Simultaneous determinations of fluorine, chlorine, and sulfur in rock samples by ion chromatography combined with pyrohydrolysis

KENJI SHIMIZU,^{1,2*} KATSUHIKO SUZUKI,² MASAFUMI SAITOH,^{3,4} UTA KONNO,^{2,5}
SHINSUKE KAWAGUCCI^{2,3,5} and YUICHIRO UENO^{3,4,6}

¹Department of Solid Earth Geochemistry (DSEG), Japan Agency for Marine-Earth Science and Technology (JAMSTEC),
2-15 Natsushima-cho, Yokosuka 237-0061, Japan

²Research and Development Center for Submarine Resources, Japan Agency for Marine-Earth Science and Technology (JAMSTEC),
2-15 Natsushima-cho, Yokosuka 237-0061, Japan

³Laboratory of Ocean-Earth Life Evolution Research (OELE), Japan Agency for Marine-Earth Science and Technology (JAMSTEC),
2-15 Natsushima-cho, Yokosuka 237-0061, Japan

⁴Department of Earth and Planetary Science, Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-ku, Tokyo 162-8551, Japan

⁵Department of Subsurface Geobiology Advanced Research (D-SUGAR), Japan Agency for Marine-Earth Science and
Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan

⁶Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 162-8551, Japan

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We present a simplified method for simultaneous determinations of fluorine (F), chlorine (Cl), and sulfur (S) contents and isotopic abundances in rock samples. After using pyrohydrolysis to extract F, Cl, and S from a sample and transfer it into a sodium hydroxide (NaOH) solution, concentrations of F, Cl, and S as sulfate are measured by ion chromatography. The method is applicable to a variety of rock materials, including peridotite, basalt, gabbro, andesite, rhyolite, sulfide minerals, and possibly to sea salt, with F, Cl, and S contents of several $\mu\text{g g}^{-1}$ to several tens of weight percent in 40 to 250 mg of rock powder. F, Cl, and S contents obtained by 5–7 repeated analyses of each of nine geological reference materials were in good agreement with previously reported values. In certain reference materials, sulfite peaks were observed, indicating incomplete oxidation to sulfate during S extraction by pyrohydrolysis. However, total S contents in those samples analysed by ICP-AES were also in good agreement with previous reported values. The RSDs of F, Cl, and S contents in reference materials were <6%, except for samples with F content <10 $\mu\text{g g}^{-1}$ (~20%) or S content <20 $\mu\text{g g}^{-1}$ (<20%). In addition, Cl isotope compositions of seawater (IAPSO Standard Seawater and Pacific Ocean water) from sample solutions in this study were identical within error to reported values, indicating that Cl isotopes do not fractionate during pyrohydrolysis. After small isotopic fractionation corrections, multiple isotope compositions of S (^{32}S , ^{33}S , ^{34}S and ^{36}S) in solutions of sulfide (IAEA-S-1, IAEA-S-2, and IAEA-S-3), IAPSO Standard Seawater, and gabbro (JGb-1), also agree well with their respective reported values. Thus, this method is applicable to obtain accurate Cl and S contents as well as their isotopic compositions from a single aliquot of sample.

Keywords: pyrohydrolysis, halogen, sulfur, ion chromatography, geological reference material

INTRODUCTION

Concentrations of fluorine (F), chlorine (Cl), and sulfur (S) vary over a wide range in geological samples. Recently F, Cl, and S contents of volcanic samples have become important in research because they behave as volatile elements in magmatic systems, and their relative abundances differ greatly between the Earth's surface and its interior. Therefore, the extent to which hydrothermal

and seawater reactions at the seafloor and degassing processes in a magma chamber have occurred can be precisely evaluated by determining the concentrations of these elements (e.g., Aiuppa *et al.*, 2004; Straub and Layne, 2003; Straub *et al.*, 2004). Moreover, because S can exist as several species, its abundance is important in studies of redox reactions, magma genesis, and ore deposit formation (e.g., Hedenquist and Lowenstern, 1994; Lee *et al.*, 2012).

Bulk data of F, Cl, and S in geologic samples are becoming increasingly available but, due to the volatility of these elements and their relatively high contents in environmental blanks, the analytical procedures used pres-

*Corresponding author (e-mail: shimmy@jamstec.go.jp)

Fig. 1. Schematic illustration of the pyrohydrolysis apparatus used in this study.

ently to determine the F, Cl, and S contents of rock samples are complicated and time-consuming. Fluorine and Cl of bulk rocks are generally extracted by pyrohydrolysis or alkali fusion, and their concentrations are measured by ion chromatography (IC) (Anazawa *et al.*, 2001; Balcone-Boissard *et al.*, 2009; Michel and Villemant, 2003; Shimizu *et al.*, 2006; Wang *et al.*, 2010). However, Wang *et al.* (2010) demonstrated that part (up to ~10%) of the F and Cl contents could be lost during alkali fusion.

The bulk S content of a sample can be measured by combustion in conjunction with gas mass spectrometry or infrared absorption spectrometry (e.g., Ackerman *et al.*, 2012; Erdman *et al.*, 2014), but large amounts of sample and standard materials whose S contents are accurately known are required. For smaller samples (<~0.1 g), powdered rock samples are dissolved in aqua regia and hydrofluoric acid, and then S is determined by using ICP-MS or ICP-AES (Ackerman *et al.*, 2012; Erdman *et al.*, 2014; Okai *et al.*, 2001). Sulfur is volatile and only slightly soluble in solution under reducing conditions; thus, aqua regia is used to oxidize S in the sample to sulfate (SO_4^{2-}), a water-soluble and non-volatile form. However, dissolution of some S-bearing minerals (e.g., barite) may be incomplete, resulting in low recovery of S (Ackerman *et al.*, 2012). Makishima and Nakamura (2001, 2012) dissolved and oxidized rock samples in a S-spiked solution of hydrofluoric and hydrobromic acids and then measured the S content by isotope dilution high mass resolution ICP-MS. By this method, they could successfully obtain reliable S concentrations from small amounts of rock sample, but it required an ultra-clean room and the large-scale analytical instrument.

Michel and Villemant (2003) reported a procedure for extraction of F, Cl, and S by pyrohydrolysis followed by their simultaneous measurement by IC. However, since their report, no additional S concentrations from geological samples analysed using this method have been reported. In order to increase the database of S data concurrently measured with F and Cl contents by IC, we optimized the pyrohydrolysis extraction procedure and applied the procedure to the extraction of F, Cl, and S from geological reference materials, followed by their measurement using IC.

