High Precision and Resolution Chlorine Isotopic Analysis of Apatite Using NanoSIMS

Jialong Hao, Sen Hu, Ruiying Li, Jianglong Ji, Huicun He, Yangting Lin, and Wei Yang*
Key Laboratory of Earth and Planetary Physics, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, P. R. China

Received: December 01, 2021; Revised: April 24, 2022; Accepted: April 24, 2022; Available online: April 25, 2022.

DOI: 10.46770/AS.2022.004

ABSTRACT: This paper reports a high analytical precision method for measuring the Cl isotopic composition of apatite using a CAMECA NanoSIMS 50L with Faraday Cup detectors (FC). Six apatite standard samples were used for calibration. Three sets of focused Cs$^+$ beams with currents of ~400 pA (~Φ 700 nm), 1 nA (~Φ 1 μm), and 2 nA (~Φ 1.5 μm) were used with different raster sizes (4 × 4 μm$^2$, 8 × 8 μm$^2$, and 10 × 10 μm$^2$, respectively). We performed depth effect experiments with three primary beam settings to optimize the instrument configuration. While using a primary beam of 2 nA with a raster size of ~10 μm, the external precision of each session varied from 0.06 to 0.48 ‰ (1SD) depending on the Cl concentration of the measured apatite. For standards with a Cl content higher than 0.5 %, the external precision was mostly higher than 0.2 ‰. Using 1 nA and 0.4 nA with spatial resolutions of ~8 μm and 5 μm, the external precision for standards with Cl contents >1 % ranged from 0.12 to 0.2 ‰ and 0.10 to 0.33 ‰, respectively. This technique enables high-precision measurements of chlorine isotopes with high spatial resolutions and can be applied to small apatite minerals in extraterrestrial samples.

INTRODUCTION

Apatite is an abundant accessory mineral found in terrestrial and extraterrestrial rocks and has been commonly used to determine the geochemical nature of its source region and the age of geologic events.\(^1\)\(^-\)\(^5\) Cl, as a highly active element, is utilized for investigating many geological processes, such as magmatic degassing, element mobility, and ore formation.\(^5\)\(^-\)\(^8\) Apatite is the major hydroxyl- and halogen-bearing mineral in extraterrestrial samples. Its chlorine isotopic composition has been intensively studied for evaluating geological and biological processes on planets and asteroids, such as for analyzing the characteristics of potential fluids and volatile abundances of planetary bodies, as well as other related planetary science applications.\(^9\)\(^-\)\(^25\)

Typically, the Cl isotope \(^{37}\)Cl/\(^{35}\)Cl is reported as $\delta^{37}$Cl in the standard per mil notation (‰):

$$\delta^{37}\text{Cl} = \left(\frac{^{37}\text{Cl}_{\text{sample}}}{^{37}\text{Cl}_{\text{standard}}} - 1\right) \times 1000 \quad (1)$$

where the standard adopted is seawater (standard mean ocean chloride (SMOC)) with a \(^{37}\)Cl/\(^{35}\)Cl value of 0.319.\(^{26}\)\(^-\)\(^27\)

Most studies on apatite Cl isotopes in extraterrestrial samples have been conducted using gas flow isotope ratio mass spectrometry (GF-IRMS). However, the application of GF-IRMS is limited as it requires a relatively large number of samples. In these cases, in situ methods, such as secondary ion mass spectrometry (SIMS), are preferable. Large-geometry SIMS, such as CAMECA IMS-1270/1280, is commonly used for Cl isotope measurements of extraterrestrial samples. For instance, apatite grains from the lunar rock were analyzed using a CAMECA 1270 ion microprobe\(^7\) to assess the potential effect of solar wind on the Cl isotope ratio of lunar regolith and soils. The $\delta^{37}$Cl analytical precision ranged from 0.4 ‰ to 1.2 ‰, depending on the apatite Cl concentration. In addition, Sarafian et al. (2016)\(^13\) determined the Cl isotope composition of apatite and merrillite in basaltic eucrites using a CAMECA IMS 1280 ion microprobe with an analytical precision of 0.17–0.32 ‰ (1SD) and a spatial resolution of ~25 μm. They suggested that the light Cl isotope reservoir may differ from that of other solar system bodies. Moreover, the Cl isotopic composition of Martian meteorites has been measured.
using a CAMECA IMS 1270/1280 to decipher the potential mantle source for Martian magmas or the halogen cycling history. Even though the in situ δ37Cl analytical precision has been improved to 0.06–0.07 ‰ (2SD) using SIMS equipped with Faraday cup (FC) detectors, the size of the Cs+ primary beam is usually ≥15 μm with an intensity of ~2 nA. The raster mode is applied to ensure flat-bottomed pits and reduce the impact of the crater effect, and the analytical spatial resolution is generally larger than 20–25 μm (spot size + raster size). This dimension limits the SIMS analysis of Cl isotopic composition in small (<10 μm) or complex-zoned apatite grains in extraterrestrial samples.16, 20

