

Articles

Major Factors Affecting the Isotopic Measurement of Chlorine Based on the Cs_2Cl^+ Ion by Thermal Ionization Mass Spectrometry

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The factors that affect isotopic measurement of chlorine based on Cs_2Cl^+ ion by thermal ionization mass spectrometry were studied. Graphite is essential for the emission of Cs_2Cl^+ ion from CsCl . No Cs_2Cl^+ ions are detected in the absence of graphite on the filament. The emission of Cs_2Cl^+ ion and the measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratio were affected by different varieties of graphite, the pH value of the sample solution, and impurities in the solution. High-precision isotopic measurement of chlorine based on Cs_2Cl^+ ion is achieved only by using graphite with a perfect crystal structure. The measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios were much higher, and even the emission of Cs_2Cl^+ ion becomes impossible when pH values of the sample solution were higher than 6, corresponding to the presence of excess Cs. The measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios were higher when SO_4^{2-} and NO_3^- anions were present. The results show that the measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios are weakly related to the amount of chlorine on filament in a range from 1 to 500 μg .

Chlorine has two natural stable isotopes, ^{37}Cl and ^{35}Cl . The large relative difference in mass causes natural variations in chlorine isotope ratios. Earlier observations suggested that there was little variation in chlorine isotopic ratios in nature, but this was due to the poor precision of the isotopic measurements. Today, with high-precision chlorine isotopic measurement methods based on the CH_3Cl^+ ion^{1,2} and the Cs_2Cl^+ ion,^{3,4} the isotope geochemistry of chlorine has been applied to hydrothermal processes,^{5,6} groundwater,⁷ evaporites,⁸ salt lake brine,^{9–11} fluid

inclusion¹² brine,^{9–11} fluid inclusions,¹² and marine aerosol particles.¹³ The observed range of natural $^{37}\text{Cl}/^{35}\text{Cl}$ ratios is $\sim 10\%$.¹⁴

Currently, three analytical techniques are used to determine the isotopic composition of chlorine. Negative thermal ionization mass spectrometry (NTIMS) based on the measurement of Cl^- ion was developed and used by Shields et al.¹⁵ to determine the absolute atomic weight of chlorine, and it was also used by Vengosh et al.¹⁶ to study the isotopic composition of chlorine in geological materials. The control of mass spectrometric discrimination in NTIMS is difficult because of the relatively light masses of the chlorine isotopes. Kaufmann et al.¹ determined the isotopic composition of chlorine based on the measurement of the CH_3Cl^+ ion produced by electronic impact ionization of methyl chloride (EIIMS). The procedure based on the measurement of the CH_3Cl^+ ion has been improved, and a total analytical precision of $\leq 0.09\%$ has been achieved.² EIIMS is widely adopted in studies of the isotopic geochemistry of chlorine.^{5–8} Positive thermal ionization mass spectrometry (PTIMS), based on the measurement of Cs_2Cl^+ , was first reported by Xiao and Zhang.^{3,4} PTIMS for the measurement of chlorine isotopes was improved by using Cs_2Cl^+ ions with multiple Faraday cups. For this technique, replicate analysis of ocean water yielded an external precision of 0.1–0.2%.¹⁷ It has also been used successfully in the investigations

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Table 1. Properties of Different Species of Graphite²³

no.	origin ^a	description of graphites	D002 (Å)	degree of graphitization (%) ^b	maximal distortion of crystal lattice (Å) ^c
1	NIST	spectral purity	3.364	88.4	±0.072
2	SFCR	spectral purity, ash, 0.001%	3.368	83.7	±0.105
3	SFCC	purity, 99.8%; ash, 0.15%	3.355	98.8	±0.112
4	BFCR	purity, 98%; ash, 0.5%	3.355	98.8	±0.174
5	NBS	high purity	3.368	83.7	±0.062
6	Carine	spectral purity	3.358	96.3	±0.106
7	SCF	spectral purity, ash, 0.005%	3.428	14.0	nd ^d

^a NIST, National Institute of Standard and Technology, U.S.A.; SFCR, Shanghai Factory of Chemical Reagents; SFCC, Shanghai Factory of Colloid Chemistry; BFCR, Beijing Factory of Chemical Reagents; NBS, National Bureau of Standards, U.S.A.; Carine, Carine Laboratory; SCF, Shanghai Carbon Factory. ^b The degree of graphitization (DG, %) is calculated as follows: $DG (\%) = [1 - (d_m - d_{gs}) / (d_{gs} - d_{cs})] \times 100$; here d_m is the measured distance of the crystal planes (002); d_{gs} and d_{cs} are the standard distances of the crystal planes for graphite and carbon powder; vis $d_{gs} = 3.354$ Å; $d_{cs} = 3.44$ Å. ^c The calculation of the maximal distortion of the crystal lattice is shown in ref 24. ^d nd, not determined.

of brine,^{9,11} aerosols,¹³ rocks,^{12,18} and subduction zone pore waters.¹⁹

A comparison between electronic impact ionization of CH_3Cl^+ and thermal ionization of Cs_2Cl^+ for the measurement of chlorine isotopes was recently carried out.¹⁴ Rosenbaum concluded that there is no significant offset between the two techniques, and EI/MS is better for the large samples (>300 µg of Cl) with a reproducibility of $\leq 0.1\%$ (2σ) and PTIMS is better for the small samples (1–50 µg of Cl) with an achievable reproducibility of $\leq 0.2\%$ (2σ). In addition, Rosenbaum's PTIMS results showed that the measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios were strongly dependent on the amount of chlorine loaded on the filament. This result is very interesting and needs to be investigated further.