EXPERIMENTAL

Samples

We measured F, Cl, and S contents of the following geological reference materials: BHVO-2, BCR-2, and BIR-1 (basalt), issued by the U.S. Geological Survey (USGS); and JP-1 (peridotite), JGb-1 (gabbro), JB-2, -3 (basalt), JA-1 (andesite), and JR-1 (rhyolite), issued by the Geological Survey of Japan (GSJ). We also measured the S content and isotopic compositions of International Atomic Energy Agency (IAEA; Vienna, Austria) silver sulfide standards (IAEA-S-1, IAEA-S-2, and IAEA-S-3) in order to estimate the S recovery yield and the isotopic fractionation of S during the pyrohydrolysis procedure. In addition, a seawater standard from the International Association for the Physical Sciences of the Oceans (IAPSO) (supplied by Ocean Scientific International Ltd., UK) and seawater collected from ~6100 m depth in the Pacific Ocean (11°36' N, 142°59' E) were evaporated, and then the chlorine content and isotope composition of the seawater-derived salts were measured.

Pyrohydrolysis

Fluorine, Cl, and S were extracted from powdered rock samples by using a pyrohydrolysis technique based on that of Michel and Villemant (2003). The pyrohydrolysis apparatus used in this study (Fig. 1) included a quartz combustion tube, 42 cm long and 2 cm in diameter, welded to a quartz collection tube ($\phi 6$ mm). Before pyrohydrolysis procedure, all quartz and platinum (Pt) components were heated at 1050°C for 4 h in a furnace to remove F, Cl and S; other components such as beakers and silicon stoppers were washed with ~2% Tama Super Cleaner (ultrapure strong alkali cleaner, Tama Chemicals Co., Ltd., Japan), and rinsed with deionized water (Milli-Q, >18 M Ω ; Millipore, USA). Next, 40–250 mg (normally ~100 mg) of sample powder was weighed in a Pt boat, and then an appropriate amount of V₂O₅ (sample: V₂O₅ ratio between 1:1 and 1:3) was weighed and mixed with the sample. In the case of the IAEA-S-1, IAEA-S-2, and IAEA-S-3, 2–5 mg of sample was mixed with 50–60 mg of V₂O₅. In the case of the seawater, ~1 g of seawater was weighed in a Pt boat. Then, it was dried in an oven at 95°C for several hours, and ~50 mg of V₂O₅ was added.

In order to place the sample boat at the hottest part of the SiC furnace (center of 30 cm long furnace) in high temperature (>800°C) quickly and safely, we put a Pt boat at the end of a long Pt plate (15 cm long $\times$ 1 cm wide) and, using tweezers, placed the other end of Pt plate near the edge of combustion tube (Fig. 1). Immediately following the insertion of the Pt plate, the quartz combustion tube was stoppered (within 2–3 seconds) leaving the Pt-plate with a sample boat in the furnace so that no F, Cl, and S in the sample would escape via the opening. Deionized water mist carried by cleaned O₂ gas (0.3 l min⁻¹) was introduced into the furnace by a peristaltic pump via a nebulizer at the rate of 0.5 ml min⁻¹ in order to collect and transport the F, Cl, and S from the sample to the NaOH solution trap. The initial concentration of the NaOH solution ranged from 0 (water) to 100 mmol l⁻¹, and the initial volume ranged from 10 to 20 ml. The NaOH solution trap consisted of a 50 ml polypropylene collection beaker resting in an ice-water bath to keep the solution cool. After extraction for ~30 min at 1200–1250°C, the tip of the quartz tube was rinsed with deionized water and the rinse water was collected in the same collection beaker. The final volume of the solution collected was ~40 ml. Then, the collection beaker was tightly capped for later IC analysis. In order to test the recovery of F, Cl, and S in the NaOH solution, in some experiments we connected a second collection beaker with NaOH solution to the outlet of the first collection beaker.

After each extraction, the Pt boat and Pt plate were removed and the combustion tube was washed with a deionized water mist at 3–4 ml min⁻¹ for ~30 min at 1250°C. Then, we conducted the next pyrohydrolysis

experiment. In order to calculate the weight of the collected solution, the empty collection beaker was weighed before the experiment and again after solution collection had been completed. The weight of the collected solution was derived by subtracting the empty beaker weight from the weight of the beaker with solution. The dilution factor (DF) of sample [total solution weight/sample weight by gram] ranged from 200 to 1000 (usually ~500).

Ion chromatography

In order to measure simultaneously F⁻, Cl⁻, and SO₄²⁻ in the same solution, we used an ICS-2100 IC system (Thermo Scientific, USA) at the Japan Agency for Marine-Earth Science and Technology (JAMSTEC), equipped with an electrolytic eluent generator (KOH) and an ionPac AS11-HC anion exchange column. For effective separation of the F⁻ and Cl⁻ peaks, we used a gradient IC separation script. During each measurement, the concentration of KOH eluent, which was 6 mmol l⁻¹ at the time of sample injection, was gradually increased to 19 mmol l⁻¹ at 30 min, and then to 45 mmol l⁻¹, where it was maintained for 10 min to wash out the remaining anions from the exchange column. An electric conductivity detector and an auto-sampler were used in the analysis, and the sample injection loop volume was 100 μ l. Under these analytical conditions, the F⁻, Cl⁻, and SO₄²⁻ peaks generally appeared at ~4.4 min, ~10.4 min, and ~29.1 min, respectively. Fluorine, Cl, and S were calibrated against diluted solutions of a commercial standard from Wako Chemicals, Japan. F⁻, Cl⁻, and SO₄²⁻ concentrations of the standard solution were 5, 10, and 40 μ g g⁻¹, respectively, and the DF of the solutions used to determine the calibration curves ranged from 5 to 10,000, which corresponds to 0.5 to 1000 ng g⁻¹ for F⁻, 1 to 2000 ng g⁻¹ for Cl⁻, and 4 to 8000 ng g⁻¹ for SO₄²⁻. We used two different calibration curves for each anion, depending on the peak intensities. If the peak areas (μ S $\cdot$ min) of F⁻, Cl⁻, and SO₄²⁻ in a sample solution were smaller than those of the standard solutions (10, 20, and 80 ng g⁻¹, respectively), we used calibration curves derived from diluted standard solutions with DFs between 500 and 10000. Otherwise, we used calibration curves generated by using diluted standard solutions with DFs from 5 to 500 (Fig. 2). If the peak areas of F⁻, Cl⁻, and SO₄²⁻ of a sample solution exceeded those of standard solutions (1000, 2000, and 8000 ng g⁻¹, respectively), the solution was diluted and remeasured. Reproducibilities of diluted standard solutions with DFs of 10,000 and 5000 were normally better than ~10% and ~5%, respectively, for F, Cl, and S. Except for blank solutions and solutions in second collection beaker, we were able to use calibration curves for high concentrations to determine F, Cl and S contents of samples.

