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A secondary isotopic reference material of chlorine from selected seawater

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Abstract

A secondary isotopic reference material of chlorine as NaCl collected from a sea water, located at 4°18′N, 161°08′E and collected on October 22, 1994, was prepared using ion exchange technique. The $\delta^{37}Cl$ of an NaCl product named ISL 354 was measured to be $-0.39 \pm 0.05‰$ (2σ) related to NIST SRM 975, an isotopic standard reference material with an absolute $^{37}Cl/^{35}Cl$ ratio of 0.31977. No contamination or isotopic fractionation was observed due to a complete recovery of chlorine and the avoidance of chemical reagents during preparation of ISL 354 from selected seawater. The isotopic composition of chlorine in ISL 354 does not change on long-term storage. So ISL 354 can be used as a secondary isotopic reference material of chlorine.

Keywords: $^{37}Cl/^{35}Cl$; Reference material; Seawater

1. Introduction

Chlorine has two naturally occurring isotopes, ^{35}Cl and ^{37}Cl. A significant variation in the chlorine isotopic composition in nature had not been observed till the development of procedure by Kaufmann et al. (1984) for high-precision isotopic measurement of chlorine based on CH_3Cl^+ ion. Using this method, the variation of chlorine isotopic composition in nature was confirmed. A few reports show that the isotopic compositions of chlorine in seawater are identical (Kaufmann et al., 1984, Long et al., 1993) within the measured precision. So seawater was usually used as standard mean ocean chlorine (SMOC) in studies of isotopic geochemistry of chlorine in nature instead of the isotopic standard reference material of chlorine NIST SRM 975 (Shields et al., 1962), which is no longer available. However, the term of SMOC is a misnomer—no accepted Cl-isotope ocean water standard currently exists. Seawaters from different locations are used by different laboratories for calibration. The seawaters being used as SMOC were collected from the Sargasso Sea and supplied by Ocean Scientific International, GPS1 (Banks et al., 2000; Rosenbaum et al., 2000), from the Pacific coast at San Diego (Eastoe and Guilbert, 1992; Long et al., 1993) and from the pier at Scripps Institution of Oceanography pier (Magenheim et al.,

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1994; Ransom et al., 1995; Volpe and Spivack, 1994), from Madeira, Atlantic Ocean (Eggenkamp and Schuiling, 1995; Eggenkamp et al., 1995), from the Atlantic Ocean at 35°24″N, 8°44″W (Gregor et al., 1997) and from the Indian Ocean at 80°00″E, 63°58″S (Liu et al., 1997; Xiao et al., 2000). The location from which the standard seawater is collected may be unimportant since the chlorine isotopic composition of seawater appears to be uniform, however variation of $\delta^{37}Cl$ in seawater may be present in unusual cases. A recent study showed that the $\delta^{37}Cl$ values of seawaters at the Central Indian Ridge at 66°21′E; 10°43′S (VM), 68°04′E; 5°39′S (VT4) and 67°33′E; 5°39′S (VT6) have high $\delta^{37}Cl$ values (0.59‰, 0.82‰ and 0.94‰, respectively) (unpublished data). No reasonable explanation for these