In the present study, we examine the factors affecting measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios based on the Cs_2Cl^+ ion by thermal ionization mass spectrometry, and we check ratio dependence on amount of chlorine loaded on the filament. Our results do not entirely agree with those reported by Rosenbaum.

EXPERIMENTAL SECTION

Sample Descriptions. In this study, the reference material ISL 354 NaCl²⁰ (ISL 354), produced from selected seawater with a measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratio of $0.319\,025 \pm 0.000\,038$, was used as the isotopic standard. The procedure for preparation of ISL 354 NaCl was indicated elsewhere.²⁰ The selected seawater was collected at $4^\circ 18' \text{N}$, $161^\circ 09' \text{E}$.²⁰ The ISL 354 (solid) was dissolved in high-purity water and passed through the columns filled with H-resin and Cs-resin to convert NaCl to CsCl.

Other samples analyzed were a Dead Sea brine (D-1318) (DS), which is a surface water and was collected in 1992; and an underground brine (UB), collected in January 1997 in the coastal area of Laizhou Bay, Shandong Province, China. This brine has a high chloride concentration of 8.705×10^4 mg of Cl/L and very high $\delta^{11}\text{B}$ of 57.7% .²¹ Brine aliquots containing ~ 20 mg of Cl were sequentially passed through columns filled with Ba-resin, H-resin, and Cs-resin to convert Cl^- to CsCl .

Analytical Methods. A VG 354 thermal ionization mass spectrometer (Micromass UK Ltd., Wythenshawe, Manchester,

U.K.) was used for all isotopic measurements of chlorine in this study. An optical pyrometer is provided with the VG 354; however, filament temperatures in this study were too low to be measured by optical pyrometer. Therefore, a thermocouple apparatus for measurement of low temperature, from room temperature to 1000 °C, was installed in the laboratory. The temperature of the filament in the ion source of the mass spectrometer can be directly measured with an accuracy of ± 3 °C by this apparatus.²²

The procedure for isotopic measurement of chlorine is basically the same as that described by Xiao and Zhang³ and Xiao et al.⁴ Flat Ta filaments (99.995%; 7.5 mm \times 0.76 mm \times 0.025 mm), degassed for 1 h with a 3.0-A current in a vacuum, were used. The center of each filament was first coated with 2.5 µL of a graphite (Johnson Matthey Co., 99.9999% purity) slurry containing ~ 75 µg of graphite. The slurry was allowed to go nearly to dryness before sample solutions of chlorine were added. The sample solutions of chlorine were then dried for 3 min with a current of 1.0 A passing through the filament.

Mass spectrometric analyses were started when filament currents reached 1.0 A after a 10-min warmup. The Cs_2Cl^+ ion was then monitored and used to focus the instrument for the isotopic measurement of chlorine. Measurements were made by magnetically switching through three m/e steps: 300.5 (baseline), 303 ($\text{Cs}_2^{37}\text{Cl}^+$) and 301 ($\text{Cs}_2^{35}\text{Cl}^+$). The $^{37}\text{Cl}/^{35}\text{Cl}$ ratio was then directly calculated from the ratio of the peaks at m/e 303 and 301. A total of 100 ratios were collected in 10 blocks in a normal analysis. Fewer than 100 ratios were collected in some analyses when the ion beams did not persist for sufficient time.

RESULTS AND DISCUSSION

Effect of Graphite on Measured $^{37}\text{Cl}/^{35}\text{Cl}$ Ratios. Recently, the characteristics of Cs_2Cl^+ ion emission for various graphites were studied in detail by Xiao et al.²³ Six kinds of graphite with different sources and high-purity carbon powder were used. The crystal structures were characterized using X-ray diffraction. The data for different kinds of graphite are shown in Table 1. The maximum distortions of the crystal lattices were calculated using the method reported by He and Cong²⁴ which determines the

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Table 2. Effect of the Kind of Graphite²³

graphite		temperature of filament (°C)	¹³³ Cs ⁺ / ^{Cs} ₂ Cl ⁺ (10 ⁻¹² A)	measured ³⁷ Cl/ ³⁵ Cl ratio (2σ)	no. of measurements
1	NIST	246	6.7/6.7	0.319 00 ± 0.000 02	8
2	SFCR	266	10/7.3	0.319 44 ± 0.000 03	8
3	SFCC	324	120/7.2	0.320 49 ± 0.000 15	3
4	BFCR	316	120/2.7	0.322 07 ± 0.000 17	3
5	NBS	217	6.3/7.6	0.319 06 ± 0.000 09	6
6	Carine	271	11.7/7.7	0.319 09 ± 0.000 04	6
7	SCF	307	13/0.23	0.320 61 ± 0.000 11	3