The CAMECA NanoSIMS 50/50L instrument was designed to obtain a higher lateral resolution. Significant efforts have been devoted to obtain micron-scale chlorine isotope information from extraterrestrial samples using NanoSIMS. The analytical spatial resolution (raster size) was improved to ~5μm using a Cs+ primary beam with an intensity of 5–40 pA. However, the analytical precision was relatively poor in the range of 0.6–2 ‰ (1SD). The main reason for this outcome is that electron multipliers (EMs) was used to detect 35Cl and 37Cl in these studies, leading to poor precision than that achieved using FC detectors owing to the aging effect or fewer available statistics. Therefore, studies on Cl isotopic analytical methods with both high precision and spatial resolution are lacking.

In this study, a high analytical precision method to measure apatite Cl isotopic composition using CAMECA NanoSIMS 50 L with FC detectors has been developed. A Cl isotopic analytical precision of <0.1‰ (1SD) could be obtained with 5–10 μm spatial resolution by optimizing the instrument configuration. To the best of our knowledge, this study presents the first demonstration of the high-precision measurement of chlorine isotopes using NanoSIMS FC detectors, possessing both high precision and spatial resolution.

EXPERIMENTAL

Sample description. Our method used sixapatite standard samples, denoted as MGMH#133648, TUBAF#37, #38, #40, #50, and MGMH# 128441A. Detailed information is provided in the paper by Wudarska et al. (2021) and a brief description is provided in Table 1.

Table 1 Summary of Cl isotopic compositions and concentrations of theapatite standards analyzed in this study

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Mineral</th>
<th>CI (%)</th>
<th>Clδ</th>
<th>Clδ</th>
<th>Clδ</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TUBAF#37</td>
<td>Fluorapatite</td>
<td>0.27</td>
<td>0.04</td>
<td>0.20</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>TUBAF#38</td>
<td>Chlorapatite</td>
<td>4.28</td>
<td>0.12</td>
<td>0.09</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>TUBAF#40</td>
<td>Fluorapatite</td>
<td>1.40</td>
<td>0.11</td>
<td>0.20</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>TUBAF#50</td>
<td>Fluorapatite</td>
<td>0.55</td>
<td>0.07</td>
<td>0.32</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>MGMH#128441A</td>
<td>Fluorapatite</td>
<td>0.99</td>
<td>0.08</td>
<td>0.42</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>MGMH#133648</td>
<td>Chlorapatite</td>
<td>6.34</td>
<td>0.16</td>
<td>0.09</td>
<td>0.16</td>
<td></td>
</tr>
</tbody>
</table>

All standards were prepared as 10 mm diameter Sn-Bi metal alloy disks, following the method of Zhang et al. (2018) and one grain of each standard was mounted. The polished metal mounts were cleaned with ultrapure water and anhydrous ethanol before drying at 70 °C in a baking oven overnight. After coating with Au, the sample holders were loaded into the airlock and baked overnight in a NanoSIMS airlock. A unique LN2 cold trap system was used to improve the vacuum in the analysis chamber. The vacuum of the analysis chamber was ~2 × 10⁻¹⁰ mbar during the Cl isotope analysis.

