

# Sulfur Concentration in Geochemical Reference Materials by Solution Inductively Coupled Plasma-Mass Spectrometry

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With implications for the origin of ore deposits, redox state of the atmosphere, and effects of volcanic outgassing, understanding the sulfur cycle is vital to our investigation of Earth processes. However, the paucity of sulfur concentration measurements in silicate rocks and the lack of well-calibrated reference materials with concentrations relevant to the rocks of interest have hindered such investigations. To aid in this endeavour, this study details a new method to determine sulfur concentration via high mass resolution solution inductively coupled plasma-mass spectrometry (ICP-MS). The method is based on an *aqua regia* leach, involving relatively rapid sample preparation and analysis, and uses small test portion masses (< 50 mg). We utilised two independently prepared standard solutions to calibrate the analyses, resulting in 4% accuracy, and applied the method to eight geochemical reference materials. Measurements were reproducible to within ~ 10%. Sulfur concentrations and isotopes of six reference materials were measured additionally by elemental analyser-combustion-isotope ratio mass spectrometry to independently evaluate the accuracy of the ICP-MS method. Reference materials that yielded reproducible measurements identical to published values from other laboratories (JGb-1, JGb-2 and MAG-1) are considered useful materials for the measurement of sulfur. Reference materials that varied between studies but were reproducible for a given test portion perhaps suffer from sample heterogeneity and are not recommended as sulfur reference materials.

Keywords: sulfur concentration, solution ICP-MS, EA-combustion-IRMS, reference materials, standard solution, sample digestion.

*La compréhension du cycle du soufre est essentielle pour les études des processus terrestres avec notamment des implications pour une meilleure connaissance de l'origine des gisements de minerai, de l'état redox de l'atmosphère et des effets du dégazage volcanique. Cependant, la rareté des mesures de concentration du soufre dans les roches silicatées et le manque de matériaux de référence bien calibrés et avec des concentrations pertinentes pour les roches d'intérêt entravent les études. Afin d'avancer dans cette problématique, cette étude détaille une nouvelle méthode pour déterminer le soufre en utilisant la technique solution ICP-MS à haute résolution de masse. La méthode est basée sur une lixiviation à base d'aqua regia, impliquant une préparation d'échantillons et un temps d'analyse relativement rapides, et qui utilise de petites portions de masses tests (< 50 mg). Nous avons utilisé deux solutions standards préparées indépendamment pour calibrer les analyses, ce qui débouche sur une précision de 4%, et nous avons appliqué la méthode à huit matériaux de référence géochimiques. Les mesures sont reproductibles à environ 10% près. Des analyses de la concentration et des isotopes du soufre de six matériaux de référence ont été également réalisées par un système analyseur élémentaire-spectromètre de masse de rapport isotopique (IRMS)-interface de combustion afin d'évaluer de manière indépendante l'exactitude de la méthode ICP-MS. Les matériaux de référence qui donnent des mesures reproductibles identiques aux valeurs publiées par d'autres laboratoires (JGb-1, JGb-2, MAG-1) sont considérés comme des matériaux utiles pour la mesure du soufre. Les matériaux de référence qui varient d'une étude à l'autre, mais sont reproductibles pour une portion test donnée sont peut-être des échantillons hétérogènes et ne sont pas recommandés comme matériaux de référence pour le soufre.*

*Mots-clés : concentration de soufre, solution ICP-MS, EA-combustion-IRMS, matériaux de référence, solution standard, digestion d'échantillon.*

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Because sulfur exists in several oxidation states, it is an important element in the study of redox reactions. With implications for the oxidation state of Earth's atmosphere through geological time, the origin of ore deposits, and weathering processes, as well as biogeochemical and inorganic reactions, the study of S has application to a wide variety of disciplines within the Earth sciences (e.g., Hedenquist and Lowenstern 1994, Arthur 2000, Wallace and Edmonds 2011).

Such investigations of the S cycle have been limited by the general dearth of S concentration measurements in silicate rocks, wherein S abundances are low but high enough to be petrologically relevant. In part, this is because few geochemical reference materials have been adequately characterised for bulk S content. In addition, the volatile nature of S makes it difficult to determine using conventional bulk-rock analytical methods. Sulfur can be reliably measured by combustion in conjunction with gas source mass spectrometers or infrared absorption spectrometers (e.g., Bach and Erzinger 1995, Studley *et al.* 2002). However, these techniques require large sample sizes and appropriate reference materials. Other bulk-rock techniques include X-ray fluorescence spectrometry (XRF), gravimetric methods (e.g., the 'Kiba' method), isotope dilution thermal ionisation mass spectrometry (ID-TIMS), isotope dilution inductively coupled plasma-mass spectrometry (ID-ICP-MS) and ion chromatography.

Although a common bulk technique in geochemistry, XRF is not routinely used for S determination in silicates because of S volatilisation during sample fusion as well as poor reference values (Leoni *et al.* 1982, Giles *et al.* 1995, Hettipathirana *et al.* 2004). The 'Kiba' method, first described by Kiba *et al.* (1955), uses a mixture of tin(II)-chloride dihydrate and strong phosphoric acid to reduce sulfides and sulfates to H<sub>2</sub>S and SO<sub>2</sub> gases; the volume of gas evolved determines the amount of S in the sample. This technique is laborious and requires a large amount of sample (Sasaki *et al.* 1979, Ueda and Sakai 1983). Isotope dilution TIMS (Paulsen and Kelly 1984) and ICP-MS (Makishima and Nakamura 2001) have also been used, even though they require complicated chemistry to extract and purify sulfur. Ion chromatography (IC) requires large sample amounts and has high detection limits (e.g., Michel and Villemant 2003). Additional routinely used bulk-rock techniques include pyrolysis of S determined by iodometric titration (Gros *et al.* 2005) and chromium reduction for recovery of total reduced inorganic sulfur (Canfield *et al.* 1986). A combination of S extraction techniques may be useful when the separate evaluation of reduced and oxidised S is desirable (e.g., Labidi *et al.* 2012).

