

NOTE

Measurement of chlorine stable isotopic composition by negative thermal ionization mass spectrometry using total evaporation technique

TATSUYA FUJITANI,^{1,2*} KATSUYUKI YAMASHITA,^{2,3} MASAHIKO NUMATA,⁴
NOBUYUKI KANAZAWA⁵ and NOBORU NAKAMURA²

¹Marine Technical College, Ashiya 659-0026, Japan

²Department of Earth and Planetary Sciences, Kobe University, Kobe 657-8501, Japan

³The Pheasant Memorial Laboratory, Institute for Study of the Earth's Interior, Okayama University,
Misasa, Tottori 682-0193, Japan

⁴National Metrology Institute of Japan, AIST, Tsukuba, Ibaraki 305-8563, Japan

⁵Thermo Fisher Scientific K.K., Moriya, Yokohama 221-0022, Japan

(Received May 9, 2009; Accepted August 7, 2009)

A total evaporation negative thermal ionization mass spectrometry (TE-N-TIMS) technique for the isotopic analysis of chlorine was developed. This technique provides fast and reliable way to determine the isotopic signature of chlorine samples as small as 100 ng. Compared to the conventional N-TIMS method, the precision of the Cl isotopic analysis is improved by a factor of up to 3 by minimizing the effect of mass fractionation. Using this method, reproducibility of 0.9‰ (R.S.D.: $n = 25$) can be achieved for $^{37}\text{Cl}/^{35}\text{Cl}$ ratio of 200 ng Cl. The analyzed results of the AgCl reagent expressed as a per-mil deviation ($\delta^{37}\text{Cl}$) relative to the Standard Mean Ocean Chloride showed good concordance with the value obtained by conventional positive thermal ionization mass spectrometry (P-TIMS).

Keywords: chlorine stable isotopes, total evaporation method, negative thermal ionization mass spectrometry, small samples

INTRODUCTION

Chlorine, which is one of the representative volatile elements in the earth's surface environment, has two stable isotopes ^{35}Cl and ^{37}Cl , with relative abundances of approximately 75% and 25%, respectively. The chlorine isotopic variations observed in geological and environmental samples are often used to trace the migration processes of volatile chemical species, or chemical reactions of chlorinated organic compound in the earth's surface environment (Stewart and Spivack, 2004). Determination of the isotopic composition of chlorine has been carried out by CH_3Cl^+ gas mass spectrometry (IRMS) (Kaufmann *et al.*, 1984), Cs_2Cl^+ thermal ionization mass spectrometry (P-TIMS) (Xiao and Zhang, 1992; Numata *et al.*, 2001) and Cl^- negative thermal ionization mass spectrometry (N-TIMS) (Vengosh *et al.*, 1989). The former two methods can offer high analytical precision (normally 0.1–0.5‰ in $^{37}\text{Cl}/^{35}\text{Cl}$ ratio). The IRMS method, however, requires a large amount of chlorine (>1 mg) for each

measurement. Even the P-TIMS method requires microgram quantity of Cl for precise analysis. For this reason, these two methods have been applied to the isotopic analysis of relatively large samples, or samples with high Cl concentration such as fluid inclusion in ore deposits (Eastoe and Guilbert, 1992), evaporites (Eggenkamp *et al.*, 1995), Cl-bearing silicate minerals (Willmore *et al.*, 2002) and Cl-rich metamorphic rocks (Barnes and Sharp, 2006; Bonifacie *et al.*, 2008). The N-TIMS technique, on the other hand, provides much higher sensitivity for chlorine relative to IRMS and P-TIMS, and only several hundred nano-grams of Cl is necessary (Fujitani and Nakamura, 2006). However, its analytical precision is worse than the former two methods mainly due to the effect of isotopic fractionation during the evaporation and ionization processes (normally in the order of few ‰).

