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Chlorine Stable Isotopes: A Comparison of Dual Inlet and Thermal Ionization Mass Spectrometric Measurements

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Chlorine stable isotope ratios, $^{37}Cl/^{35}Cl$, currently are measured using dual-inlet and thermal-ionization mass spectrometry. These two different analytical techniques, however, have never been cross calibrated. A set of samples with chlorine stable isotope δ values ranging from −4.4 to +0.3 ‰ relative to standard mean ocean water chloride has been analyzed using both of these techniques. Our data show that both techniques can yield similar results within analytical uncertainty. CsCl thermal ionization data are extremely sensitive to the amount of chlorine being measured and cannot be used to determine absolute ratios without an independent means of correcting for machine-induced mass fractionation. As long as standards and samples are of equivalent size, however, the differences between samples measured by thermal ionization remain constant. Dual inlet stable isotope mass spectrometry is suited best for samples of >10 μmol Cl, yielding chlorine stable isotope data with ≤0.1‰ reproducibilities (2σ). Thermal ionization mass spectrometry easily accommodates samples of ∼0.1−0.3 μmol Cl, with achievable uncertainties of ≤0.2‰ (2σ).

Chlorine has two stable isotopes of masses 35 and 37 amu with average abundances of 75.77% and 24.23%, respectively. The observed range of natural $^{37}Cl/^{35}Cl$ ratios is approximately 10 parts per thousand (‰).[1−4] Chlorine stable isotope ratios are becoming increasingly important in studies of the lithosphere, hydrosphere, and biosphere as tracers of terrestrial halogen cycling. Variations in $^{37}Cl/^{35}Cl$ ratios of samples are reported in the usual δ notation in parts per thousand deviation[5] relative to "standard mean ocean chloride" (SMOC). The term SMOC is a misnomer − no accepted Cl-isotope ocean water standard currently exists. Each laboratory uses its own aliquots of water for calibration. Informal tests within and between laboratories, however, have not measured any differences between various ocean-water chloride samples within current analytical precision. There are currently two analytical techniques used to determine $\delta^{37}Cl$ values, Dual Inlet Stable Isotope Ratio Mass Spectrometry and Thermal Ionization Mass Spectrometry, commonly referred to as SIRMS and TIMS. Neither method produces absolute isotope ratios. SIRMS generates raw data which give accurate δ values relative to a reference sample. TIMS gives raw data subject to machine-dependent isotope fractionation.

For dual-inlet measurements, a sample is converted to a gaseous form and aliquots are analyzed repeatedly, alternating with a reference gas of similar chemical composition, to produce a raw δ value. This type of method effectively eliminates machine effects as long as sample and reference gas introduction conditions are well-matched. The raw delta value must be corrected for multicollector effects and calibrated to the international scale using materials of accepted isotope composition, analyzed with respect to the same reference gas. As long as the raw δ values are within a few parts per million of zero, multicollector effects are negligible for Cl. There is no international standard for Cl at the present time.

In contrast to the dual inlet technique, samples are converted to salts and measured serially with standards resulting in machine-dependent abundance ratios in TIMS. Delta values are calculated from the raw data using the abundance ratios of sample and standard after accounting for any machine-induced mass fractionation. Since samples and standards are run serially and not alternately, machine effects are not always the same, as conditions can change between analyses. For most elements analyzed using TIMS, there is either an accepted value of an isotope ratio of the element measured or there are standard materials with internationally accepted values. Either of these values can be used to correct for machine-induced mass fractionation to produce absolute isotope ratios. As mentioned above, no such standards exist for the Cl isotope system. Chlorine isotope data resulting from each of the above methods have been published, but this is the first study in which the two techniques are cross-calibrated.

