Inter-element fractionation and correction in laser ablation inductively coupled plasma mass spectrometry

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Inter-element fractionation in laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analysis is one of the major challenges for using the technique for in situ trace element determination and isotopic ratio measurement of geological, environmental and biological solid samples. Attempts have been made to reduce inter-element fractionation in LA-ICP-MS analysis. However, this fractionation cannot be eliminated. The mechanism of the fractionation in LA-ICP-MS analysis is not very well understood. This study investigated the inter-element fractionation of seven elements (Ca, V, Zn, Sr, La and Nd) in three different sample matrices (NIST 613, BCR-2 and SY-4) using a UV 266 nm laser. The study showed that the inter-element fractionation depends on the sample matrices and varies with time. The inter-element fractionation behaviour of V, Zn and Ga in the synthetic sillicate glass NIST 613 is different from that in the quenched glass of fused silicate rocks (BCR-2 and SY-4). Relative to Ca, V, Zn and Ga show less fractionation in NIST 613 but larger fractionation in BCR-2 and SY-4. The relative internal standard normalized element intensity (RISNEI) is not linear with time for a laser ablation period of 210 s. Therefore, data acquisition using prolonged laser ablation without a matrix match will not improve the precision and accuracy for elements whose fractionation behavior is different from that of the internal standard element. The RISNEI versus time relationship for the first 100 s laser ablation can be treated as linear to simplify the data calculation. In this paper, the internal standard normalized fractionation factor (ISNFF) is defined as the sum of the second half average RISNEI and the difference between the second and first half average RISNEI, divided by the second half RISNEI of data acquisition, for the analytic concentration calculation. The ISNFF was applied for the correction of the data reduction in LA-ICP-MS analysis. The data accuracy for these seven elements is generally improved, particularly for an element whose calibration standard normalized ISNFF is significantly greater or less than 1 (e.g., Zn and Ga in this study). Good accuracy can be obtained for elements without ISNFF correction and matrix matches only if the calibration standard normalized ISNFF of the elements is close to 1.

Since laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was first introduced by Gray1 in 1985, it has been widely used as a powerful analytical technique in various disciplines2–7 for in situ solid micro-sampling analyses. For LA-ICP-MS analysis, a combination of external and internal standardization is most commonly used for calibration and quantification. Good precision and accuracy have been reported if an element whose fractionation is similar to those of the analytes was chosen as an internal standard.2,3,8–10 However, if the fractionation of the analyte is significantly different from that of the internal standard element, poor accuracy is obtained. The analytically suitable and naturally occurring major elements with known concentrations (e.g., Ca and Si in silicate rocks and minerals) are commonly used as an internal standard for in situ multi-element LA-ICP-MS analysis. The selection of these elements is very limited. It is difficult to choose an internal standard which is capable of standardizing elements with different chemical characteristics (e.g., chalcophile, alkali and lithophile elements).

Inter-element fractionation in LA-ICP-MS analysis has been studied by several investigators recently.9–11 Active focusing of the laser beam also reduced the inter-element fractionation in LA-ICP-MS analysis.9,11 Laser ablation using a 266 nm UV laser produced less inter-elemental fractionation than using 1064 and 532 nm lasers.9–11 More recently, Jeffries et al.12 reported that laser ablation using a frequency quintupled Nd:YAG laser (213 nm) significantly decreased the inter-element fractionation.

Despite all these efforts, inter-element fractionation in LA-ICP-MS cannot be eliminated. In this work, inter-element fractionation in three different matrices (NIST 613, BCR-2 and G-2) during laser ablation at 266 nm was investigated. Inter-element fractionation in LA-ICP-MS analysis depends on the sample matrix and varies with time during the laser ablation and transport. A fractionation factor was defined and applied to the correction of the LA-ICP-MS data reduction. Data accuracy for elements whose fractionation is different from that of an internal standard element was significantly improved after inter-element fractionation was corrected.

Experimental

Instrumentation

A VG Elemental (Winsford, Cheshire, UK) PQ II S high sensitivity ICP-MS instrument was used. The software was upgraded to the OS/2 based PQ version 4.36. A two-directional communication is interfaced between the ICP-MS and the LA systems via a serial RS-232 (i.e., COM port). With the new PQ version software, the execution of each defined time setting by
Gas flow rates—

4–5 g of rock powder were weighed into a 20 cm$^3$ Pt crucible. BCR-2 (basalt) were analysed by LA-ICP-MS. Approximately 1824

Energy and Mineral Technology (CANMET) SY-4 (diorite) were examined using a petrographic microscope and were found to be free of any crystal phases.

