A simplified procedure for the determination of stable chlorine isotope ratios (δ^{37}Cl) using LA-MC-ICP-MS

Jan Fietzke,[a] Matthias Frische,[b] Thor H. Hansteen[a] and Anton Eisenhauer[a]

Stable chlorine isotopes (^{37}Cl, ^{35}Cl) are considered as important tracers of geochemical processes, especially in subduction zone systems. However, high-quality chlorine isotope data are scarcely available. Here we present a comparatively simple procedure for the precise and accurate determination of stable chlorine isotope ratios (δ^{37}Cl) using LA-MC-ICP-MS. Chlorine was extracted from solid samples by pyrohydrolysis. After quantitative precipitation as AgCl the dried precipitates where analysed in a sample-standard bracketing approach using a weak laser ablation (0.3 J/cm^2) for sample evaporation. Atlantic Ocean sea salt and the sea water standard IAPSO were used as SMOC (standard mean ocean chloride) for normalisation (δ^{37}Cl = 0 ‰). The precision and accuracy of the presented method was validated analysing the reference materials JB-1a and JB-2. The chlorine isotope ratios of these standards were determined as δ^{37}Cl$_{JB-1a}$ = (-0.99 ± 0.06) ‰ and δ^{37}Cl$_{JB-2}$ = (-0.60 ± 0.03) ‰ (errors 2SE), respectively, in accordance with published data. Applying the presented method a total amount of less than 1 µg of chlorine was consumed during a typical measurement including 10 ablation periods on the sample.

Introduction

The element chlorine has two stable isotopes, ^{37}Cl ($\sim$25%) and ^{35}Cl ($\sim$75%), respectively. Since the pioneer study of Kaufmann et al. (1984), gas source IRMS (isotope ratio mass spectrometry) is well established as the standard tool for chlorine isotope ratio determination.[1] In the same study SMOC (standard mean ocean chloride) was introduced as a chlorine isotope reference based on the tested hypothesis that the world oceans are homogeneous with respect to chlorine isotope ratios. Thus all chlorine isotope data are presented as δ^{37}Cl relative to SMOC using the common δ-notation:

$$\delta^{37}\text{Cl} = 1000 \times \frac{(^{37}\text{Cl}/^{35}\text{Cl})_{\text{sample}}}{(^{37}\text{Cl}/^{35}\text{Cl})_{\text{SMOC}}} - 1000$$

Xiao and Zang (1992) introduced TIMS (thermal ionization mass spectrometry) as an alternative technique for chlorine isotope ratio measurements.[2]

A detailed review of the application of stable chlorine isotopes was published by Stewart and Spivack (2004).[3] Godon et al. (2004) undertook a detailed cross calibration study comparing the IRMS and TIMS techniques, and found a good agreement between the methods.[4] Recently most of the published chlorine isotope data acquired using TIMS techniques were questioned due to analytical artefacts associated with the method.[5] There is thus an urgent need for validated high-quality data. The fractionation of chlorine isotopes in terrestrial reservoirs was recently debated in the isotope geochemistry community, initiated by a study published in NATURE by Sharp et al. (2007).[5] Such a debate is, however, beyond the scope of this study.

Here we present a new and comparatively simple procedure (relative to IRMS and TIMS) for the precise and accurate determination of stable chlorine isotope ratios using LA-MC-ICP-MS, aimed at enhancing the use of chlorine isotopes as a geochemical tool.

