Combined Major and Trace Element LA-ICP-MS Analysis of Compositional Variations in Simple Solid Solutions through Cross Correlation with an EPMA-Characterized Working Standard

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Abstract: Determining correlated major and trace element zoning profiles is an important goal in modern microanalysis and is critical to some geospeedometric applications. We show that a precise determination of relative variations in major element compositions of simple solid solutions is possible by LA-ICPMS, and that low accuracy (analytical bias) can be corrected for through cross correlation with electron problem microanalyzer (EPMA)-characterized working standards. Further, the relative uncertainties on binary or quasibinary solid solution endmember proportions are always lower than the relative uncertainties on the ratio of the principle substituting elements by at least a factor of 2. In calcic plagioclase, for example, the relative uncertainty on XNa is a factor of (1 − XNa) smaller than the relative uncertainty on Ca/Na. Using a well-characterized, concentrically zoned bytownite crystal as an example, we compare reproducibilities of FE-EPMA and W-EPMA analyses with 2 μm beam diameter and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) with 16 μm beam diameter. While the accuracy of LA-ICP-MS analyses is low (analytical bias), the precision of LA-ICP-MS analyses is slightly higher than that of FE-EPMA data and comparable to that of the W-EPMA data. EPMA-corrected LA-ICP-MS data can thus be used to characterize major oxide compositional variations and potential covariations with trace elements within individual crystals.

Key words: W-EPMA, FE-EPMA, LA-ICP-MS, uncertainties, major oxide analysis

INTRODUCTION

In some minerals, e.g., the feldspars, major oxide compositions control both trace element diffusivities (Cherniak & Watson, 1994; Giletti & Casserly, 1994; Cherniak, 2002) and partitioning (Blundy & Wood, 1991; Bindeman et al., 1998), and compositional variations in major and trace elements within crystals therefore need to be determined with high precision to minimize uncertainties in geospeedometric age determinations (Costa & Dungan, 2005; Morgan & Blake, 2006). When trace elements of low concentrations are involved (e.g., Sr in plagioclase), their analysis is preferentially conducted using sufficiently sensitive methods such as laser ablation inductively coupled plasma (ICP) or secondary ion mass spectrometry, while major oxides can be determined through electron beam techniques such as electron probe microanalyzer (EPMA) (Zellmer et al., 1999). However, reliable cross correlation of major and trace element profiles is often difficult because major and trace element analyses are based on different analyte volumes. It would therefore be preferable to obtain both major oxides and trace element compositions using the same method, on the same analyte volume, and at the same time. The purpose of this contribution is to show that laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) can be successfully employed in combined major and trace element analysis in simple binary or quasibinary solid solutions.

Feasibility of accurately analyzing major and trace elements of natural silicate glasses by LA-ICP-MS has recently been demonstrated (Guillong et al., 2005; Liu et al., 2008; Humayun et al., 2010). Using ablation yield correction factors, Liu et al. (2008) also achieved accuracies of better than 10% for many major oxides in silicate minerals determined by LA-ICP-MS with a 32 μm beam diameter. However, more accurate analysis of both major and trace elements by LA-ICP-MS, particularly at smaller beam diameters to obtain higher resolution data, remains difficult because independently determined major oxide compositions are generally required to convert trace element counts into concentrations by normalizing to a major element of known composition as an internal standard (e.g., Longerich et al., 1996); and because major element analysis by LA-ICP-MS is prone to (1) molecular isobaric interferences, including NaO+ on K, Fe2+ and CO2+ on Si, and SiO+ and CO2 on Ca, where CO and CO2 may be present due to contamination from the air after sample exchange, (2) high instrumental background levels, e.g., of 23Na, and (3) a lack of suitable reference materials for accurate calibration.