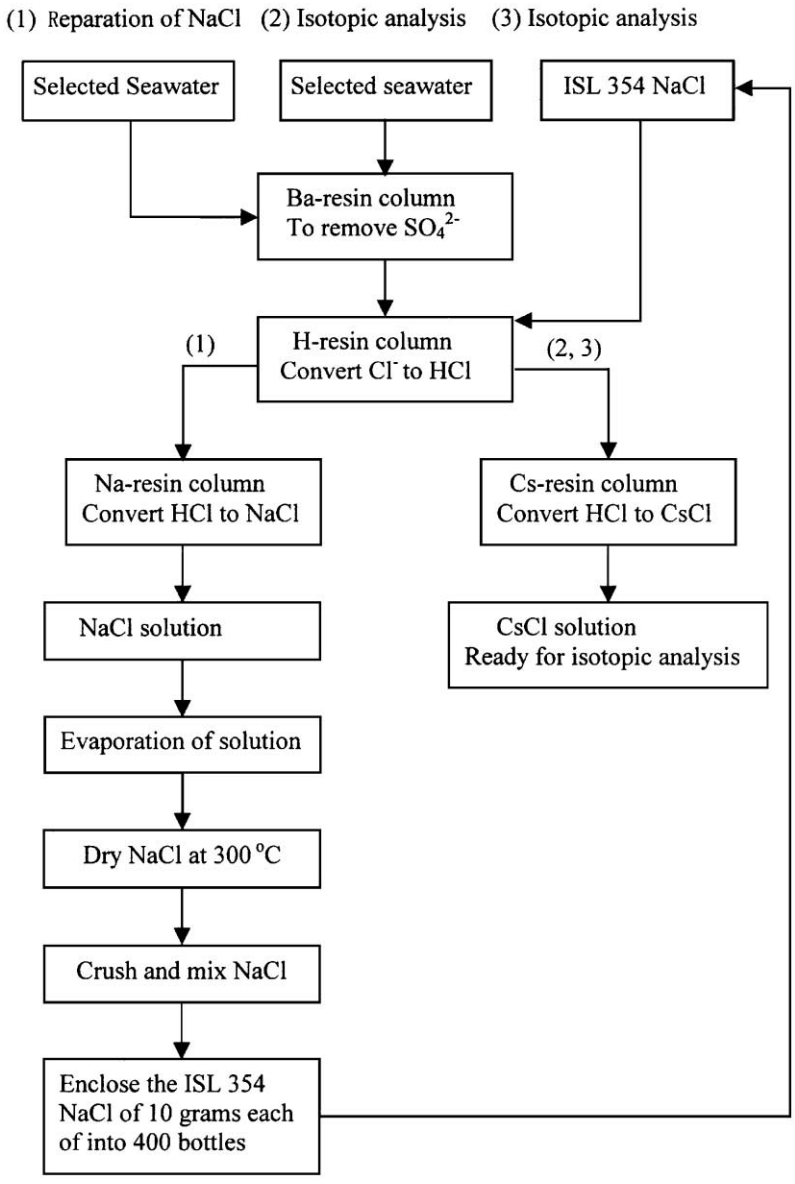

Fig. 1. Diagrammatic sketch of the preparation procedure of ISL 354 from the selected seawater.

results was found. Given the possibility of isotopic variation among the seawater standards used by different laboratories, it would be a great advantage to have a single, homogeneous seawater chloride sample to serve as a standard for the study of stable Cl isotopes.

2. Experimental

2.1. Reagents and the preparation of ion exchange resin column

Spectroscopic-grade graphite powder was mixed with 80% ethanol–20% water (v/v) to form a slurry. A normal cation exchange resin (Shanghai 732) was used in this study. High-purity water was produced by sub-boiling distillation, and high purity $Ba(NO_3)_2$, $NaNO_3$ and Cs_2CO_3 (converted to CsOH before using) were used for the preparations of Ba-resin, Na-resin and Cs-resin, respectively. No another chemical reagents were used in this study.

A glass column "A" with a diameter of 5.5 cm for the preparation of NaCl from seawater and a plastic column "B" with a diameter of 0.8 cm for isotopic analyses were used. Strongly acidic resin (Shanghai No 732) was loaded into the columns. The heights of the resin beds were 107 cm for column "A" and 1.0 cm for column "B" and the resins in the columns were eluted with 2 mol/l HNO_3 until all the resins in column were converted to H-resin form. The solutions of $Ba(NO_3)_2$, $NaNO_3$ and Cs_2CO_3 were passed through the H-resin column for the preparations of Ba-resin, Na-resin and Cs-resin, respectively, after the columns were rinsed with high-purity water to attain neutrality. The columns were rinsed again with high-purity water until Ba^{2+}, Na^+ and Cs^+ ions are not being detected in solution.

2.2. Collection of seawater

The surface seawater sample (150 kg) used to develop an isotopic reference material of chlorine was collected on October 22, 1994. The seawater was collected from the Pacific Ocean at a location of 4°18′N, 161°09′E, which is sufficiently away from the continent to prevent contamination from river waters.