Experimental

Sample preparation

Halogens were extracted from sediment and rock samples using a pyrohydrolysis technique.[6,7] A platinum boat with 0.2–1 g of powdered sample mixed with the same amount of an accelerator (V$_2$O$_5$) was put into a silica combustion tube. The platinum boat was inductively heated to 1300 °C for 30 minutes, while a mixture of water vapour, oxygen and nitrogen was passed through the tube. Released halogens and water vapour were cooled to 15 °C in a condenser and collected in a trapping solution containing NaOH (0.05 N) and Na$_2$SO$_3$ (0.005 N). After extraction the total amount of solution recovered was around 90 g. The quantitative yield of 98.5 $\pm$ 4.2 % of the extraction method was determined using IC (ion-chromatography) analysis of three reference materials (RGM-1, JB-1a, JB-2). Precipitation of chloride was achieved by adding 8 ml of a mixture containing 1 part by volume HNO$_3$ (65%) and 6 parts by volume of 0.1 N AgNO$_3$ solutions to 25 ml of the extract. In order to extract the AgCl precipitate, the sample was filtered through a membrane filter (0.2 µm). The filtrates were analyzed for quantitative precipitation of chloride using HR-ICP-MS, giving a yield of 100 $\pm$ 0.3 %. Each filter, coated with AgCl, was dried and fixed with resin (Crystalbond™) to a glass slide.

[a]Leibniz-Institute for Marine Sciences (IfM-GEOMAR), Wischhofstr. 1-3, Kiel, D-24148, Germany. E-mail: jfietzke@ifm-geomar.de
[b]SFB 574, Christian-Albrechts-University of Kiel, Wischhofstr. 1-3, Kiel, D-24148, Germany

Fractionation of Cl isotopes during the described sample preparation is not considered as significant, due to the practically quantitative chemical yield and the observed good agreement of our and published results (including samples treated with (basalts) and without pyrohydrolysis (sea water standards)). Nevertheless, fractionation cannot be ruled out totally and will be investigated in future studies.

One major advantage of the sample preparation is the fact, that the samples for the following LA-MC-ICP-MS analysis were transferred into more or less the same matrix (AgCl). This largely reduces problems of matrix effects during the measurement.

Instrumentation and data acquisition

The chlorine isotope measurements were carried out using a ThermoFisher *AXIOM* MC-ICP-MS (developed and manufactured by VG Elemental) combined with a NewWave *UP193FX* laser ablation unit. Typical operating parameters are listed in Table 1.
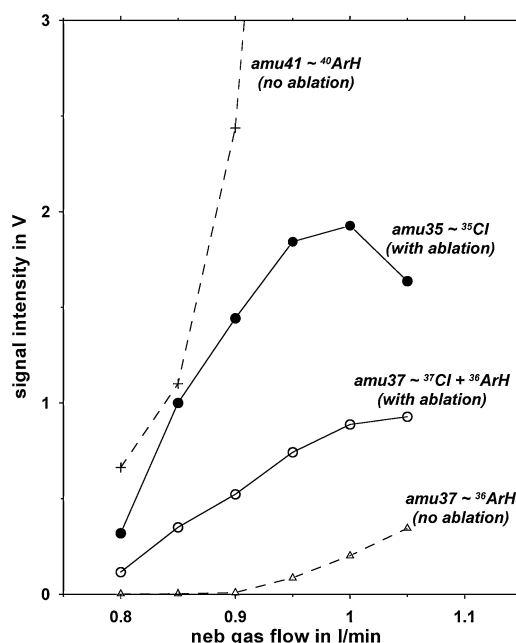
A major issue for the precise and accurate determination of chlorine isotopes *via* LA-MC-ICP-MS is the control of the hydrides ($^{36}ArH^+$) interfering with $^{37}Cl^+$. The rate of hydride generation depends on the plasma core temperature, a parameter that can be influenced *e.g.* by the gas flow. In Fig. 1 the impact of the nebulizer gas flow (mixed with the ablation cell gas after the latter left the cell) on the Cl and ArH intensities is shown. The Cl and ArH signals are influenced differently by the nebulizer gas flow. While Cl reaches its maximum intensity at about 1.0 l/min nebulizer flow, the ArH follows a more or less exponentially increasing trend.

