Major and trace analysis of basaltic glasses by laser-ablation ICP-MS

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Chemical analysis by laser-ablation ICP-MS can determine a large number of trace elements with a precision approaching traditional whole-rock analysis, but on a scale approaching that achieved by the electron microprobe. These characteristics make it a particularly attractive method for the analysis of volcanic glasses, but at present little is known about systematic errors, especially those from matrix effects. Here we investigate the precision and accuracy of LA-ICP-MS analysis of basaltic glasses for 60 elements, including rare earth elements (REE), large ion lithophile elements (LILE), high field strength elements (HFSE), the first row transition elements (FRTE), as well as less commonly analyzed elements such as Li, Be, Ge, Ga, W, Mo, As, Sb, Sn, Se, Ag, Tl, Bi, Cd and In. The rate of signal decline during ablation was found to vary systematically with the electronic structure of the element, in both calibration material (NIST SRM 612) and unknowns (natural basaltic glass VG-2 and vitrified basalt BCR-2G). These observations allow optimal analytical conditions with the available instrumentation and standards to be established. Analyses of VG-2 and seven of the MPI-DING vitrified rocks, commonly used as secondary standards, obtained under these conditions, are presented.

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1. Introduction

The advent of laser-ablation (LA) ICP-MS analysis has provided the opportunity for obtaining rapid and precise in situ major, minor and trace element analyses of geological materials. The precision of LA-ICP-MS analysis for elements with homogenous distribution in reference materials can be demonstrated by replication to be 1 to 3% [e.g., Jochum et al., 2006], attesting to the reliability of
the technique. Nearly all the trace elements traditionally analyzed in igneous rocks can be determined by this method, including rare earth elements (REE), large ion lithophile elements (LILE), high field strength elements (HFSE), the first row transition elements (FRTE), as well as less commonly analyzed elements such as Li, Be, Ge, Ga, W, Mo, As, Sb, Sn, Se, Ag, Ti, Bi, Cd and In [Hu et al., 2009; Jenner et al., 2010; Kamenetsky and Eggins, 2012]. These less commonly analyzed elements include many with geochemical properties distinct from the usual suite, which could offer new perspectives on petrogenesis.

[3] While the spatial resolution of LA-ICP-MS analysis is at present coarser than electron micro-probe analysis (EMPA), with typical sample volumes of ~10^3 µm^3 versus ~10 µm^3, respectively, the scales are similar enough that most of the advantages of EMPA are retained. Additionally, laser ablation circumvents or minimizes problems encountered using ICP-MS solution techniques, such as incomplete sample dissolution, contamination during sample preparation, and polyatomic mass interferences associated with the introduction of water and acid into the plasma [e.g., Longerich et al., 1993].

[4] Although LA-ICP-MS analysis of minerals and similar targets such as volcanic glasses is now widely undertaken, its accuracy is often not addressed. The fundamental assumption is that the background-corrected counts measured by the electron multiplier are linearly proportional to element contents for all elements. With this assumption, data reduction is simple [e.g., Longerich et al., 1996]: background-corrected counts on a selected isotope of an element X (C_X) in the unknown (unk) sample are compared as a ratio to the counts of an element whose content is known independently (e.g., by EMPA or perhaps mineral stoichiometry). These ratios ([C_X/C_SI]_unk) are then compared to the same ratios determined in an external standard (ext; [C_X/C_SI]_ext) of known composition. In addition to variability in background counts and operating conditions, systematic errors can be attributed to four factors: (1) erroneous values in the external standard; (2) differences in the ablation characteristics of the unknown compared to the external standard, which fractionates the [C_X/C_SI]_unk differently to [C_X/C_SI]_ext during ablation; (3) polyatomic interferences on the desired mass in either the unknown or the external standard and (4) non-linearity of the detector system.

[5] Here we report the results of several tests undertaken to evaluate all four types of systematic error, focusing on the optimization of the technique for the analysis of ocean floor basaltic (OFB) glasses from the Abyssal Volcanic Glass Data File (AVGDF [Melson et al., 2002]), the results of which are presented in the work of Jenner and O’Neill [2012]. The small sample volumes of LA-ICP-MS are particularly suitable for analysis of volcanic glasses, allowing their ubiquitous phenocrysts, vesicles and patches or rinds of alteration to be avoided. The values adopted for external calibration (NIST SRM 612) are checked by comparison to several glass reference materials. Potential polyatomic interferences were investigated by comparing the results obtained on different isotopes for a given element and by measuring the production rates where interferences were unavoidable. Matrix effects for 60 elements were investigated by comparing the rate of signal decay during ablation of NIST SRM 612, with those for BCR-2G and VG-2. Accuracy in the determination of contents by LA-ICP-MS were evaluated by comparing the results for the major and trace elements in the OFB glasses from the AVGDF with those previously determined by EMPA [Melson et al., 2002]. One unanticipated result worth highlighting is that we find the precision of Na analysis by LA-ICP-MS to be ~2%, better than that achieved by EMPA (~5%) and without the problem of Na loss by beam damage, which should eliminate a persistent worry about the interpretation of how natural mid ocean ridge basaltic (MORB) glasses relate to phase equilibrium experiments [McKenzie and O’Nions, 1998; Presnall and Hoover, 1984].