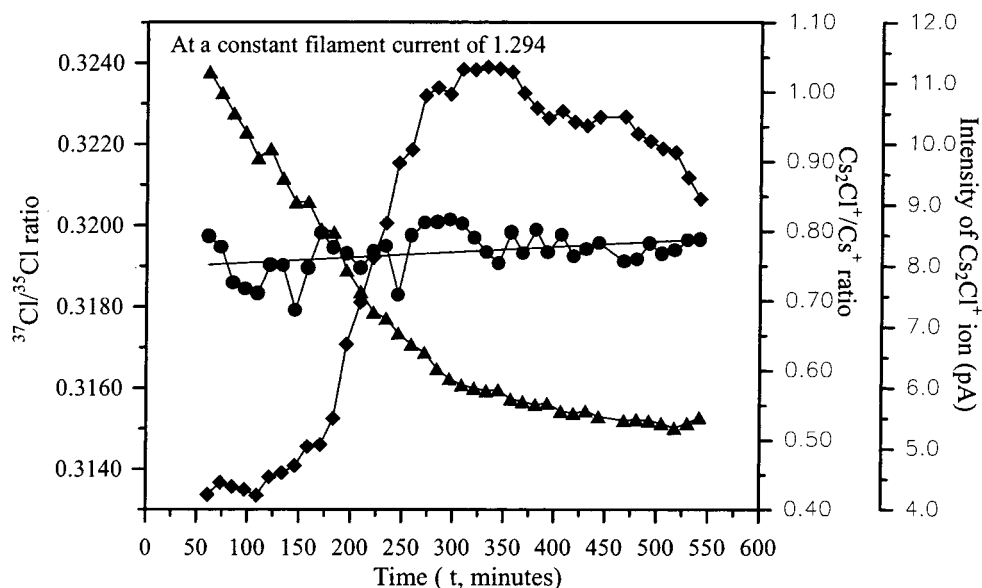


Figure 1. Variations of ³⁷Cl/³⁵Cl ratios, Cs₂Cl⁺/Cs⁺ ratios, and intensities of the Cs₂Cl⁺ ion peak for solutions doubly loaded with pH of 2.5. (●) ³⁷Cl/³⁵Cl ratio, $1.301 \times 10^{-6}t + 0.318\ 952$; average ³⁷Cl/³⁵Cl, $0.319\ 393 \pm 0.000\ 029$. (▲) Average Cs₂Cl⁺/Cs⁺ ratio is 0.6722. (◆) Average intensity of Cs₂Cl⁺ ion is 8.573 pA.

difference in the microstructure of the crystal planes (D002). All graphites were mixed with 80% ethanol/20% water to form a slurry. The measured ³⁷Cl/³⁵Cl ratios in ISL 354 corresponding to each kind of graphite and carbon powder are listed in Table 2. The results show that the ³⁷Cl/³⁵Cl ratios for ISL are strongly dependent on the kind of graphite. Graphite with different emission properties affects the precision and accuracy of isotopic determination of chlorine. The measured ³⁷Cl/³⁵Cl ratios using graphites 1, 5, and 6 are consistent and very close to the reported value of $0.319\ 025 \pm 0.000\ 038^{25}$ obtained using the same procedure mentioned above with graphite 5, which gives a high accuracy. In general, the measurement precision is better for measurements using graphites 1, 5, and 6. The precision of measurement using graphite 2 with low maximal distortion of crystal lattice is also better, but measured ³⁷Cl/³⁵Cl ratio using graphite 2 is little higher than that using graphites 1, 5, and 6. The reason for this cannot be cited at this time.

Effect of pH. The effect of the pH of the test solution on the measured ³⁷Cl/³⁵Cl ratio was reported by Xiao and Zhang.³ A suitable pH value of test solutions ranges from 2 to 5. In this study, the pH values of test solutions were examined over the range of 1–10.48 by adding HCl prepared from ISL 354 and Cs₂CO₃. The pH of the solution reflects the proportion of HCl and Cs₂CO₃. The

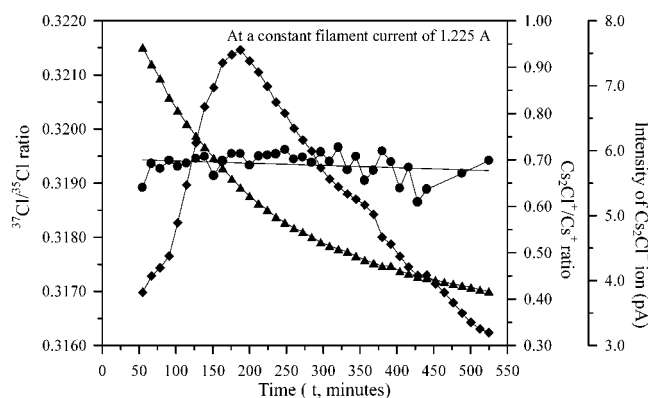


Figure 2. Variations of ³⁷Cl/³⁵Cl ratios, Cs₂Cl⁺/Cs⁺ ratios, and intensities of the Cs₂Cl⁺ ion peak for solutions doubly loaded with pH of 3.0. (●) ³⁷Cl/³⁵Cl ratio, $-4.203 \times 10^{-7}t + 0.319\ 452$; average ³⁷Cl/³⁵Cl, $0.319\ 341 \pm 0.000\ 019$. (▲) Average Cs₂Cl⁺/Cs⁺ ratio is 0.5791. (◆) Average intensity of Cs₂Cl⁺ ion is 5.264 pA.