Problem (1) can be circumvented in exceptional circumstances where stoichiometry can be assumed (e.g., in simple binary or quasibinary solid solutions like olivine or plagioclase) and totals sum to 100% (m/m) (Zellmer et al., 2003,
Problem may be circumvented if the offset in accuracy between the LA-ICP-MS analysis and the true value is systematic, so that the LA-ICP-MS data can be corrected for this offset, e.g., through compositional characterization of the same crystal growth zone by EPMA analysis and/or mapping (Zellmer et al., 2011).

In this contribution, we assess the precision with which major oxide compositional variations within simple solid solution minerals can be identified, using calcic plagioclase as an example. As a working standard, we used a well-characterized bytownitic crystal and conducted multiple LA-ICP-MS analyses along individual growth zones (cf. Fig. 1). We show that anorthite content cannot be accurately determined by LA-ICPMS at small beam diameters of 16 μm. LA-ICPMS in our specific operating conditions yielded Ca/Na ratios that were consistently a factor of 1.3 too low but did so with a high precision (1σ relative uncertainties of 0.6% by LA-ICP-MS analyses). This compares to a slightly lower precision of 0.9% by FE-EPMA and to a similar precision of 0.6–0.7% by W-EPMA, which provide more accurate results. With the help of a working standard, combined LA-ICPMS and EPMA analysis can thus be employed to facilitate cross correlation with trace element analyses without compromising precision or accuracy of major oxide microanalyses in silicate minerals.

**Consideration of Relative Uncertainties**

In simple binary or quasibinary solid solutions, the endmember proportion is a function of the ratio of the principle substituting elements. For example, the forsterite content of olivine, $X_{Fo}$, is defined as

$$X_{Fo} = \frac{Mg}{Mg + Fe},$$

(1)

where Mg and Fe are atomic abundances. Equation (1) may be rewritten as

$$X_{Fo} = \frac{Mg}{Fe + 1}.$$

(2)

Similarly, the anorthite content of plagioclase, $X_{An}$, is defined as

$$X_{An} = \frac{Ca}{Ca + Na + K},$$

(3)

where Ca, Na, and K are atomic abundances. In case of low potassium contents, equation (3) is well approximated by

$$X_{An} = \frac{Ca}{Na + 1}.$$

(4)

In general, we can write

$$y = \frac{x}{x + 1},$$

(5)

where $y$ is the solid solution endmember proportion and $x$ is the relevant ratio of the atomic abundances of the substituting elements. We show in the Appendix that in the case of uncorrelated errors, the relative uncertainty on the solid solution endmember proportion, $\sigma_y/y$, is related to the relative uncertainty on the ratio of the principle substituting elements, $\sigma_x/x$, through

$$\frac{\sigma_y}{y} = \frac{\sigma_x}{x} (1 - y).$$

(6)

For magnesian olivine, the relative uncertainty on forsterite content is thus given by

$$\frac{\sigma_{X_{Fo}}}{X_{Fo}} = \frac{\sigma_{(Mg/Fe)}}{Mg/Fe} (1 - X_{Fo}),$$

(7)

while for ferroan olivine, the relative uncertainty on fayalite content is given by

$$\frac{\sigma_{X_{Fa}}}{X_{Fa}} = \frac{\sigma_{(Fe/Mg)}}{Fe/Mg} (1 - X_{Fa}).$$

(8)

Further, for calcic plagioclase with negligible K content, the relative uncertainty on anorthite content is given by

$$\frac{\sigma_{X_{An}}}{X_{An}} = \frac{\sigma_{(Ca/Na)}}{Ca/Na} (1 - X_{An}),$$

(9)
while for sodic plagioclase with negligible K content, the relative uncertainty on albite content is given by

\[
\frac{\sigma_{X_{Ab}}}{X_{Ab}} = \frac{\sigma_{(Na/Ca)}}{Na} \left(1 - X_{Ab}\right).
\]  