2. LA-ICP-MS Analysis: Operating Conditions

[6] We used a 7500S Agilent ICP-MS (RF power = 1350 W; ablation cell gas flow = 0.3 L min^{-1} He + 0.02 L min^{-1} H_2; auxiliary gas flow = 1.0 L min^{-1} Ar; laser energy = 50 55 mJ), coupled to an ANU HeIEx laser-ablation system, which employs an 193 nm wavelength EXCIMER laser (110 (ArF) COMPex, Lambda Physik), housed at the Research School of Earth Sciences (RSES), Australian National University (ANU). Data were acquired with 20 or 30 s of background measurement, followed by between 30 and 40 s of sample ablation (longer counting times were used for analyses of elements with low-level contents in the volcanic glasses). The ICP-MS was calibrated to low oxide production rates (ThO^+ / Th^+ typically <0.4%,...
measured using NIST SRM 612) and this rate was monitored throughout each analytical session. Analyses were only undertaken >30 min after each sample change to ensure background counts and oxide production rates were minimal during data collection.

3. Laser-Ablation Spot Dimension

[7] The precision, accuracy and limit of detection (LOD) for each element obtained by LA-ICP-MS analysis is dependent on a number of variables over which the analyst has some choice, namely the diameter of the ablation spot, ablation time, laser repetition rates and the counting time per element [e.g., Jackson et al., 1992]. Two factors are at play: first, counting statistics, which depend on how much material is swept into the ICP-MS and the dwell time for each element on the electron multiplier, and second, matrix effects during ablation, which influence the ratios in the plasma of elements with different chemical properties, such as volatility [Eggins et al., 1998]. The matrix effects are known to vary with the aspect ratio (depth to diameter) of the ablation spot [Eggins et al., 1998].

[8] Increasing laser spot diameter and repetition rate results in higher count rates and hence lower detection limits [e.g., Jackson et al., 1992]. Joehum et al. [2005a] reported that the relative standard deviation (RSD) for analyses were 1–3% with their 80 μm spot size but 3–10% with 40 μm. However, ablation of large quantities of material may affect plasma conditions (e.g., temperature and electron number density) by mass loading [e.g., Chan et al., 2000] and ultimately result in a reduction in count rates, especially for elements with a low ionization potential. Furthermore, the increased flux of material to the ICP-MS may result in higher backgrounds and memory effects, because of the deposition of some ‘sticky’ elements on the skimmer cones at the interface between the ICP source and the mass spectrometer [e.g., Carter et al., 2003; McGinnis et al., 1997]. Elements identified as being ‘sticky’ are Li, U, Be and the HFSE.

[9] To identify the optimal laser spot size for analysis of OFB and other geological samples, we have undertaken a systematic study of the sizes available on our laser (12 diameters, ranging from 19 to 303 μm) at a constant repetition rate of 5 Hz, using empirical criteria of precision, accuracy and LOD for a selection of 20 elements, including some REE, HFSE and LILE. We chose BCR-2G as the example material, with NIST SRM 612 for external calibration.

[10] The LOD decrease rapidly from 19 μm, the smallest ablation diameter, to 70 μm, followed by a more conservative decrease with increasing diameter to 303 μm (Figure 1a). Three replicate analyses of BCR-2G show a rapid decrease in RSD with increasing ablation diameter (Figure 1b), likely resulting from signal loss with ablation depth when utilizing the smallest ablation sizes [Eggins et al., 1998]. This effect, known as ‘downhole fractionation’, may vary with the nature of the sample and between different elements, producing systematic errors to be discussed in Section 5. At intermediate ablation diameters (86–187 μm), the RSD for all elements is <3% and the mean RSD at each ablation diameter is ≤1.5%. At an ablation diameter of 247 μm and 303 μm the RSD is slightly higher than for the intermediate ablation diameters (Figure 1b), confirming the onset of problems of memory and other effects anticipated above for high signal intensities.