Fig. 2. Calibration curves of F^- , Cl^- , and SO_4^{2-} contents used in this study. Upper and lower panels show calibration curves for high and low concentrations respectively.

Procedural blank and V_2O_5 reagents

To estimate a procedural blank for the pyrohydrolysis procedure, we conducted four experiments without any sample or V_2O_5 reagent. We confirmed that total procedural blanks for F, Cl, and S were 0.01–0.04 μg , 0.07–0.12 μg , and 0.04–0.08 μg , respectively. In order to determine which V_2O_5 reagent had the lowest blanks, we performed the pyrohydrolysis procedure without rock powder to extract F, Cl, and S from V_2O_5 reagents purchased from two companies (Alfa Aesar, UK, Aldrich, US). Results are shown in Table 1. All tested V_2O_5 reagents contained measureable levels of F, Cl, and S. Therefore we needed to perform blank corrections to obtain the F, Cl, and S contents of unknown samples whenever these reagents were used as catalysts for the pyrohydrolysis procedure. Therefore, we chose V_2O_5 Puratronic 99.99%, purchased from Alfa Aesar, for this study. Although this reagent had a high F content (23 $\mu g g^{-1}$), the RSD was small ($\sim 11\%$), so the blank correction for F was effective even when the F content of the sample was $< 30 \mu g g^{-1}$. In addition, after most of our experiments were completed, we tested 99% V_2O_5 reagents from Wako Chemicals and Kanto Kagaku and found that they had very low contents of F, Cl, and S (Table 1). We

therefore used Kanto Kagaku 99% V_2O_5 as the catalyst in the pyrohydrolysis of some samples (see Table 2).

Cl and S isotope measurements

The stable isotope composition of chlorine in solution was analysed in the manner previously reported (Long *et al.*, 1993; Wassenaar and Koehler, 2004), with minor modifications. The Cl^- solution was first acidified to pH 1.9 with ultrapure nitric acid (HNO_3) and then heated at $85^\circ C$ for 45 min to drive off CO_2 . Then 1 ml silver nitrate solution ($0.5 \text{ mol l}^{-1} AgNO_3$) was added to precipitate $AgCl$. The solid $AgCl$ was collected on a precombusted $0.7 \mu m$ pore size Whatman glass fibre filter (GF/F). Next the filter was introduced into a glass vial, which was capped with a Teflon-lined butyl gum before evacuation. Fifteen microlitres of liquid iodomethane (CH_3I) were injected into the evacuated vial, which was then heated to $80^\circ C$ for 48 h to quantitatively convert $AgCl$ to CH_3Cl . The overall Cl content and abundance of individual stable chlorine isotopes in the CH_3Cl were determined by continuous-flow isotope ratio mass spectrometry (MAT253, Thermo Finnigan, Bremen, Germany) at JAMSTEC (Konno *et al.*, 2013). The measured chlorine isotope composition is presented by using delta notation

Table 1. F, Cl and S concentrations ($\mu\text{g g}^{-1}$) in V_2O_5 reagents after procedural blank correction

Company	Grade	<i>n</i>	F	Cl	S	F-RSD%	Cl-RSD%	S-RSD%	
Alfa Aesar	Puratronic	99.99%	9	23	0.7	0.9	11	37	44
Aldrich		99.6%	2	6.7	2.6	231	1	17	1
Aldrich		99.99%	2	0.3	3.3	9.1	8	3	10
Wako Chemicals		99%	2	0*	0.8	0*	—	1	—
Kanto Kagaku		99%	4	0.2	0.3	0.1	136	44	31

*Identical to the procedural blank.

on a per mil scale as a following:

$$\delta^{37}\text{Cl} = [({}^{37}\text{Cl}/{}^{35}\text{Cl})_{\text{sample}}/({}^{37}\text{Cl}/{}^{35}\text{Cl})_{\text{SMOC}} - 1] \cdot 1000\text{‰}$$

where SMOC is Standard Mean Ocean Chloride (Long *et al.*, 1993). In practice, chloride in IAPSO seawater was treated as SMOC. For SMOC scaling, we measured the $\delta^{37}\text{Cl}$ value of chloride in the IAPSO seawater, without first precipitating the salt and performing pyrohydrolysis. The standard deviation for the entire procedure was determined to be 0.22‰ (2 σ) by repeated measurements of Pacific Ocean water ($n = 8$).

For S isotope analysis, sulfate in the sample solution was precipitated as BaSO_4 by adding 10% BaCl_2 solution after adjusting the pH to 4–5. The precipitated BaSO_4 was cleaned by repeated centrifuging in deionized water and dried at 70°C for >12 h. The purified BaSO_4 was reacted with hot tin(II) phosphate solution at 300°C and converted into H_2S (Sasaki *et al.*, 1979; Ueno *et al.*, 2008). The H_2S was carried in a nitrogen stream, washed through a water trap, and converted to Ag_2S in a centrifuge tube containing a 0.1 mol l^{-1} AgNO_3 solution. The Ag_2S was then cleaned by repeated centrifuging with distilled water and dried at 70°C for >12 h. The dried Ag_2S was reacted with excess F_2 at 300°C in a nickel reaction vessel overnight to produce SF_6 . The SF_6 was then purified using cryogenic techniques and gas chromatography in a system equipped with a 4 m column packed with Prapak-Q (first) connected to a 2 m Molecular Sieves 5A column (second). The isotopic composition of the purified SF_6 was determined with a ThermoFischer MAT253 mass spectrometer equipped with a dual inlet system at Tokyo Institute of Technology. Sulfur isotopic compositions are reported in conventional delta notation using Vienna-Canyon Diablo Troilite (V-CDT) scaling, which is defined by the value of IAEA-S-1 having a composition on the V-CDT scale of $\delta^{34}\text{S} = -0.300\text{‰}$, $\Delta^{33}\text{S} = 0.100\text{‰}$, and $\Delta^{36}\text{S} = -0.91\text{‰}$ (Ding *et al.*, 2001; Ono *et al.*, 2006):