Instrumental setting. The in situ isotopic measurements of chlorine were performed in the NanoSIMS Lab at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). To optimize the primary beam intensity and spatial resolution, three Cs+ beams of ~400 pA (~700 nm), 1 nA (~1 μm), and 2 nA (~1.5 μm) with the same impact energy of 16 keV were tuned to achieve different raster sizes (4 × 4 μm², 8 × 8 μm², and 10 × 10 μm²), respectively. An electron gun was used to compensate for the charge effect. A mass resolution of ~6000 (M/ΔM measured at 10% peak height) was employed to separate the adjacent peaks corresponding to 35Cl and 34S. The transmission of the mass spectrometer was 50–60%, which was computed according to the assertion that the relative transmission was 100% with all slits open. The ion yields of 35Cl are ~5 × 10⁻⁶–1 × 10² cps/Cl‰/nA, depending on the different beam currents used. The ion yields were lower than ~2 × 10² from the IMS 1280-HR analysis conducted by Wudarska et al. (2021). The main reason for this outcome is that a lower Mass Resolution Power (~1800) with higher ion transmission was used in their study. In the static multicollection mode with Nuclear Magnetic Resonance-based magnet regulation, the secondary ion species of 16O, 35Cl, and 37Cl were detected with FC1, FC2, and FC3, respectively. The FC preamplifier boards were set with 10³ Ω resistors for all three FC systems, and temperature regulation was applied to stabilize the FC preamplifiers. The intensity of 37Cl ions ranged from 3.2 × 10⁵ to 1.8 × 10⁷ (cps) depending on the Cl content and the primary beam. Notably, seven secondary ion species can be simultaneously counted in NanoSIMS 50 L, and chlorine analyses can be combined with the analyses of O isotopes, volatile elements, and water content. For example, a possible configuration would be 16O, 18O, 16H, 18O, 19F, 32S, 35Cl, and 37Cl. Under this condition, the MRP should be increased to more than ~8000 to distinguish between 15O and 16OH.

Ion acquisition and data processing. Owing to the influence of the depth effect on the CI ions and isotope stability, various raster conditions of the primary beam were used to determine the appropriate analytical procedure. The primary beam intensity and raster size were the two factors considered. Three sets of focused primary beam intensities (~400 pA, 1 nA, and 2 nA) were tested. Three corresponding raster sizes of 4 × 4 μm², 8 × 8 μm², and 10 × 10 μm² were used. Thereafter, the stability of the CI ion intensity and isotope applied with the above settings were evaluated.
The analytical procedures were established separately according to the three analytical primary beam conditions based on the aforementioned tests. For the analytical condition using a ~2 nA primary beam, the sample surface was pre-sputtered at 12 × 12 μm² for 10 s to remove the coating and implant sufficient Cs⁺. Afterward, the ions of ³⁵Cl, ³⁷Cl, and ³⁹Cl were acquired using a raster setting of the same intensity primary beam (pre-sputter: 10 × 10 μm²) for 150 s. For the 1 nA primary beam, after pre-sputtering an area of 10 × 10 μm² for 30 s using a 1 nA primary beam, each area of 8 × 8 μm² was rastered to yield secondary ions, which were detected for 200 s. Similarly, using a primary beam of 400 pA, after pre-sputtering an area of 6 × 6 μm² for 30 s using a 400 pA primary beam, the raster size was reduced to 4 × 4 μm², and the counting time was increased to 300 s. The chained analysis mode in the NanoSIMS analysis software was applied to the six standard samples. Three sequences were analyzed on different areas of each standard with the analytical conditions of the three primary beam setups. The stage moved horizontally by 30 μm after each automatic spot analysis during the analysis sequence. Moreover, automated secondary ion beam centering (SIBC) at the entrance slit was conducted at the beginning of every analysis to align sputtered ions and the mass spectrometer, which was essential to the analytical stability between grains.