[11] Figure 1c shows analyses of BCR-2G with increasing ablation diameter normalized to the GeoReM preferred values for each element [Joehum and Stoll, 2008], using 29Si for internal calibration of data. The offset of the values to lower contents than those in the GeoReM compilation (measured/preferred value typically 0.9 in Figure 1c) is discussed in Section 4. At the smallest ablation diameter (19 μm), the accuracy for many elements is poor (ranging from ~0.6 to ~1.4 of preferred values), in particular, for Pb, U, Co, Ta, Th, Be, Cs and the REE. With increasing ablation diameter, the deviation in values from the preferred values becomes relatively constant, until an ablation diameter of 303 μm, where the measured/preferred again become more variable. To exploit the optimal laser-ablation and ICP-MS operating conditions (optimal field shown in Figure 1b) for targeting the contents of elements in reference materials presented here and the OFB analyses presented by Jenner and O’Neill [2012], an ablation diameter of 86 μm and a laser repetition rate of 5 Hz were used for LA-ICP-MS analysis of the majority of the elements, with a 187 μm spot for a few elements with low abundances.

4. Pulse/Analogue Counting Mode
Electron Multiplier Effects

[12] Both 29Si and 43Ca are commonly used for internal calibration of LA-ICP-MS data, because
both elements are accurately determined by EMPA. On the HP Agilent 7500S ICP-MS, signal intensity is measured using two different counting modes by the electron multiplier; the pulse counting mode measures low intensity signals by counting the individual ions at the multiplier, whereas the upper analogue stage measures the higher intensity signals through a continuously variable current, which is directly proportional to the input. The transition from pulse to analogue counting modes on our instrument takes place at $\sim 3 \times 10^6$ counts per second. The sensitivity of the detector varies with many environmental factors, so the precise location of the transition also varies. Pulse/analogue correction factors for $\sim 20$ elements spanning the mass range (depending on the analytical routine) are measured daily at the RSES.

Figure 1
The content of Si in NIST SRM 612, reference glasses and the OFB analyzed for this study is high enough that the $^{29}$Si signal is always counted using analogue mode (typically $>20 \times 10^6$ counts per second). In contrast, the range in Ca contents in the samples and reference materials analyzed here, at the optimal ablation sizes of between 86 $\mu$m and 187 $\mu$m, results in $^{43}$Ca signal intensities that overlap the boundary between pulse and analogue counting modes. Despite the linear correlation between the slopes of the pulse and analogue counting methods, differences in response between the pulse and the analogue modes have been shown to result in a significant bias when the unknown is determined in one mode and the external standard in the other [e.g., Campbell and Burns, 2001].

In order to assess this effect, the measured/preferred value for BCR-2G using $^{29}$Si and $^{43}$Ca for internal calibration are compared in Figures 1c and 1d. With $^{29}$Si, the measured/preferred values remain constant, because $^{29}$Si is measured in analogue mode during analysis of both NIST SRM 612 and BCR-2G, demonstrating the linearity in the analogue counting method at a range in signal intensities. In contrast, for $^{43}$Ca, the measured/preferred values at ablation diameters of 112 and 142 $\mu$m are higher than at both smaller and larger ablation diameters. This offset can be attributed to $^{43}$Ca being measured using analogue mode for NIST SRM 612 (11.93 cg g$^{-1}$ CaO) and pulse mode for BCR-2G (7.06 cg g$^{-1}$ CaO). Because the transition from pulse to analogue modes in $^{43}$Ca coincides with the range of ablation diameters that otherwise give the optimal analytical conditions (86–187 $\mu$m), $^{29}$Si was used for internal calibration throughout this study. A small advantage occurs from using Si rather than Ca for internal calibration, because of the higher contents of SiO$_2$ ($\sim$ 50 cg g$^{-1}$) over CaO ($\sim$10 cg g$^{-1}$) in basaltic glasses, and pertinent to the aims of this contribution, the limited range in Si contents (46.9–53.7 cg g$^{-1}$) of the OFB samples compared to that of Ca (6.01–13.9 cg g$^{-1}$). The random error on Si from EMPA is calculated to be 0.5%, but 0.8% for Ca, from the estimated uncertainties of typical EMPA given in Table 4 of Canil and O’Neill [1996]...

5. Laser-Induced Elemental Fractionation

Laser ablation at a fixed spot size results in a decrease in counts with time for all elements as the ablation pit deepens. Eggins et al. [1998] demonstrated that the rate of decrease is greater for the refractory compared to the volatile elements during early stages of ablation, resulting in a progressive relative enrichment of more volatile elements as ablation proceeds. With further ablation, they showed that this trend was reversed as the initial flat bottom of the pit, characteristic at shallow depths, degrades to an increasingly convoluted topography. The effect is attributed to the particle size distribution of laser-induced aerosols, because the volatile elements are enriched within the small particle size fraction [Košler et al., 2005; Kuhn and Günther, 2004]. This effect is the exaggerated by the ICP, because the smaller particles in the laser-induced aerosols are preferentially vaporized, atomized and ionized compared to the larger particles [Košler et al., 2005; Kuhn and Günther, 2004]. These elemental fractionations have been shown to be substantially less using short wavelength...
excimer systems (193 nm), because of the resulting smaller particle size distributions [Guillong et al., 2003; Günther and Heinrich, 1999; Jochum et al., 2007; Kuhn and Günther, 2004].