Because simple solid solutions can be considered from both ends (i.e., are equivalent if calculated as a fraction of either end-member; e.g., Fo or Fa, and An or Ab), X will never be greater than 0.5, and it follows that the relative uncertainties on endmember proportions are always lower than the relative uncertainties on the ratio of the principle substituting elements by at least a factor of 2. Further, for natural compositions close to the endmember compositions, relative uncertainties may become very small as long as the concentration of the minor substituting element (e.g., Fe in the case of magnesian olivine and Na in the case of calcic plagioclase) can be determined with reasonable precision and contributions from minor components such as Mn in olivine or K in plagioclase remain sufficiently small. The reason for the lower uncertainty on the end-member compositions compared to the uncertainty of the element ratios is the significant covariance between Mg/Fe and \(X_{Fo}\) for olivine and between Ca/Na and \(X_{An}\) for plagioclase [cf. equations (1) to (5)].

**Materials and Methods**

**Electron Microprobe Analysis and Elemental Distribution Mapping**

Quantitative analyses on plagioclase were performed by a JEOL Tungsten (W) EPMA JXA-8900R and a JEOL field emission (FE) EPMA JXA-8500F (JEOL Ltd., Tokyo, Japan) equipped with wavelength dispersive spectrometers. Both instruments are housed in the same laboratory at the Institute of Earth Sciences, Academia Sinica. The analytical procedure used standard conditions optimized for silicate analyses. Secondary and backscattered electron images were used to guide the analysis on target positions of minerals. W-EPMA and FE-EPMA were operated at acceleration voltage of 15 kV and 12 kV with beam current of 12 nA and 6 nA, respectively. Analyses were made at 10 μm intervals with a 2 μm beam diameter. For both instruments, count rates for Na and Ca were of the order of 3–4 × 10^4 cps/μA and 1–2 × 10^5 cps/μA, respectively, under these operating conditions, which were chosen to minimize Na volatilization and maximize the precision of repeat analyses. Relative standard deviations (RSD) for Si, Na, and K were less than 1%, and others were less than 0.6%. These values compare well with those commonly obtained in other laboratories.

Counting times were 10 s (peak) and 5 s (upper and lower baselines) for all elements. The measured X-ray intensities were ZAF-corrected using the standard calibration of synthetic chemical-known standard minerals with various diffracting crystals, as follows: diopside for Si with TAP crystal, orthoclase for K with PET (H) crystal, anorthite for Al (TAP) and Ca (PET), hematite for Fe with LiF crystal, jadeite, or albite for Na (TAP), and pyrope or periclase for Mg (TAP).

To aid cross correlation of EPMA and ICP-MS analyses and to evaluate the general characteristics of crystal zoning, elemental distribution mapping of plagioclase was performed with 15 kV, 50 nA, and 1 μm for the acceleration voltage, beam current, and beam size, respectively. X-ray intensities of Ca-Kα, Na-Kα, and K-Kα were counted for 0.03 s in each spot, at 1 μm intervals.

**Laser Ablation Facility**

Plagioclase major and trace elements were measured at the GeoForschungsZentrum Potsdam using a GEOLAS M Pro (Coherent, Germany) laser ablation device coupled to an ELAN DRC-e (PerkinElmer Sciex, Concord, Ontario, Canada) ICP-MS in dual detector mode. The LA device consisted of an excimer laser (COMPexPRO 102, Argon Fluoride 193 nm, Lambda Physik, Germany) with a maximum output energy of 200 mJ per pulse for repetition rates between 1 and 10 Hz, an optical beam path homogenizer to provide a homogeneous laser beam, an aperture mask with 10 circular holes with diameters of 0.125 to 4 mm (for ablation pit diameters of 5 to 160 μm), a petrographic microscope (Olympus BX 51), a 20 cm^3 sample cell, and a computer-controlled x, y, z stage. Samples were observed through the petrographic microscope with two lenses of different magnification (5- and 20-fold). During ablation, the sample image was continuously observed on a separate high-resolution monitor through a Schwarzschild objective (25-fold magnification) and a high-resolution charge-coupled device camera.