Up to the present time, the best techniques for measuring S in silicate materials are microanalytical techniques, such as electron probe microanalysis (EPMA) and secondary ion mass spectrometry (SIMS). As *in situ* techniques, they have been successful because of low detection limits and because glass or mineral reference materials have been well characterised (Hauri *et al.* 2002, Ripley *et al.* 2011). *In situ* measurements by laser ablation ICP-MS have also been explored (see Ripley *et al.* 2011), but issues with interferences, memory and calibration have not yet been fully resolved. In any case, *in situ* techniques cannot be used to measure bulk-rock S contents due to heterogeneities at the micrometre scale.

As demonstrated by the poor calibration curves for most bulk-rock techniques (Ripley *et al.* 2011), the community needs well-calibrated reference materials with appropriate S contents for the analysis of silicates. This study presents a new method for determining S concentrations by high mass resolution solution ICP-MS and applies this method to determine the S concentrations of geochemical reference materials. In particular, two standard solutions were prepared to serve as absolute calibrators of potential reference materials. Sulfur concentration and isotope ratios of reference materials were also measured by SO<sub>2</sub> combustion in an elemental analyser coupled with an isotope ratio mass spectrometer as an independent test. Agreement between S concentrations determined by both techniques lends credence to the new ICP-MS method. The technique offers the ability to rapidly measure S in small sample sizes and utilises simple chemistry.

## Methods

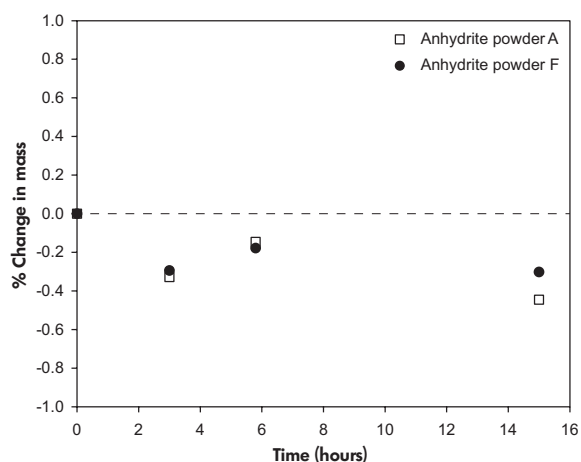
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### Standard solutions

Two independent lots of anhydrite (CaSO<sub>4</sub>) powder were purchased from Alfa-Aesar. Powder material F refers to stock number 40144 and lot F21X040 with a reported purity of 99%. Powder material A refers to stock number 11116 and lot A31X029 with a reported purity of 99.993%. These purity levels, however, do not include volatiles. In particular, any absorption of water could result in the formation of gypsum (CaSO<sub>4</sub>·nH<sub>2</sub>O), and failure to account for this would bias the calculation of S concentrations from gravimetry of anhydrite. To eliminate this problem, we heated a known mass of anhydrite powder at 170 °C for 15 hr in a gravity oven, following similar procedures outlined in Yin *et al.* (2001). Powder aliquots of > 10 g were weighed on a Mettler balance sensitive to 0.01 mg, suggesting weighing uncertainties less than 0.001–0.0001%. Gypsum breaks down to anhydrite at 70 °C at

100 kPa (Yamamoto and Kennedy 1969), so all water is driven off at these baking temperatures. After the oven was turned off, the anhydrite powder was weighed immediately and several hours later to assess the rate at which the powder reabsorbed water from the ambient Houston, TX atmosphere (Figure 1). Anhydrite powders F and A experienced 0.30 and 0.44% reductions in mass, respectively, after baking, which we interpret to indicate loss of water by dehydration of small amounts of gypsum. Monitoring the mass of the baked powders under ambient conditions showed a gradual increase in mass with time, most likely due to reabsorption of water from the atmosphere. However, over the course of 3 hr, the relative mass increase was 0.1% and hence small. Nevertheless, the mass of the powder immediately after baking was adopted as the correct mass of anhydrite in the powders. Accurately weighed powders were then transferred into a 2% m/m HNO<sub>3</sub> solution made from Seastar double-distilled concentrated HNO<sub>3</sub> and Millipore 18.2 MΩ cm water to obtain an approximate S concentration of 800–1000 μg ml<sup>-1</sup>. The total mass of the solution was recorded on a top-loading balance. Anhydrite dissolved completely within 1 hr.

These two solutions were used as our stock solutions A and F. From these we made a series of gravimetric sequential dilutions down to concentrations of ~ 0.01 μg g<sup>-1</sup>. All dilutions were then spiked with a known amount of indium to serve as an internal standard for drift correction during measurement by ICP-MS. After spiking, the total solution was weighed again, and the final concentration of S in the solution was determined from the mass of anhydrite and on the assumption of perfect stoichiometry. Calibration curves of signal intensity versus concentration in solution were linear.

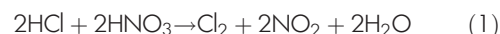


**Figure 1. Relative change of mass (in %) of anhydrite powders A and F following heating to 170 °C versus duration of heating.**

The slope for anhydrite A dilutions was 5% higher than that for anhydrite F dilutions. Assuming that the uncertainties in weighing anhydrite powders were random, we used both anhydrite A and F solutions simultaneously to define calibration curves. This gave a 4% accuracy to our measurements.

### Dissolution procedure

Sulfur concentration in bulk rocks is difficult to measure because S is volatile and/or insoluble in solution in reduced oxidation states. These complications were avoided by converting S to the S<sup>6+</sup> species in the form of SO<sub>4</sub><sup>2-</sup>, a non-volatile and water-soluble species. Sulfur was thus leached from rock powders using *aqua regia* (3 parts concentrated, for example 9 mol l<sup>-1</sup>, HCl and 1 part concentrated, for example 16 mol l<sup>-1</sup>, HNO<sub>3</sub>). The reaction of HCl and HNO<sub>3</sub> creates an oxidising environment via the reaction:



where N is in the 4<sup>+</sup> state on the right side of the equation. Reduced S is oxidised by transfer of electrons to reduce N via the following reaction:



*Aqua regia* was used instead of HF to avoid the formation of SF<sub>6</sub>, a highly stable and volatile compound. In this technique, about 50 mg of finely ground, well-mixed rock powder was added to a wrench-cap Teflon vial (3 ml) to which 1.5 ml of pure concentrated HCl was added, followed by 0.5 ml of pure concentrated HNO<sub>3</sub>. The exact amount of sample powder was determined via mass difference. The caps were then tightened with the aid of a cap wrench. We strongly encourage the sequential addition of HCl and then HNO<sub>3</sub> to the vial and discourage the dangerous and potentially lethal storage of *aqua regia* for future use. The formation of *aqua regia* rapidly evolves chlorine and nitrogen dioxide gases, both of which are dangerous chemicals. Additionally, the potency of *aqua regia* decreases with storage time.

