulfide/sulfate ratios in silicate glasses with a precision of about 5%. The mean $\delta^{34}\text{S}$ determined for the sulfate is $19.35 \pm 0.41\%$ (1σ), which is around 1.5‰ lower than the expected value. Given that the extraction of sulfate yields both good recovery and S isotope compositions when performed alone, we conclude that this shift is related to the basalt sample itself. Considering the mean extraction yields of reduced and oxidized S for this set of experiments, there is the possibility that a small amount of reduced S contributes to the sulfate pool. However, assuming that 5% of the reduced S contributes to the oxidized S and that it keeps a S isotope composition around 0‰, a simple mass balance calculation indicates that such interference can be responsible for a 0.8‰ shift at most.

An alternative is that a small amount of sulfate is naturally present in the basalt. However, the high extraction yields for reduced S over total S would not allow this component to be more than 1% of the total S budget (see Section 4.1). The observed 1.5‰ shift toward lower $\delta^{34}\text{S}$ would require the sulfate component to be ^{34}S depleted, with a $\delta^{34}\text{S}$ lower than -50% . However, at high-temperature, the sulfate pool is expected to have a $\delta^{34}\text{S}$ 2–3‰ higher than the reduced S (Miyoshi et al., 1984) disqualifying any magmatic oxidized S as the responsible agent of the observed discrepancy.

Alternatively, the 1.5‰ shift can be produced by a contaminant brought by a secondary process after the eruption or during laboratory handling. This contaminant would reside in the basalt micro-fractures and its amount would not be constrainable by the microprobe S determination. The presence of such a component may be supported by the somewhat anomalously high extraction yields of sulfate in these experiments (i.e. slightly higher although within error of 100%). Taken together, these observations allow the contaminant to have a low but realistic $\delta^{34}\text{S}$, between -5 and $+5\%$. We conclude that its likely origin might be related to a slight oxidation of the reduced S ($\approx 1\%$ or lower) by the atmospheric oxygen.

5. Sulfur isotopes in MORB: a new tool for mantle research ?

5.1. ^{33}S and ^{36}S abundances in MORB

The results on reduced S show that our method allows for precise determination of $\delta^{33-34-36}\text{S}$ in basalt glasses. Determined $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ are strikingly homogeneous, both slightly but significantly negative with mean respective values of -0.020 ± 0.005 and -0.203 ± 0.094 (all 1σ) with respect to our SF_6 tank. The narrow range of $\Delta^{33-36}\text{S}$ of the samples does not allow any distinction of one from the other. Such a result is consistent with the concept that $\Delta^{33-36}\text{S}$ of MORB would remain unchanged during melting or cooling of the melts as all the known MIF-producing processes are related to either atmospheric photochemistry or open-system chemistry and biogeochemical processes in low temperature environments (see the review of Johnston, 2011). $\Delta^{33-36}\text{S}$ of MORB can thus be considered to represent directly their mantle source. Compared to our reference gas, CDT has a mean $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ of $-0.025 \pm 0.004\%$ and $-0.11 \pm 0.05\%$, respectively, indistinguishable from our MORB estimate. The MORB source therefore lies on the same reference curve as the CDT standard, with respect to $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values.

Only limited interpretations can be made of these data as neither the chondritic reservoir (except the few data of Rai and Thiemens, 2007) nor the slab-related sulfur has yet been precisely characterized in $\Delta^{33-36}\text{S}$. Our results however support the idea that the Earth's mantle has a near-zero $\Delta^{33-36}\text{S}$ as suggested (or assumed) previously (e.g. Farquhar et al., 2002; Thomassot et al., 2009; Ono et al., 2007; Cartigny et al., 2009).

5.2. A reappraisal of $\delta^{34}\text{S}$ in MORB

In contrast with the $\Delta^{33-36}\text{S}$, the total range measured of $\delta^{34}\text{S}$ ($\sim 1.8\%$) is well above our external reproducibility ($\sim 0.1\%$), allowing the use of this method to evaluate the natural variability of $\delta^{34}\text{S}$ in MORB.