Previous studies have demonstrated the existence of large isotopic fractionation of chlorine during geological process (Stewart and Spivack, 2004; Godon *et al.*, 2004). If the precision of Cl isotopic analysis for the N-TIMS can be improved, it will provide the opportunity to investigate the chlorine isotopic composition of small samples that cannot be studied with the IRMS and P-TIMS methods. One candidate to improve the precision for N-TIMS

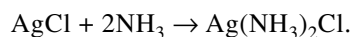
*Corresponding author (e-mail: fujitani@mail.mtc.ac.jp)

is to adopt the total evaporation method, where the ion beam of each isotope from a sample on the filament is simultaneously integrated until the sample evaporates completely. Because the entire beam is integrated, the effect of isotopic fractionation during the data acquisition is minimized. The total evaporation method using thermal ionization mass spectrometry has been developed for the isotopic analysis of uranium and plutonium in the nuclear industries (Callis and Abernathy, 1991), and neodymium in small samples (Wakaki *et al.*, 2007). The first application of isotopic analysis using total evaporation technique in a negative ion mode was the analysis of Re isotopes (Suzuki *et al.*, 2004). In this study, the total evaporation negative thermal ionization mass spectrometry (TE-N-TIMS) is applied to the analysis of chlorine stable isotope and its analytical effectiveness is discussed in detail.

EXPERIMENTAL

Reagents and seawater

The chloride mounted onto the filament for TE-N-TIMS was ammoniacal solution of AgCl (Vengosh *et al.*, 1989). The standard solution for this study was prepared by dissolving AgCl (Wako Pure Chemical Industries Ltd.) reagent with aqueous ammonia solution (30%, Kanto Chemical Co.) as shown below.



The Cl concentration of the solution was adjusted to approximately 100 mg L⁻¹. The seawater sample was taken from the Pacific Ocean (8°39.5' N, 153°56.6' E, surface) (Numata *et al.*, 2001). The chlorine ion in the seawater was precipitated as AgCl by addition of 0.03 M AgNO₃ solution in a dark room. The precipitate was then dissolved in the ammonia solution. By using ion chromatography, we confirmed that more than 94% of the chlorine in the seawater was recovered in the sample solution. The water used in this chemical procedure was obtained from a Millipore Milli-Q water purification system.

Mass spectrometry

The isotopic ratios of chlorine were measured using a Finnigan MAT262 thermal ionization mass spectrometer equipped with five Faraday detectors. The resistance of the Faraday cup amplifier was 10¹¹ Ω and a beam intensity of 1 V corresponds to 10⁻¹¹ A. The operating condition for mass spectrometry is similar to the negative thermal ionization mass spectrometry for isotope dilution analysis of Cl described in Fujitani and Nakamura (2006). Re-Re double filament assemblage using zone-refined Re ribbons (0.025 × 0.75 mm; purity: 99.999%; H. CROSS

Co.) was employed for the TE-N-TIMS analysis. About 2 μL standard solution containing 200 ng of chlorine was deposited onto a degassed flat Re filament and slowly evaporated to dryness at low filament current (~0.7 A). Filaments with 100 ng and 500 ng Cl were also prepared. For the seawater, the amount of Cl loaded onto the filament was 200 ng. The filament was then assembled into the mass spectrometer for isotopic measurement. The accelerating voltage was set to -10 kV.

Only the ionization filament (Io) current was increased automatically up to 1.8 A, which corresponds to filament temperature of about 1300°C. The sample (evaporation) filament (Ev) was fixed at 0 A throughout the analysis. When the ³⁵Cl⁻ ion beam was observed in ion counting mode, the beam was focused and the filament current was increased manually until the intensity of the ³⁵Cl⁻ ion beam reached 2 mV.

The data acquisition was performed in a multi-collector static mode to simultaneously collect ³⁷Cl⁻ (*m/z* = 37) and ³⁵Cl⁻ (*m/z* = 35). Once the data acquisition started, the filament current was automatically increased at a rate of 30 mA/scan until the ³⁵Cl⁻ ion beam intensity reached a preset maximum value. The preset maximum values were adjusted to 120 mV for 500 ng Cl, 100 mV for 200 ng Cl and 80 mV for 100 ng Cl, respectively, in order to evaporate the sample entirely within 100 to 200 scans. If the intensity increased beyond the preset value, the filament current was reduced or kept nearly constant in order to keep the ion beam intensity nearly constant. Integration time of 1 scan was 4 seconds.