For high-precision isotope measurements, the baseline drift of the FC detector affects the stability of the analysis. In a previous study regarding O isotope analysis using an IMS 1280, the baseline drift was as large as ~1000 cps, and the measured oxygen isotope ratios were biased by ~1 ‰. In this study, the background of the FCs was measured for 10 s before and after each analysis to reduce the impact of the baseline drift. Normally, the standard deviation of the FC background noise of the NanoSIMS with a 10¹¹ Ω resistance is in the range of 2–3 × 10⁻¹⁶ A (~2000 cps), which was recorded over 10 min with an integration time of 5 s. Noise is defined as the standard deviation of the signal over 10 min. The raw results of ³⁵Cl/³⁷Cl are given with a background correction during the acquisition. Instrumental mass fractionation (IMF) was estimated for each standard by comparing the measured ³⁷Cl/³⁵Cl ratio with the reference values measured using gas source isotope ratio mass spectrometry (GS-IRMS) for the IMF. The widely employed notation IMF = (³⁷Cl/³⁵Cl)measured / (³⁷Cl/³⁵Cl)recommended was employed in this study. The corrected ratio was then transformed into the delta (δ) notation. The reproducibility of the Cl isotopic measurements on the reference samples was 1SD. The δ³⁷Cl result was reported with the associated 2SE uncertainties (error bar), including the reproducibility of the δ³⁷Cl measurements on the corresponding reference apatite and the internal uncertainty of each analysis. Uncertainties in the reference values for apatite standards were not included. However, when applied to unknown samples, the uncertainty of the IMF can be estimated as the square sum of the standard deviation of the measurement and uncertainties of the reference values for the apatite standards.

**RESULTS AND DISCUSSION**

**Depth effect.** The depth effect is expected in the in situ analysis using high-density primary beams, such as NanoSIMS. The scanning mode was applied to reduce depth effect compared to spot analysis. However, improving the spatial resolution by reducing the size of the scanning area may also cause a severe depth effect.31, 39

We conducted depth effect experiments with various primary beam settings (400 pA, 1 nA, and 2 nA) and raster sizes (4 × 4 μm², 8 × 8 μm², and 10 × 10 μm²). Fig. 1 shows the variation of the ³⁵Cl⁻ content varying with time. Under conditions of 400 pA (4 × 4 μm²), 1 nA (8 × 8 μm²), and 2 nA (10 × 10 μm²), the signal was relatively stable within the statistical time. Under the conditions of 1 nA (8 × 8 μm²) and 2 nA (10 × 10 μm²), the isotopic ratio was stable.
within the statistical time, and the standard deviations of the variation were 0.20 % and 0.15 % (1SE), respectively (Fig. 1b). When the scanning area was reduced to 1 nA (4 × 8 μm²) and 2 nA (8 × 8 μm²), a pronounced depth effect was observed, and the standard deviations of the variation were 0.50 % and 0.22 % (1SE), respectively (Fig. 1b).

The mechanism of the SIMS depth effect remains unclear and may be influenced by multiple factors. In our Cl isotopic analysis, presumably, the main contributing factor is that the rate of production of sputtered ions changes with the electronic properties of the surface, which is related to the erosion depth.45

**Internal precision.** Based on the fundamental statistical theory of isotopic analysis, the internal precision of the isotope ratio depends on two factors: the signal-to-noise ratio and the drift of the ratio. When using SIMS for isotope ratio measurements, the depth effect may cause a drift in the ratio. When the stability of the signal is sufficiently high (= the statistical error), improving the signal-to-noise ratio of the analysis is key to obtaining high internal accuracy.

In a previous study of NanoSIMS Pb-Pb isotope measurements using EMs, we improved the signal statistics to reduce the impact of shot noise, which reduced the Poisson error and enhanced internal precision.31, 39

Compared with detection using EMs, employing dual-FC to measure Cl isotopes, the within-spot uncertainty is limited to a minimum value by shot noise (Poisson error) and Johnson–Nyquist (JN) noise, which has been discussed in detail in a previous study.46 JN noise is the fluctuation of current induced in the resistor owing to the thermal agitation of electrons. Consequently, the relative internal error was estimated using Eq. 2 as follows:

\[
RSE_{est.}(\%) = \sqrt{\text{Poisson}(\%)^2 + \text{SNR}(\%)^2} \quad (2)
\]

In Eq. 2, the Poisson error is calculated using Eq. 2 as follows:

\[
\text{Poisson}(\%) = 1000 \times \frac{1}{\sqrt{\sum_i N_i(^{35}\text{Cl}) + \sum_i N_i(^{37}\text{Cl})}}
\]

where \( n \) is the total number of cycles; \( N_i(^{35}\text{Cl}) \) and \( N_i(^{37}\text{Cl}) \) are the counts integrated with cycle \( i \); \( \text{SNR}(\%) \) is the error owing to the signal-to-noise ratio, which was calculated from the total counts of each isotope (\(^{35}\text{Cl} \) and \(^{37}\text{Cl} \)) and the FC baseline variation (~2000 cps) using Eq. 4 as follows:

\[
\text{SNR}(\%) = 1000 \times \sqrt{\frac{FC_{35\text{Cl}}}{N_{35\text{Cl}} \times \sqrt{n}}} + \sqrt{\frac{FC_{37\text{Cl}}}{N_{37\text{Cl}} \times \sqrt{n}}} \quad (4)
\]