2.3. Preparation of NaCl product from seawater

The chlorine extracted as NaCl was named ISL 354. It can be permanently stored without changing the isotopic composition of chlorine. The process for extraction and purification of chlorine for isotopic measurement of ISL 354 and the selected seawater is shown in Fig. 1.

The selected seawater was sequentially passed through the columns filled with Ba-resin, H-resin and Na-resin. The Cl content of the column effluent was monitored. All effluent prior to the detection of chloride was discarded. This effluent liquids are actual water retained by the columns. In this process, the chlorine blank from high-purity water was eliminated and chlorine in selected seawater was completely recovered with no isotopic fractionation. So the isotopic composition of ISL 354 accurately reflects that of the selected seawater. The solution of NaCl collected from the Na-resin column was evaporated to dryness at a temperature below 80 °C and then dried in a super-clean environment at 300 °C till the weight of NaCl remained constant. The NaCl was stored in plastic bottles after being crushed and mixed.

The sample solution with chloride concentration of 10–15 mg Cl/ml was continuously passed through the Ba-resin (only for the selected seawater sample), H-resin and Cs-resin columns. The effluent liquids through the columns were collected when Cl^- ions were detected. The solution of CsCl was used for isotopic measurement of chlorine.

2.4. Mass spectrometry

The mass spectrometry is basically the same as that reported by Xiao and Zhang (1992) and Xiao et

Table 1
The chemical compositions (%, w/w) of NaCl in ISL 354 NaCl

Ions	Cl^-	SO_4^{2-}	NO_3^-	Br^-	I^-	Mg^{2+}	K^+	NaCl	Impurities[a]
Contents	60.3	0.01	$< 8 \times 10^{-4}$	0.11	4.5×10^{-6}	0.01	0.10	99.5	$\leqslant 0.5\%$

[a] Impurities are total amount of all ions except for Na^+ and Cl^- ions.

al. (1995) and is as follows: A VG 354 thermal ionization mass spectrometer, made in VG Isotope, England, was used for chlorine isotopic measurements. The single tantalum filament ($0.75 \times 0.076 \times 0.0025$ cm) heated at a current of 3.0 A for 1 h in a vacuum system, was first treated with the graphite slurry of 3 μl to coat the center of the filament. The sample solution containing Cl of about 10 μg as CsCl was loaded when the graphite was near to dryness and then dried by passing a current of 1.0 A through the filament for 5 min. The sample was then loaded into the mass spectrometer. The current through the filaments was increased to 0.8 A in 10 min. The Cs_2Cl^+ ion was monitored and used to focus the instrument. The intensity of the Cs_2Cl^+ ion beam was adjusted to $5–6 \times 10^{-12}$ A by controlling the filament current, which was typically 1.0–1.2 A producing a temperature of 230–250 °C. The filament temperature was measured by an improved electric thermo-couple. The ion intensities at m/z of 301 ($^{133}Cs_2{}^{35}Cl^+$) and 303 ($^{133}Cs_2{}^{37}Cl^+$) were measured by magnetically switching between the two peaks. The $^{37}Cl/^{35}Cl$ ratio equals to the ratio of ion intensities of m/z 303 peak to 301 peak. The $\delta^{37}Cl$ value of the secondary isotopic reference material of seawater is calculated as follows:

$$\delta^{37}\mathrm{Cl}(‰) = \left\{\left[\left(^{37}\mathrm{Cl}/^{35}\mathrm{Cl}\right)_{\mathrm{sam}} \div \left(^{37}\mathrm{Cl}/^{35}\mathrm{Cl}\right)_{975}\right] - 1\right\} \times 1000,$$

where $(^{37}Cl/^{35}Cl)_{975}$ is the measured isotopic composition of chlorine in NIST SRM 975, 0.319519 ± 0.000089 using the same chemical and mass spectrometric procedures as for samples (cf. the absolute value, 0.31977).