[16] Although there are broad differences in the ablation characteristics of the volatile versus the refractory elements, no systematic patterns predicting the behavior of a given element have been reported. To investigate this further, we have calculated the rate of decrease in counts for a given element \([C_X]\) normalized to the rate of decrease in counts of the internal standard \([C_Si]\) during ablation of NIST SRM 612, corrected to the mean of the ratio (i.e., \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\)). The slopes for 60 elements were calculated from the average \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\) of between 3 and 8 analyses of NIST SRM 612 for a given analytical routine (typically four different analytical routines, were undertaken during each analytical session to achieve the limit of detection required for each element; see Section 8 for a description of each of the analytical routines). The averages for each routine undertaken during various analytical sessions conducted over a two year time period were compiled as an average to give the final \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\) and its standard deviation for 60 elements, which is typically ~40% for the REE; the scatter reflects variations in laser energy (i.e., laser pit depth), the error on the slope resulting from the pulsing of the laser, the dwell time on each mass during counting by the electron multiplier, as well as counting statistics and linearity of the ion-counting system.

[17] The normalized slopes \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\) are plotted in Figure 2a as a function of the 50% condensation temperatures of the element from the solar nebula [from Lodders, 2003], taken as an approximate indication of the element’s volatility, following the suggestion of Gaboardi and Humayun [2009]. There is a broad change in the behavior of elements at 50% condensation temperatures ~1100 K; the counts for volatile elements decrease more slowly than Si (positive \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\)), whereas for refractory elements \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\) decrease more quickly. However, there is considerable scatter within each group. There is a broad increase in \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\) with increasing first ionisation energy of an element (Figure 2b). The REE behave coherently, with \(R^2 = 0.76\), but elsewhere there is considerable scatter. In particular, most of the Group 1 elements (Na, K, Rb and Cs) have a higher \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\) compared to the overall trend.

[18] A more compelling correlation is found by comparing variations in \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\) against atomic number (Figure 2c). An obvious zigzag pattern defined by the atomic structure emerges (highlighted in gray in Figure 2c). This pattern is also observed using the alternative normalization to \([d[C_X/C_Ca]/dt]/[C_X/C_Ca]_{\text{mean}}\), demonstrating that the pattern itself is not a detector linearity effect. Excluding Group 1 elements, \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\) for elements within a given period increase with increasing atomic number, reflecting the fundamental atomic Aufbau principle by which electron orbital shells are progressively filled as atomic number increases. Where the increase in atomic number coincides with the transition from one period to the next, there is a sharp decrease in \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\). The minimum \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\) for Periods 2, 3, 4, 5 and 6 are typically around ~0.002, and the maximum \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\) for Periods 3, 4 and 5 are around 0.002 (dashed lines, Figure 2c). The Group 1 alkali metals (i.e., K, Rb, Cs and arguably Na) fall on the “zag” of the zigzag pattern (Figure 2c), indicating that the effect is related to volatility as well as ionisation potential (cf. Figure 2b). The slope of the trends within each Period decreases from Period 3 to Period 6 (Figure 2c), perhaps because the relative change in atomic mass within a given period decreases as atomic number increases through the Periodic Table from Group 3 to 6. The only elements that deviate significantly from the pattern are Ba (both \(^{137}\)Ba and \(^{138}\)Ba) and Ta. The lower \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\) of Ba compared to elements of similar atomic number (i.e., the REE), may be due to its lower ionisation potential (Figure 2b) compared to the REE, but this explanation does not account for the anomalous behavior of Ta. Both Th and U have lower \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\) than the overall trend and differ considerably from Pb, which could be a limiting factor in the accuracy obtainable for U-Th-Pb geochronology by LA-ICP-MS.

6. Matrix Matching Between Calibration Material and Unknown

[19] The behavior of elements during sample ablation matters to analytical accuracy if the slopes \([d[C_X/C_Si]/dt]/[C_X/C_Si]_{\text{mean}}\) differ between the unknown and the external standard. NIST SRM 612 is commonly used as the external calibration material for LA-ICP-MS analyses. This glass was doped with ~40 \(\mu g \, g^{-1}\) of a large number of trace
Figure 2
elements (see Eggins and Shelley [2002] for an overview of the production of this reference material), including all those sought in this study, and in amounts well above limits of detection. The contents of many of the less commonly analyzed elements in the available glass standards made from natural samples are often poorly known and near their limits of detection (e.g., for BCR-2G and the