SAMPLE DESCRIPTIONS

Five samples were chosen for this study: Sargasso seawater (GPS1); a solution of Spec Pure $CsCl_{(s)}$ (SPCS); water from the Dead Sea, Israel (DSW); a solution of $NaCl_{(s)}$ from the Dead Sea

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(1) Kaufmann, R.; Long, A.; Bentley, H.; Davis, S. *Nature (London)* **1984**, *309*, 338−40.
(2) Ransom, B.; Spivack, A. J.; Kastner, M. *Geology* **1995**, *23*, 715−8.
(3) Eastoe, C. J.; Guilbert, J. M.; Kaufmann, R. S. *Geology* **1989**, *17*, 285−8.
(4) Eggenkamp, H. G. M. The Geochemistry of Chlorine Isotopes, Ph.D. Thesis, Utrecht University, Utrecht, The Netherlands, 1994.
(5) Rollinson, H. R. *Using Geochemical Data: Evaluation, Presentation, Interpretation*; Longman Group, Ltd.: Harlow, UK, 1993; p 352.

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(DSS); and a brine sample from a North Sea oil field (NSOF). Salt solutions of ~8−10 mg/g Cl were made by dissolving the salts in deionized, distilled water. Seawater samples were filtered and irradiated with ultraviolet radiation after collection. The total spread in δ^{37}Cl values of these samples is ~5 ‰, equivalent to almost half the observed variation in nature.

ANALYTICAL TECHNIQUES

Thermal Ionization Mass Spectrometry (TIMS). Recent years have seen large technical advances in the measurement of Cl isotopes by TIMS.[6−9] We have adopted the mass spectrometric technique described by Xiao and co-workers,[6,7] using the Cs_2Cl^+ ion to determine the $^{37}Cl/^{35}Cl$ ratio of the sample. This is accomplished by monitoring masses 303 ($Cs_2{}^{37}Cl^+$), 301 ($Cs_2{}^{35}Cl^+$), and 304.5 (baseline). The use of the heavy species, Cs_2Cl^+, helps to minimize the effects of instrumental mass fractionation. The TIMS measurement yields a 303/301 mass ratio for each sample. As natural Cs is monoisotopic, this ratio is equivalent to the 37/35 ratio.

TIMS measurements were made on a VG Micromass 30 thermal ionization mass spectrometer at the University of Leeds. Samples were converted to CsCl in solution using three cation exchange columns[7,8] to produce CsCl solutions of 2−5 μg of Cl per microliter (0.06−0.15 μmol of Cl per microliter). The SPCS solution was not usually processed through the exchange columns. Five to 40 microliters of CsCl solution was loaded onto a single Ta filament, mixed with Ultra F carbon (Johnson Matthey), and dried gently at ~0.8 amps. Sample loads ranged from 3 to 200 μg of Cl equivalent (0.1−6.0 μmol of Cl). Samples were heated to 1.3−1.6 A (<400 °C). Data were collected with a Faraday collector at 0.5−100 pA currents through a 100 Gohm resistor. A typical measurement consisted of 30−100 blocks with 12 ratios/block, collected over 2−3 h. Mass 133 (Cs^+) was examined periodically as were other masses of potential contaminants. No other contaminant peaks were significant relative to the baseline. Analytical Cl blanks were below detection limits and are considered negligible.

Two types of TIMS replicates were measured during the course of this study. Several aliquots of each sample were processed through ion-exchange columns, and each aliquot was subsampled for replicate TIMS analyses. Reproducibilities between and within aliquots were similar. The data for the ~3−5 μg loads are for replicate TIMS analyses of a single aliquot of each sample; all other data are for at least two aliquots of each sample. Data were collected in two batches over two years. Only data showing no machine-induced mass fractionation are summarized in Table 1.

Dual Inlet Stable Isotope Ratio Mass Spectrometry (SIRMS). We measured the $^{37}Cl/^{35}Cl$ ratio of $CH_3Cl^+_{(g)}$ using a modified positive ion method on a dual inlet stable isotope ratio mass spectrometer.[10] Masses 52 and 50 (predominantly $CH_3{}^{37}Cl^+$ and $CH_3{}^{35}Cl^+$) are monitored to determine a 52/50 ratio which is equivalent to the 37/35 ratio of the sample. Corrections for the presence of ^{2}H, ^{13}C, and molecular fragments are unnecessary for samples within 10‰ of the working standard. Unlike TIMS data, SIRMS data are collected with respect to a reference gas, in our laboratory, tank CH_3Cl (BDH no. 60026 3L), yielding a δ value relative to this gas. Two to four 75-μL aliquots of seawater from Kimmeridge Bay (KimBay) were analyzed with each set of samples to calibrate the reference gas. Mass fractionation is not a problem with SIRMS as long as sample and reference gas pressures and volumes are well-matched. Large pressure differences result in delta values which change continuously with time.