**ICP-MS Data Acquisition and Reduction**

Helium was used as carrier gas (1.0 L min⁻¹) and argon as plasma (15 L min⁻¹), auxiliary (1.2 L min⁻¹), and make-up gas (0.7 L min⁻¹). Isotopes of elements of interest (²³Na, ²⁴Mg, ²⁷Al, ²⁸Si, ⁳⁹K, ⁴²Ca, ⁵⁶Fe) were measured using an output energy of 100 mJ (reduced by an attenuator to achieve an energy density of 6 J cm⁻²), with 10 ms dwell time and 3 ms quadrupole settling time. With exception of ⁴²Ca, these isotopes were chosen to allow to maximize count rates at small spot sizes required for detailed crystal profiling. Background intensities from the gas blank were measured for 30 s (laser firing, shutter closed) followed by acquiring transient signals of the analytes for 60 s (laser firing, shutter open). Each analytical batch consisted of up to 20 samples. Samples were measured using a repetition rate of 5 Hz, an energy density of 6 J cm⁻², and a spot size of 16 μm. The same operating conditions will be suitable for contemporaneous trace element analyses, e.g., Sr (cf. Zellmer et al., 2011). A reference glass standard (NIST 610) was measured twice at the beginning and twice at the end of an analytical batch for external calibration, using a repetition rate of 5 Hz, an energy density of 6 J cm⁻², and a spot size of 32 μm.
Due to the lower ablation yield when using small spot sizes for detailed crystal profiling, isotopes measured by LA-ICP-MS were chosen to maximize count rates using the following criteria: (1) isotopes that are free of isobaric interferences from isotopes of other elements; (2) isotopes with high isotopic abundance; (3) isotopes with low contribution of polyatomic species (gas blank composed of Ar, He, H, C, N, O); (4) isotopes with high signal-to-noise ratio (SNR). Used isotopes are summarized in Table 1 together with potential interferences from polyatomic species, average gas blank intensities, typical sample count rates and related SNR. The choice of two isotopes deviates from the above-mentioned criteria: $^{42}\text{Ca}$ was used instead of $^{44}\text{Ca}$, which has an approximately three times higher isotopic abundance, because the higher gas blank intensity for $^{44}\text{Ca}$ results in a better SNR for $^{42}\text{Ca}$ at sufficient count rates. Additionally, the intensity ratio $^{44}\text{Ca}/^{42}\text{Ca}$ of 3.6 (obtained for NIST 610 and 16 quartz samples) compared to the isotopic abundance ratio of 3.2, indicating a polyatomic interference by $^{40}\text{Ca}^{4}\text{He}$ on $^{44}\text{Ca}$. Further, $^{56}\text{Fe}$ was used instead of $^{57}\text{Fe}$: although $^{57}\text{Fe}$ shows a much lower gas blank contribution and a higher SNR, its 40 times lower isotopic abundance results in significantly lower count rates with worse counting statistics. Interferences by polyatomic $^{40}\text{Ar}^{16}\text{O}$ and $^{40}\text{Ca}^{16}\text{O}$ may be neglected due to the good agreement between the intensity ratio $^{56}\text{Fe}/^{57}\text{Fe}$ of 40.8 (obtained for NIST 610 and 16 quartz samples) and the isotopic abundance ratio of 41.7.

For data reduction, the LOTUS 123 macro-based spreadsheet program LAMTRACE was employed. A short, general description of its capabilities is given by van Achterbergh et al. (2001), and its algorithms are described in Longerich et al. (1996). The program performs background correction, correction for instrumental drift, internal calibration, choice of integration intervals, and calculation of element concentrations using external calibration.

$^{42}\text{Ca}$ was used for all elements of interest as internal standard to convert integrated intensities into element concentrations. For the NIST 610 glass standard, a value of 11.45% (m/m) for CaO was used (Jochum & Nehring, 2006). For all plagioclase samples an initial value of 12% (m/m) for CaO was taken as a first approximation and then corrected together with other elements of interests following stoichiometric calculations (see below). The choice of the initial value is essentially arbitrary, as the corrected values are a function of Ca/Na ratios.