Figure 3. (a–b) Values of \(\frac{d[C_{X}/C_{Si}]/dt}{[C_{X}/C_{Si}]_{\text{mean}}}\) and (c–d) \(\frac{d[C_{X}/C_{Ca}]/dt}{[C_{X}/C_{Ca}]_{\text{mean}}}\) versus atomic weight. For NIST SRM 612 an overall zigzag pattern is defined by an increase in atomic weight and variations in the behavior of the elements within each period of the Periodic Table. For \(^{29}\text{Si}\) normalized slopes, \((\frac{d[C_{X}/C_{Si}]/dt}{[C_{X}/C_{Si}]_{\text{mean}}})\), there is an offset between NIST SRM 612 with VG-2 and BCR-2G. In contrast, for Ca normalized slopes, \((\frac{d[C_{X}/C_{Ca}]/dt}{[C_{X}/C_{Ca}]_{\text{mean}}})\), there is no offset between NIST SRM with VG-2 or BCR-2G. Hence, use of \(^{29}\text{Si}\) for internal standardization with NIST SRM 612 for external calibration introduces systematic error. However, as discussed in the text, the contents of Ca in volcanic glass samples produce signal intensities on \(^{43}\text{Ca}\) that are at the transition between pulse and analogue counting modes of the electron multiplier. Ergo, data were reduced using \(^{29}\text{Si}\) and then corrected for the measured offset.

Figure 2. The normalized relative decrease in counts \(\frac{d[C_{X}/C_{Si}]/dt}{[C_{X}/C_{Si}]_{\text{mean}}}\) versus (a) 50% condensation temperature from Lodders [2003] and (b) first ionisation energy (eV) and (c) atomic number (A). The values of \(\frac{d[C_{X}/C_{Si}]/dt}{[C_{X}/C_{Si}]_{\text{mean}}}\) show considerable scatter when compared to variations in condensation temperature and first ionisation energy (eV). In contrast, values of \(\frac{d[C_{X}/C_{Si}]/dt}{[C_{X}/C_{Si}]_{\text{mean}}}\) show a systematic zigzag pattern when compared against atomic number (A). The slope of the trends within each period shows a steady decrease from Periods 3–6. Notably, the maximum \(\frac{d[C_{X}/C_{Si}]/dt}{[C_{X}/C_{Si}]_{\text{mean}}}\) for Periods 3, 4, and 5 and the minimum \(\frac{d[C_{X}/C_{Si}]/dt}{[C_{X}/C_{Si}]_{\text{mean}}}\) for Periods 2, 3, 4, 5 and 6 are almost identical, demonstrating the systematic nature of elemental behavior during laser ablation.
MPI-DING glasses), making them less suitable for external calibration than NIST SRM 612. However, the major element composition of NIST SRM 612 is considerably different from natural volcanic glasses (Table S1 in the auxiliary material), and this glass appears to ablate quite differently to basaltic glasses [e.g., Gaboardi and Humayun, 2009; Jochum et al., 2007].

To test the suitability of NIST SRM 612 for external calibration of analyses of volcanic glasses, we compare the systematic variations in (d[CX/CSi]/dt)/[CX/CSi]mean for NIST SRM 612 against natural volcanic glasses VG-2 and BCR-2G (Figure 3). The higher degree of scatter in (d[CX/CSi]/dt)/[CX/CSi]mean values compared to analyses of NIST SRM 612 is attributed to the lower contents of many elements in BCR-2G and VG-2. During ablation of VG-2 and BCR-2G, the values of (d[CX/CSi]/dt)/[CX/CSi]mean are systematically lower than NIST SRM 612, regardless of differences in condensation temperature or first ionization energy of the element (Figures 3a and 3b, respectively). In contrast to 29Si, when normalizing the slope to 43Ca, (d[CX/CCa]/dt)/[CX/CCa]mean for both VG-2 and BCR-2G overlap the values for NIST SRM 612 (Figures 3c and 3d, respectively), demonstrating (d[CX/CCa]/dt)/[CX/CCa]mean for all elements other than 29Si are unaffected by differences in the matrix compositions between the natural volcanic glasses and the synthetic NIST SRM 612 glasses. This effect militates against using 29Si as the element for internal standardization, but the feasible alternatives, 43Ca and 27Al, are affected by the transition from pulse to analogue mode in the detector. We therefore arrived at a compromise: we first reduced the data using 29Si, and then applied a matrix correction for the systematic offset. Because the (d[CX/CCa]/dt)/[CX/CCa]mean for a given element are comparable for NIST SRM 612, BCR-2G and VG-2, the offset for (d[CX/CSi]/dt)/[CX/CSi]mean can be measured by comparing the contents of CaO in the Smithsonian volcanic glasses and BCR-2G with results obtained using EMPA (Figure 4; EMPA analyses from Melson et al. [2002]). At an ablation diameter of 86 μm this offset to lower Ca contents is 6.4 ± 0.2% (Figure 4; data collected over a two year period demonstrating the systematic nature of the offset) and ~2% at a larger ablation diameter of 187 μm. No such correction is needed, of course, for those elements calibrated against BCR-2 G as opposed to NIST SRM 612 (Na, Mg, Al, P, K and Fe).