Once sealed, the vials were heated overnight in a gravity oven at 125–140 °C. The next day, after allowing the vials to cool to room temperature, the vials were opened slowly and carefully using a cap wrench under a fume hood (protective wear is highly recommended in case of rupture). The full contents of the vials were transferred to a centrifuge tube and diluted up to 10 ml with 2% m/m HNO<sub>3</sub>. The contents were centrifuged for ~ 15 min to separate the undissolved solids from the solution. The supernatant was then transferred to an empty 125 ml polypropylene bottle. The cycle of dilution, centrifuging and transfer of solution was

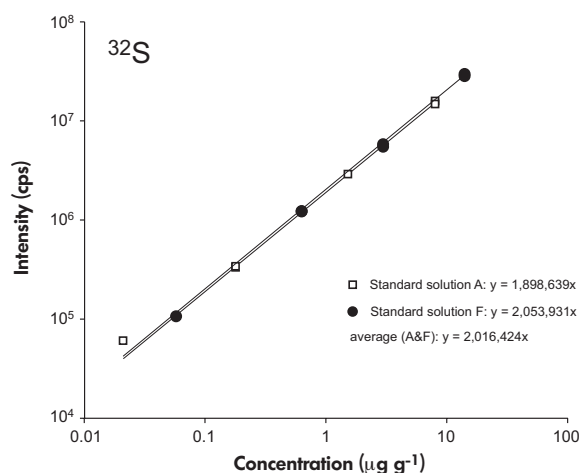
repeated three times to ensure complete removal of the leachate from the residual rock powder. The contents of the polypropylene bottle were measured via mass difference. Before analysis by ICP-MS, a known quantity of indium was added to the final solution to serve as an internal standard element. A procedural blank was also prepared.

### Inductively coupled plasma-mass spectrometry

**Instrumentation:** All measurements were conducted on a ThermoFinnigan Element 2 magnetic sector ICP-MS at Rice University. The magnetic sector mass analyser allowed operation at the high mass resolutions necessary to resolve S isotopes from isobaric interferences that cannot be resolved by conventional quadrupole ICP-MS. Samples were introduced by free aspiration using an Elemental Scientific 100  $\mu\text{l min}^{-1}$  Teflon nebuliser attached to a 25-ml cyclonic spray chamber. Samples were allowed a 1.2 min uptake time and 3 min wash in 2%  $\text{HNO}_3$ .

**Data acquisition:** The Element 2 instrument was operated at medium mass resolution ( $M/\Delta M \approx 3000$  at 10% intensity) to resolve  $^{32}\text{S}$  from  $^{16}\text{O}^{16}\text{O}$  and  $^{31}\text{P}^1\text{H}$ ;  $^{33}\text{S}$  from  $^{16}\text{O}^{17}\text{O}$ ; and  $^{34}\text{S}$  from  $^{17}\text{O}^{17}\text{O}$ ,  $^{16}\text{O}^{17}\text{O}^1\text{H}$  and  $^{16}\text{O}^{18}\text{O}$ . We also measured  $^{115}\text{In}$  as an internal standard and  $^{40}\text{Ar}^{40}\text{Ar}$  to correct for long-term magnet drift. Sulfur and In were measured at a 100% mass window and  $^{40}\text{Ar}^{40}\text{Ar}$  at a 200% mass window. The magnet mass was fixed to 31.972 u for S isotope measurements, 79.921 u for  $^{40}\text{Ar}^{40}\text{Ar}$ , and 114.903 u for In, and each scan was executed by sweeping the voltage in the electrostatic analyser (Escan mode). We permitted both ion counting and analogue mode detection. Small mass offsets due to magnetic hysteresis were empirically corrected in the method file. Overall magnetic drift during operation was corrected in real time by locking onto the  $^{40}\text{Ar}^{40}\text{Ar}$  dimer. Ten slices of 0.01 s each were measured for each peak, and a complete measurement consisted of seventy-five passes. Signals for each spectrum were integrated at a 50% mass window; the  $^{40}\text{Ar}^{40}\text{Ar}$  integration window was 80%. During data acquisition, sensitivity was  $\sim 5 \times 10^4$  cps  $\text{In}/\text{ng ml}^{-1}$  and  $\sim 2 \times 10^3$  cps total S/ $\text{ng ml}^{-1}$ .

**Data reduction:** Geochemical reference materials, standard solutions and procedural blanks, all run in the same sequence, were first corrected for drift by normalising In signals to the beginning of the sequence. The procedural blank was then subtracted from the sample unknowns. Assuming a linear relationship forced through zero, a calibration curve was then generated for each set of standard solutions (Figure 2) and the drift- and blank-corrected signal was converted to solution concentration using the calibration curve. The solution concentration was

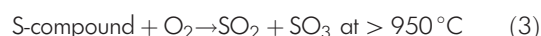


**Figure 2. Calibration curves for  $^{32}\text{S}$  determined by standard solutions (A series, F series and both) differ by  $\pm 4\%$ . The  $0.02 \mu\text{g g}^{-1}$  solution suffered from unresolved molecular interferences, but these values are far below any natural sample of interest.**

then converted to rock-powder concentration using the known mass of the dissolved powder and applying the appropriate dilution correction.