The hydride generation is additionally influenced by the ablation procedure itself, as the ArH signal decreases during ablation. To illustrate this in Fig. 2 an example of the signal responses before, during and after an 8 s ablation test on the sea salt standard is provided. When ablation starts, the ablated material introduced into the plasma results in a decreased rate of hydride generation.
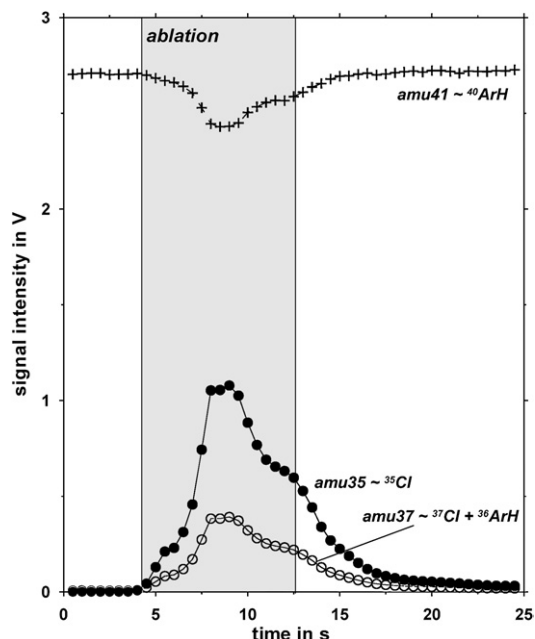
The above stated issues demonstrate the importance of monitoring the hydrides when measuring Cl isotopes *via* ICP-MS. We have tested and evaluated two approaches to deal with that problem:

Fig. 1 Influence of varied nebulizer gas flow on the intensities of Cl and ArH.

Fig. 2 Responses of the Cl and ArH signals to the introduction of ablated material into the plasma.

a) using a reduced nebulizer gas flow, adjusted to provide a Cl intensity of about 50 % of the maximum value. In this case the ArH signal is reduced by about two orders of magnitude.

b) using a nebulizer gas flow which produces about 3 V on amu41. This provides higher Cl intensities and the amu41 signal is used to correct the amu37, applying a $^{36}Ar/^{40}Ar$ abundance ratio of 0.003.

The results of both approaches are presented and compared in the next chapter.

Table 1 Instrumental parameters

AXIOM MC-ICP-MS	
Cool gas	14 l/min
Auxiliary gas	1.8 l/min
Nebulizer gas	0.8–0.95 l/min
RF power	1300 W
Reflected power	2 W
Ion energy	4968 V
Cones	R.A. Chilton RAC19/RAC705
Resolution	500res
UP193solid state / UP193FX	
Ablation cell gas	0.7 l/min (He)
Spot size	150 μm
Fluency	0.3 J/cm^2
Repetition rate	30 Hz
Scan mode	Line scan with 50 μm/s scan speed, 1250 μm length

A second, but minor issue was the determination of the appropriate laser fluency. With a high value we found strong contributions by ablating parts of the filter and resin, respectively, and, thus, reduced it below the ablation threshold of both materials. With a laser fluency of about 0.3 J/cm^2 we observed no ablation of either the filter or the resin. The AgCl filtrate was nevertheless decomposed. We consider this filtrate decomposition to be more an evaporation than a clean ablation, but the result was anyway a stable and reproducible chlorine signal.

To provide a maximal chlorine signal we chose a 150 μm spot size, the largest one available on our laser ablation system, and a repetition rate of 30 Hz. Analytical data were acquired using line scans of 1250 μm length applying a scan speed of 50 μm/s. After ablating for 25 s the laser paused for 90 s. Applying a standard-sample-standard bracketing approach, we ran measurements alternating between the SMOC standard and the sample, repeating ablations of each material at least 10 times.

Sample exchange (ablation cell gas bypassed, cell opened, sample holder exchange, cell closed, cell purged, cell gas back online) took about 10 minutes. After that period the plasma was in a similar condition as prior to the exchange procedure. The latter could be controlled *via* the $^{40}ArH^+$ level.

One sample can, thus, be analysed relative to a standard within one hour.