3. Results

3.1. Purity of ISL 354

The chemical composition of seawater shows characteristically high Cl^- with minor SO_4^{-2} and trace NO_3^-, Br^- and I^-. The NO_3^-, Br^- and I^- ions cannot be removed using the described process of sample preparation, so ISL 354 retains all of NO_3^-, Br^- and I^- ions from the seawater. These are the main impurities in ISL 354 and constitute less than 0.5% by weight (Table 1). The impurities in ISL 354 have no matrix effects for the isotopic measurement of chlorine based on the measurement of Cs_2Cl^+ ion.

3.2. Homogeneity of $\delta^{37}Cl$ in ISL 354

The homogeneity of the isotopic composition of chlorine in ISL 354 is important. Fourteen of 400 bottles containing ISL 354 were randomly analyzed for isotopic compositions of chlorine. Sixteen beads, including ISL 354 in 14 bottles, one selected seawater, and one NIST SRM 975 were run together on each wheel. The sample beads were randomly ordered. The results are shown in Table 2 and plotted in Fig. 2. The discrepancy of $^{37}Cl/^{35}Cl$ ratios in ISL 354 is less than 0.006% with an average $^{37}Cl/^{35}Cl$ ratio of 0.319393 ± 0.000018.

3.3. The $\delta^{37}Cl$ value and corrected $^{37}Cl/^{35}Cl$ ratio in ISL 354 produced from selected seawater

The $^{37}Cl/^{35}Cl$ ratio of NIST SRM 975, an isotopic standard reference material of chlorine with absolute $^{37}Cl/^{35}Cl$ ratio of 0.31977 ± 0.00081, was measured together with ISL 354. The average measured $^{37}Cl/^{35}Cl$ ratio of NIST SRM 975 for nine repeated measurements is 0.319519 ± 0.000089 (2σ). The corrected factor from instrument system is $0.31977/0.319519 = 1.000786$. The measured $\delta^{37}Cl$ values in 14 ISL 354 bottles are shown in Table 2 and plotted in Fig. 3. The average $\delta^{37}Cl$ value of ISL 354 is $-0.39 \pm 0.06‰$ (2σ) related to NIST SRM 975. The corrected $^{37}Cl/^{35}Cl$ ratio of ISL 354 relative to NIST SRM 975 is 0.319644 ± 0.000917. The uncertainty of $^{37}Cl/^{35}Cl$ ratio is mainly from that of NIST SRM 975.

In order to compare results with another laboratory, three measurements each of SRM 975 and ISL 354 were made by isotope ratio mass spectrometry (IRMS) on CH_3Cl at the University of Arizona (Table 3). Long et al. (1993) had previously reported a value of $0.52 \pm 0.02‰$ (1σ) for SRM 975 relative to their sample of seawater chloride. The new result

Table 2
The measured $^{37}Cl/^{35}Cl$ ratios and $\delta^{37}Cl$ values in ISL 354 NaCl, selected seawater and NIST SRM 975

Measured isotopic composition of chlorine in ISL 354							
Number (bottle)	1 (15)	2 (23)	3 (30)	4 (69)	5 (75)	6 (131)	7 (134)
$R_{37/35}$	0.319400	0.319379	0.319409	0.319402	0.319346	0.319448	0.319408
(2σ)	$\pm$0.000057	$\pm$0.000101	$\pm$0.000131	$\pm$0.000066	$\pm$0.000106	$\pm$0.000110	$\pm$0.000096
$\delta^{37}Cl$	$-$0.37	$-$0.44	$-$0.34	$-$0.37	$-$0.54	$-$0.22	$-$0.35
‰ (2σ)	$\pm$0.18	$\pm$0.32	$\pm$0.41	$\pm$0.21	$\pm$0.33	$\pm$0.34	$\pm$0.30
Run Times	8	7	7	8	6	9	7
Number (bottle)	8 (179)	9 (197)	10 (231)	11 (311)	12 (314)	13 (388)	14 (399)
$R_{37/35}$	0.319364	0.319369	0.319460	0.319399	0.319395	0.319385	0.319340
2σ	$\pm$0.000103	$\pm$0.000100	$\pm$0.000062	$\pm$0.000100	$\pm$0.000067	$\pm$0.000109	$\pm$0.000055
$\delta^{37}Cl$	$-$0.48	$-$0.47	$-$0.18	$-$0.38	$-$0.39	$-$0.42	$-$0.56
‰ (2σ)	$\pm$0.32	$\pm$0.31	$\pm$0.19	$\pm$0.31	$\pm$0.21	$\pm$0.34	$\pm$0.17
Run times	7	7	6	8	7	6	7
Average isotopic composition of chlorine in ISL 354 NaCl	$^{37}Cl/^{35}Cl$ ratio	0.319393 $\pm$ 0.000018 (2σ, $n = 14$)					
	$\delta^{37}Cl$ (‰)	-0.39 ± 0.06 (related to NIST SRM 975)					