Mineral stoichiometric calculations proceeded as follows: first, the number proportions of the cations Ca, Na, Mg, Fe, and Ti were calculated by division of the oxide proportions (as determined by LAMTRACE, see above) through the molecular weights of CaO, NaO$_{1/2}$, KO$_{1/2}$, MgO, FeO, and TiO$_2$, respectively. Then number proportions of Si and Al were determined following feldspar stoichiometric constraints that

$$\text{Si} = 2 \left(\text{Ca} + \text{Mg}\right) + 3 \left(\text{Na} + \text{K}\right) - \text{Ti}$$

and

$$\text{Al} = 2 \left(\text{Ca} + \text{Mg}\right) + \text{Na} + \text{K} - \text{Fe},$$

assuming substitution of Mg for Ca, Fe for Al, and Ti for Si. Note that although other substitution mechanisms for trace elements are possible, particularly for Fe that may occur as Fe$^{2+}$, this would only have a very small effect on the calculated proportions of Si and Al.

The oxides were then recalculated and normalized to total 100% (m/m) using number proportions and the respective molecular weights of the oxides. Note that if trace elements are analyzed at the same time, they can be normalized to the corrected CaO value after these stoichiometric calculations are performed.

### Sample Description and Sampling Strategy

The data presented here were collected as part of a systematic study of zoning patterns in mid-ocean ridge basalt (MORB) plagioclase crystals. As a working standard, we employed a concentrically zoned bytownitic plagioclase crys-

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Potential Interferences from Polyatomic Species</th>
<th>Gas Blank Intensity (cps)</th>
<th>Typical Sample Intensity (cps)</th>
<th>SNR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{23}\text{Na}$</td>
<td>No significant one</td>
<td>850</td>
<td>22,000</td>
<td>26</td>
</tr>
<tr>
<td>$^{24}\text{Mg}$</td>
<td>$^{23}\text{Na}^{1}\text{H}$</td>
<td>3</td>
<td>1,300</td>
<td>530</td>
</tr>
<tr>
<td>$^{27}\text{Al}$</td>
<td>No significant one</td>
<td>780</td>
<td>190,000</td>
<td>250</td>
</tr>
<tr>
<td>$^{28}\text{Si}$</td>
<td>$^{11}\text{C}^{16}\text{O}, ^{14}\text{N}_{2}$</td>
<td>47,000</td>
<td>150,000</td>
<td>3</td>
</tr>
<tr>
<td>$^{39}\text{K}$</td>
<td>$^{39}\text{Ar}^{1}\text{H}$</td>
<td>34,000</td>
<td>34,000</td>
<td>1</td>
</tr>
<tr>
<td>$^{42}\text{Ca}$</td>
<td>$^{12}\text{C}^{14}\text{N}^{16}\text{O}_{2}, ^{38}\text{Ar}^{1}\text{He}, ^{40}\text{Ca}^{4}\text{He}$</td>
<td>22,000</td>
<td>31,000$^b$</td>
<td>1.4$^b$</td>
</tr>
<tr>
<td>$^{47}\text{Ti}$</td>
<td>No significant one</td>
<td>30</td>
<td>60</td>
<td>2</td>
</tr>
<tr>
<td>$^{56}\text{Fe}$</td>
<td>$^{40}\text{Ar}^{16}\text{O}, ^{40}\text{Ca}^{16}\text{O}$</td>
<td>11,000</td>
<td>22,000</td>
<td>2</td>
</tr>
<tr>
<td>$^{57}\text{Fe}^a$</td>
<td>$^{40}\text{Ar}^{16}\text{O}^{1}\text{H}$</td>
<td>60$^a$</td>
<td>300$^b$</td>
<td>5$^b$</td>
</tr>
</tbody>
</table>

$^a$Not used for this study, data from measurements of other projects for discussion.

