Precise measurement of chlorine stable isotopic ratios by thermal ionization mass spectrometry

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An improved method for chlorine isotopic analysis by thermal ionization mass spectrometry of Cs_2Cl^+ has been investigated for precise measurement of $^{37}\text{Cl}/^{35}\text{Cl}$ isotopic ratios for small amount of samples. Chlorine in organic and inorganic samples was recovered as AgCl and converted to CsCl with metallic Mg and Cs -form ion exchange resin. The CsCl (containing 2 μg of Cl) was loaded on a Ta filament together with graphite powder. The $^{37}\text{Cl}/^{35}\text{Cl}$ ratio measurement was carried out using Cs_2Cl^+ ions with multi Faraday cup (static mode) for 80–100 min each single run. Replicate analysis of ocean water and laboratory standard (CsCl reagent) yield the in-run precision of 0.1–0.2‰ ($2\sigma_m$) for 300–400 ratios and external precision of 0.1–0.2‰ ($1\sigma_{SD}$). This method has been tested on a variety of chemical reagents including metal chlorides, hydrochloric acid and chlorinated organic solvents. It was found that the artificial chlorine compound show large variations of $^{37}\text{Cl}/^{35}\text{Cl}$ ratio (total ranges from –5 to +3‰ relative to standard mean ocean chloride) depending upon manufacturing processes. We suggest that the high sensitivity and precision technique established in this work would allow us to detect small isotopic variations of chlorine in small amounts of natural samples such as terrestrial materials (minerals/rocks, sediments, groundwater, etc., as well as environmental materials), meteorites and other planetary materials.

INTRODUCTION

Variations in the isotopic compositions of chlorine ($^{37}\text{Cl}/^{35}\text{Cl}$) are useful diagnostic tool for processes associated with important geochemical reactions in the atmosphere, surface fluids and the lithosphere (Hoefs, 1997). The chlorine isotopes are chiefly fractionated by phase change of Cl -bearing materials, e.g., evaporites crystallized from brine (Vengosh *et al.*, 1989; Eggenkamp *et al.*, 1995; Liu *et al.*, 1997; Lyons *et al.*, 1999), reaction between hydrous silicate minerals and aqueous phase (Eastoe and Guilbert, 1992; Magenheimer *et al.*, 1995; Ransom *et al.*, 1995), and volatilization of HCl from acidic aerosols (Volpe and Spivack, 1994; Volpe *et al.*, 1998; Lyons *et*

al., 1999). Although the isotopic abundances are generally utilized as conservative tracers in hydrology (Phillips, 1995), not only mixing of waters from different sources (Kaufmann *et al.*, 1993) but also difference of diffusion rate between $^{35}\text{Cl}^-$ and $^{37}\text{Cl}^-$ (Desaulniers *et al.*, 1986; Eggenkamp *et al.*, 1994), and ion filtration effect in clay layers (Phillips and Bentley, 1987) cause variation of Cl isotopic ratio in groundwater. The studies of nonconservative behavior of Cl have potential for constraining the distribution and chemical evolution of volatile elements on the Earth (Magenheimer *et al.*, 1995; Eggenkamp and Koster van Groos, 1997; Markl *et al.*, 1997).

Chlorinated organic compounds that are produced for industrial use or formed as by-product,

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have resulted in many environmental problems. Tanaka and Rye (1991) reported large variations of Cl isotopic compositions in some volatile organic compounds, and suggested that it could be used to quantify the flux of stratospheric Cl derived from artificial chlorinated compounds. Isotopic compositions of chlorinated organic solvents would also be useful to distinguish sources of groundwater contaminants (van Warmerdam *et al.*, 1995) and to evaluate their degradation in aquifers (Sturchio *et al.*, 1998).

Several techniques, involving electron impact ionization mass spectrometry (Boyd *et al.*, 1955; Hoering and Parker, 1961; Taylor and Grimsrud, 1969; Kaufmann *et al.*, 1984; Long *et al.*, 1993), negative thermal ionization mass spectrometry (Shields *et al.*, 1962; Vengosh *et al.*, 1989) and fast atom bombardment-mass spectrometry (Wastaway *et al.*, 1998) have been developed to determine the isotopic composition of Cl. However, the study of Cl isotopes was limited by lack of precision or sensitivity. Sensitivity of isotopic analysis is much important for the samples like meteorites and environmental pollutants because their size and concentration of Cl are sometimes limited.

Thermal ionization mass spectroscopy (TIMS) of Cs_2Cl^+ has small mass dependent fractionation, high sensitivity and low filament blank (Xiao and Zhang, 1992; Magenheimer *et al.*, 1994; Xiao *et al.*, 1995; Rosenbaum *et al.*, 2000). It has been used successfully in the investigation of brines (Liu *et al.*, 1997), aerosols (Magenheimer *et al.*, 1994; Volpe and Spivack, 1994; Volpe *et al.*, 1998), rocks (Magenheimer *et al.*, 1994; Magenheimer *et al.*, 1995; Boudreau *et al.*, 1997; Banks *et al.*, 2000), and subduction-zone pore waters (Ransom *et al.*, 1995) in magnetic scanning (peak jumping) mode.

In this work, in order to develop an improved method of the Cl isotopic analysis using TIMS which is applicable to tiny planetary materials, repeated analysis of ocean water and a reagent standard have been carried out in different conditions. We have established a high sensitivity, precision method which enable us to analyze Cl isotopes with precision of $\sim 0.1\text{‰}$ for 2 μg -size Cl,

demonstrated detailed methods and presented analytical results for ocean water and Cl-bearing commercial inorganic and organic reagents in this work.

EXPERIMENTAL PROCEDURES

Seawater samples and reagents

Seawater samples from the Pacific Ocean were taken during the KH-98-1 expedition by research vessel Hakuho-maru of the Ocean Research Institute (University of Tokyo). In addition, in order to find possible variation of Cl isotopic composition caused by human activities, coast water from Setouchi area (Setonaikai) was analyzed. The seawater samples were stored at -20°C until use, and filtered with a $0.45\text{ }\mu\text{m}$ membrane filter before pretreatment for isotopic measurement.