7. LA-ICP-MS: Interferences and Choice of Isotope

[21] Quantitative analysis of elemental abundances using LA-ICP-MS is complicated by polyatomic interferences, in particular oxides, argides, dimers and doubly charged ions. The differences in compositions of NIST SRM 612 from natural samples makes accurate accounting for these interferences essential. Thus, multiple isotopes of a number of elements (Mg, Ca, Fe, Ni, Ti, Cu, Zn, Ga, Ge, Mo, Ag, In, Sb, Ba, Sm, Yb, W and Pb) in a range of OFB glasses were analyzed and compared by regression of the content calculated from one isotope against another (Figure 5). Where a discrepancy was found (e.g., Cu, Zn, Ag and Se), the differences in the calculated contents were compared against contents of major and other abundant elements to identify the interference and select a reliable isotope for analysis. For example, 63Cu versus 65Cu shows a linear correlation (Figure 5b), but 65Cu is considerably higher than 63Cu. Both 63Cu and 65Cu have potential titanium oxide interferences (47Ti16O and 46Ti16OH on mass 63; 49Ti16O and 48Ti16OH on mass 65), but there is no correlation between either isotope with the Ti contents of the analyzed samples. The systematic nature of the correlation and the lower contents using 63Cu compared to 65Cu point to a 23Na40Ar interference on 63Cu, whereby the higher content of Na in NIST SRM 612 relative to the OFB results in an underestimation in the derived values for 63Cu.
in the OFB. The content of Zn measured on mass 64 is 3% higher than on mass 66 (Figure 5c), which likely results from a mass interference from $^{24}\text{Mg}^{40}\text{Ar}$, because the Ni content of these glasses are too low for significant $^{64}\text{Ni}$ (natural abundance of $^{64}\text{Ni}$ is only 0.926%). The offset of 3% using $^{24}\text{Mg}^{40}\text{Ar}$ demonstrates that the interference $^{26}\text{Mg}^{40}\text{Ar}$ on mass 66 is negligible, since the ratio of $^{24}\text{Mg}/^{26}\text{Mg}$ is 7.2. The overestimation of the content of Zn on mass 67 compared to 66 (Figure 5c) is attributed to a major $^{27}\text{Al}^{40}\text{Ar}$ mass interference, reflecting higher aluminum contents of the OFB (12.6 19.0 cg g$^{-1}$) than NIST SRM 612 (2.03 cg g$^{-1}$).

[22] Analysis of both isotopes of Sb and multiple isotopes of W, Ti, Ca and Yb in OFB show excellent agreement with each other (Figure 5). The potential mass interference of $^{27}\text{Al}^{16}\text{O}$ on $^{43}\text{Ca}$ was checked because of the common use of $^{43}\text{Ca}$ for internal calibration. The production of $^{27}\text{Al}^{16}\text{O}$ on mass 43 was assessed by measuring the apparent

**Figure 5.** Examples of measurements of multiple isotopes with the aim of assessing the most appropriate one to use for LA-ICP-MS analysis. Values ($\mu g$ g$^{-1}$) show results of regression of content data for one isotope against another.
CaO in a gem quality MgAl2O4 rich spinel from Sri Lanka with 70 cg g⁻¹ Al2O3. We detected 0.07 cg g⁻¹ apparent CaO. Assuming a worst-case scenario, whereby spinel contains no Ca and all the measured Ca is from the $^{27}$Al$^{16}$O interference, the correction would be 0.1 cg g⁻¹ Al2O3, which is negligible (i.e., it would amount to 0.015 cg g⁻¹ in a typical MORB glass with 15 cg g⁻¹ Al2O3). $^{43}$Ca was also checked against $^{42}$Ca in 107 back arc basin samples from the S.W Pacific, because hydrous melts evolving in back arc basins display a larger range in major element contents (CaO ranging from ~2–14 cg g⁻¹) than nominally anhydrous within plate ocean floor basalts (CaO ranging from ~9.5–12.5 cg g⁻¹), providing a more rigorous statistical test for interferences over a range of contents. Calcium contents from $^{42}$Ca and $^{43}$Ca agreed to 1.4%, with an uncertainty of 1.3% on each isotope. The masses chosen for analysis by LA-ICP-MS are given in Table S1.

Of the element contents reported in this study, polyatomic interferences cannot be avoided for Sc, Ga, Ge, As, Se, Ag, In, Re, Pt and Au. Production ratios of interfering species on the necessary masses were estimated using natural minerals (zircon, apatite, olivine and rutile) and synthetic experimental glasses with varying contents of REE and/or cones had no effect. Consequently, experimental glasses with a range in REE contents (considerably higher than apatite), producing $^{154}$Sm$^{++}$ and $^{154}$Gd$^{++}$ interferences on mass 77 substantially higher than either the background or blank, were chosen to measure interference corrections. A similar memory effect was noted during attempts to determine boron, producing ‘phantom’ ~8 ng g⁻¹ boron signals in presumably boron-free San Carlos olivine.