Herein, we determined the relationship between the signal statistics (\(^{35}\text{Cl} \) intensity) and the estimated analytical relative internal precision \((RSE_{est.}(\%))\) and Poisson error \((\%o)\) for three different integration times (150 s, 200 s, and 300 s) (Fig. 2). The \(RSE_{est.}(\%)\) and Poisson error \((\%o)\) decreased exponentially relative to the \(^{33}\text{Cl} \) count rate. However, the relationship between \(RSE_{est.}\) and Poisson error was not entirely consistent. For example, at a low \(^{35}\text{Cl} \) intensity, the Poisson error accounted for a smaller proportion of \(RSE_{est.}\) (\(RSE_{est.} \) was one order of magnitude higher), and the difference between \(RSE\) and Poisson error decreased with increasing \(^{35}\text{Cl} \) intensity. Consequently, analyzing a low-content standard sample or using a small beam current for isotope analysis (FC mode) was insufficient to reduce the influence of the propagation Poisson error by increasing the accumulation amount. It is also necessary to reduce the thermal noise of resistance and can be achieved using a higher resistance.30, 47

**External reproducibility.** An external reproducibility test was performed on the six apatite standards under the conditions described in Section 2. Three raster conditions are used in this provided in the Supplementary Materials. Each session corresponded to a different standard sample and analysis condition. Table 2 summarizes the Cl isotopic composition, concentration results, and the external uncertainty of each session ISD. All the measured \(\delta^{37}\text{Cl} \) values corrected using the IMF of each session are also plotted in Fig. 3. TUBAF #37 is not plotted in Fig. 3 owing to its low Cl content and larger uncertainty values than other standards. The uncertainties of each spot (error bar) are reported with the associated 2SD levels, including the internal precision (2SE) and external precision (reproducibility) of the spot-to-spot analysis (2SD). The external precision of each session varied within 0.06–0.49 % (1SD) depending on the apatite Cl concentration while using the primary beam of 2 nA and a spatial

---

**Fig. 2** Relationship between signal statistics (\(^{35}\text{Cl} \) intensity); estimated analytical relative internal precision \((RSE_{est.}(\%))\) and Poisson error \((\%o)\) for three different integration times (150 s, 200 s, and 300 s). Analytical relative internal precision is estimated using square sum of errors due to counting statistics (Poisson error) and S/N ratios.
Table 2 Results of Cl isotopic composition and concentration analyses of the apatite standards