### Elemental analyser mass spectrometry

Sulfur concentrations and isotope compositions ( $\delta^{34}\text{S}$ ) were determined by  $\text{SO}_2$  combustion in an Elemental Analyser coupled with an isotope ratio mass spectrometer (EA-combustion-IRMS). The measurement was performed using a GV Isoprime isotope ratio mass spectrometer and Eurovector elemental analyser (EuroEA3028-HT) in the Laboratory for Environmental and Sedimentary Isotope Geochemistry (LESIG) at the University of California at Berkeley. Bulk powder samples (containing  $> 3 \mu\text{g}$  sulfur) were mixed with  $\text{V}_2\text{O}_5$  powder (used as a catalyst) and thermochemically decomposed with copper wires at  $1020^\circ\text{C}$  to yield  $\text{SO}_2$  gas for S isotope determinations following these reactions:



Small amounts of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  were also produced during these reactions, depending on the nature of the sample.  $\text{H}_2\text{O}$  was removed by passing through a Mg  $(\text{ClO}_4)_2$  trap, and  $\text{CO}_2$  by passing through a dilutor. Several replicates of one international reference material (NBS 127)

**Table 1.**  
Analytical results by ICP-MS

	Lot No.	<sup>32</sup> S (µg g <sup>-1</sup> ) concentration	<sup>33</sup> S (µg g <sup>-1</sup> ) concentration	<sup>34</sup> S (µg g <sup>-1</sup> ) concentration	LOD <sup>32</sup> S (µg g <sup>-1</sup> )	LOD <sup>33</sup> S (µg g <sup>-1</sup> )	LOD <sup>34</sup> S (µg g <sup>-1</sup> )	Blank correction
<b>BCR-2: basalt powder</b>								
Analysis 1	0468	301	353	307	9	125	40	14–22%
Analysis 2	0468	299	322	299	5	75	24	9–15%
Analysis 3	0468	307	302	295	4	23	8	8–9%
Analysis 4	0468	325	305	295	3	21	8	8–9%
Mean ± s		308 ± 11.8	321 ± 23.4	299 ± 5.4				
% RSD		3.8	7.3	1.8				
<b>BHVO-1: basalt powder</b>								
Analysis 1	40–17	47.5	52.6	48.4	3	37	12	26–33%
Analysis 2	40–17	46.0	49.4	47.8	3	46	15	30–39%
Analysis 3	40–17	45.7	56.7	46.3	4	55	18	35–40%
Analysis 4	40–17	55.4	61.4	55.7	2	31	9	16–24%
Analysis 5	40–17	57.2	60.0	56.7	3	48	14	23–33%
Analysis 6	40–17	55.5	57.3	57.0	2	26	8	14–22%
Analysis 7	40–17	52.7	58.7	52.0	4	50	16	27–40%
Analysis 8	40–17	59.9	76.5	61.0	7	93	30	37–48%
Analysis 9	43–12	55.4	65.3	54.5	6	81	26	36–49%
Analysis 10	43–12	59.8	65.5	59.7	3	12	5	14–16%
Mean ± s		53.5 ± 5.4	60.3 ± 7.6	53.9 ± 5.1				
% RSD		10.0	12.6	9.5				
<b>BHVO-2: basalt powder</b>								
Analysis 1	0223	111	106	103	0.5	5	1	4–5%
Analysis 2	0223	147	151	147	2	9	4	4–6%
Analysis 3	0223	145	151	145	3	10	4	5–7%
Analysis 4	0223	125	140	130	3	43	14	13–17%
Analysis 5	0223	121	132	127	2	29	10	10–13%
Analysis 6	0223	134	147	140	2	28	9	8–12%
Analysis 7	0223	138	144	144	2	34	10	8–13%
Analysis 8	0223	144	152	145	2	36	11	8–13%
Analysis 9	0223	149	153	151	1	21	6	5–8%
Analysis 10	0223	142	166	141	3	37	12	9–15%
Analysis 11	0223	137	149	137	4	60	19	14–24%
Analysis 12	0223	135	132	128	1	5	2	4–5%
Analysis 13	0223	144	136	134	1	8	3	7–8%
Mean ± s		136 ± 11	143 ± 15	136 ± 13				
% RSD		8.3	10.2	9.2				
<b>BIR-1: basalt powder</b>								
Analysis 1	0898	0.5	5.9	0.6	2	32	10	79–97%
Analysis 2	0898	1.0	7.3	0.5	2	27	9	72–96%
Analysis 3	0898	1.6	3.7	1.0	4	53	17	92–96%
Analysis 4	0898	3.7	8.8	3.0	2	26	8	70–79%
Analysis 5	0898	3.5	7.1	2.9	2	27	9	75–80%
Analysis 6	0085	1.3	8.0	0.4	3	46	15	82–98%
Analysis 7	0097	0.8	8.2	1.5	3	38	12	76–95%
Analysis 8	0097	2.0	7.8	1.1	2	34	11	77–93%
Analysis 9	0097	2.5	6.9	1.4	2	30	10	77–90%
Analysis 10	0097	13.8	18.3	14.1	2	21	7	40–44%
<b>JGb-1: gabbro powder</b>								
Analysis 1	8–45	1996	2078	2052	3	13	5	≤ 1%
Analysis 2	8–45	1814	1970	1922	2	9	4	≤ 1%
Analysis 3	8–45	1754	1749	1672	0.3	3	1	< 1%
Analysis 4	8–45	1739	1734	1656	0.4	3	1	< 1%
Analysis 5	8–45	2139	2045	1905	4	56	18	1–2%
Analysis 6	8–45	2496	2186	2041	3	43	14	1–2%
Analysis 7	8–45	1927	1988	1911	1	12	5	< 1%