High purity CsCl (99.999% purity, Aldrich) and commercial grade CsCl ($>99\%$, Nacalai tesque; $>99\%$, Wako Pure Chemical Industries) were stored as 9.5 g/l (2g-Cl/l) solutions.

NaCl (99.99%, Matsunaga Chemical), HCl (reagent grade hydrochloric acid, Wako Pure Chemical Industries; High-purity HCl gas, Sumitomo Seika Chemicals), KCl ($>99.5\%$, Wako Pure Chemical Industries), tetrachloromethane ($>99\%$, Nacalai tesque), 1,1,1-trichloroethane (97%, Wako Pure Chemical Industries), 1,1-dichloroethene (99%, GL Sciences), trichloroethene ($>99.5\%$, Wako Pure Chemical Industries), and tetrachloroethene ($>99\%$, Wako Pure Chemical Industries) were used for Cl isotopic measurements. Other chemicals were analytical or reagent grades.

Ion chromatography

Analysis of chloride ion and other anions was performed on a Hitachi ion chromatograph L-7000. A 20 μl volume of the sample was injected into the mobile phase. Separations were performed with a Hitachi 2740 guard column and a Hitachi 2740 analytical column with a mixed eluent of 2.3 mM phthalic acid, and 2.5 mM 2-amino-2-hydroxymethyl-1,3-propanediol. A Shodex IC

YK-421 guard column and a Shodex IC YK-421 analytical column with a mixed eluent of 1.0 mM 2,6-pyridinedicarboxylic acid, 5.0 mM L-tartaric acid, and 24 mM boric acid were used for analysis of alkali metal and alkali earth ions.

Preparation of CsCl

Chloride ion in aqueous solution (seawater, dissolved inorganic reagents and decomposition products of organic compounds) was isolated as AgCl and converted into CsCl by the method of

Fig. 1. Procedures of CsCl preparation from seawater, inorganic reagents and chloride ion recovered from organic compounds.

Hoering and Parker (1961) and Magenheimer *et al.* (1994) with some modifications (Fig. 1). For analysis of chlorinated organic compounds, covalently bonded Cl atoms were liberated as Cl^- with sodium biphenyl reagent by the method of Liggett (1954) with some modifications (Fig. 2).

The chlorinated organic compounds (1.2 to 1.6 mg) were added to 2 ml of toluene in test tubes with screw stoppers. The reductive dechlorination reaction was performed under nitrogen atmosphere in a polyethylene bag to prevent degradation of the sodium biphenyl reagent with moisture and oxygen. The air in the bag was replaced with nitrogen gas, and 0.2 ml of sodium biphenyl reagent (1 M solution in dimethoxyethane, Dojindo Laboratory) was added to the each tube. After 30 min, 0.5 ml of water was added and shaken to

Fig. 2. Procedures of reductive dechlorination of chlorinated organic compounds with Na-biphenyl reagent.

extract Cl^- and to destroy the excess reagent. After separation of the lower aqueous layer, residual Cl^- was extracted with 0.5 ml of 1 M HNO_3 and 1 ml of H_2O respectively. The extracted fractions were combined and washed with 2 ml of toluene and n-hexane to remove organic compounds. Finally, the water layer was diluted to 10 ml with H_2O .

Sample solutions that contain 50 μg of Cl^- were put into polypropylene centrifuge tubes. Fifty microliters of 1 M HNO_3 and 100 μl of 30 mM AgNO_3 solution was added to each tube, and then kept for 2 hours at room temperature in the dark. The solution was centrifuged at 15,000 rpm for 5 min, and the supernatant was discarded. Precipitation of AgCl was washed with 500 μl of 0.01 M HNO_3 twice and 50 μl of H_2O once by centrifugation, and then 50 μl of 1 M NH_3 was added to dissolve the AgCl . In order to remove Ag ion, *ca.* 1 mg of Mg powder was added to the solution. After one-hour reaction, the solution was centrifuged and the supernatant was recovered. The precipitation was washed with 50 μl of water twice. All supernatant fractions were combined and evaporated to dryness on hot plate (120°C). The residue ($\text{NH}_4\text{Cl} + \text{MgCl}_2$) was dissolved in 50 μl of water and loaded on a column (i.d. 2 mm) that contained 0.1 ml of Cs-form cation exchange resin (DOWEX 50W $\times$ 8, 200–400 mesh). The column was washed with 170 μl of water. For the isotopic analysis of organic compounds, organic contaminants that would prevent ionization were removed from the eluent by addition of activated charcoal powder (1 mg, GL Sciences GX-60). The charcoal powder was washed with H_2O to remove Cl^- and then added to the eluent as suspension, after 30 min it was removed from the eluent by centrifugation. The concentration of the Cl^- in the eluent was measured by ion chromatography, and the eluent was evaporated to dryness on hot plate. The amount of Cl^- was calculated from the Cl^- concentration and volume of the eluent, and then water was added to the solid residue (CsCl) to form a 2 g- Cl/l solution.

Seawater samples were treated by a different procedure as follows. Seawater (*ca.* 25 μl , con-

taining 0.5 mg of Cl) was passed through Ba-form cation exchange resin (50W $\times$ 8, 0.2 ml in a column), and Cs-form cation exchange resin (50W $\times$ 8, 0.1 ml in a column). The eluent (*ca.* 250 μl) was recovered, and concentrations of Cs^+ and Cl^- were measured by ion chromatography.

Mass spectrometry

Measurements of isotopic composition were performed using a Finnigan MAT Model 262 thermal ionization mass spectrometer. This instrument has an equivalent radius of 64 cm and a 90° geometry. The instrument has five Faraday cup detectors, coupled to $10^{11} \Omega$ resistors, a secondary electron multiplier, and a retarding potential quadrupole system. Flat undegassed Ta ribbons (purity: 99.95%; 0.025×1.5 mm, Nilaco) were used for single filament mode measurements (Table 1).