<table>
<thead>
<tr>
<th>FCO (nA)</th>
<th>Filename</th>
<th>Raster (μm)</th>
<th>δ$^37$Cl Ref.*</th>
<th>Cl (%) Ref.</th>
<th>$^{35}$Cl/^{37}Cl$_{Exp}$</th>
<th>IMF$_{Exp}$</th>
<th>δ$^{35}$Cl$_{Exp}$</th>
<th>ISD</th>
<th>Cl/O$_{Exp}$</th>
<th>ISD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>20211015-TUBAF#50-1</td>
<td>0.26</td>
<td>0.55</td>
<td>0.3216</td>
<td>1.0055</td>
<td>0.23</td>
<td>0.17</td>
<td>0.0092</td>
<td>0.0012</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211015-128441A-1</td>
<td>0.36</td>
<td>0.99</td>
<td>0.3214</td>
<td>1.0046</td>
<td>0.66</td>
<td>0.26</td>
<td>0.0158</td>
<td>0.0014</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211015-TUBAF#40-1</td>
<td>0.23</td>
<td>1.40</td>
<td>0.3213</td>
<td>1.0045</td>
<td>0.39</td>
<td>0.16</td>
<td>0.0199</td>
<td>0.0006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211015-TUBAF#38-1</td>
<td>0.11</td>
<td>4.28</td>
<td>0.3211</td>
<td>1.0041</td>
<td>0.19</td>
<td>0.11</td>
<td>0.0665</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211015-133648_1</td>
<td>0.10</td>
<td>6.34</td>
<td>0.3210</td>
<td>1.0038</td>
<td>0.07</td>
<td>0.06</td>
<td>0.1088</td>
<td>0.0014</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211015-TUBAF#37-1</td>
<td>0.14</td>
<td>0.27</td>
<td>0.3214</td>
<td>1.0049</td>
<td>0.44</td>
<td>0.41</td>
<td>0.0085</td>
<td>0.0002</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>20211016-TUBAF#50-2</td>
<td>0.26</td>
<td>0.55</td>
<td>0.3214</td>
<td>1.0049</td>
<td>0.44</td>
<td>0.41</td>
<td>0.0085</td>
<td>0.0002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211016-TUBAF#37-2</td>
<td>0.14</td>
<td>0.27</td>
<td>0.3216</td>
<td>1.0055</td>
<td>-0.83</td>
<td>0.67</td>
<td>0.0041</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211016-128441A-1</td>
<td>0.36</td>
<td>0.99</td>
<td>0.3213</td>
<td>1.0045</td>
<td>0.29</td>
<td>0.39</td>
<td>0.0160</td>
<td>0.0002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211016-TUBAF#40-1</td>
<td>0.23</td>
<td>1.40</td>
<td>0.3213</td>
<td>1.0044</td>
<td>-0.15</td>
<td>0.21</td>
<td>0.0209</td>
<td>0.0003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211016-TUBAF#38-1</td>
<td>0.11</td>
<td>4.28</td>
<td>0.3211</td>
<td>1.0040</td>
<td>-0.13</td>
<td>0.13</td>
<td>0.0687</td>
<td>0.0006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211016-133648-1</td>
<td>0.10</td>
<td>6.34</td>
<td>0.3211</td>
<td>1.0041</td>
<td>-0.06</td>
<td>0.15</td>
<td>0.1037</td>
<td>0.0010</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>20211017-#50-1</td>
<td>0.26</td>
<td>0.55</td>
<td>0.3214</td>
<td>1.0049</td>
<td>0.66</td>
<td>0.69</td>
<td>0.0112</td>
<td>0.0004</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211017-#40-1</td>
<td>0.23</td>
<td>1.40</td>
<td>0.3212</td>
<td>1.0041</td>
<td>0.67</td>
<td>0.34</td>
<td>0.0277</td>
<td>0.0002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211017-#38-1</td>
<td>0.11</td>
<td>4.28</td>
<td>0.3211</td>
<td>1.0040</td>
<td>0.12</td>
<td>0.19</td>
<td>0.0885</td>
<td>0.0009</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211017-#37-1</td>
<td>0.14</td>
<td>0.27</td>
<td>0.3216</td>
<td>1.0054</td>
<td>2.90</td>
<td>2.17</td>
<td>0.0054</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211017-133648-1</td>
<td>0.10</td>
<td>6.34</td>
<td>0.3210</td>
<td>1.0037</td>
<td>0.03</td>
<td>0.10</td>
<td>0.1348</td>
<td>0.0004</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20211017-128441a-1</td>
<td>0.36</td>
<td>0.99</td>
<td>0.3211</td>
<td>1.0038</td>
<td>0.27</td>
<td>0.26</td>
<td>0.0203</td>
<td>0.0002</td>
<td></td>
</tr>
</tbody>
</table>

* Determined using SIMS by Wudarska et al.\(^{41}\)

---

Fig. 3 Measured δ$^37$Cl corrected using the IMF of each session. Under the condition: (a) using a primary beam of 2 nA to raster a 10 × 10 μm$^2$ area; (b) using a primary beam of 1 nA to raster an 8 × 8 μm$^2$ area; (c) using a primary beam of 400 pA to raster a 4 × 4 μm$^2$ area.

Fig. 4 Relation of the Cl concentration and external reproducibility under various conditions: using a primary beam of 2 nA to raster a 10 × 10 μm$^2$ area; using a primary beam of 1 nA to raster an 8 × 8 μm$^2$ area; using a primary beam of 400 pA to raster a 4 × 4 μm$^2$ area.