8. Grouping of Elements for LA-ICP-MS Analysis

Counting statistics depend on the dwell times on each mass number on the electron multiplier and the number of times each mass number is visited during an ablation, with the total time constrained by the depth of ablation, which should not exceed the spot diameter to minimize the downhole fractionation effects. This consideration argues against
trying to determine all elements in one routine, and instead the sought elements were initially split into four routines (Table S3). Elements intended to be compared as ratios during evaluation of data (e.g., Nb/Ta and Zr/Hf in OFB analyses presented by Jenner et al. [2010] and Jenner and O'Neill [2012]) were placed in the same groups: Routine 1, transition elements; Routine 2 targeted the REE and Routine 3 focused on the ‘lesser analyzed elements’. The number of elements in Routine 4 was limited to eight, to permit longer counting times per element, where contents were near the detection limit. A higher laser repetition rate of 10 Hz was used in Routine 4 to increase sensitivity. Several elements were analyzed in more than one routine to check for internal consistency. Following a preliminary evaluation of the results from Routines 1 to 4, a further analytical campaign (Routine 5) was undertaken using a larger spot size of 187 μm and a repetition rate of 15 Hz, to reanalyze a number of elements that were previously close to or below the LOD (i.e., W, Bi and Sb) or not previously attempted (Re, Pt and Au). Comparison of peak/background counts for all elements in Routine 5 (Table S3) shows a substantial decrease in the LOD compared to those of Routines 1–4 (e.g., LOD for W decreases from 0.012 to 0.002 μg g⁻¹, Bi decreases from 0.005 to 0.001 μg g⁻¹ and Th decreases from 0.020 to 0.001 μg g⁻¹). Routine 6 analyzed major elements for comparison with EMPA, which provides insight into matrix effects while also testing for internal consistency and identifying outliers in the data set (in particular, for volcanic glass analyses presented by Jenner and O'Neill [2012]).

[26] A few elements such as P, As, Se, Ag and Sb with high ionisation potentials, hence low sensitivity, pose additional problems because they are also prone to memory effects [Spandler et al., 2011, supplementary material]. For P, the content in the NIST SRM 612 is much lower than in volcanic glasses, causing a memory effect in the external standard, similar to that described for Se in (section 7). This effect was minimized by standardizing to BCR-2G instead of NIST SRM 612.

9. NIST SRM 612 External Calibration Values

[27] In general, the GeoReM preferred values for NIST SRM 612 [Jochum et al., 2011] were used for calibration (Table S1), with the exception of values for SiO₂, Se, Ti and Cr. For Ti, we adopted a value of 39.4 μg g⁻¹ in order to bring the LA-ICP-MS analyses into agreement with EMPA of a global range in ocean floor basalts [Jenner and O’Neill, 2012; Melson et al., 2002] and the GeoRem preferred value for Ti in BCR-2G [Jochum et al., 2005a]; the content of Ti (14100 μg g⁻¹) in BCR-2G is considerably higher than NIST SRM 612, making it ideal for calibration. The value for Cr of 39.0 μg g⁻¹ was taken from a comparison with EMPA analyses of 28 synthetic glasses and crystals from O’Neill and Berry [2006] and Mallmann and O’Neill [2009], with ~4000 μg g⁻¹ Cr. Similar studies of the solubilities of Ni, Co and Mo in the same glass compositions have established the reliability of this approach for these elements [O’Neill and Egging, 2002] and W [O’Neill et al., 2008]. The major elements Na, Mg, Al, Fe, and P and K were externally calibrated to BCR-2G, which is much closer in composition to the volcanic glasses. The high backgrounds on ³¹P and especially ⁴⁰K make NIST SRM 612, with only ~40 μg g⁻¹ of both these elements, a poor choice for their external calibration. The effects of the high background and low signal/background on the reproducibility in ⁴⁰K measurements in NIST SRM 612 compared to all other elements are evident from the error bars on the (d[C × / CSi]) / [C × / CSi]mean in Figure 3.

[28] All samples and standards were analyzed in batches of ~12, with NIST SRM 612 and BCR-2G (Na, Mg, Al, P, K and Fe) used for external calibration analyzed at the beginning and end of each batch to allow corrections to be made for instrumental drift. The values for elements in NIST SRM 612 and BCR-2G used for calibration are given in Table S1, permitting recalibration of data presented here if more accurate values for the standards become available.