Data evaluation and results

The described method was tested using the two basaltic reference materials JB-1a and JB-2. North Atlantic sea salt and sea water reference material IAPSO were used as SMOC standards for normalisation.

Stable chlorine isotope ratios $^{37}Cl/^{35}Cl$ were calculated from the slope of the best linear fits for individual data sets using the simultaneous dynamic responses of the amu37 and amu35

signals (Fig. 3). In Fig. 3a the responses for amu35, amu37 and amu41 prior to, during and after ablation are plotted. Additionally the resulting ^{37}Cl signal after correcting the amu37 for the hydrides using 0.003*amu41 is provided. In Fig. 3b it can be seen, how perfectly linear the amu37 and amu35 signals evolve. Starting from the baseline both signals parallely increase during ablation and end at the baseline again after ablation. The slope of the best linear fit is used as the isotope ratio. It is visible, that the hydride-corrected $^{37}Cl/^{35}Cl$ ratio is typically higher than the raw ratio, because the ArH interference contributes a lower background during ablation and, thus, the correction is smaller at the upper end of the amu37/amu35 trend line. This leads to the at first look paradox effect that the corrected ratio is higher than the uncorrected one.

It can also be seen that the correlation improves when applying the correction (indicated by the closer to 1 R^2 value).

A more detailed description of the merits of the applied data reduction will be presented elsewhere.

$\delta^{37}Cl$ relative to SMOC was calculated as the mean of the individual standard-bracketed sample results (typically 10 repetitions) using the above mentioned slope values as Cl isotope ratios.

In Fig. 4 a comparison of the data calculated with and without the amu41 correction using method **b)** is displayed. Here we repeatedly measured the SMOC standard. Applying the correction reduces the scatter of the data by a factor of 12.

The results and published reference data are presented in Table 2. All reported results were true replicates, including individually prepared standards and samples. The $\delta^{37}Cl$ values of the basaltic reference materials determined in this study are in accordance with published data.[8] These authors quoted the reproducibility of their method as 0.12 ‰ (SD). A comparable internal precision (about 0.1 ‰ (SD)) is achieved for the individual standard-bracketed samples applying method **b)**.
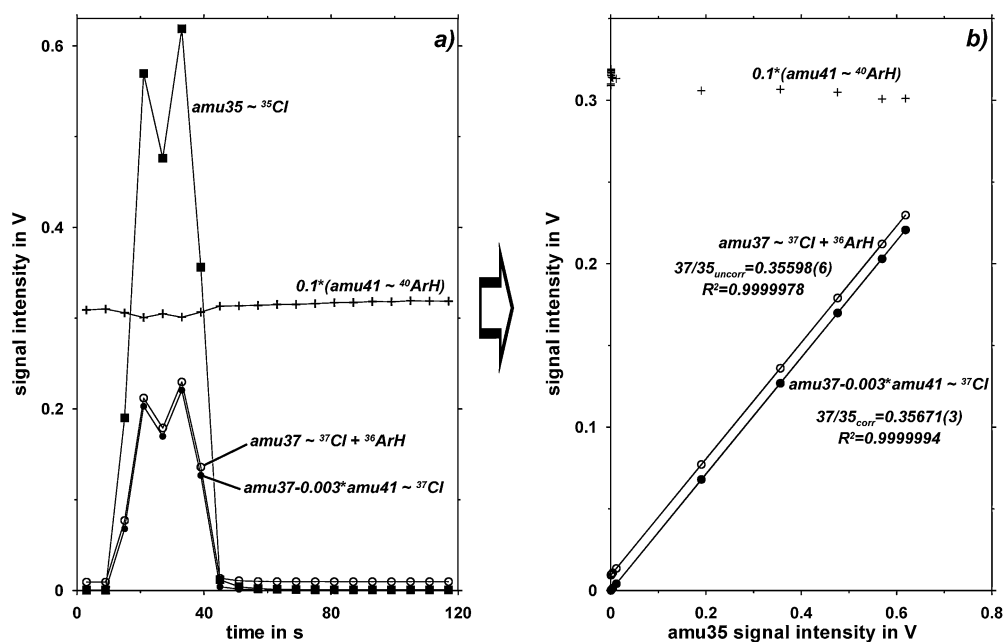
Fig. 3 Simultaneous dynamic responses of the acquired signals (a) and the transfer into isotope ratios (b). The 1σ uncertainties of the slopes are provided in brackets.
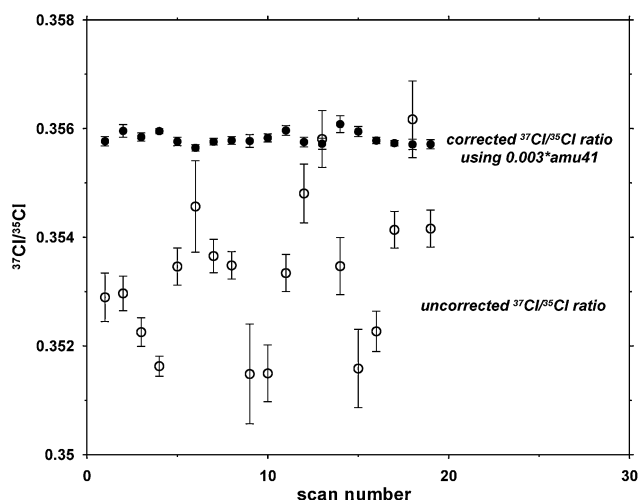
Fig. 4 Impact of the use of ArH correction on the scatter of determined $^{37}Cl/^{35}Cl$ ratios.