---

resolution of ~10 μm (Table 2 and Fig. 3). For standards with Cl contents higher than 0.5 %, the external precision was mainly better than 0.25 %. When using 1 nA and 0.4 nA at spatial resolutions of ~8 μm and 5 μm, the external precisions for the standards with Cl contents >1 % are in the range of 0.13–0.21 % and 0.10–0.34 %, respectively. Fig. 4 depicts the relationship between the Cl concentration and external reproducibility. The concentration increased from 0.27 to 1, and the analytical external precession decreased significantly. This outcome may be owing to a lower intensity, leading to a larger internal precision due to the FC noise and Poisson error. However, when the concentration was higher than 1 %, under the primary beam conditions of 1 nA and 2 nA, the analytical external precession did not decrease significantly with increased content. In summary, the results show that the analysis accuracy of chlorapatite in extraterrestrial samples with a chlorine content of more than 1%, especially Martian meteorites, can be better than 0.1–2 % at a spatial resolution of 5–8 μm. However, for TUBAF#37 (Cl wt. 0.27%) using a 400 pA beam current, the 37 Cl signals were as low as ~3 × 10$^3$ cps. The external reproducibility (~2.2 % 1SD) was mainly influenced by the standard deviation of the Faraday cup noise (~2.2 % 1SD). For such a low counting rate of $^{37}$Cl, EM or higher resistance (10 E12 or 13 Ω) should be used.

Matrix effect and IMF. IMF represents an integrated parameter that combines the ionization process and transmission process from the mass spectrometer to the detection system. In SIMS analysis, IMF is mainly a function of the composition and structure of the material analyzed. In the previous study in which $^{37}$Cl was measured using SIMS, a slight variation of IMF with the Cl content was observed.\(^{30, 41}\)

The measured Cl isotopic IMF values of our study are plotted against the Cl content in Fig. 5 and the date are presented in Table 2. Our study also revealed correlations between the IMF and Cl
was more significant in this study. This outcome may explain the
Therefore, fractionation resulting from background deductions
was not linear in our study. The IMF declined rapidly at a low Cl
content. However, the IMF used to correct the $\delta^{35}$Cl of the unknown sample should be acquired using the standards with the corresponding Cl content or corrected using the linear relation determined in a small range containing the content of the sample.

Concentration calibration. Figure 6 shows the linear correlation between the Cl content and the $^{35}$Cl/$^{16}$O ratio. The slope of the Cl content calibration curve was not constant for the different primary beams. The slope of the plot was 47.1 ($R^2 = 0.9956$), 60.9 ($R^2 = 0.9996$), and 58.9 ($R^2 = 0.9956$) for the for the 400 pA, 1 nA, and 2 nA primary beams, respectively. Using 400 pA primary beam, the ion yield of $^{35}$Cl and $^{16}$O were $9.6 \times 10^6$ (cps/Cl%/nA) and 1.3 $\times 10^7$ (cps/Cl%/nA), respectively. For 1 nA and 2 nA primary beams, the ion yield of $^{35}$Cl and $^{16}$O were $5.4 \times 10^6$ (cps/Cl%/nA) and $9.1 \times 10^6$ (cps/Cl%/nA), respectively. This result may be because of the relative sensitivity factor, which changed with the bombardment ion intensity, which influenced the Cl and O differently. Therefore, different slopes are required for Cl content calibration when measuring Cl isotopes using primary beams with different intensities.

CONCLUSIONS

This study developed a method with high analytical precision to measureapatite Cl isotopic composition using CAMECA NanoSIMS 50 L with FC detectors. Considering the crater effect in SIMS isotope analysis and larger spatial resolution than the spot size, we optimized the instrument configuration to obtain high spatial resolution while reducing depth effects. The factors related to shot noise (Poisson error) and JN noise, which affect the internal analytical precision in the FC detector mode, were assessed. In addition, correlations between IMF and Cl concentrations were observed in this study. Cl isotopic external precisions of $<0.1$‰ (1SD and Cl content >4%) can be obtained with spatial resolutions of 5–10 μm. The IMF values of the two end members, TUBAF#37 and MGMH#133648, differ by 1.8‰ (1SD and Cl content >4%) can be obtained with spatial resolutions of 5–10 μm. The IMF values of the two end members, TUBAF#37 and MGMH#133648, differ by $\pm 1.8$‰ (1SD and Cl content >4%).