When most of the sample was evaporated from the sample filament, the ion beam intensity decreased rapidly. The data acquisition was terminated when the ³⁵Cl⁻ ion beam intensity fell below a preset threshold value of 5 mV. The final isotope ratio was calculated from the integrated ion intensities of each isotope after subtraction of the baseline intensity. Because the entire beam is integrated to calculate the isotope ratio, the analytical error for each analysis is not available. The time required for each analysis is less than twenty minutes.

For the comparison of the data, we have undertaken isotopic analyses of the AgCl reagent and seawater using P-TIMS method. The details of the analytical technique for P-TIMS are described in Numata *et al.* (2001).

RESULTS AND DISCUSSION

A typical profile of ³⁵Cl⁻ ion beam intensity and its corresponding filament current as a function of scan number is shown in Fig. 1a. In this example, the sample on the filament was totally evaporated after 166 scans. The beam intensities of both ³⁵Cl⁻ and ³⁷Cl⁻ ions rose rapidly up to the preset value, where it was held until most of the sample was evaporated. The filament current also

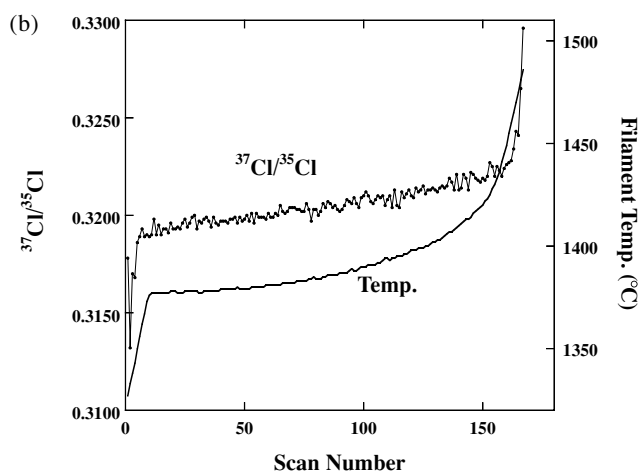
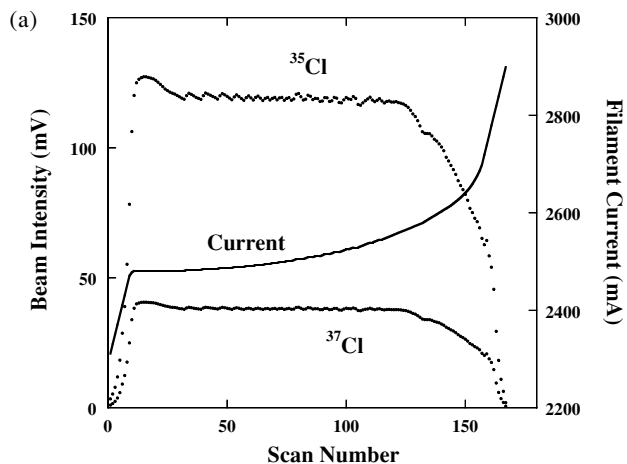


Fig. 1. (a) The representative profiles of the $^{35}\text{Cl}^-$ and $^{37}\text{Cl}^-$ ion beam intensities for 500 μg Cl sample and the filament current during the total evaporation procedure against the scan number. (b) The fluctuations of $^{37}\text{Cl}/^{35}\text{Cl}$ ratio and their corresponding filament temperature against the scan number for the same analysis in (a).

rose rapidly until the preset beam intensity but gradually increased during the analysis to keep the beam intensity constant. When the filament current reached around 2600 mA, the ion beam intensity dropped suddenly.