$$\delta^x\text{S} = ({}^xR_{\text{sample}}/{}^xR_{\text{VCDT}} - 1) \cdot 1000\text{‰}$$

where xR is the isotopic ratio (${}^x\text{S}/{}^{32}\text{S}$, where $x = 33, 34$, or 36) of the sample. For the ${}^{33}\text{S}/{}^{32}\text{S}$ and ${}^{36}\text{S}/{}^{32}\text{S}$ ratios, we

report $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values defined as follows:

$$\Delta^{33}\text{S} = 1000 \cdot \ln(1 + \delta^{33}\text{S}/1000) - 0.515 \cdot 1000 \cdot \ln(1 + \delta^{34}\text{S}/1000)\text{‰}$$

$$\Delta^{36}\text{S} = 1000 \cdot \ln(1 + \delta^{36}\text{S}/1000) - 1.90 \cdot 1000 \cdot \ln(1 + \delta^{34}\text{S}/1000)\text{‰}.$$

Note that definitions of capital delta (Δ) values are different from conventional δ notation ($\Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \cdot (\delta^{34}\text{S}/1000 + 1)^{0.515} - 1000$), though the difference between the two capital delta values is smaller than 0.1‰ when $\delta^{34}\text{S}$ varies within $\pm 10\text{‰}$. The analytical reproducibility of $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ values determined by replicate analyses of IAEA-S-1 were 0.43‰, 0.015‰, and 0.16‰ (1 σ), respectively ($n = 7$).

RESULTS AND DISCUSSION

Optimizing pyrohydrolysis conditions

There are many parameters to optimize pyrohydrolysis conditions that may affect recovery yields of F, Cl and S, including the sample amount, kind of oxidizing catalyst (V_2O_5 or WO_3), sample/catalyst ratios, flow rates of carrier gas and water mist, temperature, duration, sample insertion temperature, and the initial concentration and volume of NaOH solution in the collection beaker. Based on the results of previous works (Balcone-Boissard *et al.*, 2009; Michel and Villemant, 2003; Wang *et al.*, 2010), the initial concentration and volume of NaOH solution in the collection beaker and sample insertion temperature are not well-constrained effective parameters for the recovery yields. Therefore, we conducted the pyrohydrolysis experiments with BHVO-2 under various volumes and concentrations of initial NaOH solutions and sample insertion temperatures to optimize the condition (Table 2). Under all experimental conditions, concentrations of F and Cl derived from the sample solution of the second beaker were negligible, indicating that $\sim 100\%$ entrapment of F^- and Cl^- in the sample solution in the first beaker was achieved. F (and Cl) concentrations of BHVO-2 after blank correction were identical regardless of the insertion temperature and the NaOH solution con-

Table 2. *F, Cl and S concentrations ($\mu\text{g g}^{-1}$) in selected reference materials determined by ion chromatography following pyrohydrolysis*

Sample name	Sample insertion temp. [°C]	Initial NaOH conc. [mmol l ⁻¹] vol. (ml)	Sample [mg]	V ₂ O ₅ [mg]	V ₂ O ₅ grade ^a	from 1st solution			from 2nd solution			Blank corrected (total conc.)			Published data			Method	Ref.
						F			F			F			F				
						Cl	S		Cl	S		Cl	S		Cl	S			
BHVO-2																			
analysis1	25	100 (10)	89.34	133.48	A	430	82	125	0.9	0.4	0.7	396	80	124	402	150	168	pyrohydrolysis-IC	MV
analysis2	800	water (20)	88.50	117.19	A	419	86	98	0.6	0.2	19.6	410	92	116	376	89		pyrohydrolysis-IC	B
analysis3	800	1 (20)	105.69	132.07	A	438	92	144	0.6	0.5	2.2	389	86	146	409	81		pyrohydrolysis-IC	W
analysis4	800	20 (20)	91.85	107.27	A	449	91	136	3.6	0.6	0.9	426	91	136			190	combustion-SPEC	A
analysis5	1200	20 (10)	90.62	101.24	A	421	80	155	0	0.9	2.3	395	80	157			184	aqua regia-ICPAES	A
analysis6	1250	13 (30)	82.78	128.39	A	448	87	162	1.4	0.4	0.3	414	87	161			136	aqua regia-ICPMS	E
analysis7	1250	20 (20)	156.14	173.58	A	431	86	162	0.3	0.4	0.7	406	86	161			132	combustion-IRMS	E
analysis8	1250	20 (20)	118.38	158.29	A	439	85	161	0.3	0.3	0.7	418	84	160					
analysis9	1250	20 (20)	79.80	243.03	K	419	77	155				418	76	154					
analysis10	1250	20 (20)	64.06	196.90	K	421	80	156				421	80	155					
analysis11	1250	20 (20)	99.22	—		349	62	120				349	62	120					
analysis12	1250	20 (20)	129.40	—		345	64	122				345	64	122					
BHVO-2 average ^b												408	84	158					
RSD (%)												3	6	2					
BCR-2																			
analysis1	1250	20 (10)	116.80	129.57	A	557	95	319	0.8	0.5	1.7	532	95	319	448	98	158, 165	pyrohydrolysis-IC	MV
analysis2	1250	20 (10)	130.00	147.64	A	549	93	308	0.8	0.2	10	523	93	316	485	89		pyrohydrolysis-IC	W
analysis3	1250	20 (10)	42.23	76.35	A	588	99	327	0.6	0.5	1.8	546	99	327			407	combustion-SPEC	A
analysis4	1250	20 (20)	54.27	74.93	A	588	90	362				556	89	361			291	aqua regia-ICPAES	A
analysis5	1250	20 (20)	72.02	110.67	A	574	97	327				538	96	326			308	aqua regia-ICPMS	E
BCR-2 average												539	94	330			340	combustion-IRMS	E
RSD (%)												2	4	5			334	ID-HR-MC-ICPMS	MN12
BIR-1^c																			
analysis1	1250	20 (20)	127.16	134.28	A	56	6.4	8.1				32	5.6	7.2	44	26		proposed	G
analysis2	1250	20 (20)	103.72	95.94	A	54	6.5	6.0				33	5.8	5.2	55	44	47, 104	pyrohydrolysis-IC	MV
analysis3	1250	20 (20)	48.96	74.46	A	54	5.8	7.9				32	5.2	7.1			<10	aqua regia-ICPMS	E
analysis4	1250	20 (20)	87.76	84.80	A	54	6.5	6.6				32	5.9	5.8					
analysis5	1250	20 (20)	122.67	111.55	A	57	6.6	8.6				36	6.0	7.8					
BIR-1 average												33	5.7	6.6					
RSD (%)												5	5	16					
JP-1^c																			
analysis1	1250	20 (20)	111.92	110.89	A	29	75	33				6.0	75	32	14	50	26.9	recommended	I
analysis2	1250	20 (20)	147.23	152.88	A	27	74	30				2.9	73	29	18.4	82		alkali fusion-IC	Sh
analysis3	1250	20 (20)	66.72	76.83	A	28	74	33				1.8	74	32			42	combustion-SPEC	A
analysis4	1250	20 (20)	179.92	165.92	A	22	74	31				0.3	74	30			33	aqua regia-ICPAES	A
analysis5	1250	20 (20)	43.89	137.09	K	3.3	80	29				2.7	79	29			29.4	aqua regia-ICPMS	E
analysis6	1250	20 (20)	67.44	227.34	K	2.4	73	32				1.8	72	31			33	aqua regia-ICPAES	O
analysis7	1250	20 (20)	96.87	369.01	K	2.8	75	33				2.0	74	32			28.0	ID-ICPMS	MN01
JP-1 average ^d												2.2	74	31			29.4	ID-HR-MC-ICPMS	MN12
RSD (%)												23	3	5					