We duplicated 3 of the 5 EPR samples reported in Chaussidon et al. (1991) and obtained reproducible $\delta^{34}\text{S}$, systematically lower than that of the original publication, with a shift between 0.4 and 1.5‰ towards negative values. The 3 other samples from the same location (EPR 12°N, see Table 6) also yielded negative $\delta^{34}\text{S}$ between -0.84 and -0.62% . This leads to a consistent local mean $\delta^{34}\text{S}$ of $-0.55 \pm 0.30\%$ ($n=6$, 1σ), contrasting with the generally accepted MORB

Table 6

Replicate S isotope compositions of additional worldwide MORB. (a): versus V-CDT. (b): versus our SF_6 tank.

Sample	S (ppm)	$\delta^{34}\text{S}^a$ (‰)	$\Delta^{33}\text{S}^b$ (‰)	$\Delta^{36}\text{S}^b$ (‰)
<i>North Atlantic ridge</i>				
CH98 DR11	967	-0.87	-0.030	-0.329
		-1.17	-0.013	-0.261
		-1.02 ± 0.21	-0.022 ± 0.012	-0.295 ± 0.049
CH98 DR10	1085	-1.00	-0.030	-0.284
		-0.94	-0.007	-0.441
		-0.97 ± 0.04	-0.019 ± 0.017	-0.362 ± 0.111
CH98 DR09	1048	-1.33	-0.021	-0.332
		-1.42	-0.029	-0.187
		-1.37 ± 0.06	-0.025 ± 0.006	-0.259 ± 0.102
CH98 DR08	1176	-0.62	-0.027	-0.345
		-0.56	-0.014	-0.226
		-0.59 ± 0.05	-0.021 ± 0.009	-0.286 ± 0.084
CH98 DR06	1064	-1.74	-0.017	-0.001
		-1.90	-0.016	-0.029
		-1.82 ± 0.11	-0.016 ± 0.001	-0.015 ± 0.020
<i>South West Indian ridge</i>				
ED DR73-2	978	-1.81	-0.032	-
		-1.72	-0.024	-
		-1.91	-0.021	-0.176
ED DR11 1-9	728	-1.81 ± 0.09	-0.026 ± 0.006	-0.176
		-0.18	-0.006	-0.079
		0.21	-0.006	-0.065
SWF DR09 1-3	1154	0.02 ± 0.28	-0.006 ± 0.000	-0.072 ± 0.010
		-0.65	-0.025	-0.122
		-0.54	-0.023	-0.231
		-0.60 ± 0.08	-0.024 ± 0.001	-0.177 ± 0.077
<i>East Pacific ridge, 12°N</i>				
CY82 18-1	1135	-0.68	-0.013	-
		-0.56	-0.017	-0.192
		-0.62 ± 0.09	-0.015 ± 0.003	-0.192
CY84 24-03	984	-0.74	-0.013	-0.089
		-0.88	-0.025	-0.052
		-0.81 ± 0.10	-0.019 ± 0.008	-0.071 ± 0.026
CY84 30-06	1221	-0.77	-0.010	-0.091
		-0.90	-0.015	-
		-0.84 ± 0.10	-0.013 ± 0.004	-0.091
<i>East Pacific ridge, 17°S</i>				
CY84 06-02	1196	-1.12	-0.015	-0.083
		-1.19	-0.024	-0.124
		-1.15 ± 0.05	-0.020 ± 0.006	-0.104 ± 0.029
CY84 07-03	1131	-1.15	-0.015	-0.156
		-1.13	-0.014	-0.096
		-1.14 ± 0.01	-0.015 ± 0.001	-0.126 ± 0.042

$\delta^{34}\text{S}$ value of $+0.51 \pm 0.64\%$ (Sakai et al., 1984; Chaussidon et al., 1991). In contrast to our measurements, the previous MORB data were acquired using the heterogeneous CDT standard. However, the magnitude of the observed $\delta^{34}\text{S}$ shift is higher than the CDT overall heterogeneity and therefore cannot be related to the standard used.