Table 1 (continued).  
Analytical results by ICP-MS

	Lot No.	$^{32}\text{S}$ ( $\mu\text{g g}^{-1}$ ) concentration	$^{33}\text{S}$ ( $\mu\text{g g}^{-1}$ ) concentration	$^{34}\text{S}$ ( $\mu\text{g g}^{-1}$ ) concentration	LOD $^{32}\text{S}$ ( $\mu\text{g g}^{-1}$ )	LOD $^{33}\text{S}$ ( $\mu\text{g g}^{-1}$ )	LOD $^{34}\text{S}$ ( $\mu\text{g g}^{-1}$ )	Blank correction
Analysis 8	8-45	2036	2038	1934	2	11	4	$\leq 1\%$
Mean $\pm$ s		1988 $\pm$ 249	1974 $\pm$ 157	1887 $\pm$ 149				
% RSD		12.5	8.0	7.9				
<b>JGb-2: gabbro powder</b>								
Analysis 1	5-39	681	718	691	5	67	22	4-7%
Analysis 2	5-39	635	682	622	4	51	16	3-6%
Analysis 3	5-39	736	697	662	3	21	7	3-4%
Mean $\pm$ s		684 $\pm$ 50	699 $\pm$ 18	659 $\pm$ 35				
% RSD		7.4	2.6	5.2				
<b>JP-1: peridotite powder</b>								
Analysis 1	6-26	28.5	37.2	30.0	2	31	10	29-39%
Analysis 2	6-26	24.5	33.2	26.1	2	24	8	27-36%
Analysis 3	6-26	35.2	39.6	31.3	1	9	3	24-25%
Mean $\pm$ s		29.4 $\pm$ 5.4	36.7 $\pm$ 3.3	29.1 $\pm$ 2.7				
% RSD		18.4	8.9	9.4				
<b>MAG-1: marine mud powder</b>								
Analysis 1	7-21	3692	3834	3675	3	12	5	< 1%
Analysis 2	7-21	3947	3977	3889	1	13	4	< 1%
Analysis 3	7-21	3724	3677	3499	1	9	3	< 1%
Analysis 4	7-21	3856	3983	3856	4	56	18	$\leq 1\%$
Analysis 5	7-21	3573	3670	3619	4	60	20	$\leq 1\%$
Analysis 6	7-21	3922	4113	3936	5	60	20	$\leq 1\%$
Analysis 7	7-21	3981	3952	3918	5	79	23	$\leq 1\%$
Analysis 8	7-21	3987	4028	3940	7	102	30	1-2%
Analysis 9	7-21	4023	3952	3931	3	48	14	$\leq 1\%$
Analysis 10	7-21	4227	4068	3686	10	137	44	1-3%
Analysis 11	7-21	5164	4078	3826	4	54	17	$\leq 1\%$
Analysis 12	7-21	3993	3747	3624	10	64	22	2%
Analysis 13	7-21	3800	3520	3380	12	78	27	2%
Mean $\pm$ s		3894 $\pm$ 176	3892 $\pm$ 186	3752 $\pm$ 185				
% RSD		4.5	4.8	4.9				

and two laboratory reference samples were measured along with samples in each batch run for data calibration and quality control. Measurement reproducibility (1s) for these materials was better than 0.2‰ for  $\delta^{34}\text{S}$ . For natural samples, any measurement reproducibilities greater than 0.2‰ were due to sample heterogeneity or low S abundance. All data are reported with respect to the Vienna Canyon Diablo Troilite RM.

## Results

### Background and detection limit for ICP-MS measurements

Inductively coupled plasma-mass spectrometry offers very low detection limits, defined here as 3s of the background. The instrumental limits of detection in solution were 5, 36 and 11  $\text{ng ml}^{-1}$  for  $^{32}\text{S}$ ,  $^{33}\text{S}$  and  $^{34}\text{S}$ , respectively. The detection limits listed in Table 1, however, denote the limit of detection for rock samples, which was higher because dissolution of the

rock results in dilution of the rock concentration. We calculated the detection limit of the rock to be

$$\text{LOD}_{\text{rock}} = \text{LOD}_{\text{solution}} * M_{\text{solution}}/M_{\text{rock}} \quad (5)$$

where LOD is the limit of detection (3s) and M is the mass of the solution or rock sample. Thus, the dilution factor determines the detection limit of the rock and always results in a greater  $\text{LOD}_{\text{rock}}$  than  $\text{LOD}_{\text{solution}}$ . All samples measured in this study reported S concentrations above detection limit except BIR-1 (discussed below). Our rock detection limits were  $\sim 1\text{--}50 \mu\text{g g}^{-1}$ .

Analyses were considered resolvable in this study if the drift-corrected sample signal differed from the background by 2s or more. The background/signal ratio, or the blank correction, denotes how much of the total signal is attributable to the background level of the ICP-MS. Of the geochemical reference materials measured, JGb-1 and MAG-1 had negligible ( $\leq 3\%$ ) background/signal ratios,

JGb-2 had very low values (3–7%), and BHVO-2 and BCR-2 ranged from 4 to 24%, depending on the dilution factor. Those with higher background/signal ratios include BHVO-1, JP-1 and the only resolvable analysis of BIR-1 (Analysis 10) – all with less than half of the signal attributable to noise.

### Geochemical reference materials

Powdered geochemical reference materials analysed in this study included four basalts (USGS BCR-2, BHVO-1, BHVO-2 and BIR-1), two gabbros (Geological Survey of Japan, JGb-1 and JGb-2), a peridotite (Geological Survey of Japan, JP-1) and a marine mud (USGS MAG-1). To assess sample heterogeneity, different test portions and lot numbers were measured when possible and are denoted in Table 1. Values were reproducible to within 18% relative standard deviation (RSD). Analysis 1 for BHVO-2 and the  $^{32}\text{S}$  measurement of analysis 11 for MAG-1 differed from the mean by more than 2s and were thus disregarded. For most samples, averages calculated for  $^{32}\text{S}$ ,  $^{33}\text{S}$  and  $^{34}\text{S}$  were indistinguishable within uncertainty, but in some cases, results for  $^{33}\text{S}$  were higher. In the hundreds of  $\mu\text{g g}^{-1}$  range, averages calculated from  $^{33}\text{S}$  may be up to 11% greater than averages calculated for  $^{32}\text{S}$  or  $^{34}\text{S}$ . The low isotopic abundance of  $^{33}\text{S}$  renders it more susceptible to blank-subtraction uncertainties. We have reported  $^{33}\text{S}$  values but, from here on, only give  $^{32}\text{S}$  and  $^{34}\text{S}$  concentrations.