pH value of a CsCl solution produced by the reaction of HCl and Cs₂CO₃, is 3.92. A pH of <3.92 or >3.92 shows excesses of HCl or Cs₂CO₃, respectively. For solutions with different pH, the ³⁷Cl/³⁵Cl ratio, Cs₂Cl⁺/Cs⁺ ratio, and intensity of the Cs₂Cl⁺ ion peak were measured for nearly 8 h at a constant filament current. The results are shown in Figures 1–5, which indicate the following:

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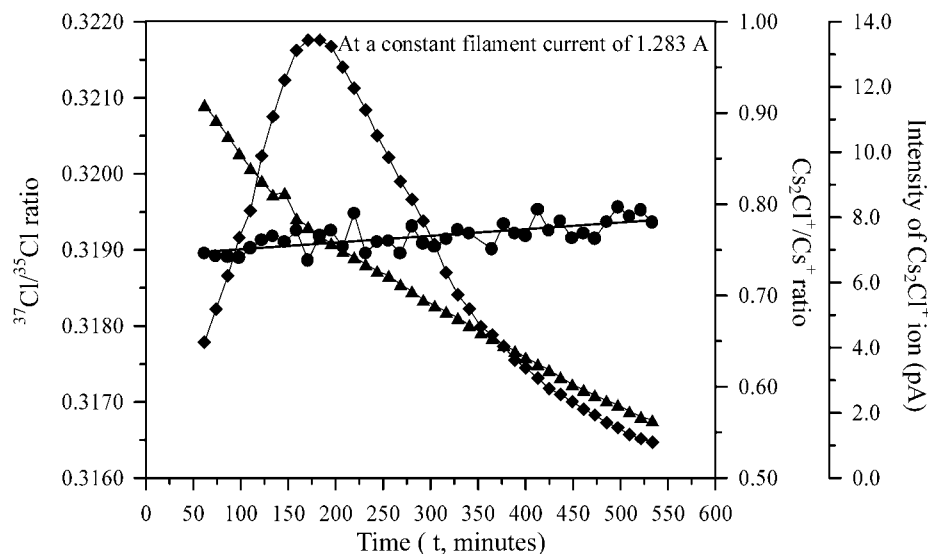


Figure 3. Variations of $^{37}\text{Cl}/^{35}\text{Cl}$ ratios, $\text{Cs}_2\text{Cl}^+/\text{Cs}^+$ ratios, and intensities of the Cs_2Cl^+ ion peak for solutions doubly loaded with pH of 4.0. (●) $^{37}\text{Cl}/^{35}\text{Cl}$ ratio, $7.682 \times 10^{-7}t + 0.318920$; average $^{37}\text{Cl}/^{35}\text{Cl}$, 0.319181 ± 0.000016 . (▲) Average $\text{Cs}_2\text{Cl}^+/\text{Cs}^+$ ratio is 0.7037. (◆) Average intensity of Cs_2Cl^+ (pA) is 6.430 pA.

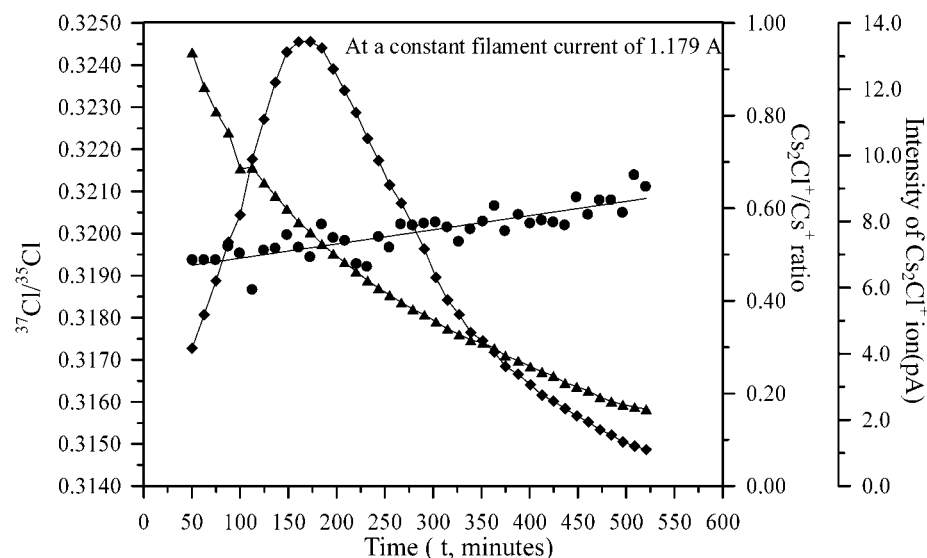


Figure 4. Variations of $^{37}\text{Cl}/^{35}\text{Cl}$ ratios, $\text{Cs}_2\text{Cl}^+/\text{Cs}^+$ ratios, and intensities of the Cs_2Cl^+ ion peak for solutions loaded with pH of 5.5. (●) $^{37}\text{Cl}/^{35}\text{Cl}$ ratio, $3.369 \times 10^{-6}t + 0.319076$; average $^{37}\text{Cl}/^{35}\text{Cl}$, 0.32004 ± 0.000038 . (▲) Average $\text{Cs}_2\text{Cl}^+/\text{Cs}^+$ ratio is 0.4229. (◆) Average intensity of Cs_2Cl^+ ion is 6.633 pA.