$^b$Estimated data, calculated using isotopic abundances.
tional growth zones on repeat analyses along three compositionally homogeneous growth zones within this crystal. Laser ablation spots are marked in Figure 1, which represents a Na map of this crystal produced by FE-EPMA. FE-EPMA and W-EPMA quantitative analyses were conducted within close proximity of these spots, within the same growth zones. Reproducibilities of EPMA analyses from within each individual growth zone are comparable to those of repeat analyses of the homogeneous gem labradorite AMNH 95557 (unpublished data), providing evidence for growth zone homogeneity.

**Results**

FE-EPMA, W-EPMA, and LA-ICPMS data are given in Supplementary Tables 1, 2, and 3, respectively, and the results are summarized in Table 2.

**Supplementary Tables 1, 2, and 3**

Supplementary Tables 1, 2, and 3 can be found online. Please visit journals.cambridge.org/jid_MAM.

When LA-ICP-MS- and EPMA-derived Ca/Na ratios are compared, it becomes evident that the LA-ICP-MS data does not yield accurate results: LA-ICP-MS-derived Ca/Na ratios are consistently a factor of 1.3 too low. However, the reproducibility of LA-ICP-MS-derived Ca/Na ratios as based on repeat analyses along three compositionally homogeneous growth zones (RSD = 2.2%, n = 17; 2.2%, n = 17; 1.7%, n = 16) is slightly better than for FE-EPMA-derived Ca/Na ratios (RSD = 3.3%, n = 43; 4.1%, n = 15; 4.9%, n = 35), and comparable to W-EPMA-derived Ca/Na ratios (RSD = 2.0%, n = 38; 2.9%, n = 16; 2.5%, n = 38).

The relative uncertainty on anorthite content is a function of anorthite content and the relative uncertainty on the Ca/Na ratio [cf. equation (9)]. Hence, when comparing the relative uncertainties on anorthite content, the anorthite content itself must be accurately known. Using equation (9), we thus combine the EPMA-derived anorthite content and the LA-ICPMS-derived uncertainty on the Ca/Na ratios to assess the uncertainty in anorthite content measured by LA-ICPMS. We obtain 1σ relative standard deviations on anorthite content of 0.6%, 0.5%, and 0.5% for LA-ICPMS data of the three respective growth zones. This compares to 0.9%, 0.9%, and 1.3% for FE-EPMA data and 0.6%, 0.6%, and 0.7% for W-EPMA data of the three respective growth zones [where equation (9) yields the same result as the uncertainty based on the reproducibility of the sample population].

In summary, in this study the precision on LA-ICP-MS analyses of plagioclase composition was a factor of 1.5 to 2.6 better than for FE-EPMA analyses and similar to that of (or up to a factor of 1.4 better than for) W-EPMA analyses.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Average</th>
<th>Relative Standard Deviation of Repeat Analyses along Growth Zones of Working Standard.</th>
<th>Zone #1</th>
<th>Zone #2</th>
<th>Zone #3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(FE-EPMA, W-EPMA, LA-ICPMS)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SiO2 (%)</td>
<td>50.38 0.9</td>
<td>50.72 0.6</td>
<td>51.34 1.1</td>
<td>50.49 0.3</td>
</tr>
<tr>
<td></td>
<td>Al2O3 (%)</td>
<td>31.16 0.8</td>
<td>30.54 1.1</td>
<td>30.34 1.1</td>
<td>30.71 0.7</td>
</tr>
<tr>
<td></td>
<td>FeOa (%)</td>
<td>0.52 0.2</td>
<td>0.53 0.3</td>
<td>0.53 0.3</td>
<td>0.54 0.5</td>
</tr>
<tr>
<td></td>
<td>MgO (%)</td>
<td>0.23 0.5</td>
<td>0.24 0.6</td>
<td>0.24 0.6</td>
<td>0.23 0.5</td>
</tr>
<tr>
<td></td>
<td>CaO (%)</td>
<td>14.34 0.6</td>
<td>14.49 0.6</td>
<td>14.53 0.6</td>
<td>14.49 0.6</td>
</tr>
<tr>
<td></td>
<td>Na2O (%)</td>
<td>3.12 0.6</td>
<td>3.23 0.7</td>
<td>3.14 0.6</td>
<td>3.24 0.7</td>
</tr>
<tr>
<td></td>
<td>K2O (%)</td>
<td>0.04 0.2</td>
<td>0.05 0.2</td>
<td>0.05 0.2</td>
<td>0.05 0.2</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>99.81 c 0.0</td>
<td>99.84 c 0.0</td>
<td>99.84 c 0.0</td>
<td>99.84 c 0.0</td>
</tr>
</tbody>
</table>