SIRMS measurements were made on a VG Isogas SIRA 12 dual inlet stable isotope ratio mass spectrometer at the University of Reading. Samples were converted to CH_3Cl in two steps.[10] Cl was quantitatively extracted from samples by precipitation with Ag in a nitrate solution. AgCl was then converted to CH_3Cl by reaction with CH_3I. Ten to 40 μmol of Cl (350−1425 μg Cl) were used for each analysis. A typical measurement consisted of 12 blocks with 20 ratios/block, collected over 12 min. Masses 28−130 were scanned after each measurement to check for contamination of the sample gas. All analyses showing signs of contamination were rejected from further processing. Data were collected in two batches over two years.

Error Propagation. Two types of uncertainties are reported in this study, reflecting the two different systems usually used to report SIRMS and TIMS data. Reproducibility of independent replicate analyses alone are often used for the reporting of dual-inlet delta values which ignores the uncertainty introduced through calibration of the reference gas (Rep). Both sources of uncertainty are normally included in reported TIMS data (Tot). We cite both calculated uncertainties in the data from this study.

Table 1. TIMS Cl Isotope Data[a]

sample	μg of Cl	303/301	n	δ^{37}Cl	rep	total
GPS1	3−5	0.318630 ± 21	8			
SPCS	3−5	0.318759 ± 80	7	0.41	±0.25	±0.26
NSOF	3−5	0.317230 ± 20	6	−4.39	±0.06	±0.09
GPS1	5−10	0.318741 ± 64	12			
DSW	5−10	0.318594 ± 37	7	−0.46	±0.12	±0.23
DSS	5−10	0.318759 ± 35	7	0.06	±0.11	±0.23
GPS1	25−35	0.319533 ± 48	9			
SPCS	25−35	0.319633 ± 43	17	0.31	±0.13	±0.20
GPS1[b]	~100	0.320524 ± 53				
SPCS	~100	0.320339 ± 90	8	−0.58	±0.28	±0.33
SPCS[c]	~100			2.52	±0.28	±0.32
GPS1	~150	0.320502 ± 135	5			
DSW	~150	0.320378 ± 33	1	−0.39	±0.10	±0.43
DSS	~150	0.320507 ± 62	1	−0.02	±0.19	±0.46
GPS1[b]	~200	0.321947 ± 56				
SPCS	~200	0.321832 ± 26	3	−0.36	±0.08	±0.19
SPCS[c]	~200			7.20	±0.08	±0.17

[a] 303/301 and 37/35 mass ratios are equivalent. SPCS samples were not purified through columns. δ^{37}Cl values (in ‰) were calculated relative to GPS1 data, defined as 0 on the SMOC scale. n = number of analyses; rep = reproducibility (2σ); total = total uncertainty (2σ). [b] Calculated from 25−35-μg GPS1 data corrected for the mass loaded. [c] Delta value relative to 25−35-μg GPS1 data for comparison purposes. See text for discussion.

DISCUSSION

TIMS Data. TIMS δ^{37}Cl values are calculated relative to the average 303/301 ratios for aliquots of GPS1 for each set of loading

(6) Xiao, Y. K.; Zhou, Y. M.; Liu, W. G. *Anal. Lett.* **1995**, *28*, 1295−304.
(7) Xiao, Y. K.; Zhang, C. G. *Int. J. Mass Spectrom. Ion Processes* **1992**, *116*, 183−92.
(8) Magenheim, A. J.; Spivak, A. J.; Volpe, C.; Ransom, B. *Geochim. Cosmochim. Acta* **1994**, *58*, 3117−21.
(9) Cliff, R. A.; Dodson, M. H. in *Seventh Annual V. M. Goldschmidt Conference*; Lunar and Planetary Institute: Houston, **1997**, *Vol. 921*, p 52.
(10) Eggenkamp, H. G. M.; Kreulen, R.; Koster van Groos, A. F. *Geochim. Cosmochim. Acta* **1995**, *59*, 5169−75.