The mass spectrometric procedure was the modified method of Xiao and Zhang (1992), Magenheimer *et al.* (1994), and Xiao *et al.* (1995). Two micrograms of chlorine as CsCl aqueous solution (9.5 g- $\text{CsCl}/\text{l} \times 1.0 \mu\text{l}$) and *ca.* 50 μg of graphite powder as a slurry in 80% ethanol were mixed on a polytetrafluoroethylene sheet. The mixture was loaded on the center of the filament and then dried with a filament current of 1.5 A. The filaments were loaded in the ion source of the mass spectrometer and the analysis was started when the pressure in the ion source reached less than 10^{-5} Pa. The filament current was automatically increased to 1.2 A in 10 min, and then increased manually to detect and focus $\text{Cs}_2^{35}\text{Cl}^+$ ion

Table 1. Conditions of mass spectrometry

Filament	undegassed Ta
Sample loading	
Amount of chloride ion	2 μg
pH	5–6
$\text{Cs}^+:\text{Cl}^-$ (molar ratio)	1:1
Drying (filament current)	1.5 A, 0.5 min
Filament current	
Preheat	0 $\rightarrow$ 1.2 A (0.12 A/min)
Measurement	1.42–1.48 A
Ion current ($\text{Cs}_2^{35}\text{Cl}^+$)	$2\text{--}5 \times 10^{-13}$ A

beam. The intensity of $\text{Cs}_2^{35}\text{Cl}^+$ ion current was adjusted to $(2-3) \times 10^{-13}$ A by the filament current, which was typically 1.4–1.5 A. In order to detect the target ions ($\text{Cs}_2^{35}\text{Cl}^+$: $m/z = 301$ and $\text{Cs}_2^{37}\text{Cl}^+$: $m/z = 303$), the accelerating voltage was set to 8 kV.

Data were acquired in static (multi-Faraday cup) mode for less than 100 min. Typically 400 to 500 ratios were collected in blocks from 20 to 25.

RESULTS AND DISCUSSION

Seawater

The results of Cl isotopic measurements of seawater ($8^\circ 39.5' \text{ N}$, $153^\circ 56.6' \text{ E}$) chloride are shown in Table 2 and Fig. 3. The results of runs 1 to 11 were obtained for chloride recovered by treatment with Ba and Cs-form ion exchange resin, and the results of runs 12 to 25 were obtained for those recovered as AgCl. The mean $^{37}\text{Cl}/^{35}\text{Cl}$ ratios obtained by latter method appear to be lower, but the difference was not significant. The recovery yield of Cl as CsCl ranged from 79 to 94%

Fig. 3. Chlorine isotopic compositions of seawater and a CsCl reagent for the period between June 1998 and July 1999. The seawater was taken from the Pacific Ocean ($8^\circ 39.5' \text{ N}$, $153^\circ 56.6' \text{ E}$) in March 1998 (Seawater-1: The seawater was treated with Ba-form resin and Cs-form resin; Seawater-2: The seawater was treated with AgNO_3 , Mg, and Cs-form resin). The commercial grade (purity: >99%) CsCl reagent was obtained from Nacalai tesque, Kyoto. Error bars represent $2\sigma_m$ (σ_m : internal standard error).

Table 2. Measured Cl isotopic compositions of the seawater sample ($8^\circ 39.5' \text{ N}$, $153^\circ 56.6' \text{ E}$, depth: 0 m)

Run	Ion exchange ^(a) $^{37}\text{Cl}/^{35}\text{Cl}^{(c)}$	Run	Recovered as AgCl ^(b) $^{37}\text{Cl}/^{35}\text{Cl}^{(c)}$
1	0.319852 ± 0.000018	12	0.319838 ± 0.000102
2	0.319806 ± 0.000031	13	0.319756 ± 0.000080
3	0.319885 ± 0.000027	14	0.319744 ± 0.000123
4	0.319760 ± 0.000033	15	0.319799 ± 0.000053
5	0.319821 ± 0.000021	16	0.319764 ± 0.000050
6	0.319734 ± 0.000015	17	0.319729 ± 0.000103
7	0.319849 ± 0.000027	18	0.319807 ± 0.000064
8	0.319797 ± 0.000022	19	0.319823 ± 0.000041
9	0.319856 ± 0.000026	20	0.319784 ± 0.000068
10	0.319811 ± 0.000041	21	0.319712 ± 0.000075
11	0.319857 ± 0.000029	22	0.319707 ± 0.000067
—	—	23	0.319811 ± 0.000050
—	—	24	0.319725 ± 0.000102
—	—	25	0.319834 ± 0.000070
average	$0.319821 \pm 0.000045^{(d)}$	average	$0.319774 \pm 0.000046^{(d)}$

^(a)Seawater was treated with Ba-resin and Cs-resin.

^(b)Seawater was treated with AgNO_3 , Mg and Cs-resin.

^(c)Error for the individual runs is $2\sigma_m$ (σ_m : standard error).

^(d)Error for the average value is $1\sigma_{SD}$ (σ_{SD} : standard deviation).