Moreover, the correlation between the Cl content and $^{35}$Cl/$^{16}$O changes with the intensity of the primary beam. It is recommended that the corresponding slope be used for Cl content calibration. This paper presents the first report of high-precision measurements of Cl isotopes using NanoSIMS, which can be applied to small apatite-group minerals from extraterrestrial samples.

Fig. 5 Relation of the Cl isotopic IMF and Cl content under various conditions: using a primary beam of 2 nA to raster a $10 \times 10$ μm$^2$ area; using a primary beam of 1 nA to raster an 8 $\times$ 8 μm$^2$ area; using a primary beam of 400 pA to raster a 4 $\times$ 4 μm$^2$ area. Error bars are the analytical external precision of each standard samples (1SD).

Fig. 6 Linear correlation between Cl contents and $^{35}$Cl/$^{16}$O ratios under various conditions: using a primary beam of 2 nA to raster a $10 \times 10$ μm$^2$ area; using a primary beam of 1 nA to raster an 8 $\times$ 8 μm$^2$ area; using a primary beam of 400 pA to raster a 4 $\times$ 4 μm$^2$ area.

concentrations. The IMF values of the two end members TUBAF#37 and MGMH#133648 differ by $\pm 1.8$‰ (1.0055–1.0037), which is larger than the values of $\pm 0.24$‰ and $\pm 0.7$‰ reported by Wudarska et al. and Cui et al., respectively, using an IMS 1280HR. The reason for IMF variations remains unclear. Wudarska et al. have mentioned potential orientation effects in their paper; however, the potential effect and IMF variations should not be significant in NanoSIMS, in which the sample is bombarded from a perpendicular angle. In addition, compared with the correlation determined for the same standard samples by Wudarska et al., the relationship between Cl content and IMF was not linear in our study. The IMF declined rapidly at a low Cl content. However, the $^{35}$Cl intensity reported by Wudarska et al. ($>3 \times 10^5$ CPS) was higher than that in this study ($<8 \times 10^5$ CPS). Therefore, fractionation resulting from background deductions was more significant in this study. This outcome may explain the variations in IMF between high and low Cl mass fractions and the different IMF relations between this study and those by Wudarska et al. and Cui et al. using the IMS 1280HR system. In addition, because the relationship between IMF and the content is not truly linear in the range where the content varies considerably in our study, the IMF used to correct the $\delta^{35}$Cl of the unknown sample should be acquired using the standards with the corresponding Cl content or corrected using the linear relation determined in a small range containing the content of the sample.

www.at-spectrosc.com/as/article/pdf/2022004 XXX At. Spectrosc. 2022, 43(1), XXX-XXX.
AUTHOR INFORMATION

Wei Yang is a Professor at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), operating a NanoSIMS laboratory. He received his B.S. (2001) and Ph.D. (2007) degrees in geochemistry from the University of Science and Technology of China. After completing his Ph.D., he came to IGGCAS for post-doctoral research and joined the comparative planetary science group as an Associate Professor in 2011. His main interest in the past decade was Mg isotope geochemistry and its application in tracing the deep carbon cycle. He is currently working on instrumentation developments on secondary ion mass spectrometry and its application in Earth and planetary sciences, the formation and evolution of the Moon based on the exploration data and returned samples of the Chinese Lunar Exploration Program. He has published over 70 peer-reviewed scientific papers in ISI-indexed journals.

Corresponding Author

*W. Yang

Email address: yangw@mail.iggcas.ac.cn

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We would like to thank G. Q. Tang and Y. Liu for illuminating discussions. We are grateful to two anonymous reviewers who provided valuable suggestions for improving this manuscript. This study was funded by the Key Research Program of Chinese Academy of Sciences (ZDRW-KF-2019-5-2, ZDBS-SSW-JSC007-15), the Strategic Priority Research Program of Chinese Academy of Sciences (XDB41000000), National Natural Science Foundation of China (42173036), the Key Research and Development Program of China (2018YFA0702601), the Key Deployment Program of IGGCAS (IGGCAS-202101), and the Pre-research Project on Civil Aerospace Technologies of China National Space Administration (D20203).

REFERENCES

24. A. Stephant, M. Anand, X. Zhao, Q. H. S. Chan, M. Bonifacie, and