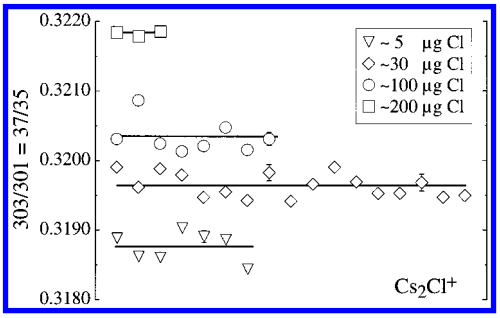

Figure 1. TIMS data for 5-, 30-, 100-, and 200-μg loads of SPCS solution. The 2σ uncertainties are smaller than the symbols except where indicated. Lines show average values.

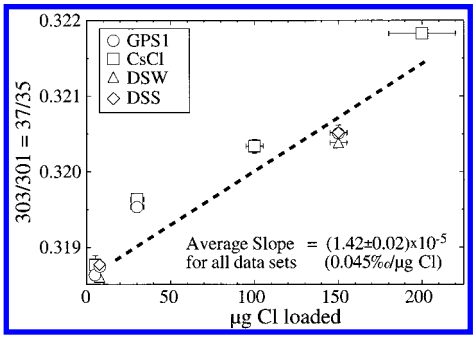

Figure 2. TIMS data for samples from this study as a function of the micrograms of Cl loaded on the filament. The 2σ uncertainties are smaller than the symbols except where indicated. The line indicates the machine-dependent change in the 303/301 ratio as a function of the amount of Cl loaded, averaged for each set of samples (0.045 ‰ per microgram of Cl), and is for illustration purposes only.

conditions (Table 1). Several observations can be drawn from these data. For loads of 25−35 μg of Cl, sample reproducibility was ≤0.2‰ (2σ). The larger uncertainty of the ~5-μg analyses of the SPCS sample reflects a deterioration in the purity of the sample after ~2 years of storage in a PTFE bottle, as it was not processed through columns prior to analysis (Table 1). The δ^{37}Cl values for the ~100-μg and ~200-μg loads of SPCS are calculated relative to the average value of 25−35 μg loads of GPS1 analyzed at the same time to show how mismatched loads of standards and samples affect calculated delta values. The measured 303/301 ratio is strongly dependent on the amount of CsCl loaded on the filament (Figure 1). If this effect is not taken into account, as much as 7‰ offset is observed for differences of ~170 μg of Cl equivalent (Table 1). Consistent intersample differences are obtained when similar amounts of Cl are loaded for analysis, though absolute ratios differ considerably (Table 1). The average change in the 303/301 ratio as a function of the amount of Cl analyzed for all sets of samples was 0.045‰/microgram of Cl loaded (Figure 2). Although we expect the value of this slope to be machine-dependent, the effect itself is endemic to TIMS measurements.

Two types of mass fractionation were observed in our TIMS analyses, lighter isotopes preferentially ionizing relative to heavier ones. Fractionation occurred during loading of several samples which contained slight excess acidity resulting from incomplete cation replacement. This may explain the slightly larger errors associated with the ~150-μg loads of GPS1. The second type of fractionation occurred during TIMS analysis. A few analyses showed continually increasing 303/301 ratios with time (Figure 3). These trends were accompanied by large increases in the 133/301 ratio ($Cs^+/Cs_2{}^{35}Cl^+$), indicating increasing breakdown of the Cs_2Cl^+ ion, into Cs^+ and presumably Cl^- ions. Given the rapid increase in both the 133/301 and 303/301 ratios, it is likely that $Cl^\bullet$ radicals were produced, further destabilizing the Cs_2Cl^+. Rapid heating of samples, in under ~10 min, and insufficient carbon often results in this type of fractionation.