Table 2 LA-ICP-MS results of the basaltic reference materials JB-1a and JB-2, respectively, relative to SMOC (Atlantic Ocean sea salt, IAPSO sea water standard). Errors for data from this study are given as 2SEM (n = 10). Reference data (Bonifacie *et al.*, 2007) are provided as the mean of two data points each (individual data points in brackets)[8]

Sample	$\delta^{37}Cl$ relative to SMOC in ‰ this work	$\delta^{37}Cl$ relative to SMOC in ‰ Bonifacie *et al.*, 2007
JB-1a	-0.98 ± 0.20^{a}	-0.96 (-0.90, -1.01)
	-0.99 ± 0.06^{b}	
JB-2	-0.50 ± 0.14^{a}	-0.56 (-0.50, $-0,62$)
	-0.59 ± 0.04^{b}	
	-0.62 ± 0.04^{b}	

^{a} Refers to data using reduced hydride tuning. ^{b} Refers to data using the hydride (amu41) correction, respectively.

For method **a)** the latter is about 3 times higher. Note, each sample measurement consists typically of 10 repeated standard-bracketed sample ablations.

Both methods are able to produce accurate $\delta^{37}Cl$ results but method **b)** is definitely the more precise one. The comparison of both method's results indicate that for high precision $\delta^{37}Cl$ data the correction of $^{36}ArH^{+}$ using simultaneously collected $^{40}ArH^{+}$ data is indispensable.

The precision is mostly limited by the amount of Cl in the sample and the resulting Cl signal intensity. For accurate results, so far 25 µg of the pyrohydrolytically extracted chlorine were prepared for the precipitation. Considering the fact, that we

used for the measurement (10 ablation lines, 1250 µm length, 150 µm spot size) just 2.5 % of the total precipitate (filter area $\sim$80 mm^2, ablated area $\sim$ 2 mm^2) the analysis consumed less than 1 µg Cl yielding a $\delta^{37}Cl$ uncertainty of 0.06 ‰ (2SE). The latter demonstrates the great potential of the described method to produce high quality Cl data using smaller or more depleted samples while concentrating the precipitate on a smaller filter.

Our reference material results underline that the method presented here is able to produce accurate and precise $\delta^{37}Cl$ data. Providing a sufficient amount of Cl on the filter $\delta^{37}Cl$ data can be determined with a precision of about 0.05 ‰ (2SE) within one hour of measurement time.

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