Reference materials with S concentrations greater than  $30 \mu\text{g g}^{-1}$  were measured additionally by the EA-combustion-IRMS method (Table 2). Results agree well with our solution ICP-MS determinations (Figure 3), suggesting that complete oxidation of sulfur was achieved via *aqua regia* digestion, volatile loss was negligible and matrix effects were minimal.

For comparison, Table 3 lists published values of S concentration for the same reference materials analysed here but using different techniques. MAG-1, JGb-1, JGb-2 and JP-1 report S concentrations that are indistinguishable within uncertainty from our EA-combustion-IRMS results as well as published reference values (Imai *et al.* 1999, Okai *et al.* 2001, Kubota 2009). Table 4 lists recommended values for the geochemical reference materials analysed in this study.

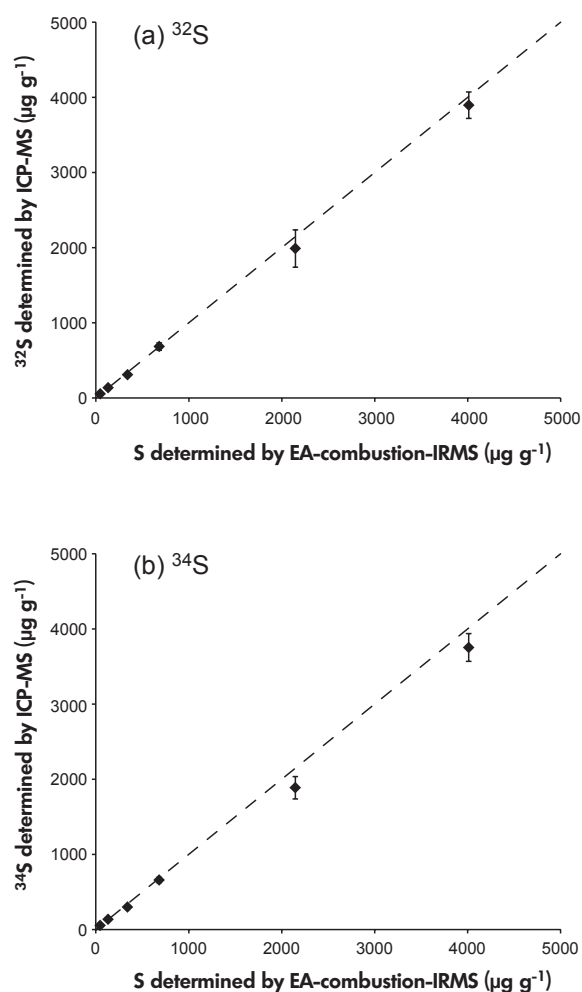
Our measurements of S in BHVO-1 and BHVO-2 were lower than those previously determined, but identical to the EA-combustion-IRMS results. The solution ICP-MS determinations appear to be reproducible and showed good agreement between the three S isotopes. The

**Table 2.**  
EA-combustion-IRMS results

	S ( $\mu\text{g g}^{-1}$ ) concentration	$\delta^{34}\text{S}$ (‰)
<b>BCR-2</b>		
Analysis 1	326	4.07
Analysis 2	352	3.83
Analysis 3	341	5.85
Mean $\pm$ s	$340 \pm 13$	$4.58 \pm 1.10$
% RSD	4	24
<b>BHVO-1</b>		
Analysis 1	50.1	5.92
Analysis 2	43.3	6.15
Mean $\pm$ s	$47 \pm 5$	$6.03 \pm 0.16$
% RSD	10	3
<b>BHVO-2</b>		
Analysis 1	134	5.62
Analysis 2	130	5.46
Analysis 3	133	6.06
Mean $\pm$ s	$132 \pm 2$	$5.71 \pm 0.31$
% RSD	1	5
<b>JGb-1</b>		
Analysis 1	2185	1.24
Analysis 2	2089	1.42
Analysis 3	2163	1.07
Mean $\pm$ s	$2146 \pm 50$	$1.24 \pm 0.17$
% RSD	2	14
<b>JGb-2</b>		
Analysis 1	653	4.69
Analysis 2	749	4.42
Analysis 3	639	4.23
Mean $\pm$ s	$681 \pm 60$	$4.45 \pm 0.23$
% RSD	9	5
<b>MAG-1</b>		
Analysis 1	4001	-2.34
Analysis 2	3985	-2.46
Analysis 3	4048	-2.70
Mean $\pm$ s	$4011 \pm 33$	$-2.50 \pm 0.18$
% RSD	1	7

agreement between our ICP-MS and EA-combustion-IRMS results suggests that S determinations are accurate for the split and lot numbers that were measured. If published S measurements are assumed to be correct, the disagreement with previously published values suggests that BHVO-1 and BHVO-2 are heterogeneous with regard to S.

BCR-2 gave reproducible results that were well above detection limit. Averages calculated for  $^{32}\text{S}$  and  $^{34}\text{S}$  were indistinguishable, but were slightly lower than results from the EA-combustion-IRMS method. Sulfur concentration determined in this study overlaps within uncertainty with the values of Fehr *et al.* (2010), but was much greater than the values of Michel and Villemant (2003). The



**Figure 3. Comparison between solution ICP-MS and EA-combustion-IRMS determinations of (a)  $^{32}\text{S}$  and (b)  $^{34}\text{S}$  (in  $\mu\text{g g}^{-1}$ ). Error bar values are listed in Table 1. The dashed line marks the 1:1 line of equivalence.**

disagreement with EA-combustion-IRMS results and published S abundances may result from incomplete oxidation of S from rock powders using our *aqua regia* method or from heterogeneity in the powder reference materials between different aliquots. We attribute this disagreement to sample heterogeneity and not the method employed here because our new method generates S contents indistinguishable from EA-combustion-IRMS results and published values for nearly all other samples.