Data acquisition and calibration

After the instruments had been optimised and a procedure set up, both LA and ICP-MS were run automatically following the analytical procedure from the first to last analysis. Experiments were carried out in the following cycle sequences: NIST 613, BCR-2, SY-4, NIST 613, …, NIST 613, BCR-2, SY-4, NIST 613.

Each analysis consists of a 100 s pre-ablation delay for the background (data collected), 210 s lasering for signal (data collected) and a 90 s sample delay for flush (no data collected). Seven elements ($^{42}$Ca, $^{51}$V, $^{66}$Zn, $^{69}$Ga, $^{88}$Sr, $^{139}$La and $^{146}$Nd) which range from the highest (Zn) to least (Nd) fractionation relative to Ca were investigated for their fractionation behaviour and correction procedure. Data were acquired in the peak-jumping mode with a dwell time of 10.24 ms. Background levels for each element were obtained by acquiring data for a gas blank for 100 s prior to laser sampling. Sample data were corrected from 210 s ablation and data acquisition. Count rates were collected and exported as CSV (comma delimited values) files by PQ Version 4.36 Time Resolved Analysis (TRA) software. All subsequent data manipulations were later accomplished off-line using a commercial spreadsheet program by manual operation and by in-house written software.

All sample data reported were background subtracted. The first few data after initial laser ablation were not included in the data reduction to avoid potential surface contamination. Calibration and quantification of the analysis utilized both external and internal calibrations. NIST 613 was used as an external calibration standard and Ca as an internal standard.

Results and discussion

Matrix effect

The relative internal standard (e.g., Ca in this study) normalized element intensity (RISNEI) is defined here as

\[
\text{RISNEI} = \frac{I_{\text{element}}/I_{\text{internal standard}}}{I_{\text{Initial ablation}}/I_{\text{Initial ablation}}}
\]

Fig. 1 shows the RISNEI of Zn, Ga, V and La in three different matrices (NIST 613, BCR-2 and SY-4). The data shown in the figures are averages of every nine readings from TRA data acquisition to smooth the curve. The RISNEI versus time relationship of Sr and Nd in the three matrices is similar to that of La, and is not shown in the figure. Inter-element fractionation of the elements depends on the sample matrices. The inter-element fractionation behaviour of the elements in the synthetic silicate glass NIST 613 is different from that in the fused silicate rocks (BCR-2 and SY-4). Relative to Ca, V and Ga show less fractionation in NIST 613 but greater fractionation in BCR-2 and SY-4. The fractionation of an element in SY-4 is higher than that of the same element in BCR-2. Although the fractionation of the same element is different in three sample matrices (Fig. 1), the RISNEI of all elements in the same sample matrix displays a similar trend, e.g., the RISNEI of all the...
elements in SY-4 increases with time after the initial ablation and transport, reaches its maximum at approximately 275 s, and then decreases with time. The RISNEI is not linear with time for a period of 210 s during laser ablation and transport. Therefore, data acquisition using prolonged laser ablation without a matrix match will not improve the precision and accuracy for elements whose fractionation behaviour is different from that of the internal standard.

Variations with time

Fig. 2 shows the RISNEI of Zn and Ga in SY-4 and BCR-2 of the first and last analyses. The last analysis was repeated using the same LA-ICP-MS operating conditions approximately 2 h after the first analysis. Fig. 2 indicates that the inter-element fractionation varies with time. Physical conditions during the laser ablation and transport may cause this variation. The oxygen content in the sample chamber significantly affects the inter-element fractionation during the laser ablation and transport and the mechanism is still under investigation. It was observed that different laser beam focusing may also affect the fractionation.9,11 The local temperature of the sample is an important factor in fractionation.11 Despite the RISNEI changes for the two different analyses, interestingly, all the elements in the same sample matrix displayed the same RISNEI versus time trend described above (Fig. 2).

Internal standard normalized fractionation factor (ISNFF)