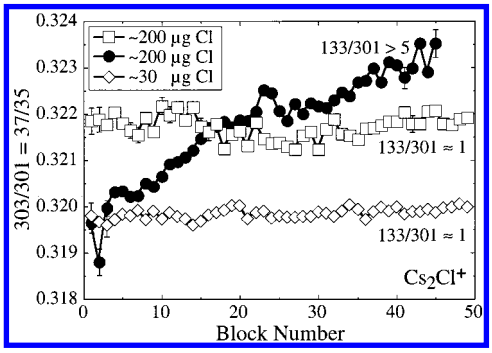

Figure 3. Indication of mass fractionation during TIMS analysis of the SPCS sample as evidenced by strongly increasing 303/301 ratios with time (circles) and elevated 133/301 ($Cs^+/Cs_2{}^{35}Cl^+$) ratios. Shown for comparison are analyses of another aliquot of the same sample not showing measurable mass fractionation.

The δ^{37}Cl values reported in Table 1 are each calculated relative to a small set of data from similar size loads of GPS1. Their propagated uncertainties consequently include a significant contribution from those of the GPS1 data. This error component can be minimized in the future by standardizing the amount analyzed and building a larger GPS1 data set. Under these conditions, the predicted uncertainty for a single analysis of an unknown sample would be comparable to that reported for the single ~150-μg loads of DSW or DSS.

Evaluation of Published TIMS Data. The large changes in the measured 303/301 ratio, relative to the amount of Cl loaded on the filament, may explain some of the variability seen in published TIMS data. Vengosh et al.[11] state that they did not use a constant amount of Cl on the filament to generate their δ^{37}Cl negative-ion TIMS data, though they later adopted a procedure of using "approximately constant amounts of Cl". Although the style of ionization is different, the data of Vengosh et al.[11] strongly suggest that there is a mass dependence in negative-ion TIMS similar to that seen in the TIMS analyses of this study. If so, variable loads might explain the several per mil differences between their Qaidam Basin data and those of Liu et al.,[12,13] and their Dead Sea data and the current results.

The study of Xiao et al.[7] explored the relationship between filament load and measured ratio in the 3−6 μg Cl range. Their data display 1−3‰ differences for replicate loads, which is at least as large as the 1−4‰ variability between loads. Given this sort of reproducibility, it is not surprising that their data show no systematic change with load in 303/301 ratios. These authors standardize to ~10-μg Cl loads in their later studies,[6,12−14] though

(11) Vengosh, A.; Chivas, A. R.; McCulloch, M. T. *Chem. Geol. (Isot. Geosci.)* **1989**, *79*, 333−43.
(12) Liu, W. G.; Xiao, Y. K.; Sun, D. P.; Qi, H. P.; Wang, Y. H.; Jin, L.; Zhou, Y. M. *Chin. Sci. Bull.* **1995**, *40*, 699−700.
(13) Liu, W. G.; Xiao, Y. K.; Wang, Q. Z.; Qi, H. P.; Wang, Y. H.; Zhou, Y. M.; Shirodkar, P. V. *Chem. Geol.* **1997**, *136*, 271−9.
(14) Xiao, Y.; Liu, W.; Zhou, Y. *38th IUPAC General Assembly*, Guilford, UK **1995**; IUPAC.

Table 2. Summary of IRMS and TIMS δ^{37}Cl Data[a]

	IRMS				TIMS			
	(‰)	rep	total	*n*	(‰)	rep	total	*n*
KimBay	0.00	±0.08	±0.08	14				
GPS1	−0.01	±0.09	±0.12	19				
SPCS[b]	0.34	±0.11	±0.14	8	0.34	±0.17	±0.22	24
DSW	−0.43	±0.09	±0.12	8	−0.45	±0.11	±0.26	8
DSS	0.01	±0.06	±0.10	9	0.05	±0.12	±0.26	8
NSOF	−4.39	±0.08	±0.11	5	−4.39	±0.06	±0.09	6

[a] δ^{37}Cl calculated relative to KimBay (IRMS) or GPS1 (TIMS), defined as 0 on the SMOC scale. rep = reproducibility (2σ); total = total uncertainty (2σ); *n* = number of analyses. [b] TIMS data calculated from 3−5-μg and 25−35-μg loads.