JGb-1												
analysis1	1250	20 (20)	97.25	105.88	A	141	62	1719	0.3	0.5	19.7	117
analysis2	1250	20 (20)	82.94	108.39	A	146	63	1868	0.3	0.3	3.3	116
analysis3	1250	20 (20)	78.17	104.18	A	148	64	1874				117
analysis4	1250	20 (20)	141.02	191.36	A	149	55	1793				118
analysis5	1250	20 (20)	189.61	546.66	K	117	60	1910				116
analysis6	1250	20 (20)	239.59	695.53	K	118	64	1891				118
JGb-1 average												117
RSD (%)												6
JB-2^a												
analysis1	1250	20 (20)	72.93	93.33	A	130	300	29				100
analysis2	1250	20 (20)	77.69	97.82	A	129	295	22				100
analysis3	1250	20 (20)	89.22	153.95	A	149	296	27				109
analysis4	1250	20 (20)	185.64	196.69	A	126	301	22				101
analysis5	1250	20 (20)	96.15	269.08	K	99	291	19				99
analysis6	1250	20 (20)	57.82	215.28	K	99	292	24				98
analysis7	1250	20 (20)	51.99	129.55	K	99	285	17				101
JB-2 average												4
RSD (%)												2
JB-3												
analysis1	1250	20 (20)	217.95	216.95	A	289	298	6.8	0.7	0.2	0	267
analysis2	1250	20 (20)	105.16	128.05	A	290	285	7.0	0.2	0.6	0	262
analysis3	1250	20 (20)	89.25	106.52	A	300	290	7.3	0.2	1.1	0	272
analysis4	1250	20 (20)	66.41	99.53	A	314	295	8.0				279
analysis5	1250	20 (20)	129.30	142.10	A	296	298	6.8				271
JB-3 average												270
RSD (%)												2
JA-1^c												
analysis1	1250	20 (20)	121.76	147.95	A	213	44	26				185
analysis2	1250	20 (20)	93.76	123.79	A	222	41	25				192
analysis3	1250	20 (20)	96.79	133.12	A	209	41	25				177
analysis4	1250	20 (20)	108.43	124.07	A	202	41	26				176
analysis5	1250	20 (20)	48.33	230.55	K	176	41	24				176
analysis6	1250	20 (20)	62.62	187.02	K	177	40	24				176
analysis7	1250	20 (20)	66.95	185.67	K	176	37	28				180
JA-1 average												4
RSD (%)												5
JR-1^c												
analysis1	1250	20 (20)	106.46	106.27	A	1056	918	13				1033
analysis2	1250	20 (20)	119.00	150.52	A	1006	883	10				977
analysis3	1250	20 (20)	95.18	123.68	A	1093	923	12				1063
analysis4	1250	20 (20)	43.05	66.58	A	1128	940	15				1092
analysis5	1250	20 (20)	49.72	166.80	K	1101	889	14				1101
analysis6	1250	20 (20)	87.34	250.56	K	1084	936	8.6				1084
JR-1 average												1058
RSD (%)												4
												3
												19

^aA, Alfa Aesar Puratronic 99.99%; K, Kanto Kagaku 99%.

^bFor F and Cl concentrations, all data are used except those obtained by V₂O₅-free extraction. For S, data obtained by extractions from ≥1200°C are used (except data obtained by V₂O₅-free extraction).

^cSulfite peaks in sample solutions were observed by ion chromatographic analyses. Total S contents of samples were derived by ICP-AES analyses.

^dFor F concentrations, data obtained by extractions using Kanto Kagaku 99% V₂O₅ are shown.

Method: IC, ion chromatograph; SPEC, infrared spectrometry; RIMS, isotope ratio mass spectrometer; NAA, neutron activation analysis; ID, isotope dilution; HR, high resolution.

Ref.: MV, Michel and Villemant (2003); Ba, Balcone-Boissard et al. (2009); W, Wang et al. (2010); A, Ackerman et al. (2012); E, Erdman et al. (2014); MN01, MN12, Makishima and Nakamura (2001, 2012); G, Govindaraju (1994); I, Imai et al. (1995); O, Okai et al. (2001); Sa, Sano et al. (2004); Sh, Shimizu et al. (2006); Bu, Burton (1996).