Table 3. Measured Cl isotopic compositions of seawater samples

Location	Depth (m)	Salinity (‰)	Temp. (°C)	Sampling date	$^{37}\text{Cl}/^{35}\text{Cl}^*$
Pacific Ocean					
8°39.5' N, 153°56.6' E	0	34.873	28.0	03/04/1998	0.319820 ± 0.000037 ($n = 7$)
12°06.9' N, 138°52.3' E	0	34.387	26.4	03/08/1998	0.319894 ± 0.000171 ($n = 5$)
12°58.4' N, 143°43.7' E	0	34.397	—	03/10/1998	0.319847 ± 0.000041 ($n = 3$)
18°12.9' N, 144°42.0' E	0	34.843	27.0	03/11/1998	0.319829 ± 0.000079 ($n = 4$)
18°12.7' N, 144°42.2' E	992	34.470	4.1	03/11/1998	0.319870 ± 0.000087 ($n = 4$)
18°12.7' N, 144°42.2' E	3235	34.667	1.7	03/11/1998	0.319883 ± 0.000091 ($n = 5$)
18°12.7' N, 144°42.2' E	3725	34.669	1.7	03/11/1998	0.319856 ± 0.000079 ($n = 6$)
26°30.2' N, 142°39.4' E	0	34.947	22.9	03/13/1998	0.319853 ± 0.000117 ($n = 4$)
Setonaikai					
34°38.3' N, 135°07.0' E	0	31.6	—	02/08/1998	0.319849 ± 0.000093 ($n = 4$)

*Error: $2\sigma_m$ (σ_m : external standard error).

Period of the analysis: June 1998–July 1998.

(average: 88%) by the AgCl-precipitation procedure.

The ion current intensities for runs 1 to 11 were higher ($4\text{--}7 \times 10^{-13}$ A) than values of runs 12 to 25 ($2\text{--}4 \times 10^{-13}$ A). Although the internal errors ($2\sigma_m$: standard error of the mean of individual ratios in each run) of runs 12 to 25 were larger than errors of runs 1 to 11 by difference of ion current intensity, there was no difference in external reproducibility ($1\sigma_{SD}$: standard deviation of the mean of individual runs) between both pretreatment procedures. The average value (0.319794 : run 1–25) was used as standard (standard mean ocean chloride: SMOC (Long *et al.*, 1993), $\delta^{37}\text{Cl} = 0\text{‰}$) in the following results.

Nine seawater samples from different locations were repeatedly analyzed (Table 3). Those samples were treated with Ba-form resin and Cs-form resin before isotopic measurement. The results revealed the isotopic composition of Cl in seawater is homogeneous as reported previously (Hoering and Parker, 1961; Kaufmann *et al.*, 1984). Hydrothermal activity was found near one of sampling point in the Pacific Ocean ($18^\circ 12.7'$ N, $144^\circ 42.2'$ E; depth 992 m: minimum salinity layer; depth 3235 m: center of plume from hydrothermal vent; depth 3725 m: just above seafloor). Because the samples were not directly collected from hydro-

thermal vent, hydrothermal fluid would be highly diluted with seawater. Even if isotopic composition of chloride in hydrothermal fluid was different from seawater, the influence on Cl isotopic composition in the samples might be negligible. A sample from the In-land Sea (Setonaikai) must be affected by industrial and municipal discharge, but no difference of $\delta^{37}\text{Cl}$ was observed.

CsCl reagents

Because NIST SRM 975 (NaCl) is not available now, there is no international standard for Cl stable isotopic composition. Although Cl in seawater is isotopically homogeneous with variations less than the analytical precision, it is possible that the analytical methods could be improved to detect these variations (Xiao *et al.*, 1995). In the case of mass spectrometry of CH_3Cl , reference CH_3Cl gas is introduced into the spectrometer, and ion beams are measured alternately in the sample and the reference for precise relative measurement (Long *et al.*, 1993; Musashi *et al.*, 1998). In order to compare precision and accuracy between laboratories and to check day-to-day reproducibility in a laboratory by thermal ionization mass spectrometry of Cs_2Cl^+ , CsCl reagent would be suitable as a laboratory reference standard.

Table 4. Measured Cl isotopic compositions of the CsCl reagent (Nacalai tesque, >99%)

Run	$^{37}\text{Cl}/^{35}\text{Cl}$	$\delta^{37}\text{Cl}$ (‰)
Directly loaded ^(a)		
1	0.318913 ± 0.000039	-2.76 ± 0.12
2	0.318948 ± 0.000049	-2.65 ± 0.15
3	0.318981 ± 0.000071	-2.54 ± 0.22
4	0.319020 ± 0.000057	-2.42 ± 0.18
5	0.319015 ± 0.000044	-2.44 ± 0.14
6	0.319007 ± 0.000040	-2.46 ± 0.13
7	0.318955 ± 0.000043	-2.62 ± 0.13
8	0.319047 ± 0.000033	-2.33 ± 0.10
9	0.319096 ± 0.000061	-2.18 ± 0.19
10	0.318862 ± 0.000054	-2.91 ± 0.17
11	0.318977 ± 0.000060	-2.55 ± 0.19
12	0.319067 ± 0.000057	-2.27 ± 0.18
13	0.319007 ± 0.000075	-2.46 ± 0.24
14	0.319072 ± 0.000086	-2.26 ± 0.27
15	0.318973 ± 0.000090	-2.57 ± 0.28
16	0.318943 ± 0.000048	-2.66 ± 0.15
17	0.319005 ± 0.000044	-2.47 ± 0.14
18	0.318902 ± 0.000053	-2.79 ± 0.17
19	0.319012 ± 0.000090	-2.45 ± 0.28
20	0.319065 ± 0.000070	-2.28 ± 0.22
average	0.318993 ± 0.000061 (1 σ_{SD})	-2.49 ± 0.21 (1 σ_{SD})
Recovered Cl ^(b)		
1	0.318896 ± 0.000040	-2.81 ± 0.12
2	0.319001 ± 0.000041	-2.48 ± 0.13
3	0.319071 ± 0.000055	-2.26 ± 0.17
4	0.318851 ± 0.000046	-2.95 ± 0.14
5	0.319030 ± 0.000047	-2.39 ± 0.15
average	0.318970 ± 0.000093 (1 σ_{SD})	-2.58 ± 0.29 (1 σ_{SD})

Error for the individual runs is 2 σ_m (σ_m : standard error).

^(a)CsCl reagent was directly loaded on the filaments.

^(b)Cl⁻ was recovered from CsCl as AgCl, and converted to CsCl.