Figure 1b shows the fluctuation of $^{37}\text{Cl}/^{35}\text{Cl}$ and its corresponding filament temperature of the same sample shown in Fig. 1a. The $^{35}\text{Cl}^-$ ion beam intensity reached its preset value at approximately 1380°C. At this temperature, the effect of isotopic fractionation was already apparent. Isotopic fractionation gradually proceeded as the filament current increased. It is noteworthy that the isotopic fractionation of chlorine began at a much lower temperature of around 1340°C (Fujitani and Nakamura, 2006). This may be the reason why conventional N-TIMS

Table 1. Results of the Cl isotope composition of AgCl reagent (Cl content 200 ng)

Run #	^{35}Cl total voltage (V)	$^{37}\text{Cl}/^{35}\text{Cl}$
1	5.28	0.32118
2	6.81	0.32025
3	9.89	0.32098
4	10.69	0.32054
5	4.90	0.32051
6	7.95	0.32114
7	11.46	0.32052
8	4.45	0.32087
9	6.32	0.32088
10	5.10	0.32027
11	8.84	0.32078
12	5.07	0.32058
13	8.80	0.32113
14	7.08	0.32070
15	6.68	0.32046
16	5.50	0.32066
17	7.48	0.32052
18	6.68	0.32080
19	5.85	0.32043
20	3.63	0.32042
21	13.87	0.32102
22	5.56	0.32114
23	5.35	0.32065
24	20.13	0.32091
25	15.11	0.32029
Average \pm 1SD		0.32071 \pm 0.00029
R.S.D. (%)		0.9

analysis could not provide highly reproducible chlorine isotopic data compared to other methods. Since the isotope ratio of TE-N-TIMS is derived from the integrated ion intensities of each isotope, the effect of isotopic fractionation is likely minimized.

The results of the chlorine isotopic compositions of the 200 ng Cl in AgCl reagent are given in Table 1 and Fig. 2. Isotopic measurements were carried out 25 times. The average number of scans was 110 and the average of the ^{35}Cl total voltage was approximately 7.9 V. This corresponds to an electric charge of approximately 7.9×10^{-11} C. The mean value of the $^{37}\text{Cl}/^{35}\text{Cl}$ ratios was 0.32071 and the reproducibility was 0.00029 (1SD), which corresponds to R.S.D. of 0.9‰. The Cl isotopic ratios of the 100 ng and 500 ng Cl in AgCl reagent were also determined. The mean value of the $^{37}\text{Cl}/^{35}\text{Cl}$ ratios of thirteen measurements of 500 ng sample was 0.32081. The reproducibility was 0.00028 (1SD, $n = 13$), which was the same as the reproducibility of the 200 ng Cl sample. The measurements of the 100 ng Cl ($n = 9$) showed somewhat larger reproducibility of 0.00066 (R.S.D. = 2.0‰) compared to 200 ng and 500 ng samples, with the mean value of 0.32088. While the reproducibility of 100 ng analysis reaches 2‰, the reproducibility of 200–500 ng

Table 2. Measured Cl isotopic compositions and the deviation of the $^{37}\text{Cl}/^{35}\text{Cl}$ from the SMOC

Sample	Cl content (ng)	Number of run	Average of ^{35}Cl total voltage (V)	$^{37}\text{Cl}/^{35}\text{Cl}$	$\delta^{37}\text{Cl}$ (‰)
AgCl reagent	100	9	2.9	$0.32088 \pm 0.00066^a)$	$+2.1 \pm 2.0^b)$
	200	25	7.9	0.32071 ± 0.00029	$+1.5 \pm 0.9$
	500	13	25.4	0.32081 ± 0.00028	$+1.8 \pm 0.9$
Seawater	200	9	4.7	0.32022 ± 0.00036	0 ± 1.1
Seawater (P-TIMS)	2000	8		0.31910 ± 0.00010	0 ± 0.31

^{a)}1SD, ^{b)}R.S.D.