Fig. 3 shows the relative Ca normalized Ga and Zn intensity in SY-4 versus time for the first 100 s laser ablation. A very good linear relationship was observed. To simplify the calculation here, it is assumed that the RISNEI is linear with time for the first 100 s during the laser ablation and transport. This is reasonable for our routine LA-ICP-MS analysis which uses 60 s for data acquisition. Fig. 4 is a schematic diagram shown the RISNEI versus time. AB is the RISNEI when the laser is initially fired, CD the RISNEI when the laser is off, EF the average RISNEI of the data acquisition, GH the average RISNEI of the first half of the data acquisition and IJ an average RISNEI of the second half of the data acquisition. The internal standard normalized fractionation factor (ISNFF) is defined here as the sum of the second half average RISNEI and the difference between the second and first half average RISNEI, divided by the second half RISNEI:

$$\text{ISNFF} = \frac{IJ \cdot (IJ - GH)}{IJ \cdot (IJ - GH) - J I J}$$

The ISNFF calculated varies with the time interval selected for data reduction. An average ISNFF of individual elements for the first 100 s laser ablation in three different matrices is presented in Table 3. Relative to Ca, six elements show different fractionation behaviour in three sample matrices during the LA-ICP-MS analysis. ISNFF ranges from 0.965 for La to 1.259 for Zn in NIST 613, from 0.991 for La to 1.332 for Zn in BCR-2 and from 0.992 for La to 1.432 for Zn in SY-4. The fractionation behaviour of the elements in fused glass chips of two geological silicate reference materials (BCR-2 and SY-4) is different from those in synthetic silicate glass standard. The relationship between ISNFF and the major components (SiO$_2$ and Al$_2$O$_3$) in three sample matrices is shown in Fig. 5. The ISNFF increases and decreases with Al$_2$O$_3$ and SiO$_2$ contents in the sample matrices, respectively. The relationship between the fractionation and elemental properties such as field strength and melting temperature has been investigated previously,7 but no significant correlation was observed. A linear relationship between the ISNFF and the sum of first and second ionization enthalpies is shown in Fig. 6, indicating that inter-element fractionation during laser ablation depends on ionization energy. This suggests that a low ionization energy element was ablated easier than that of high ionization energy, which lead to the progressive enrichment of high ionization-energy elements in the ablation.

Fig. 1 Relative Ca normalized element intensity of (a) Zn, (b) Ga, (c) V and (d) La in NIST 613, BCR-2 and SY-4 in LA-ICP-MS analysis.

The mechanism of inter-element fractionation in LA-ICP-MS is not very well understood, and will be investigated further.

Inter-element fractionation correction

The ISNFF for individual elements in NIST 613 standard and samples was calculated using the equation described above.

Fig. 2 Relative Ca normalized element intensity of (a) Zn and (b) Ga in SY-4 and of (c) Zn and (d) Ga in BCR-2 for the first and last analyses. The last analysis was repeated using the same LA-ICP-MS operating conditions approximately 2 h after the first analysis.

Fig. 3 Relative Ca normalized element intensity of (a) Zn and (b) Ga versus time, showing linearity for the first 100 s laser ablation and transport of LA-ICP-MS.

Fig. 4 Simplified diagram of relative internal standard normalized element intensity (RISNEI) versus time. AB is the RISNEI when the laser is initially fired, CD the RISNEI when the laser is off, EF the average RISNEI of the data acquisition, GH the average RISNEI of the first half of the data acquisition and IJ the average RISNEI of the second half of the data acquisition. The internal standard normalized fractionation factor (ISNFF) is defined here as the sum of the second half average RISNEI and the difference between the second and first half average RISNEI, divided by second half RISNEI of data acquisition.
The ISNFF of the element in the samples was then normalized to that of the same element in standard, and applied to the final elemental concentration calculation described previously: \[ C_{\text{Sample analyte, corrected}} = C_{\text{Sample analyte}} \times \frac{\text{ISNFF (Standard analyte)}}{\text{ISNFF (Sample analyte)}} \]

The results with and without inter-element fractionation correction are present in Table 4. The accuracy expressed as the relative difference between this work and literature value is shown in Fig. 7. The data accuracy by LA-ICP-MS with ISNFF correction developed in this study (using the equation described above) is significantly improved, particularly for Zn and Ga. The relative difference for Zn is reduced from 53.5 to 2.6% for BCR-2 and from 81.5 to 7.2% for SY-4, and that for Ga from 16.3 to 5.4% for BCR-2 and from 30.9 to 5.4% for SY-4. Since Gray performed the first LA-ICP-MS analysis in 1985, good precision and accuracy by LA-ICP-MS have been obtained without inter-element fractionation correction and matrix matches if an element whose fractionation is similar to