In order to establish a laboratory standard, three lots of commercial CsCl reagents were analyzed (Tables 4 and 5). We noted that mass spectrometric runs of a commercial grade reagent (Nacalai tesque) were most successful in obtaining stable isotopic ratios over an extended time period (Fig. 3). On the other hand, ion currents from high purity CsCl (Aldrich, 99.999%) analyses were occasionally unstable and hence some data which are not given in Table 5 were of poor quality. The reason for the unstable runs of high purity CsCl is not clear. Therefore, we tentatively concluded that the Nacalai reagent was most safely

Table 5. Measured $\delta^{37}\text{Cl}$ values of the CsCl reagents

Run	Aldrich (99.999%) $\delta^{37}\text{Cl}$ (‰)	Wako (>99%) $\delta^{37}\text{Cl}$ (‰)
1	-0.74 ± 0.22	0.36 ± 0.15
2	-0.68 ± 0.41	0.15 ± 0.12
3	-0.81 ± 0.14	0.00 ± 0.14
4	-1.00 ± 0.15	-0.06 ± 0.15
5	-0.80 ± 0.22	
6	-0.66 ± 0.14	
7	-0.61 ± 0.43	
8	-0.96 ± 0.17	
9	-0.96 ± 0.23	
average	-0.80 ± 0.14 (1 σ_{SD})	0.11 ± 0.19 (1 σ_{SD})

Error for the individual runs is 2 σ_m (σ_m : standard error). CsCl was directly loaded on the filaments with graphite.

employed as a laboratory standard.

Xiao *et al.* have reported that the pH of loading solution affected on efficiency and stability of Cs₂Cl⁺ beam and that the optimum beam was obtained at pH = 2–5 (Xiao and Zhang, 1992). The pH values of CsCl solutions (56.4 mM) analyzed in this work were 5.7–6.1, which were slightly higher than these of Xiao and Zhang (1992).

Inorganic compounds

Isotopic composition of Cl recovered as AgCl from a CsCl reagent was measured to check isotopic fractionation by the procedure (Table 4). A significant difference was not observed between the composition obtained by this treatment and that of directly loaded CsCl reagent. The recovery yield of Cl ranged from 89 to 96% (average: 92%).

Four kinds of inorganic chlorine compounds were used for Cl isotopic measurement. Chloride ion (50 μg) in each compounds was recovered as AgCl and converted to CsCl (recovery yield: 88 to 96%, average: 93%). The range of $\delta^{37}\text{Cl}$ in the inorganic compounds, including CsCl, was -2.5 to +0.9‰ (Tables 4–6). Difference in raw materials, processing of salts and production of Cl₂ and HCl gas would cause differences of $\delta^{37}\text{Cl}$ in inorganic compounds.

Main resources of Cl are seawater, brine and

Table 6. Measured $\delta^{37}\text{Cl}$ values of the inorganic compounds

Run	HCl (gas) $\delta^{37}\text{Cl}$ (‰)	HCl $\delta^{37}\text{Cl}$ (‰)	NaCl $\delta^{37}\text{Cl}$ (‰)	KCl $\delta^{37}\text{Cl}$ (‰)
1	0.88 ± 0.14	-0.26 ± 0.33	-0.95 ± 0.34	-2.30 ± 0.31
2	1.03 ± 0.28	-0.24 ± 0.32	-1.04 ± 0.28	-2.26 ± 0.32
3	0.85 ± 0.16	-0.22 ± 0.25	-0.96 ± 0.47	-2.16 ± 0.37
4		0.05 ± 0.18	-0.70 ± 0.31	
average	0.92 ± 0.10 ($1\sigma_{\text{SD}}$)	-0.17 ± 0.15 ($1\sigma_{\text{SD}}$)	-0.91 ± 0.15 ($1\sigma_{\text{SD}}$)	-2.24 ± 0.07 ($1\sigma_{\text{SD}}$)

Error for the individual runs is $2\sigma_m$ (σ_m : standard error).

evaporites. Chlorine isotopic composition in seawater is homogeneous ($\delta^{37}\text{Cl}$: 0‰), and the variations in brine and halite is small (in most of the case $\delta^{37}\text{Cl}$: -1 to +1‰, Eggenkamp *et al.*, 1995; Liu *et al.*, 1997). Difference in raw materials would not be enough to explain the variation.

Crystallization of salts for purification from the raw materials and electrolysis for production of Cl_2 gas, the most important intermediate of chlorine industry may be the steps that cause the isotopic variation in manufacturing process of inorganic and organic chlorine compounds (Eggenkamp *et al.*, 1995; Johnston and Hutchinson, 1942; Madorsky and Straus, 1947).

Chlorinated organic compounds

The sodium biphenyl reagent, known as a reactive reductant, is used for complete extraction and qualification of organic chlorine in industrial waste. Although yield of reductive dechlorination from *ca.* 1 mg of chlorinated organic solvents was high (96 to 99%, average: 98%), yield of Cl recovery as CsCl (78 to 97%, average: 85%) was lower than the yield of CuO-oxidation methods for CH_3Cl preparation (Holt *et al.*, 1997; Jendrzewski *et al.*, 1997). Since isotopic fractionation in the procedure of CsCl preparation from Cl^- is negligible (Table 4), low recovery yield of the step would not be a problem during the analysis. Chloride ion was not detectable by ion chromatography through blank test of the pretreatment procedure. Possible contamination in the CsCl preparation step was less than 0.05% of Cl^- from organic compounds.