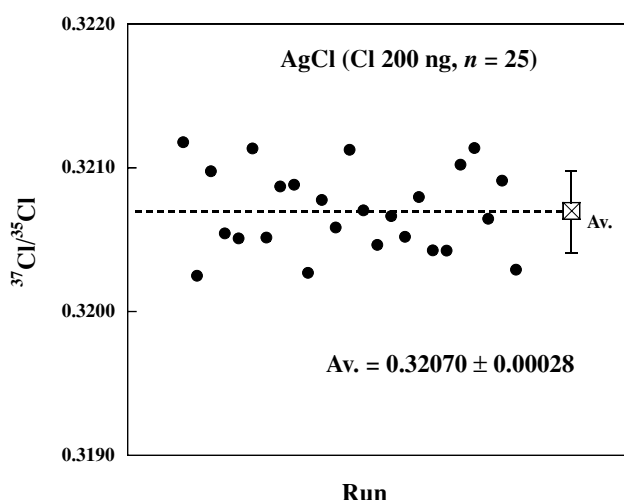


Fig. 2. The results of measurements of the chlorine isotope compositions in AgCl reagent. 200 ng Cl was loaded onto the filament. Error bar shows 1SD.

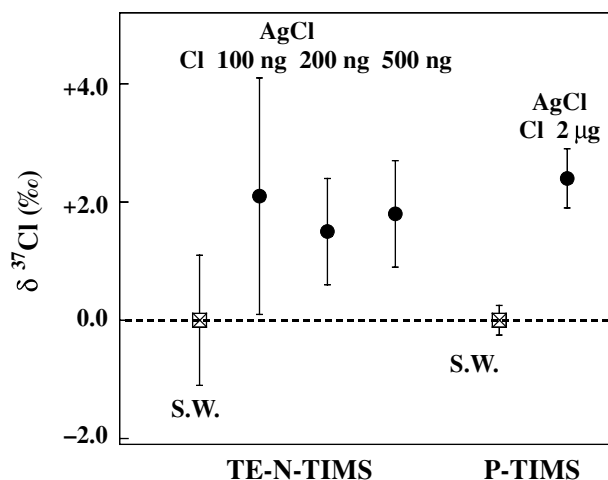


Fig. 3. The $\delta^{37}\text{Cl}$ of chlorine isotope measurements of AgCl reagent by different technique, namely N-TIMS using total evaporation method and the conventional P-TIMS. Error bars refer to 1SD. S.W., seawater.

Cl is significantly better than that of conventional N-TIMS analysis (Vengosh *et al.*, 1989). Furthermore, the isotopic compositions of all three cases showed good agreement, implying that the amount of Cl loaded onto the filament did not affect the result of the final data if they were kept in the range of 100 to 500 ng.

The Cl isotopic composition of seawater was also determined to serve as the Standard Mean Ocean Chloride (SMOC) reference standard (Kaufmann *et al.*, 1984). The amount of chlorine used to determine the isotopic composition of the seawater sample was fixed at 200 ng. The mean value of the $^{37}\text{Cl}/^{35}\text{Cl}$ ratios obtained from nine repeated analyses was 0.32022 and the reproducibility was 0.00036 (R.S.D = 1.1‰).

The isotopic data for the samples analyzed during the course of this study are summarized in Table 2. The final Cl isotopic ratio of the sample is expressed as a per-mil deviation ($\delta^{37}\text{Cl}$) relative to SMOC. In order to check the quality of the data obtained by TE-N-TIMS method, the $^{37}\text{Cl}/^{35}\text{Cl}$ ratios of the AgCl reagent and seawater were

also determined by P-TIMS. Chlorine loaded onto the filament for P-TIMS analysis was about 2 μg . The results were 0.31988 ± 0.00017 for the AgCl reagent and 0.31910 ± 0.00010 for the seawater, respectively. The absolute values of Cl isotopic compositions analyzed by P-TIMS were 2.5~3.5‰ lower than those of the total evaporation technique for both AgCl reagent and seawater. However, in most geological and environmental applications, we are only concerned about relative difference in Cl isotopic signatures, typically expressed as the deviation from the SMOC. The $\delta^{37}\text{Cl}$ value of the AgCl reagent analyzed by P-TIMS method was $2.4 \pm 0.5\%$. This is within the range of reproducibility of the values determined using TE-N-TIMS method, confirming the reliability of the technique (see Fig. 3).