Given that the Kiba reagent does not distinguish between sulfate and sulfide, the systematic differences between the Kiba and the CrCl_2 – HF methods might be related to a widespread presence of ^{34}S -enriched sulfates in the samples. In this scenario, the sulfate contaminant would however have a surprisingly high $\delta^{34}\text{S}$ ($>50\%$). More likely, the observed positive $\delta^{34}\text{S}$ values for the Kiba-extracted S are the result of an incomplete S extraction (see Section 2). The systematic shift is of the order of magnitude of the overall MORB variability making the Kiba extraction protocol inappropriate for MORB analyses.

The mean MORB $\delta^{34}\text{S}$ ($n = 19$) is significantly negative, at $-0.91\% \pm 0.50$ (1σ) (see Fig. 4). We are aware that the small number of glasses analyzed in this study ($n = 19$) is insufficient to be representative of the whole MORB reservoir, especially when its natural geochemical variability is taken into account. However, this new data set is comparable in size to the whole literature dataset allowing a first re-appraisal of the geological meaning of MORB sulfur isotope compositions based on the new negative values of $\delta^{34}\text{S}$.

Unlike for $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, whether the mean negative $\delta^{34}\text{S}$ of MORB characterizes the mantle source or is acquired during melting and differentiation needs to be clearly addressed. Several parameters have to be taken into account: first, the temperature at which all the potential sulfur exsolution occurs is high, typical of magmatic processes ($T > 1200$ °C). Secondly, S in MORB is principally associated with iron (and to a lesser extent to Ni and Cu), whether it is in sulfides or dissolved in the silicate melt. Therefore, the surrounding atomic environment of sulfur does not change between the dissolved and the exsolved phase. In this context, the classical stable isotope theory would predict that the fractionation between dissolved sulfur and any segregated sulfide is negligible (see the reviews of Taylor, 1986; Ohmoto and Goldhaber, 1997). Moreover, whereas all the abiotic fractionations of sulfur isotopes are driven by redox changes, both the

results of Métrich et al. (2009) and our data show that S is likely to be completely reduced in most MORB. Taken together, all these inferences allow the safe assumption that $\delta^{34}\text{S}$ of MORB represents the value of their mantle source. This may be particularly true for non-differentiated basalts ($\text{MgO} > 6.0\%$) for which the typical magmatic temperatures are the highest and the quantity of sulfides lost by exsolution are the lowest. This view was challenged by Chaussidon et al. (1989) who suggested a $\alpha_{\text{exsolved-dissolved}}^{34} = 1.003 \pm 0.003$. This result relies on previously determined peridotite $\delta^{34}\text{S}$ and ion probe measurements of exsolved sulfides. Taking the present MORB $\delta^{34}\text{S}$ of $\approx -1\%$ leads to a $\alpha_{\text{exsolved-dissolved}}^{34} \approx 1.004$. This would predict a decrease of $\delta^{34}\text{S}$ during differentiation as the result of sulfide fractionation. We do not observe such trends and therefore suggest that the $\alpha_{\text{exsolved-dissolved}}^{34}$ might be smaller or negligible, in accordance with the Mandeville et al. (2009) study.

Assuming that $\delta^{34}\text{S}$ of MORB reflects that of their mantle source, the consistent negative deviation compared to the CDT standard would clearly distinguish the Earth's mantle from chondrites. Actually, available data on undifferentiated meteorites cluster around a mean $\delta^{34}\text{S}$ of $0.04 \pm 0.31\%$ (1σ , $n = 24$, Orgueil excluded) when all classes of chondrites are considered (Gao and Thiemens, 1993a,b). Again, these data have been acquired using the heterogeneous CDT standard. However, Rai and Thiemens (2007) determined $\delta^{34}\text{S}$ of five chondrites and confirmed that these materials have $\delta^{34}\text{S}$ statistically indistinguishable from 0.00% even when the V-CDT standard is used. Therefore, the significant difference in ^{34}S abundance between the chondrite reservoir(s) and the Earth's mantle makes sulfur isotope composition a potential tool for addressing crust–mantle complementarity, the role of subduction or core/mantle differentiation.