Five kinds of chlorinated aliphatic hydrocarbons were used for isotopic measurements, and the results were shown in Table 7. The variation of isotopic compositions (-5 to +3‰) was consistent with reported values, e.g., -6.8 to +2.6 (Tanaka and Rye, 1991), -2.9 to +4.1 (van Warmerdam *et al.*, 1995), -2.9 to +2.1 (Holt *et al.*, 1997), +1.0 to +3.9 (Jendrzewski *et al.*, 1997). The chlorinated organic solvents are formed by addition of Cl_2 or HCl to carbon of CH_4 , CH_3OH , C_2H_4 , C_2H_2 , C_3H_8 (Grayson, 1985). Chlorine kinetic isotope effects (k_{35}/k_{37}) on nucleophilic substitution by $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reaction mechanisms showed that ^{37}Cl is bound more firmly to the carbon atom than ^{35}Cl (Turnquist *et al.*, 1973). Therefore isotopic fractionation during the synthesis of chlorinated compounds would have a cumulative effect on isotopic variations of Cl_2 and HCl. More information on the manufacturing processes of the chlorinated organic compounds is necessary to qualify fractionation effects.

Comparison of mass spectrometric methods

Negative thermal ionization mass spectrometry (N-TIMS) of Cl^- from AgCl was developed by Shields *et al.* (1962). Vengosh *et al.* (1989) reported a simple procedure of N-TIMS using directly loaded geochemical samples. However, these techniques based on N-TIMS of Cl^- have high discrimination factor and large filament blank (Magenheim *et al.*, 1994). Their high sensitivity is suitable for Cl qualification by isotope dilution mass spectrometry (Heumann *et al.*, 1987;

Table 7. Measured $\delta^{37}\text{Cl}$ values of the chlorinated organic solvents

Run	Tetrachloromethane $\delta^{37}\text{Cl}$ (‰)	1,1,1-Trichloroethane $\delta^{37}\text{Cl}$ (‰)	1,1-Dichloroethene $\delta^{37}\text{Cl}$ (‰)	Trichloroethene $\delta^{37}\text{Cl}$ (‰)	Tetrachloroethene $\delta^{37}\text{Cl}$ (‰)
1	-0.22 ± 0.16	-4.89 ± 0.33	2.93 ± 0.15	-1.76 ± 0.16	-1.74 ± 0.17
2	-0.20 ± 0.19	-4.94 ± 0.25	3.20 ± 0.29	-1.80 ± 0.18	-1.50 ± 0.19
3	-0.79 ± 0.35	-5.20 ± 0.30	2.41 ± 0.25	-1.55 ± 0.23	-1.96 ± 0.30
4	-0.10 ± 0.20			-1.72 ± 0.23	-2.35 ± 0.27
5				-1.79 ± 0.27	
average	-0.33 ± 0.31 ($1\sigma_{\text{SD}}$)	-5.01 ± 0.16 ($1\sigma_{\text{SD}}$)	2.85 ± 0.40 ($1\sigma_{\text{SD}}$)	-1.72 ± 0.10 ($1\sigma_{\text{SD}}$)	-1.89 ± 0.36 ($1\sigma_{\text{SD}}$)

Error for the individual runs is $2\sigma_m$ (σ_m : standard error).

Shinonaga *et al.*, 1994), but they are not precise enough (uncertainty: 2‰) for isotopic analysis of most geochemical samples. This study showed that TIMS of Cs_2Cl^+ was sensitive and precise enough for some purpose.

Xiao *et al.* loaded CsCl solution after loading of graphite on the filaments, and Magenheim's procedure was opposite. In the former case, graphite repels aqueous solution. In the latter case, ethanol easily spread on the filaments. In order to load the samples and graphite as small and homogeneous spot on the Ta filament, CsCl solution and graphite slurry were mixed before loading. Coarse graphite powder gave high ion current, but the mixture of CsCl and graphite was fragile and easily dropped from filaments. In order to prevent dropping, graphite powder was crushed with an alumina mortar. Use of wider filaments (1.5 mm width) gave slightly high ion current and easier control of filament current.

The ion current intensity obtained in this study ($2\text{--}3 \times 10^{-13}$ A, 2 μg -Cl loaded) was much lower than the intensity reported by Xiao *et al.* (1995) (7×10^{-12} A, 10 μg -Cl loaded), but higher than the value reported by Magenheim *et al.* (1994) (4×10^{-14} A, 2 μg -Cl loaded). The Cl isotopic ratio of seawater measured in this study was 0.319794 ± 0.000051 (average of run 1–25 $\pm 1\sigma_{\text{SD}}$). This value is significantly higher than the one obtained by Xiao *et al.* (1995) (0.318988 ± 0.000049 ; $1\sigma_{\text{SD}}$), but similar to the ones reported by Magenheim *et al.* (1994) (0.31944 ± 0.00009 or 0.31970 ± 0.00008 ; $1\sigma_{\text{SD}}$). As many parameters

(e.g., amount of Cl, graphite species, Cl/graphite ratio, pH of sample solution, impurities) affect the mass spectrometry of Cs_2Cl^+ (Magenheim *et al.*, 1994; Xiao *et al.*, 1995, 2000; Banks *et al.*, 2000; Rosenbaum *et al.*, 2000), the main reason of the differences of ion current and isotopic ratio is not clear. The modifications of loading conditions and the use of the multi-Faraday cup mode employed in this work yielded precision better than or comparable (0.16‰) to the level previously reported (0.15‰ using 10 μg of Cl: Xiao *et al.*, 1995; 0.25‰ using 2 μg of Cl: Magenheim *et al.*, 1994) using a smaller sample size (2 μg of Cl).

Impurities or degradation products of some chlorinated organic solvent inhibited ionization of CsCl without activated charcoal treatment. Also, trace amount of impurity affected ionization of CsCl reagent, this effect would be more serious for organic compounds (external reproducibility: inorganic Cl, 0.1 to 0.2‰; organic Cl, 0.1 to 0.4‰). Although the precision of the measurements (0.10 to 0.40‰: external reproducibility, $1\sigma_{\text{SD}}$) was slightly lower compared to electron impact ionization mass spectrometry of CH_3Cl (0.07‰: Holt *et al.*, 1997; 0.04 to 0.32‰: Jendrzewski *et al.*, 1997), vacuum lines and furnaces are not necessary for the sodium biphenyl degradation procedure. Also, the mass spectrometry of CsCl requires smaller amounts of sample as chloride ion (50 μg), and it is possible that the organic chlorine sample quantity for the measurements could be reduced further.