Conventional IRMS and P-TIMS measurements have revealed a large fractionation of Cl isotopic composition during geological process, ranging from -14% to $+16\%$ in $\delta^{37}\text{Cl}$ value (Godon *et al.*, 2004). Recently, Sharp and co-workers have performed an IRMS analyses of MORB

glasses and abyssal peridotites and argued that there is no large difference in the chlorine isotope signature between mantle and crustal materials, both of which have $\delta^{37}\text{Cl}$ values close to 0‰ (Barnes and Sharp, 2006; Sharp *et al.*, 2007). On the other hand, Wei *et al.* (2008) reported $\delta^{37}\text{Cl}$ values of +1.2 to +6.0‰ from serpentines from the subduction zones using P-TIMS. TE-N-TIMS may serve as the third method of the chlorine isotopic analysis to clarify such a discrepancy.

In addition to the reduced sample size for analysis, TE-N-TIMS has two additional advantages over IRMS and P-TIMS. One is the simple chemical procedure for sample preparation. The three different methods follow a common chemical procedure until the purification of chlorine from the samples by precipitation of AgCl. While no further purification is necessary for N-TIMS analysis, P-TIMS and IRMS techniques require additional troublesome procedures to convert the Cl^- ions into the Cs_2Cl^+ ions or CH_3Cl^+ ions, respectively. Second is the short analytical time required for mass spectrometry. Typical analytical time using TE-N-TIMS is about twenty minutes. This is a factor of ten shorter than the P-TIMS method.

The chlorine isotopic variation observed in the environmental pollutants such as chlorinated solvents (Numata *et al.*, 2002) and perchlorates (Coates and Achenbach, 2004) is larger than that of typical geological samples. On the other hand, a large number of sample analysis is often necessary in the field of environmental chemistry. For this reason, a fast and simple analytical procedure developed in this study will be highly useful.

CONCLUSION

A fast and simple method for chlorine isotopic analysis using TE-N-TIMS was developed. Using this method, the $^{37}\text{Cl}/^{35}\text{Cl}$ ratio of 0.32071 ± 0.00029 (1SD) for AgCl reagent containing 200 ng of Cl^- was obtained. Reproducibility of 0.9‰ is slightly worse than that of the conventional thermal ionization mass spectrometry using Cs_2Cl^+ ions. However, the sample size is reduced by a factor of ten, and the analytical time is also dramatically reduced. Although the absolute value of $^{37}\text{Cl}/^{35}\text{Cl}$ determined by the TE-N-TIMS does not perfectly match the value from the conventional P-TIMS, the per-mil deviation from the Standard Mean Ocean Chloride (SMOC) agrees within the analytical uncertainty, confirming the reliability of the method. The TE-N-TIMS method can therefore be used as a powerful tool in the study of very small amount of chlorine extracted from terrestrial and extraterrestrial samples. In addition, its simple analytical procedure and short analytical time will allow us to investigate a large number of samples, as required in the field of environmental sciences.

Acknowledgments—We thank Drs. T. Tanaka and K. Suzuki for helpful comments on the manuscript. This work was supported in part by Grants-in-Aid for Scientific Research (No. 1434017) from Ministry of Education, Culture, Sports Science and Technology of Japan.