BIR-1 has been reported to contain between 47 and 104  $\mu\text{g g}^{-1}$  S (Michel and Villemant 2003, Savard *et al.* 2006); however, our analyses never exceeded 19  $\mu\text{g g}^{-1}$ . All but one analysis reported here were below detection limit. Sulfur concentrations greater than 50  $\mu\text{g g}^{-1}$  were resolvable using the method employed here, and the reproducibility among ten analyses of concentrations

**Table 3. Published sulfur values for reference materials**

S concentration ( $\mu\text{g g}^{-1}$ )	Method <sup>a</sup>	Reference
<b>BCR-2</b>		
158	IC	Michel and Villemant (2003)
165	IC	Michel and Villemant (2003)
400 ± 15%	ICP-AES	Fehr <i>et al.</i> (2010)
<b>BHVO-1</b>		
102		Govindaraju (1994)
93 ± 6%	ID-ICP-MS	Makishima and Nakamura (2001)
<b>BHVO-2</b>		
168 ± 2%	IC	Michel and Villemant (2003)
<b>BIR-1</b>		
47	IC	Michel and Villemant (2003)
104	IC	Michel and Villemant (2003)
60	INAA	Savard <i>et al.</i> (2006)
<b>JGb-1</b>		
1950		Govindaraju (1994)
1910		Imai <i>et al.</i> (1995)
1980 ± 30	ICP-AES	Okai <i>et al.</i> (2001)
<b>JGb-2</b>		
707		Govindaraju (1994)
400		Imai <i>et al.</i> (1999)
707		Imai <i>et al.</i> (1999)
<b>JP-1</b>		
30		Govindaraju (1994)
28 ± 8%	ID-ICP-MS, ID-FI-ICP-MS	Makishima and Nakamura (2001)
26.9		Imai <i>et al.</i> (1995)
33 ± 3	ICP-AES	Okai <i>et al.</i> (2001)
27 ± 1	IODOM	Gros <i>et al.</i> (2005)
<b>MAG-1</b>		
3900		Govindaraju (1994)
4096 ± 592	CEA	Kubota (2009)

ID-ICP-MS, isotope dilution inductively coupled plasma-mass spectrometry; IC, ion chromatography; ICP-AES, inductively coupled plasma-atomic emission spectrometry; CEA, combustion elemental analyser; INAA, instrumental neutron activation analysis; ID-FI-ICPMS, isotope dilution flow injection ICP-MS; IODOM, iodometry.

<sup>a</sup> Left blank for compiled values.

below the LOD suggests that the extremely low concentrations are real. In any case, because of the low concentrations, BIR-1 should not be used as a geochemical reference material.

Finally,  $\delta^{34}\text{S}$  values are known to range between +20 and -20‰ in materials ranging from modern seawater to sulfides in organic-rich sediments (Holland 1973). This could generate an uncertainty as great as 4% for S concentrations determined from standard solutions with unknown  $\delta^{34}\text{S}$ . For the reference materials with known  $\delta^{34}\text{S}$  (listed in Table 2), the uncertainty of S concentration



**Table 4.**  
Recommended values from this study

	<sup>32</sup> S (μg g <sup>-1</sup> ) concentration	<sup>34</sup> S (μg g <sup>-1</sup> ) concentration	Average S (μg g <sup>-1</sup> ) concentration
<b>BHVO-1</b>			
Mean ± s	53.5 ± 5.4	53.9 ± 5.1	54.7 ± 5.1
<b>BHVO-2</b>			
Mean ± s	136 ± 11	136 ± 13	136 ± 12
<b>JGb-1</b>			
Mean ± s	1988 ± 249	1887 ± 149	1937 ± 204
<b>JGb-2</b>			
Mean ± s	684 ± 50	659 ± 34	671 ± 41
<b>JP-1</b>			
Mean ± s	29.4 ± 5.4	29.1 ± 2.7	29.3 ± 3.8
<b>MAG-1</b>			
Mean ± s	3894 ± 176	3752 ± 185	3820 ± 191

determined via solution ICP-MS is at most 2.6% (BHVO-2) and is thus not considered here to be a serious problem.

## Conclusions

The new method to determine S concentration by solution ICP-MS presented here produced reproducible measurements using small sample aliquots (< 50 mg). Sample preparation and analytical time were rapid and straightforward. Accuracy was assessed using two independently prepared standard solutions, resulting in 4% accuracy, as well as comparison with results utilising the EA-combustion-IRMS method. Measurement reproducibility on sample unknowns was ~ 10% for samples with > 50 μg g<sup>-1</sup> S, and was mostly limited by uncertainties in procedural blanks, weighing, δ<sup>34</sup>S variations and intrinsic sample heterogeneity. Reproducible measurements that were identical to EA-combustion-IRMS values and published values make GSJ JGb-1, JGb-2 and JP-1, and USGS marine mud MAG-1 good reference materials for S concentration measurement. Although USGS basalt reference materials BHVO-1 and BHVO-2 concentrations were reproducible for a given test portion or lot number using both methods employed here, our results differ from other studies. BCR-2 gave reproducible S concentrations for each method, but differed by ~ 35 μg g<sup>-1</sup> between methods. Our study also gave significantly lower S concentrations (< 50 μg g<sup>-1</sup>) than published measurements (50–100 μg g<sup>-1</sup>) for USGS basalt BIR-1. These differences in the USGS basalt geochemical reference materials may be due to sample heterogeneity between test portions.

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## References

- Arthur M.A. (2000)**  
Volcanic contributions to the carbon and sulfur geochemical cycles and global change. In: Sigurdsson H., Houghton B., McNutt S.R., Rymer H. and Stix J. (eds), *Encyclopedia of volcanoes*. Academic Press (San Diego, USA), 1045–1056.
- Bach W. and Erzinger J. (1995)**  
Volatile components in basalts and basaltic glasses from the EPT at 9°30'N. In: Batiza R., Storms M.A. and Allan J.F. (eds), *Proceedings of the Ocean Drilling Program, Scientific Results*. (College Station, USA), 23–29.
- Canfield D.E., Raiswell R., Westrich J.T., Reaves C.M. and Berner R.A. (1986)**  
The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chemical Geology*, 54, 149–155.
- Fehr M.A., Andersson P.S., Hälenius U., Gustafsson Ö. and Mörh C.-M. (2010)**  
Iron enrichments and Fe isotopic compositions of surface sediments from the Gotland Deep, Baltic Sea. *Chemical Geology*, 277, 310–322.
- Giles H., Hurley P. and Webster H. (1995)**  
Simple approach to the analysis of oxides, silicates and carbonates using X-ray fluorescence spectrometry. *X-Ray Spectrometry*, 24, 205–218.
- Govindaraju K. (1994)**  
Compilation of working values and sample description for 383 geostandards. *Geostandards Newsletter*, 18 (Special Issue), 158pp.
- Gros M., Lorand J.-P. and Bezos A. (2005)**  
Determination of total sulfur contents in the international rock reference material SY-2 and other mafic and ultramafic rocks using an improved scheme of combustion/iodometric titration. *Geostandards and Geoanalytical Research*, 29, 123–130.
- Hauri E., Wang J., Dixon J.E., King P.L., Mandeville C. and Newman S. (2002)**  
SIMS analysis of volatiles in silicate glasses: 1. Calibration, matrix effects and comparisons with FTIR. *Chemical Geology*, 183, 99–114.