| Ca/Na | 2.53 0.3 | 3.57 0.6 | 3.57 0.6 | 3.57 0.6 | 3.57 0.6 | 3.57 0.6 |

**Table 2.**
of bytownitic plagioclase. In general, broadly comparable precision of LA-ICP-MS and EPMA data of major element composition allows the use of laser data to give precision major element chemistry for the same analyte volume that trace element chemical measurements are made on, if an EPMA-characterized working standard is employed to improve accuracy.

**DISCUSSION**

As outlined in the Introduction, the reasons for the discrepancy of the major element oxide concentrations determined by LA-ICP-MS compared to EPMA data include isobaric interferences, instrumental background, and the lack of suitable reference materials for accurate calibration of the ICP-MS signal. Part of the discrepancy is therefore likely attributably to a matrix effect, namely the use of NIST 610 glass standard for determining oxide concentrations in plagioclase feldspar. A better calibration would likely be achieved by using a plagioclase standard instead, as NIST 610 appears to be a less than ideal internal standard for silicate analyses by using a plagioclase standard instead, as NIST 610 appears to be a less than ideal internal standard for silicate analyses (cf. Liu et al., 2008). However, most LA-ICP-MS laboratories do not have a range of large and homogenous enough mineral standards at their disposal, so even if more accurate major element analyses were possible by employing such standards, it may be difficult to use this matrix-matching approach in practice. Our approach is to correct for the observed discrepancy by adjusting the Ca/Na ratio of the LA-ICP-MS data using an EPMA-characterized working standard. This correction is feasible because the LA-ICP-MS derived Ca/Na ratios are systematically different (namely lower by a factor of 1.3 under our analytical conditions) compared to those determined by EPMA. Our methodology not only solves the issue of poor matrix matching between feldspar and the NIST 610 glass standard, but in addition corrects for any potential discrepancies arising from isobaric interferences and instrumental background, and can therefore easily be adopted by other laboratories.

In the following, we provide a worked example of how to determine variations in major element composition along a traverse of a compositionally zoned feldspar phenocryst using LA-ICPMS (see Supplementary Spreadsheet 4).

**Supplementary Spreadsheet 4**

Supplementary Spreadsheet 4 can be found online. Please visit journals.cambridge.org/jid_MAM.

The working standard used above (Fig. 1) lends itself to be used as an example. We have collected LA-ICPMS data of a rim-to-rim traverse across this crystal (cf. Fig. 2). Following the stoichiometric approach outlined above, we obtain an anorthite profile that resolves very well the observed calcic core overgrown by a more sodic rim (large open diamonds in Fig. 3).

However, this profile significantly underestimates the true anorthite content of the crystal, as LA-ICP-MS-derived Ca/Na ratios were shown above to be consistently a factor of 1.3 too low for the specific matrix under consideration and the specific beam conditions used here. Hence, we may derive a corrected profile, which more accurately reflects the anorthite content of this crystal, by reducing the number proportion of Na by a factor of 1.3 prior to the stoichiometric calculation of the number proportions of Si and Al. The resulting profile is shown with black diamonds in Figure 3. Note that the absolute 2σ uncertainties of each point have slightly decreased compared to the uncorrected LA-ICPMS profile due to the slightly higher overall anorthite content [cf. equation (9) and Supplementary Spreadsheet 4].