Fig. 4. Results of chlorine isotopic measurements of seawater, inorganic reagents, and chlorinated organic solvents. CsCl reagents were purchased from three companies (Nacalai tesque, Aldrich, Wako Pure Chemicals). CT: tetrachloromethane (carbon tetrachloride), TCA: 1,1,1-trichloroethane, 1,1-DCE: 1,1-dichloroethene, TCE: trichloroethene, PCE: tetrachloroethene. Error bars are $2\sigma_m$ (σ_m : external standard error).

CONCLUSIONS

Thermal ionization mass spectrometry of Cs_2Cl^+ was applied for chlorine isotopic measurements of inorganic and organic chlorine compounds. Representative results in this study are shown in Fig. 4. The $\delta^{37}\text{Cl}$ range of inorganic samples (-2.5 to $+0.9\text{‰}$) was similar to the range of that of most Cl in surface and subsurface water. On the other hand, the range of $\delta^{37}\text{Cl}$ in organic compounds (-5.0 to $+2.9\text{‰}$) was almost twice as large.

The precision (external reproducibility) of the analytical method (0.1 to 0.4‰ ; $1\sigma_{\text{SD}}$) was not better than the precision of the mass spectrometry of CH_3Cl , but was precise enough to distinguish Cl isotopic composition of chlorine compounds. In order to reduce the error of the method, improvement of sample preparation and loading procedure are necessary because many factors affect CsCl ionization process. Since it was possible to reveal Cl isotopic fractionation in most of the reagents and perhaps natural materials using small

amounts of samples and without expensive equipment for pretreatment, this analytical procedure could be applied to solve geochemical, cosmochemical and environmental issues.

No variations in isotopic composition of seawater sample and commercial grade CsCl reagent from the corresponding average values were observed during the period of this study (more than 7 months). Thus, CsCl reagent can be used as laboratory reference standard.

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REFERENCES

- Banks, D. A., Green, R., Cliff, R. A. and Yardley, B. W. D. (2000) Chlorine isotopes in fluid inclusions: Determination of the origins of salinity in magmatic fluid. *Geochim. Cosmochim. Acta* **64**, 1785–1789.
- Boudreau, A. E., Stewart, M. A. and Spivack, A. J. (1997) Stable Cl isotopes and origin of high-Cl magmas of the Stillwater Complex, Montana. *Geology* **25**, 791–794.
- Boyd, A. W., Brown, F. and Lounsbury, M. (1955) Mass spectrometric study of natural and neutron-irradiated chlorine. *Can. J. Phys.* **33**, 35–42.
- Desaulniers, D. E., Kaufmann, R. S., Cherry, J. A. and Bentley, H. W. (1986) ^{37}Cl - ^{35}Cl variations in a diffusion-controlled groundwater system. *Geochim. Cosmochim. Acta* **50**, 1757–1764.
- Eastoe, C. J. and Guilbert, J. M. (1992) Stable chlorine isotopes in hydrothermal processes. *Geochim. Cosmochim. Acta* **56**, 4247–4255.
- Engenkamp, H. G. M. and Koster van Groos, A. F. (1997) Chlorine stable isotopes in carbonatites: evidence for isotopic heterogeneity in the mantle. *Chem. Geol.* **140**, 137–143.