Table 2. (continued)

Sample name	Sample insertion temp. [°C]	Initial NaOH conc. [mmol l ⁻¹] vol. (ml)	Sample [mg]	V ₂ O ₅ [mg]	V ₂ O ₅ grade ^a	from 1st solution			from 2nd solution			Blank corrected (total conc.)			Published data			Method	Ref.
						F	Cl	S	F	Cl	S	F	Cl	S	F	Cl	S		
IAEA-S-1	1250	20 (10)	2.15	45.73	A	391	2151	111742	80	12	10373	—	2148	1.22 × 10 ⁵	—	—	1.29 × 10 ⁵	pure Ag ₂ S base	
IAEA-S-2	1250	20 (20)	5.07	63.19	A	260	48	120906	36	8	4632	7	47	1.26 × 10 ⁵	—	—	1.29 × 10 ⁵	pure Ag ₂ S base	
IAEA-S-3	1250	20 (20)	3.27	47.26	A	299	84	122439	25	8	2445	—	82	1.25 × 10 ⁵	—	—	1.29 × 10 ⁵	pure Ag ₂ S base	
IAPSO Standard Seawater																			
analysis1	1000	20 (20)	1012	53.42	A	2.5	18848	526	0	167	432	1.4	1.90 × 10 ⁴	958	1.3	19354	904	recommended	Bu
analysis2	1000	20 (20)	1012	57.84	A	2.6	19111	460	0	137	688	1.3	1.92 × 10 ⁴	1148					
analysis3	600	20 (20)	1030	63.84	K	1.2	18332	609	0	655	161	1.2	1.90 × 10 ⁴	769					
Pacific Ocean water																			
analysis1	1000	20 (20)	1022	58.91	A	2.5	18959	523	0	74	504	1.2	1.90 × 10 ⁴	1027	1.3	19328.7	879	IC-analyses	
analysis2	1000	20 (20)	1021	49.63	A	2.6	18894	430	0	123	662	1.5	1.90 × 10 ⁴	1092					

centration and volume, and are in good agreement with published values. Concentrations of S derived from the sample solutions of the second beaker were also negligible for many conditions. However, when the initial volume of the NaOH solution was 10 ml and its concentration was <1 mmol l⁻¹, entrapment of S in the sample solution of the first beaker was <99%. In particular, not all S extracted by pyrohydrolysis may be trapped in pure water (Table 2, BHVO-2 analysis2). Blank-corrected S concentrations in BHVO-2 obtained by sample insertion at room temperature and 800°C (BHVO-2 analysis1–4) were ~15% lower than those obtained by sample insertion at 1200°C or 1250°C (BHVO-2 analysis5–9). Because the melting temperature of V₂O₅ is 690°C, V₂O₅ melts before the S is extracted from a sample. As a result, it may not efficiently catalyse the oxidation of S to SO₃. Therefore, some S in the sample may escape as slightly soluble and volatile H₂S or remain in a sample residue as sulfide. Our experimental results indicate that the initial concentration and volume of the NaOH solution should be 20 mmol l⁻¹ and 20 ml, respectively, and that the temperature at sample insertion should be as high as the heating temperature (1250°C), but a second collection beaker is not necessary for a low-S sample.

We extracted S from Ag₂S (IAEA-S-1, IAEA-S-2, and IAEA-S-3) under the appropriate conditions and confirmed the high recovery (94–97%) of S and the complete oxidation of sulfide to sulfate (Table 2). However, S leakage to the second collection beaker was significantly high when the volume of the initial NaOH solution was 10 ml (IAEA-S-1). The S content in the sample solutions of the second beaker was also not negligible even when the volume of the initial NaOH solution was 20 ml. Therefore, for high-S samples, a second collection beaker and a higher concentration NaOH solution may be required. We confirmed that Cl recovery from seawater (salt) using the pyrohydrolysis procedure was from 98.1 to 99.5% (Table 2). This result shows that the method is also applicable to samples with extremely high Cl.

In addition, we conducted pyrohydrolysis experiments with BHVO-2 without any V₂O₅ reagent (Table 2, BHVO-2 analysis11, 12). The obtained F, Cl, and S contents were all ~20% lower than those obtained by extraction with the V₂O₅ reagent, thus confirming that V₂O₅ is required to extract F, Cl, and S by pyrohydrolysis. The sample: V₂O₅ ratio in the pyrohydrolysis procedure does not affect recovery of F, Cl, and S as long as the sample: V₂O₅ ratio is between 1:1 and 1:3.

F, Cl, and S contents of reference materials

We conducted five to seven repeat analyses of each reference material and averaged the values to obtain their F, Cl, and S concentrations (Table 2, Fig. 4). The F content of JP-1 was very low and, subsequently, the data ob-

Fig. 3. Correlations of multiple sulfur isotopic compositions for IAEA-S-1, IAEA-S-2 and IAEA-S-3 obtained by direct Ag_2S fluorinations vs. sulfate sample solutions via pyrohydrolysis.

Fig. 4. Mean measured values (this study) of F, Cl and S concentrations compared with published values (PV). Lower panels are close-up diagrams of upper panel diagrams indicated as shaded squares. Sulfur concentrations of JGb-1 are out of range of the shown diagram ($S \sim 2000 \mu\text{g g}^{-1}$). References for published values with methods are listed in Table 2.

tained using the Alfa Aesar V_2O_5 extraction catalyst (Table 2, JP-1 analysis1–4) required a large blank correction ($>1000\%$). Therefore, we used data obtained using the Kanto Kagaku reagent (JP-1 analysis5–7) for the F content of JP-1.

In certain sample solutions (BIR-1, JP-1, JB-2, JA-1, and JR-1), sulfite (SO_3^{2-}) peaks were identified by IC,

indicating that S was not completely oxidized to sulfate during the pyrohydrolysis procedure. Therefore, we analysed total S contents of these samples by ICP-AES equipped with a semiconducting detector and pure nitrogen purging of the spectrometer optics (SPS5500, SII Nano Technology, Chiba, Japan). Two emission wavelengths can be used to measure S content (180.669 nm or