To show that this corrected LA-ICPMS profile does indeed accurately characterize the chemistry of the crystal, we have used W-EPMA to obtain a compositional traverse parallel and close to the LA-ICPMS pits (small gray diamonds in Fig. 3). The two profiles are clearly within an error of one another. The corrected LA-ICPMS profile, however, yields a smoother zoning pattern, which likely reflects the averaging of small-scale heterogeneities by the 16 μm laser beam. This smoother profile would be more suitable for cross correlation with trace element data, which may be collected during the same analytical session and at the same time.

**Conclusions**

1. We provide formulas for the calculation of relative uncertainties on simple solid solution endmember proportions from the relative uncertainties on the ratio of the principle substituting elements. Relative uncertainties on endmember proportions are always lower by at least a factor of 2.
2. For plagioclase, the precision of W-EPMA data is at present slightly better than the precision of FE-EPMA data. This may due to a higher power density of the FE beam, which would increase beam damage for some silicates, or due to greater beam intensity fluctuations inherent to the design of the relatively new FE source.

3. Compared to EPMA analyses with a beam diameter of 2 μm, LA-ICP-MS measurements of major oxide composition of bytownitic plagioclase with a beam diameter of 16 μm is less accurate, but similarly (~W-EPMA) or slightly more (~FE-EPMA) precise.

4. In simple binary or quasibinary solid solution, cross correlation of LA-ICP-MS derived data with an EPMA-characterized working standard therefore makes it possible to obtain precise major element chemistry for the same analyte volume that the trace element chemical measurements are determined from, without compromising accuracy. At present, this approach therefore represents one of the most viable methods for obtaining high-resolution correlated major and trace element data on simple solid solution minerals.

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REFERENCES


**Appendix**

Here we show that if \( y = x/(x + 1) \) [cf. equation (5)], the relative uncertainties \( \sigma_y/y \) and \( \sigma_x/x \) are related [cf. equation (6)] through \( \sigma_y/y = \sigma_x/x(1 - y) \) if \( \sigma_x \) and \( \sigma_y \) are uncorrelated.

We take the reciprocal of

\[
y = \frac{x}{x + 1}
\]  

(A.1)

to obtain

\[
\frac{1}{y} = 1 + \frac{1}{x}
\]  

(A.2)

Substituting

\[
a = 1/y
\]  

(A.3)

and

\[
b = 1/x,
\]  

(A.4)

we obtain

\[
a = 1 + b
\]  

(A.5)

and therefore

\[
\sigma_a = \sigma_b.
\]  

(A.6)

Further, it follows from equation (A.3) that

\[
\left( \frac{\sigma_a}{a} \right)^2 = \left( \frac{\sigma_y}{y} \right)^2
\]  

(A.7)

and backsubstitution of equation (A.3) yields

\[
\sigma_a = \sigma_y/y^2.
\]  

(A.8)

Similarly, it follows from equation (A.4) that

\[
\sigma_b = \sigma_x/x^2.
\]  

(A.9)

Combining equations (A.6), (A.8), and (A.9) then yields

\[
\frac{\sigma_y}{y} = \frac{\sigma_x}{x}
\]  

(A.10)

and therefore

\[
\frac{\sigma_y}{y} = \frac{\sigma_x}{x} \frac{y}{x}.
\]  

(A.11)

Further, rearranging equation (A.1) yields

\[
x = \frac{y}{1 - y}
\]  

(A.12)

and thus

\[
\frac{y}{x} = 1 - y.
\]  

(A.13)

Substituting equation (A.13) into equation (A.11) finally yields

\[
\frac{\sigma_y}{y} = \frac{\sigma_x}{x} (1 - y).
\]  

(A.14)

Q.E.D.