- Eggenkamp, H. G. M., Middelburg, J. J. and Kreulen, R. (1994) Preferential diffusion of ^{35}Cl relative to ^{37}Cl in sediments of Kau Bay, Halmahera, Indonesia. *Chem. Geol. (Isotope Geosci. Sect.)* **116**, 317–325.
- Eggenkamp, H. G. M., Kreulen, R. and Koster van Groos, A. F. (1995) Chlorine stable isotope fractionation in evaporite. *Geochim. Cosmochim. Acta* **59**, 5169–5175.
- Grayson, M. (ed.) (1985) *Kirk-Othmer Concise Encyclopedia of Chemical Technology*. John Wiley & Sons, New York.
- Heumann, K. G., Gall, M. and Weiss, H. (1987) Geochemical investigations to explain iodine-overabundances in Antarctic meteorites. *Geochim. Cosmochim. Acta* **51**, 2541–2547.
- Hoefs, J. (1997) *Stable Isotope Geochemistry*. Springer-Verlag, Berlin, pp. 62–63.
- Hoering, T. C. and Parker, P. L. (1961) The geochemistry of the stable isotopes of chlorine. *Geochim. Cosmochim. Acta* **23**, 186–199.
- Holt, B. D., Sturchio, N. C., Abrajano, T. A. and Heraty, L. J. (1997) Conversion of chlorinated volatile organic compounds to carbon dioxide and methyl chloride for isotopic analysis of carbon and chlorine. *Anal. Chem.* **69**, 2727–2733.
- Jendrzewski, N., Eggenkamp, H. G. M. and Coleman, M. L. (1997) Sequential determination of chlorine and carbon isotopic composition in single microliter samples of chlorinated solvent. *Anal. Chem.* **69**, 4259–4266.
- Johnston, H. L. and Hutchison, D. A. (1942) Efficiency of the electrolytic separation of chlorine isotopes. *J. Chem. Phys.* **10**, 469–472.
- Kaufmann, R. S., Long, A., Bentley, H. and Davis, S. (1984) Natural chlorine isotope variations. *Nature* **309**, 338–340.
- Kaufmann, R. S., Frape, S. K., McNutt, R. and Eastoe, C. (1993) Chlorine stable isotope distribution of Michigan Basin formation waters. *Appl. Geochem.* **8**, 403–407.
- Liggett, L. M. (1954) Determination of organic halogen with sodium biphenyl reagent. *Anal. Chem.* **26**, 748–750.
- Liu, W. G., Xiao, Y. K., Wang, Q. Z., Qi, H. P., Wang, Y. H., Zhou, Y. M. and Shirodkar, P. V. (1997) Chlorine isotopic geochemistry of salt lakes in the Qaidam Basin, China. *Chem. Geol.* **136**, 271–279.
- 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.
- Lyons, W. B., Frape, S. K. and Welch, K. A. (1999) History of McMurdo Dry Valley lakes, Antarctica, from stable chlorine isotope data. *Geology* **27**, 527–530.
- Madorsky, S. L. and Straus, S. (1947) Concentration of isotopes of chlorine by the counter-current electromigration method. *J. Res. Natl. Bur. Stand.* **38**, 185–189.
- Magenheim, A. J., Spivack, A. J., Volpe, C. and Ransom, B. (1994) Precise determination of stable chlorine isotopic ratios in low-concentration natural samples. *Geochim. Cosmochim. Acta* **58**, 3117–3121.
- Magenheim, A. J., Spivack, A. J., Michael, P. J. and Gieskes, J. M. (1995) Chlorine stable isotope composition of the oceanic crust: Implications for earth's distribution of chlorine. *Earth Planet. Sci. Lett.* **131**, 427–432.
- Markl, G., Musashi, M. and Bucher, K. (1997) Chlorine stable isotope composition of granulites from Lofton, Norway: Implications for the Cl isotopic composition and for the source of Cl enrichment in the lower crust. *Earth Planet. Sci. Lett.* **150**, 95–102.
- Musashi, M., Markl, G. and Kreulen, R. (1998) Stable chlorine-isotope analysis of rock samples: New aspects of chlorine extraction. *Anal. Chim. Acta* **362**, 261–269.
- Phillips, F. M. (1995) The use of isotopes and environmental tracers in subsurface hydrology. *Rev. Geophys. Supplement*, 1029–1033.
- Phillips, F. M. and Bentley, H. W. (1987) Isotopic fractionation during ion filtration: I. Theory. *Geochim. Cosmochim. Acta* **51**, 683–695.
- Ransom, B., Spivack, A. J. and Kastner, M. (1995) Stable Cl isotopes in subduction-zone pore waters: Implications for fluid-rock reactions and the cycling of chlorine. *Geology* **23**, 715–718.
- Rosenbaum, J. M., Cliff, R. A. and Coleman, M. L. (2000) Chlorine stable isotopes; A comparison of dual inlet and thermal ionization mass spectrometric measurements. *Anal. Chem.* **72**, 2261–2264.
- Shields, W. R., Murphy, T. J., Garner, E. L. and Dibeler, V. H. (1962) Absolute isotopic abundance ratio and the atomic weight of chlorine. *J. Am. Chem. Soc.* **84**, 1519–1522.
- Shinonaga, T., Ebihara, M., Nakahara, H., Tomura, K. and Heumann, K. G. (1994) Cl, Br and I in igneous standard rocks. *Chem. Geol.* **115**, 213–225.
- Sturchio, N. C., Clausen, J. L., Heraty, L. J., Huang, L., Holt, B. D. and Abrajano, T. A., Jr. (1998) Chlorine isotope investigation of natural attenuation of trichloroethene in an aerobic aquifer. *Environ. Sci. Technol.* **32**, 3037–3042.
- Tanaka, N. and Rye, D. M. (1991) Chlorine in the stratosphere. *Nature* **353**, 707.
- Taylor, J. W. and Grimsrud, E. P. (1969) Chlorine isotopic ratios by negative ion mass spectrometry. *Anal.*

- Chem.* **41**, 805–810.
- Turnquist, C. R., Taylor, J. W., Grimsrud, E. P. and Williams, R. C. (1973) Temperature dependence of chlorine kinetic isotope effects for aliphatic chlorides. *J. Am. Chem. Soc.* **95**, 4133–4138.
- van Warmerdam, E. M., Frape, S. K., Aravena, R., Drimmie, R. J., Flatt, H. and Cherry, J. A. (1995) Stable chlorine and carbon isotope measurements of selected chlorinated organic solvents. *Appl. Geochem.* **10**, 547–552.
- Vengosh, A., Chivas, A. R. and McCulloch, M. T. (1989) Direct determination of boron and chlorine isotopic compositions in geological materials by negative thermal-ionization mass spectrometry. *Chem. Geol. (Isotope Geosci. Sect.)* **79**, 333–343.
- Volpe, C. and Spivack, A. J. (1994) Stable chlorine isotopic composition of marine aerosol particles in the western Atlantic Ocean. *Geophys. Res. Lett.* **21**, 1161–1164.
- Volpe, C., Wahlen, M., Pszeny, A. A. P. and Spivack, A. J. (1998) Chlorine isotopic composition of marine aerosols: Implications for the release of reactive chlorine and HCl cycling rates. *Geophys. Res. Lett.* **25**, 3831–3834.
- Wastaway, K. C., Koemer, T., Fang, Y. R., Rudziński, J. and Paneth, P. (1998) A new method of determining chlorine kinetic isotope effect. *Anal. Chem.* **70**, 3548–3552.
- Xiao, Y. K. and Zhang, C. G. (1992) High precision isotopic measurement of chlorine by thermal ionization mass spectrometry of the Cs_2Cl^+ ion. *Int. J. Mass Spectrom. Ion Proc.* **116**, 183–192.
- Xiao, Y. K., Zhou, Y. M. and Liu, W. G. (1995) Precise measurement of chlorine isotopes based on Cs_2Cl^+ by thermal ionization mass spectrometry. *Anal. Lett.* **28**, 1295–1304.
- Xiao, Y. K., Wei, H. Z., Zhou, Y. M., Wang, Y. H. and Liu, W. G. (2000) Investigation of characteristics of non-reductive thermal ion emission of various graphites in thermal ionization mass spectrometry. *Anal. Chim. Acta* **420**, 95–101.