Table 3. Sulfur and chlorine isotopic compositions using NaOH sample solutions

	Measured					Comparison			Reference
	$\delta^{34}\text{S}$ [‰]	$\Delta^{33}\text{S}$ [‰]	$\Delta^{36}\text{S}$ [‰]	$\delta^{37}\text{Cl}$ [‰]	$\delta^{34}\text{S}$ [‰]	$\Delta^{33}\text{S}$ [‰]	$\Delta^{36}\text{S}$ [‰]	$\delta^{37}\text{Cl}$ [‰]	
JGB-1-analysis4	2.16	0.076	-1.27		1.24 $\pm$ 0.17				Ackerman <i>et al.</i> (2012)
JGB-1-analysis5	0.51	0.040	-0.55						
JGB-1-analysis6	0.16	0.011	-0.23						
JGB-1-average	0.95	0.043	-0.68						
JGB-1-corrected $\pm 1\sigma$	0.12 $\pm$ 1.07	0.020 $\pm$ 0.033	-0.21 $\pm$ 0.53						
IAEA-S-1	0.15	0.138	-1.44		-0.30	0.100	-0.91		Ono <i>et al.</i> (2006) direct Ag_2S flourination direct Ag_2S flourination
IAEA-S-2	22.67	0.067	-1.03		22.29	0.040	-0.72		
IAEA-S-3	-30.83	0.110	-0.96		-32.84	0.084	-0.44		
IAPSO-analysis1				-0.10				0	Long <i>et al.</i> (1993)
IAPSO-analysis2				-0.18	21.11				Craddock <i>et al.</i> (2008)
IAPSO-analysis3	21.46	0.089	-1.15		21.34	0.050	-0.33		Ono <i>et al.</i> (2012) (present seawater)
IAPSO-corrected	21.29	0.061	-0.70						
Pacific Ocean water-analysis1				0.08				-0.04	AgCl precipitation from seawater
Pacific Ocean water-analysis2				0.07					

1 sigma errors of $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ were 0.43‰, 0.015‰ and 0.16‰, respectively.

2 sigma error of measured $\delta^{37}\text{Cl}$ was 0.22‰.

181.972 nm) by an ICP-AES system. We used the 181.972 nm line because the sensitivity, reproducibility, and linearity of the calibration curve for S at the 181.972 nm line were slightly better than those at the 180.669 nm line. The detection limit of S in solution at 181.972 nm was 10 ng g⁻¹, as calculated from the 3 σ value of the instrumental background. This value corresponds to 5 μ g g⁻¹ of S in a sample for the usual sample DF (~500) used in this study. The RSD of each measurement near the detection limit was 15% and was derived by repeated analyses of a ~10 ng g⁻¹ solution.

In most cases, the RSD of the F, Cl, and S contents of reference materials was <6%, indicating that the reference materials were relatively homogeneous among the distributed portions. The large uncertainty in the F content of JP-1 (RSD, 23%) can be explained by the relatively large blank correction (up to 35%). Although the S contents of BIR-1, JB-2, and JR-1 had relatively large uncertainty (up to 20%), the data were close to the ICP-AES detection limit; therefore, these large uncertainties are inevitable.

The F, Cl, and S contents of most of the reference materials were in relatively good agreement with previously reported values (Table 2, Fig. 4). However, reported F, Cl, and S contents of BIR-1 and the F contents of BCR-2 and JP-1 are clearly different from values determined in this study. Even so, there are so few reported values that it is difficult to judge whether or not they are reliable. The distributed test portions of the reference materials might also be heterogeneous, as described by Erdman *et al.* (2014). Systematically lower F and Cl contents of certain reference materials (i.e., JB-2, JB-3, and JA-1) extracted by alkali fusion (Shimizu *et al.*, 2006) may indicate F and Cl loss during extraction, as demonstrated by Wang *et al.* (2010).

Cl and S isotopic compositions

The Cl isotope compositions of seawater-derived salts (from IAPSO Standard Seawater and Pacific Ocean water) were analysed after extraction by pyrohydrolysis (Table 3). The $\delta^{37}\text{Cl}$ values scaled by the IAPSO Standard Seawater analysis were identical within the analytical error between the salts derived from the IAPSO (−0.18‰) and the Pacific Ocean water (+0.07‰).

The S isotopic compositions of the sulfide (IAEA-S-1, IAEA-S-2, and IAEA-S-3) and gabbro (JGb-1) sample solutions were measured (Table 3). Before the S isotope measurements of IAEA-S-1, IAEA-S-2, IAEA-S-3 and IAPSO Standard Seawater, the solutions in the first and second collection beakers were combined into one beaker in order to determine the S isotope composition of the total extracted S. We only analysed the S isotopic composition for IAPSO-analysis3, because for the other seawater measurements, a substantial amount of S escaped

to the second beaker (Table 2), indicating incomplete recovery of S from seawater. The higher S contents of seawater extracted with pyrohydrolysis (S: 958–1148 μ g g⁻¹) compared with that measured without pyrohydrolysis (S: 879 or 904 μ g g⁻¹) may indicate a degree of S contamination during the evaporation process. The various S isotope compositions for IAEA-S-1, IAEA-S-2 and IAEA-S-3 are slightly different from those measured by the direct Ag₂S fluorinations, but were linearly correlated (Fig. 3). Therefore the actual isotope compositions can be obtained using a mass fractionation correction. Although analysis3 of IAPSO Standard Seawater had ~15% lower S content than expected (Table 2), its corrected $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$ values were identical within the analytical error to reported values of IAPSO Standard Seawater (e.g., Craddock *et al.*, 2008) and present seawater (e.g., Ono *et al.*, 2012). Reproducibilities of $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ for JGb-1 were significantly larger than those for the standard, IAEA-S-1. Although it is uncertain whether JGb-1 is heterogeneous in terms of S isotopes or if a larger than expected S isotope fractionation occurred during extraction or reduction processes, $\delta^{34}\text{S}$ value of JGb-1 is still within analytical error of the range of reported values (Ackerman *et al.*, 2012).

These results indicate that Cl isotopic compositions do not fractionate during pyrohydrolysis and that the multiple S isotopic compositions can be obtained using small isotope fractionation corrections. Therefore, this extraction method can be used to obtain accurate Cl and S contents as well as their isotopic composition from a single aliquot of sample.

CONCLUSIONS

We established a simple method for determining F, Cl, and S in small (as little as 40 mg) rock samples by using IC after pyrohydrolysis extraction. We determined their contents in reference materials ranging from peridotite to rhyolite containing F, Cl, and S contents ranging from <10 μ g g⁻¹ to >1000 μ g g⁻¹ and achieved analytical results in good agreement with values reported in the literatures. We were also able to determine the Cl and S isotope compositions of sample solutions obtained by the pyrohydrolysis procedure.