REFERENCES

- Barnes, J. D. and Sharp, Z. D. (2006) A chlorine isotope study of DSDP/ODP serpentinized ultramafic rocks: Insights into the serpentinization process. *Chem. Geol.* **228**, 246–265.
- Bonifacie, M., Busigny, V., Mevel, C., Philippot, P., Agrinier, P., Jendrzewski, N., Scambelluri, M. and Javoy, M. (2008) Chlorine isotopic composition in seafloor serpentinites and high-pressure metaperidotites. Insights into oceanic serpentinization and subduction processes. *Geochim. Cosmochim. Acta* **72**, 126–139.
- Callis, E. L. and Abernathy, R. M. (1991) High-precision analyses of uranium and plutonium by total sample volatilization and signal integration. *Int. J. Mass Spectrom. Ion Proc.* **103**, 93–105.
- Coates, J. D. and Achenbach, L. A. (2004) Microbial perchlorate reduction: rocket-fuelled metabolism. *Nature Rev. Microbiol.* **2**, 569–580.
- Eastoe, C. J. and Guilbert, J. M. (1992) Stable chlorine isotopes in hydrothermal systems. *Geochim. Cosmochim. Acta* **56**, 4247–4255.
- Eggenkamp, H. G. M., Kreulen, R. and Koster van Groos, A. F. (1995) Chlorine stable isotope fractionation in evaporates. *Geochim. Cosmochim. Acta* **59**, 5169–5175.
- Fujitani, T. and Nakamura, N. (2006) Determination of chlorine in nine rock reference materials by isotope dilution mass spectrometry. *Geostandard Geoanal. Res.* **30**, 113–120.
- Godon, A., Webster, J. D., Layne, G. D. and Pineau, F. (2004) Secondary ion mass spectrometry for the determination of $\delta^{37}\text{Cl}$: Part I. Intercalibration of SIMS and IRMS for aluminosilicate glasses. *Chem. Geol.* **207**, 291–303.
- Kaufmann, R. S., Long, A., Bentley, H. and Davis, S. (1984) Natural chlorine isotope variations. *Nature* **309**, 338–340.
- Numata, M., Nakamura, N. and Gamo, T. (2001) Precise measurement of chlorine stable isotopic ratios by thermal ionization mass spectrometry. *Geochem. J.* **35**, 89–100.
- Numata, M., Nakamura, N., Koshikawa, H. and Terashima, Y. (2002) Chlorine stable isotope measurements of chlorinated aliphatic hydrocarbons by thermal ionization mass spectrometry. *Anal. Chim. Acta* **455**, 1–9.
- Sharp, Z. D., Barnes, J. D., Brearley, A. J., Fischer, T. P., Chaussidon, M. and Kamenetsky, V. S. (2007) Chlorine isotope homogeneity of the mantle, crust and carbonaceous chondrites. *Nature* **446**, 1062–1065.
- Stewart, M. A. and Spivack, A. J. (2004) The stable-chlorine isotope compositions of natural and anthropogenic materials. *Rev. Mineral. Geochem.* **55**, 231–254.
- Suzuki, K., Miyata, Y. and Kanazawa, N. (2004) Precise Re isotope ratio measurements by negative thermal ionization mass spectrometry (NTI-MS) using total evaporation technique. *Int. J. Mass Spectrom.* **235**, 97–101.
- Vengosh, A., Chivas, A. R. and McCulloch, M. T. (1989) Direct determination of boron and chlorine isotopic composition

- tions in geological materials by negative thermal-ionization mass spectrometry. *Chem. Geol. (Isotope Geosci. Sect.)* **79**, 333–343.
- Wakaki, S., Shibata, S. and Tanaka, T. (2007) Isotope ratio measurements of trace Nd by the total evaporation normalization (TEN) method in thermal ionization mass spectrometry. *Int. J. Mass Spectrom.* **264**, 157–163.
- Wei, W., Kastner, M. and Spivack, A. (2008) Chlorine stable isotopes and halogen concentrations in convergent margins with implications for the Cl isotopes cycle in the ocean. *Earth Planet. Sci. Lett.* **266**, 90–104.
- Willmore, C. C., Boudreau, A. E., Spivack, A. J. and Kruger, F. J. (2002) Halogens of the Bushveld Complex, South Africa: $\delta^{37}\text{Cl}$ and Cl/F evidence for hydration melting at the source region in a back-arc setting. *Chem. Geol.* **182**, 503–511.
- Xiao, Y. K. and Zhang, C. G. (1992) High precision isotopic measurement of chlorine by thermal ionization mass spectrometry of Cs_2Cl^+ ion. *Int. J. Mass Spectrom. Ion Proc.* **116**, 183–192.