1. A strong and stable Cs_2Cl^+ ion beam is obtained for solutions with pH 2.5–5.5 for runs of more than 8 h. The Cs_2Cl^+ ion beam becomes weak and unstable with solutions of pH 6 or more.

2. The measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios usually increase with time over the course of an 8-h run. The variation can be described by the equation $Y = at + b$; here a is slope of the curve, which indicates the rate of change in measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios with time. The values of a are 1.30×10^{-6} for a solution with pH 2.5, -4.02×10^{-7} for a solution with pH 3.0, 8.79×10^{-7} for a solution with pH 4.0, 3.37×10^{-6} for a solution with pH 5.5, and 3.07×10^{-6} for a solution with pH 6. Data are acquired for only ~90 min in a normal measurement. According to the a values above, the variation of measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratio in a period of 90 min is only about 0.02–0.03%, which is comparable to the precision of the PTIMS procedure.

3. The results reported by Xiao et al.²³ indicated that the $\text{Cs}_2\text{Cl}^+/\text{Cs}^+$ ratio is a very important indicator for judging the

capabilities of thermal ion emission. We also hope to produce an intense Cs_2Cl^+ ion beam and restrain emission of Cs^+ ion here. The $\text{Cs}_2\text{Cl}^+/\text{Cs}^+$ ratios continually decrease with increasing time. This decrease is accompanied by an increase in the measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratio. This observation is consistent with results reported by both Xiao et al.²³ and Rosenbaum et al.¹⁴ The $\text{Cs}_2\text{Cl}^+/\text{Cs}^+$ ratios decrease from ~1 at the beginning to ~0.4 at the end for solutions of pH 2.5–5.5, but not for pH 6.0. The average $\text{Cs}_2\text{Cl}^+/\text{Cs}^+$ ratios in each loading are 0.6722 for solution of pH 2.5, 0.5791 for solutions of pH 3.0, 0.7037 for solutions of pH 4.0, 0.4229 for solutions of pH 5.5, and 0.04926 for solutions of pH 6.0. The low average $\text{Cs}_2\text{Cl}^+/\text{Cs}^+$ ratios suggest that a large fractionation occurs. As can be seen in Figures 1–5, the measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios are higher than usual when a solution of pH 6.0 is loaded.

Repeated measurements of $^{37}\text{Cl}/^{35}\text{Cl}$ ratios for loading solution with pH ranging from 1.03 to 10.48 are plotted in Figure 6. The results show that measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios are high for solutions

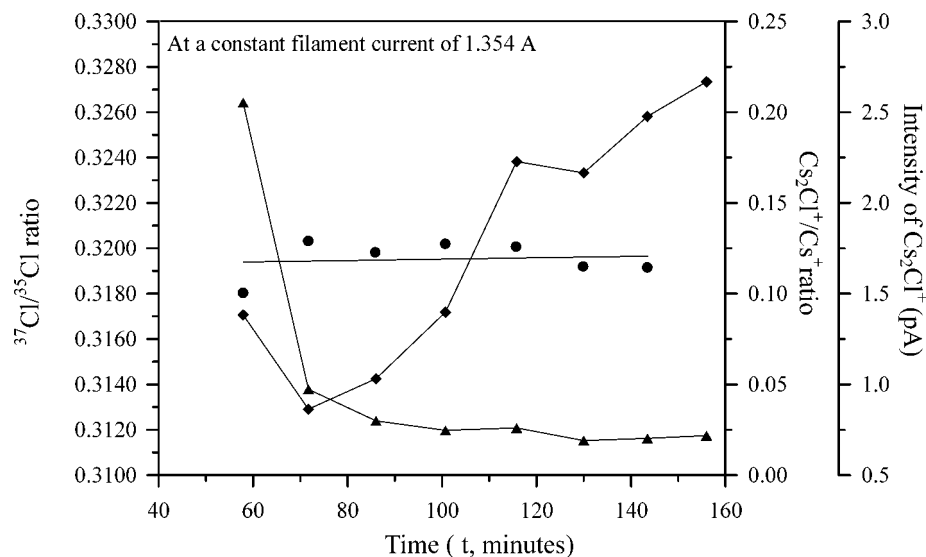


Figure 5. Variations of $^{37}\text{Cl}/^{35}\text{Cl}$ ratios, $\text{Cs}_2\text{Cl}^+/\text{Cs}^+$ ratios, and intensities of the Cs_2Cl^+ ion peak for solutions loaded with pH of 6.0. (●) $^{37}\text{Cl}/^{35}\text{Cl}$ ratio, $3.086 \times 10^{-6}t + 0.319213$; average $^{37}\text{Cl}/^{35}\text{Cl}$, 0.319522 ± 0.000179 . (▲) Average $\text{Cs}_2\text{Cl}^+/\text{Cs}^+$ ratio is 0.04926. (◆) Average intensity of Cs_2Cl^+ ion is 1.777 pA.