Measured isotopic composition of chlorine in the selected seawater	
$^{37}Cl/^{35}Cl$ ratio	0.319400 $\pm$ 0.000073 (2σ, $n = 7$)
$\delta^{37}Cl$ (‰)	-0.37 ± 0.23 (related to NIST SRM 975)

Calculated isotopic composition of chlorine in mean seawater[a]	
$^{37}Cl/^{35}Cl$ ratio	0.319409 (41 seawater samples)
$\delta^{37}Cl$ (‰)	-0.34 (related to NIST SRM 975)

Measured isotopic composition of chlorine in NIST SRM 975	
$^{37}Cl/^{35}Cl$ ratio	0.319519 $\pm$ 0.000089 (2σ, $n = 9$)
$\delta^{37}Cl$ (‰)	0.0 ± 0.28 (isotopic standard of chlorine)

[a] The isotopic composition of chlorine for mean ocean is calculated based on the two measured $^{37}Cl/^{35}Cl$ ratios of 0.319025 and 0.319400 for the selected seawater reported previously (Xiao et al., 1998) and this study, as well as the average measured $^{37}Cl/^{35}Cl$ ratio of 0.319034 for the seawater in Pacific and Indian Ocean (Xiao et al., 1998).

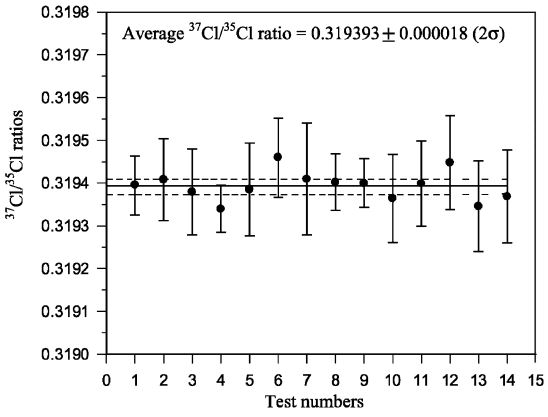

Fig. 2. The measured isotopic compositions of chlorine in ISL 354.

for SRM 975 differs slightly from the 1993 result, but the difference between SRM 975 and ISL 354, 0.38 ± 0.03‰, agrees closely with the difference determined by thermal ionization measurements.

3.4. The difference of chlorine isotopic compositions between ISL 354 and original selected seawater and mean seawater

The chlorine isotopic composition of the selected seawater, from which ISL 354 was produced, was measured together with the ISL 354. The average measured $^{37}Cl/^{35}Cl$ ratio in the selected seawater is 0.319400 ± 0.000073 (2σ) with the $\delta^{37}Cl$ value of -0.37 ± 0.23‰ (2σ). The corrected $^{37}Cl/^{35}Cl$ ratio

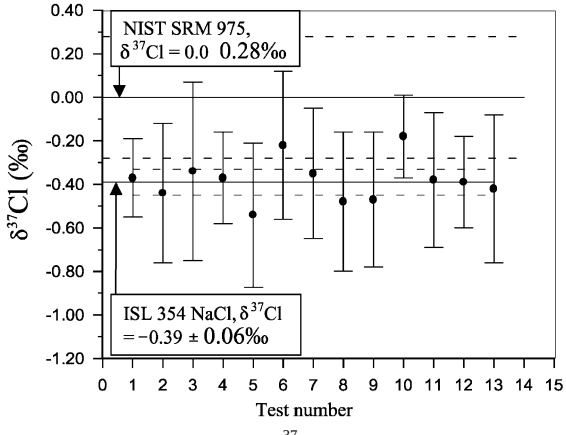

Fig. 3. The measured $\delta^{37}Cl$ values in ISL 354.