### Table 3 ISSF of elements for the first 100 s laser ablation in three different matrices

<table>
<thead>
<tr>
<th>Element</th>
<th>51V</th>
<th>64Zn</th>
<th>69Ga</th>
<th>87Sr</th>
<th>138La</th>
<th>146Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST 613 (average, (n=5))</td>
<td>1.057</td>
<td>1.259</td>
<td>1.142</td>
<td>1.012</td>
<td>0.965</td>
<td>0.974</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>1.8</td>
<td>3.0</td>
<td>2.3</td>
<td>0.3</td>
<td>1.6</td>
<td>1.3</td>
</tr>
<tr>
<td>BCR-2 (average, (n=5))</td>
<td>1.109</td>
<td>1.332</td>
<td>1.199</td>
<td>0.991</td>
<td>0.983</td>
<td>0.985</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>1.4</td>
<td>1.6</td>
<td>2.1</td>
<td>2.0</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>SY-4 (average, (n=5))</td>
<td>1.131</td>
<td>1.432</td>
<td>1.286</td>
<td>0.992</td>
<td>0.998</td>
<td>0.980</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>2.1</td>
<td>3.0</td>
<td>3.0</td>
<td>1.3</td>
<td>1.1</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The accuracy of LA-ICP-MS with ISNFF correction developed in this study (using the equation described above) is significantly improved, particularly for Zn and Ga. The relative difference for Zn is reduced from 53.5 to 2.6% for BCR-2 and from 81.5 to 7.2% for SY-4, and that for Ga from 16.3 to 5.4% for BCR-2 and from 30.9 to 5.4% for SY-4. Since Gray performed the first LA-ICP-MS analysis in 1985, good precision and accuracy by LA-ICP-MS have been obtained without inter-element fractionation correction and matrix matches if an element whose fractionation is similar to those of the analytes was chosen as an internal standard. This can be very clearly explained in Table 3. Relative to Ca, the elements Sr, La and Nd have ISNFFs very close to 1 in both the external calibration standard (NIST 613) and samples (BCR-2 and SY-4). The results calculated using NIST 613 as an external standard and Ca as an internal standard are not very different between the data with and without ISNFF correction (Table 4). However, if the calibration standard normalized ISNFF of the elements (e.g., Zn and Ga in this study) is significantly greater or less than 1, an error is introduced into the calculated results of LA-ICP-MS analysis if the procedure used here is not adopted.

**Conclusions**

Inter-element fractionation of seven elements (Ca, V, Zn, Ga, Sr, La and Nd) in three different sample matrices (NIST 613, BCR-2 and SY-4) during LA-ICP-MS analysis using a UV 266 nm laser was investigated. The fractionation depends on the sample matrices and varies with time. A linear relationship between the ISNFF and the ionization enthalpy indicates that...
inter-element fractionation during laser ablation depends on ionization energy. In this paper, the internal standard normalized fractionation factor (ISNFF) is defined as the sum of the ionization energy. In this paper, the internal standard normalized fractionation during laser ablation depends on matrix matches only if the calibration standard is close to 1. Further work is needed to investigate the inter-element fractionation of more elements in various matrices, e.g., Pb, Th and U in zircons. The isotopic ratio measurement by LA-ICP-MS in zircons has been used for geochronology. However, owing to the inter-element fractionation, this measurement has been limited to the determination of only Pb²⁰⁷/Pb²⁰⁶ ratios. With the inter-element fractionation correction, it will be possible to measure more useful U/Pb and Th/Pb ratios.

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References

Table 4 Concentrations determined by LA-ICP-MS before and after the ISNFF correction, and literature values for reference materials BCR-2 and SY-4

<table>
<thead>
<tr>
<th>Element</th>
<th>Before ISNFF correction</th>
<th>After ISNFF correction</th>
<th>Literature value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BCR-2 (average, n=5)/µg g⁻¹</td>
<td>SY-4 (average, n=5)/µg g⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RSD (%)</td>
<td>RSD (%)</td>
<td>Before ISNFF correction</td>
</tr>
<tr>
<td>⁵¹V</td>
<td>1.1</td>
<td>2.8</td>
<td>23.2</td>
</tr>
<tr>
<td>⁶⁶Zn</td>
<td>8.8</td>
<td>12.7</td>
<td>32.2</td>
</tr>
<tr>
<td>⁶⁹Ga</td>
<td>3.8</td>
<td>5.0</td>
<td>1130</td>
</tr>
<tr>
<td>⁸⁸Sr</td>
<td>2.2</td>
<td>13.6</td>
<td>571</td>
</tr>
<tr>
<td>¹³⁹La</td>
<td>3.9</td>
<td>9.1</td>
<td>1191</td>
</tr>
<tr>
<td>¹⁴⁶Nd</td>
<td>4.8</td>
<td>3.4</td>
<td>58</td>
</tr>
</tbody>
</table>

Fig. 7 Accuracy expressed as the relative difference between results obtained in this work (A) before and (B) after ISNFF correction, and literature values for (a) BCR-2 (ref. 16) and (b) SY-4 (ref. 17).