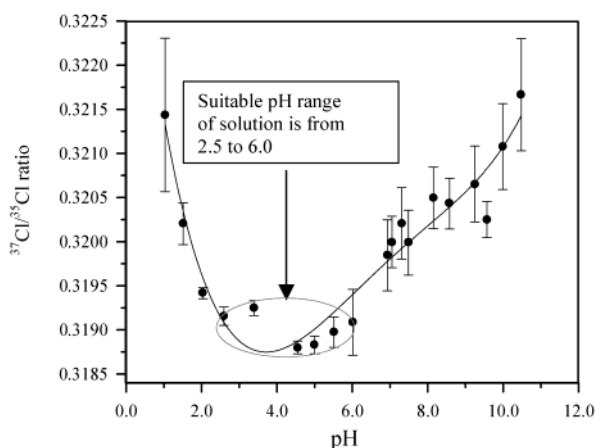


Figure 6. Measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios for solutions with different pH values.

with both low pH and high pH. According to our study, it thus appears that the suitable range of pH values is from 2.5 to 6.0, for which the measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios have high precision and accuracy. At low pH, fractionation tends to take place due to evaporation of excess HCl in the solution. The emission of Cs_2Cl^+ ion is perhaps suppressed by excess Cs^+ , and a normal ion beam will be emitted at higher temperature. The fractionation will take place due to quick decomposition of CsCl at higher temperature for a solution with high pH. As shown in Figure 7, Cs/Cl ratios are 0.9551 and 1.0616 for solutions with pH 2.5 and 5.5, respectively. This result indicates that a slight excess of Cl or Cs does not significantly affect measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios. As shown in Figure 6, however, large fractionations occur for samples with pH of <2.5 or ≥ 6.0 .

A stoichiometric (1:1) CsCl solution can generally be produced by passing sample solutions through a Cs-resin column. It is, however, possible to introduce small excesses of Cs or H^+ during sample preparation using this column if Cs in the column is not moved completely during the preparation of Cs-resin column and Cs-resin in the column is not enough to convert HCl to CsCl. The

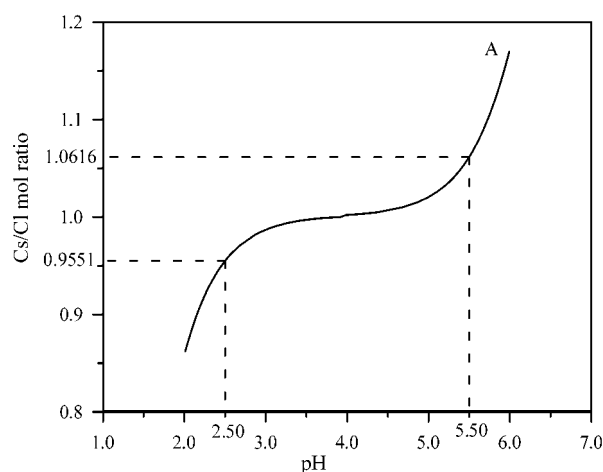


Figure 7. Cs/Cl ratios for solutions with pH ranging from 2.0 to 6.0 (line A). Cs/Cl ratios for the solution of pH 2.5 and 5.5 are 0.9551 and 1.0616, respectively (dashed lines).

pH of a sample solution prepared in the Cs-resin column should therefore always be measured, and solutions that are too acid or too alkaline should be discarded. This means that the sample preparation has failed.

Effect of Other Anions. Solutions of ISL 354 containing various amounts of NaNO_3 , and Na_2SO_4 were passed through columns filled with H-resin and Cs-resin and were converted to solutions of CsCl plus CsNO_3 and of CsCl plus Cs_2SO_4 . The measured isotopic compositions of chlorine in these mixed solutions are listed in Figures 8 and 9, which show that the measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios are much higher than the standard value of 0.319025. This occurs when the $\text{CsNO}_3/\text{CsCl}$ and the $\text{Cs}_2\text{SO}_4/\text{CsCl}$ ratios are greater than 1.0 and 3.0, respectively. Large amounts of NO_3^- and SO_4^{2-} and possibly other anions (e.g., F or organic liquids) in solution must be removed to obtain high-precision measurements.

The SO_4^{2-} can be removed as BaSO_4 by passing the solution through a column filled with Ba-resin. In general, the concentration of NO_3^- is much lower than that of Cl^- in natural samples;

Table 3. Effect of Removing SO_4 and NO_3

sample	measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratio			
	without removing SO_4 and NO_3		after removing SO_4 and NO_3	
	for single load	average $^{37}\text{Cl}/^{35}\text{Cl}$ ratio	for single load	average $^{37}\text{Cl}/^{35}\text{Cl}$ ratio
SO_4/Cl with mole ratio, 5	$0.320\,287 \pm 0.018\%$	$0.320\,344 \pm 0.000\,326\ (1\sigma)$	$0.319\,405 \pm 0.006\%$	$0.319\,379 \pm 0.000\,019\ (1\sigma)$
	$0.320\,935 \pm 0.013\%$		$0.319\,395 \pm 0.005\%$	
	$0.319\,810 \pm 0.005\%$		$0.319\,336 \pm 0.005\%$	
NO_3/Cl with mole ratio, 3	$0.320\,168 \pm 0.012\%$	$0.319\,983 \pm 0.000\,096\ (1\sigma)$	$0.319\,137 \pm 0.003\%$	$0.318933 \pm 0.000\,119\ (1\sigma)$
	$0.319\,934 \pm 0.003\%$		$0.318\,724 \pm 0.002\%$	
	$0.319\,848 \pm 0.005\%$		$0.318\,937 \pm 0.002\%$	