Table 3
IRMS measurements, University of Arizona

Material	*n*	Mean $\delta^{37}Cl$ (‰)	σ	Standard error
SRM 975	3	0.43	0.044	0.025
ISL 354	3	0.05	0.020	0.012
Difference		0.38 ± 0.03		

of original selected seawater relative to NIST SRM 975 is 0.319651 ± 0.000972. The difference between $\delta^{37}Cl$ value of the ISL 354 and that of the original selected seawater is -0.02‰, which is within the measurement precision in this study.

The average isotopic compositions of chlorine in 41 ocean water samples and the selected seawater were recently reported to be 0.319034 and 0.319025 (Zhou et al., 1998). The recently reported $^{37}Cl/^{35}Cl$ ratio of 0.319025 is different from the measured $^{37}Cl/^{35}Cl$ ratio of 0.319400 in this study for the same selected seawater due to the use of a different kind of graphite. The isotopic compositions of chlorine in other seawaters were not measured in this study. However, a normalized $^{37}Cl/^{35}Cl$ value and $\delta^{37}Cl$ value of mean seawater can be calculated to be 0.319409 and -0.34‰ relative to SRM 975 based

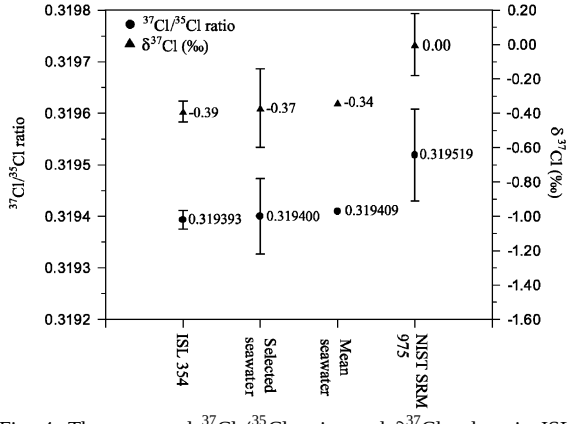

Fig. 4. The measured $^{37}Cl/^{35}Cl$ ratios and $\delta^{37}Cl$ values in ISL 354, selected seawater and NIST SRM 975. The measured $^{37}Cl/^{35}Cl$ ratios in ISL 354, selected seawater, mean seawater and NIST SRM 975 are 0.319393 ± 0.000018, 0.319400 ± 0.000073, 0.319409 and 0.319519 ± 0.000089, respectively. The $\delta^{37}Cl$ values of ISL 354, selected seawater and mean seawater relative to NIST SRM 975 are -0.39 ± 0.06‰, -0.37 ± 0.23‰, and -0.34‰, respectively.

on the above data. The $^{37}Cl/^{35}Cl$ values and $\delta^{37}Cl$ values in ISL 354, the selected seawater, mean seawater and NIST SRM 975 are shown in Fig. 4. The $\delta^{37}Cl$ value of ISL 354 is 0.05‰ lower than that of mean seawater and 0.02‰ lower than that of the selected seawater. It is 0.05‰ higher than that of the Sand Diego seawater used at the University of Arizona. Together, these results suggest that that ISL 354 can be used as the Standard Mean Ocean Chlorine (SMOC).

4. Conclusions

ISL 354 NaCl produced from a selected seawater sample collected in the Pacific Ocean (4°18′N, 161°08′E) is available. The measured $^{37}Cl/^{35}Cl$ value of ISL 354 is 0.319393 ± 0.000018 and the $\delta^{37}Cl$ relative to NIST SRM 975 is -0.39 ± 0.06‰. The corrected $^{37}Cl/^{35}Cl$ value is 0.319644 ± 0.000917. The isotopic composition of chlorine in ISL 354 is unaltered from that of the original selected seawater. The difference in $\delta^{37}Cl$ values between ISL 354 and mean seawater is -0.05‰. Therefore, the ISL 354 can be recommended as a secondary reference material of chlorine isotope for the study of isotopic geochemistry of chlorine.

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