they do not address the large differences between their observations and those of Vengosh et al.[11] The TIMS measurements of Magenheim and co-workers involve the use of 2−3 μg of Cl consistently and should not be affected by differential loads.[2,8,15]

As we have shown, TIMS results are highly sensitive to the amount of Cl on the filament during analysis. Since it is not possible to correct for machine-induced mass fractionation during Cs_2Cl^+ analysis, it is surprising that Xiao et al.[6,14] proposed a new atomic weight be adopted by IUPAC on the basis of their TIMS measurements of Cl isotopes in natural substances. Our data show that this suggestion is not reasonable and should be rejected until such time as the method is calibrated using well-characterized mixtures of ^{35}Cl and ^{37}Cl gravimetric standards or an internal correction for machine-induced mass fractionation is developed.[9]

Comparison of SIRMS and TIMS Data. SIRMS data are reported as δ^{37}Cl values relative to a sample of seawater from Kimmeridge Bay, UK, KimBay (Table 2). Reproducibility was ≤0.1‰ (2σ) for 50−100 μmol aliquots of GPS1 throughout this study. The δ^{37}Cl value of GPS1 is indistinguishable from SMOC as represented by the KimBay sample. The SIRMS and TIMS δ^{37}Cl data for all our samples are within error of each other (Table 2).

If both techniques produced identical results, a plot of SIRMS δ^{37}Cl data relative to TIMS data should yield a line of slope 1 passing through the origin. An error-weighted, least-squares fit [16] to our data has a slope and intercept within error of this theoretical line (Figure 4), $\delta^{37}Cl_{TIMS} = (1.002 \pm 0.028)\delta^{37}Cl_{SIRMS} + (0.007 \pm 0.068)$, with propagated 2σ uncertainties.

SUMMARY

Neither TIMS nor SIRMS can be used to determine absolute ^{37}Cl/^{35}Cl ratios of samples unless calibrated with independent, gravimetric standards. The dependence of the 303/301 ratio on the amount of Cl loaded in TIMS measurements adds an extra level of complexity to this problem.

SIRMS and TIMS have been successfully cross-calibrated for Cl stable isotope measurements using samples covering a range of ~5‰, from −4.3 to 0.4‰ relative to SMOC. There is no significant offset between the two techniques. SIRMS is best for large samples (>300 μg of Cl) with a reproducibility ≤0.1‰ (2σ). TIMS is best for small samples (~1−50 μg of Cl) with an achievable reproducibility ≤0.2‰ (2σ).

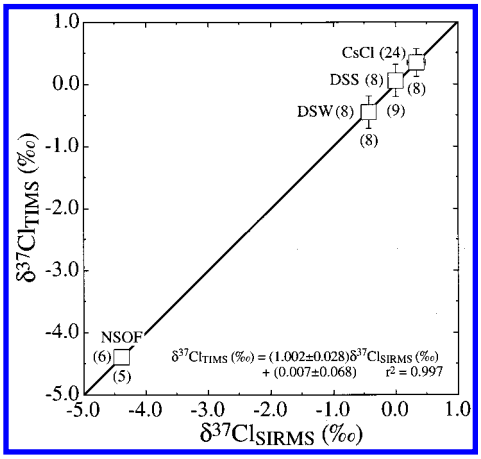

Figure 4. Comparison of TIMS data calculated relative to GPS1 and SIRMS data calculated relative to KimBay. Parentheses below the symbol indicate the number of SIRMS analyses of each sample; those to the left show the number of TIMS analyses. Equation and line indicate error-weighted, least-squares fit to the data.[16] Slope and intercept of the line are within error of the expected 1:1 line. Total 2σ uncertainties are as indicated.

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(15) Magenheim, A. J.; Spivak, A. J.; Michael, P. J.; Gieskes, J. M. *Earth Planet. Sci. Lett.* **1995**, *131*, 427−32.

(16) Williamson, J. H. *Can. J. Phys.* **1968**, *46*, 1845−7.