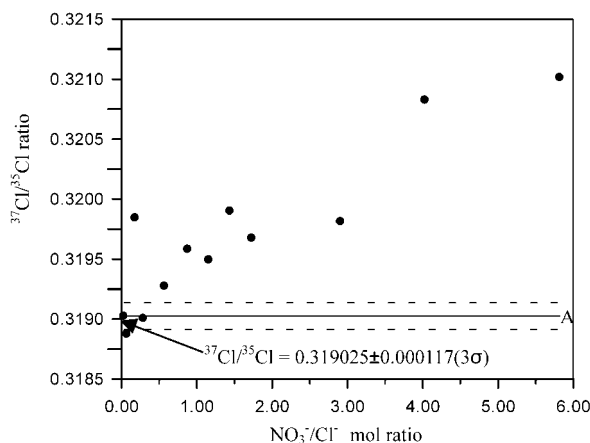


Figure 8. Variation of measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios with the $\text{NO}_3^-/\text{Cl}^-$ ratios in solution. The measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios are significantly higher when the $\text{NO}_3^-/\text{Cl}^-$ ratio in solutions are >1.00 . The solid line "A" expresses the reported $^{37}\text{Cl}/^{35}\text{Cl}$ ratio of 0.319 025, and dashed lines are its uncertainties (3σ).

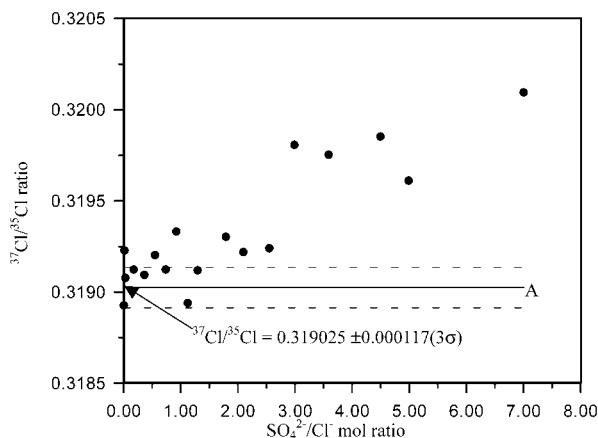


Figure 9. Variation of measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios with the $\text{SO}_4^{2-}/\text{Cl}^-$ ratios in solutions. The measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios are significant higher when the $\text{SO}_4^{2-}/\text{Cl}^-$ ratios in solutions are >3.00 . The solid line "A" expresses the reported $^{37}\text{Cl}/^{35}\text{Cl}$ ratio of 0.319 025 and dashed lines are its uncertainties (3σ).

thus, the presence of NO_3^- in the natural samples generally does not affect the measurement of the $^{37}\text{Cl}/^{35}\text{Cl}$ ratio. Any large amounts of NO_3^- can be removed by passing the solution through an Ag-resin column. The AgCl that is produced is held by the resin and can be dissolved by adding NH_4OH . The resulting solutions free of NO_3^- and SO_4^{2-} can then be passed sequentially through H-resin and Cs-resin columns. Thus, the isotopic compositions of chlorine in brines containing high concentration of

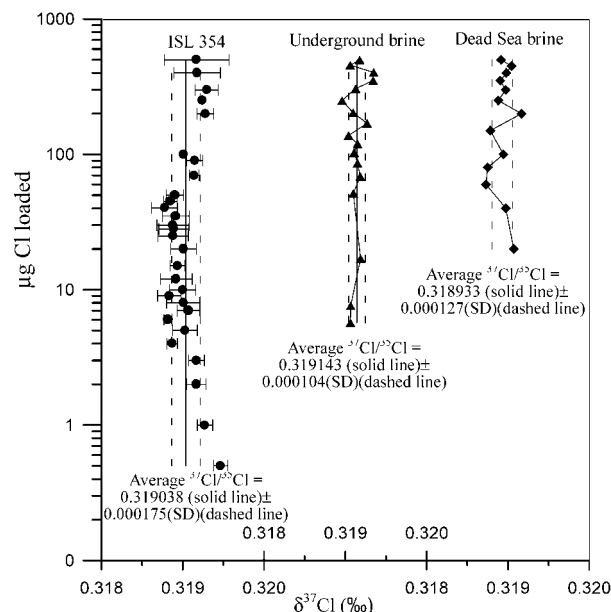


Figure 10. Variation of measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratio with micrograms of Cl loaded for ISL 354, underground brine, and Dead Sea brine loaded.

NO_3^- and SO_4^{2-} can be measured (Table 3). The procedures described above effectively eliminate the interference of NO_3^- and SO_4^{2-} and improve measurement precision.