## references

- Hedenquist J. and Lowenstern J. (1994)**  
The role of magmas in the formation of hydrothermal ore deposits. *Nature*, 370, 519–527.
- Hettipathirana T.D., Grey N.A. and Naidu R. (2004)**  
Analysis of silicates using wavelength-dispersive X-ray fluorescence spectrometry for major elements: Effects of loss elimination and catch-weights. *X-Ray Spectrometry*, 33, 117–123.
- Holland H.D. (1973)**  
Systematics of the isotopic composition of sulfur in the oceans during the Phanerozoic and its implications for atmospheric oxygen. *Geochimica et Cosmochimica Acta*, 37, 2605–2616.
- Imai N., Terashima S., Itoh S. and Ando A. (1995)**  
1994 Compilation of analytical data for minor and trace elements in seventeen GSJ geochemical reference samples, "Igneous Rock Series". *Geostandards Newsletter*, 19, 135–213.
- Imai N., Terashima S., Itoh S. and Ando A. (1999)**  
1998 Compilation of analytical data for five GSJ geochemical reference samples: The "Instrumental Analysis Series". *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 23, 223–250.
- Kiba T., Takagi T., Yoshimura Y. and Kishi I. (1955)**  
Tin (II)-strong phosphoric acid. A new reagent for the determination of sulfate by reduction to hydrogen sulfide. *Bulletin of the Chemical Society of Japan*, 28, 641–644.
- Kubota R. (2009)**  
Simultaneous determination of total carbon, nitrogen, hydrogen and sulfur in twenty-seven geological reference materials by elemental analyser. *Geostandards and Geoanalytical Research*, 33, 271–283.
- Labidi J., Cartigny P., Birck J.L., Assayag N. and Bourrand J.J. (2012)**  
Determination of multiple sulfur isotopes in glasses: A reappraisal of the MORB  $\delta^{34}\text{S}$ . *Chemical Geology*, 334, 189–198.
- Leoni L., Menichini M. and Saitta M. (1982)**  
Determination of S, Cl and F in silicate rocks by X-ray fluorescence analyses. *X-Ray Spectrometry*, 11, 156–158.
- Makishima A. and Nakamura E. (2001)**  
Determination of total sulfur at microgram per gram levels in geological materials by oxidation of sulfur into sulfate with *in situ* generation of bromine using isotope dilution high-resolution ICP-MS. *Analytical Chemistry*, 73, 2547–2553.
- Michel A. and Villemant B. (2003)**  
Determination of halogens (F, Cl, Br, I), sulfur and water in seventeen geological reference materials. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 27, 163–171.
- Okai T., Terashima S. and Imai N. (2001)**  
Determination of total sulfur in thirty-one geochemical reference materials using an inductively coupled plasma-atomic emission spectrometer fitted with a semiconductor photodiode detector. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 25, 133–136.
- Paulsen P.J. and Kelly W.R. (1984)**  
Determination of sulfur as arsenic monosulfide ion by isotope dilution thermal ionization mass spectrometry. *Analytical Chemistry*, 56, 708–713.
- Ripley E.M., Li C., Moore C.H., Elswick E.R., Maynard J.B., Paul R.L., Sylvester P., Seo J.H. and Shimizu N. (2011)**  
Analytical methods for sulfur determination in glasses, rocks, minerals and fluid inclusions. *Reviews in Mineralogy and Geochemistry*, 73, 9–39.
- Sasaki A., Arikawa Y. and Folinsbee R. (1979)**  
Kiba reagent method of sulfur extraction applied to isotopic work. *Bulletin of the Geological Survey of Japan*, 30, 241–245.
- Savard D., Bédard L.P. and Barnes S.-J. (2006)**  
TCF selenium preconcentration in geological materials for determination at sub- $\mu\text{g g}^{-1}$  with INAA (Se/TCF-INAA). *Talanta*, 70, 566–571.
- Studley S., Ripley E.M., Elswick E.R., Dorais M.J., Fong J., Finkelstein D. and Pratt L.M. (2002)**  
Analysis of sulfides in whole rock matrices by elemental analyzer-continuous flow isotope ratio mass spectrometry. *Chemical Geology*, 192, 141–148.
- Ueda A. and Sakai H. (1983)**  
Simultaneous determinations of the concentration and isotope ratio of sulfate- and sulfide-sulfur and carbonate-carbon in geological samples. *Geochemical Journal*, 17, 185–196.
- Wallace P.J. and Edmonds M. (2011)**  
The sulfur budget in magmas: Evidence from melt inclusions, submarine glasses and volcanic gas emissions. *Reviews in Mineralogy and Geochemistry*, 73, 215–246.
- Yamamoto H. and Kennedy G.C. (1969)**  
Stability relations in the system  $\text{CaSO}_4\text{-H}_2\text{O}$  at high temperatures and pressures. *American Journal of Science*, 267-A, 550–557.
- Yin Q.Z., Jacobsen S.B., Lee C.-T., McDonough W.F., Rudnick R.L. and Hom I. (2001)**  
A gravimetric  $\text{K}_2\text{OsCl}_6$  standard: Application to precise and accurate Os spike calibration. *Geochimica et Cosmochimica Acta*, 65, 2113–2127.