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REFERENCES

- Ackerman, L., Rohovec, J. and Sebek, O. (2012) Determination of total sulfur in fifteen geological materials using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and combustion/infrared spectrometry. *Geostand. Geoanal. Res.* **36**, 407–414.
- Aiuppa, A., Federico, C., Giudice, G., Gurrieri, S., Paonita, A. and Valenza, M. (2004) Plume chemistry provides insights into mechanisms of sulfur and halogen degassing in basaltic volcanoes. *Earth Planet. Sci. Lett.* **222**, 469–483.
- Anazawa, K., Tomiyasu, T. and Sakamoto, H. (2001) Simultaneous determination of fluorine and chlorine in rocks by ion chromatography in combination with alkali fusion and cation-exchange pretreatment. *Anal. Sci.* **17**, 217–219.
- Balcone-Boissard, H., Michel, A. and Villemant, B. (2009) Simultaneous determination of fluorine, chlorine, bromine and iodine in six geochemical reference materials using pyrohydrolysis, ion chromatography and inductively coupled plasma-mass spectrometry. *Geostand. Geoanal. Res.* **33**, 477–485.
- Burton, J. D. (1996) The Ocean: a global chemical system. *Oceanography an Illustrated Guide* (Summerhayes, C. P. and Thorpe, S. A., eds.), 165–181, John Wiley.
- Craddock, P. R., Rouxel, O. J., Ball, L. A. and Bach, W. (2008) Sulfur isotope measurement of sulfate and sulfide by high-resolution MC-ICP-MS. *Chem. Geol.* **253**, 102–113.
- Ding, T., Valkiers, S., Kipphardt, H., De Bievre, P., Taylor, P. D. P., Gonfiantini, R. and Krouse, R. (2001) Calibrated sulfur isotope abundance ratios of three IAEA sulfur isotope reference materials and V-CDT with a reassessment of the atomic weight of sulfur. *Geochim. Cosmochim. Acta* **65**, 2433–2437.
- Erdman, M. E., Lee, C. T. A., Yang, W. and Ingram, L. (2014) Sulfur concentration in geochemical reference materials by solution inductively coupled plasma-mass spectrometry. *Geostand. Geoanal. Res.* **38**, 51–60.
- Govindaraju, K. (1994) 1994 compilation of working values and sample description for 383 geostandards. *Geostand. Newsl.* **18** (Special Issue), 158.
- Hedenquist, J. W. and Lowenstern, J. B. (1994) The role of magmas in the formation of hydrothermal ore-deposits. *Nature* **370**, 519–527.
- 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. *Geostand. Newsl.* **19**, 135–213.
- Konno, U., Takai, K. and Kawagucci, S. (2013) Stable chlorine isotope ratio analysis of subnanomolar level methyl chloride by continuous-flow isotope ratio mass spectrometry. *Geochem. J.* **47**, 469–473.
- Lee, C. T. A., Luffi, P., Chin, E. J., Bouchet, R., Dasgupta, R., Morton, D. M., Le Roux, V., Yin, Q. Z. and Jin, D. (2012) Copper systematics in arc magmas and implications for crust-mantle differentiation. *Science* **336**, 64–68.
- Long, A., Eastoe, C. J., Kaufmann, R. S., Martin, J. G., Wirt, L. and Finley, J. B. (1993) High-precision measurement of chlorine stable-isotope ratios. *Geochim. Cosmochim. Acta* **57**, 2907–2912.
- 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 ICPMS. *Anal. Chem.* **73**, 2547–2553.
- Makishima, A. and Nakamura, E. (2012) High-resolution MC-ICPMS employing amplifiers with a 10 (12) ohm resistor for bulk sulfur determination in biological and geological samples. *J. Anal. Atom. Spectrom.* **27**, 891–895.
- Michel, A. and Villemant, B. (2003) Determination of halogens (F, Cl, Br, I), sulfur and water in seventeen geological reference materials. *Geostand. Newsl.* **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. *Geostand. Newsl.* **25**, 133–136.
- Ono, S., Wing, B., Johnston, D., Farquhar, J. and Rumble, D. (2006) Mass-dependent fractionation of quadruple stable sulfur isotope system as a new tracer of sulfur biogeochemical cycles. *Geochim. Cosmochim. Acta* **70**, 2238–2252.
- Ono, S. H., Keller, N. S., Rouxel, O. and Alt, J. C. (2012) Sulfur-33 constraints on the origin of secondary pyrite in altered oceanic basement. *Geochim. Cosmochim. Acta* **87**, 323–340.
- Sano, T., Fukuoka, T. and Hasenaka, T. (2004) Determination of chlorine contents in geological survey of Japan reference materials by prompt gamma neutron activation analysis. *Geostand. Geoanal. Res.* **28**, 443–448.
- Sasaki, A., Arikawa, Y. and Folinsbee, R. E. (1979) Kiba reagent method of sulfur extraction applied to isotopic work. *Bull. Geol. Surv. Japan* **30**, 241–245.
- Shimizu, K., Itai, T. and Kusakabe, M. (2006) Ion chromatographic determination of fluorine and chlorine in silicate rocks following alkaline fusion. *Geostand. Geoanal. Res.* **30**, 121–129.
- Straub, S. M. and Layne, G. D. (2003) The systematics of chlorine, fluorine, and water in Izu arc front volcanic rocks: Implications for volatile recycling in subduction zones. *Geochim. Cosmochim. Acta* **67**, 4179–4203.
- Straub, S. M., Layne, G. D., Schmidt, A. and Langmuir, C. H. (2004) Volcanic glasses at the Izu arc volcanic front: New perspectives on fluid and sediment melt recycling in subduction zones. *Geochem. Geophys. Geosyst.* **5**, doi:10.1029/2002gc000408.
- Ueno, Y., Ono, S., Rumble, D. and Maruyama, S. (2008) Quadruple sulfur isotope analysis of ca. 3.5 Ga Dresser Formation: New evidence for microbial sulfate reduction in the early Archean. *Geochim. Cosmochim. Acta* **72**, 5675–5691.
- Wang, Q. Y., Makishima, A. and Nakamura, E. (2010) Determination of fluorine and chlorine by pyrohydrolysis and ion chromatography: Comparison with alkaline fusion digestion and ion chromatography. *Geostand. Geoanal. Res.* **34**, 175–183.
- Wassenaar, L. I. and Koehler, G. (2004) On-line technique for the determination of the delta Cl-37 of inorganic and total organic Cl in environmental samples. *Anal. Chem.* **76**, 6384–6388.