Effect of the Amount of Loaded Chlorine. Rosenbaum et al.¹⁴ showed that the measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratio is highly sensitive to the amount of Cl on the filament. We also studied the effect of the amount of loaded chlorine in detail for three samples: ISL 354, an underground brine, and a Dead Sea brine. The amount of loaded chloride ranged from 0.5 (only for ISL 354) to 500 μg . The results are shown in Table 4 and plotted in Figure 10. Our result is inconsistent with the result reported by Rosenbaum et al.¹⁴ We did not observe any significant overall increase in the measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios of the three samples studied with the amount of Cl loaded within acceptable precision. However, the measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios are slightly higher for solutions loaded with $<1\ \mu\text{g}$ of Cl. An amount of Cl ranging from 2 to 10 μg was loaded for isotope analyses of chlorine in natural samples using the measurement of Cs_2Cl^+ ion. Thus, our results appear to indicate that the $^{37}\text{Cl}/^{35}\text{Cl}$ ratios are reasonably insensitive to the amount of Cl loaded on the filament when working with PTIMS.

CONCLUSIONS

$^{37}\text{Cl}/^{35}\text{Cl}$ ratios, based on the measurement of Cs_2Cl^+ ion with a graphite load, by thermal ionization mass spectrometry are

Table 4. Effect of the Amount of CsCl Loaded on the Filament^a

ISL 354 NaCl		underground brine		Dead Sea brine	
μg of Cl loaded	$^{37}\text{Cl}/^{35}\text{Cl}$ ratio	μg of Cl loaded	$^{37}\text{Cl}/^{35}\text{Cl}$ ratio	μg of Cl loaded	$^{37}\text{Cl}/^{35}\text{Cl}$ ratio
0.5	0.319 466 \pm 0.000 085 (6)	6	0.319 063 (1)	20	0.319 072 (1)
1	0.319 273 \pm 0.000 095 (8)	8	0.319 478 (2)	40	0.318 974 (2)
2	0.319 166 \pm 0.000 120 (6)	17	0.319 188 (2)	60	0.318 977 (1)
3	0.319 168 \pm 0.000 098 (12)	52	0.319 100 (1)	80	0.318 752 (2)
4	0.318 870 \pm 0.000 065 (5)	69	0.319 184 (2)	100	0.318 945 (2)
5	0.319 029 \pm 0.000 152 (9)	86	0.319 151 (2)	150	0.318 784 (2)
6	0.318 819 \pm 0.000 050 (5)	103	0.319 108 (2)	200	0.319 168 (2)
7	0.319 074 \pm 0.000 140 (6)	120	0.319 150 (2)	250	0.318 883 (1)
8	0.319 006 \pm 0.000 205 (7)	138	0.319 038 (2)	300	0.318 972 (1)
9	0.318 835 \pm 0.000 145 (5)	170	0.319 267 (1)	350	0.318 906 (2)
10	0.318 998 \pm 0.000 161 (6)	203	0.319 097 (2)	400	0.318 981 (2)
12	0.318 920 \pm 0.000 195 (5)	250	0.318 959 (1)	450	0.319 046 (1)
15	0.318 935 \pm 0.000 092 (5)	306	0.319 127 (3)	500	0.318 916 (2)
20	0.319 011 \pm 0.000 158 (7)	352	0.319 342 (4)		
25	0.318 881 \pm 0.000 188 (5)	404	0.319 349 (3)		
28	0.318 890 \pm 0.000 184 (5)	456	0.319 061 (2)		
30	0.318 881 \pm 0.000 199 (5)				
35	0.318 913 \pm 0.000 164 (7)				
40	0.318 775 \pm 0.000 160 (5)				
45	0.318 847 \pm 0.000 084 (5)				
50	0.318 904 \pm 0.000 106 (4)				
70	0.319 139 \pm 0.000 062 (3)				
90	0.319 146 \pm 0.000 100 (3)				
100	0.319 008 (2)				
200	0.319 279 \pm 0.000 104 (4)				
250	0.319 244 (1)				
300	0.319 294 \pm 0.000 141 (4)				
400	0.319 177 \pm 0.000 287 (3)				
500	0.319 170 \pm 0.000 398 (3)				

^a The numbers in parentheses are the numbers of measurement.

affected by emission characteristics of graphite, impurities in the sample, and the pH of the sample solution. Graphite with a large maximal distortion of crystal lattice, corresponding to an imperfect crystal lattice, should not be used for the high-precision isotopic measurement of chlorine. This study notes that measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios increase with the content of impurity anions, such as NO_3^- and SO_4^{2-} ions. It also shows that measured $^{37}\text{Cl}/^{35}\text{Cl}$ ratios are sensitive to the pH of the sample solution. Samples with pH lower than 2.5 and higher than 6.0 produced high $^{37}\text{Cl}/^{35}\text{Cl}$ ratios when the working solutions of CsCl were prepared using Cs_2CO_3 solution to neutralize HCl solution produced from the sample. Our results also show that $^{37}\text{Cl}/^{35}\text{Cl}$ ratios are relatively insensitive to

the amounts of Cl, ranging from 2 to 500 μg , loaded on the filament.

ACKNOWLEDGMENT

The authors express their gratitude to two anonymous reviewers for their useful comments. This project was supported by National Natural Foundation of China (40173013).

Received for review July 2, 2001. Accepted February 5, 2002.

AC0107352