6. Conclusion

We developed a HF- CrCl_2 and a H_3BO_3 -Thode solution method allowing a complete and specific extraction of reduced and oxidized sulfur in glassy matrices. This protocol is valid for silicate glasses showing either only reduced S (e.g. MORB) or coexistence of sulfate–sulfide (e.g. arc magmas or BABB). Our results confirm that MORB do not contain significant amounts of sulfate, in agreement with Métrich et al. (2009), and suggest that such oxidized sulfur in MORB, if any, may result from post-emplacment sample contamination (in the laboratory or on the seafloor).

MORB show homogeneous negative $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ with respect to our SF_6 tank. However, these values are likely to be indistinguishable from our CDT estimate, revealing that the Earth's mantle lies on the same fractionation curves as the CDT standard.

In contrast, all samples show negative $\delta^{34}\text{S}$ ranging down to -1.80% . These negative values contrast with the mainly positive data previously reported for comparable or even for the same samples. In this respect, we propose that the use of the Kiba reagent is associated with an incomplete recovery of sulfur leading to a systematic isotope fractionation. The mean $\delta^{34}\text{S}$ of MORB is $-0.91 \pm 0.50\%$ (1σ , $n = 19$), statistically distinct from the chondrite value of 0.04 ± 0.31 (1σ , $n = 24$) determined in Gao and Thiemens (1993a,b), revealing the potential of S isotopes to constrain mantle geodynamics or core/mantle differentiation.

Importantly, the total $\delta^{34}\text{S}$ range is well above our analytical precision ($\approx 0.1\%$), showing that ocean ridge basalts do not have a homogeneous source from the S isotope point of view. Applied in a regionally-focused study, the relative abundances of S isotopes may help to decipher between the different models usually advocated to account for MORB source heterogeneity and hence be a potential new tracer for chemical geodynamic studies.

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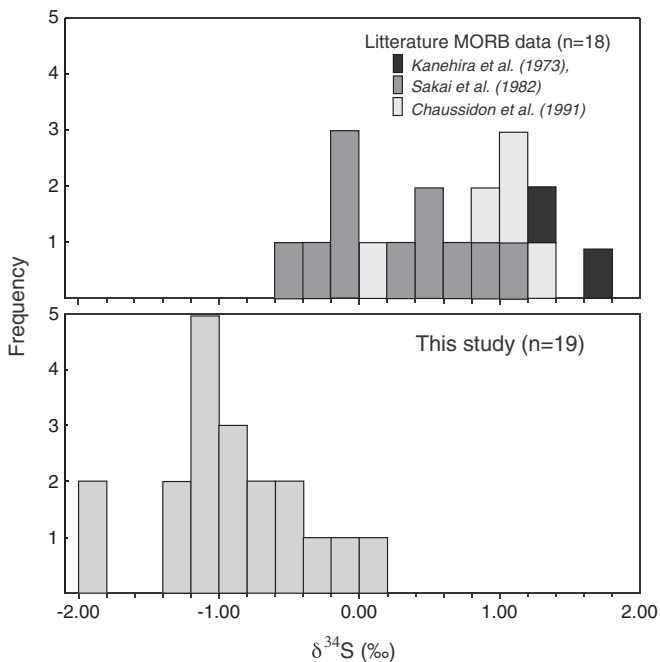


Fig. 4. Histograms comparing previously published $\delta^{34}\text{S}$ data for MORB (upper) to the newly obtained data (lower). Previous data are from (Kanehira et al., 1973; Sakai et al., 1984; Chaussidon et al., 1991).

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