10. Compilation of Routines 1–6 Data

[29] The major and minor elements in OFB from the AVGDF determined by EMPA [Melson et al., 2002] were also determined by LA-ICP-MS in 616 samples (using BCR-2G as the external standard). This offers the opportunity for estimating precision and internal consistency for a range of elements with different properties during laser ablation, by regressing the analyses from one method against another (Figure 6). We assumed the relationship

\[ [X]_{\text{LA-ICP-MS}} = k_{X}[X]_{\text{EMPA}} \]
Although the relationship is linear, the regression is not, because both variables are subject to uncertainties, and need to be weighted accordingly [e.g., York, 1966]. The uncertainties on the EMPA analyses were taken from Canil and O’Neill [1996]. They have the form \( \sigma([X]) = \sigma_0 + \sigma_1[X] \), where \( \sigma_0 \) is taken as one third of the conventional limit of detection, calculated from counting statistics (Tables S4 and S5). The \( \sigma_1 \) term incorporates several factors including instrument drift, and should therefore be treated as an unknown where possible. For the major and minor elements, the \( \sigma_0 \) term for the LA-ICP-MS analyses is insignificant compared to the \( \sigma_1 \) term, so the uncertainty is assumed to be of the simplified form \( \sigma([X]) = \sigma_1[X] \), which enables the value of \( \sigma_1 \) term to be calculated by

**Figure 6.** Comparison of major element data collected using EMPA versus LA-ICP-MS. Ratios are from regression with weighting of both variables (see text).
setting the reduced chi squared of the regression to unity. The form of the weighting may have a significant effect on the results of this type of regression analysis. Assuming only the $s_0$ term (i.e., constant uncertainty) would overemphasize the data at higher contents, whereas assuming only the $s_1$ term where $s_0$ is significant (i.e., near the limit of detection) would give unwarranted influence to the data at low abundances. Results are given in Table S4 and Figure 6. For all the elements treated here except P, the values of $s_1$ fall between 2 and 4%. The regression for P is likely affected by pixelation of the EMPA data: the average value of P in our data set is 0.15 cg g$^{-1}$, but contents determined by EMPA are reported only to the nearest 0.01 cg g$^{-1}$. To show the potential effects of this pixelation on the regression, the regression was repeated using a larger uncertainty on the EMPA data (P2; Table S4). Confirmation that it is indeed the EMPA data for P that carries the extra uncertainty comes from the statistics of the correlation between P determined by LA-ICP-MS and Nd in OFB glasses [Jenner and O’Neill, 2012].

Consistency between the LA-ICP-MS and the EMPA data is tested by the value of the slopes ($k_X$) from the regressions (Figure 6 and Table S4). There are systematic discrepancies for Na, Mg and Al of a few percent, which may reflect corresponding errors for these elements either in BCR-2G, affecting the LA-ICP-MS data, or in VG-2, to which the EMPA were corrected in the work of Melson et al. [2002]. The largest discrepancy is for Na, which is 6.4% higher by LA-ICP-MS. However, Melson et al. [2002] highlight that other laboratories [i.e., Langmuir et al., 1992] have also identified a 6 to 8% offset in Na values, indicating a problem in the referencing of the Smithsonian data to the wet chemical analysis of VG-2.

A number of elements such as Ti, Zr, La, Ce and Yb were analyzed in multiple routines to ensure consistency between routines. For natural volcanic...
glasses, discrepancies could indicate overlap with microphenocrysts, real variations in glass composition, or instrument problems. Figure 7 gives an example of the reproducibility in Ti, Zr, La and Ce analyses undertaken using a combination of the six analytical routines for 616 OFB glasses reported in the work of Jenner and O’Neill [2012], and 106 back-arc basin glasses, which increase the range in compositions. Precision can also be estimated by regressing the analyses from one routine against another (Table S5). For the weighting, \( \sigma_0 \) was taken as one third of the limit of detection (from counting statistics) given in Table S3, with \( \sigma_1 \) assumed to be equal in the two routines. For many isotopes, LOD is <1% of the abundances, hence inconsequential. We find values of \( \sigma_1 \) between 2 and 4% for all elements, similar to the regressions against the EMPA data (Table S5).

Some elements were determined on different isotopes in subsets of the samples to check for interferences. These data may also be used to evaluate precision, if there are no interferences (e.g., Ti, Sb, Yb and W; Figure 5). Several of these elements have abundances that are typically within a factor of ten or so of their LOD, i.e., Sb and W. For these elements, the good agreement in results using different isotopes also demonstrates the effectiveness of the LA-ICP-MS technique for measuring the contents of elements at low abundances. The reported values in Tables S6 and S7 are a compilation of the data collected in Routines 1–6 using averages where replicate analyses were undertaken on a given element in multiple routines. The contents of As, Se, Ag and Sb in volcanic glasses are all typically <0.6 \( \mu g \) g\(^{-1}\), and memory effects from the relatively high amounts in NIST SRM 612 were found to produce anomalously high contents in volcanic glasses in a few analytical sessions. This is a pernicious kind of analytical error, which may be hard to identify, especially when only a few samples or a few analytical sessions are involved; but it can be identified by ensuring that secondary standards with suitably low contents of the effected elements are analyzed routinely along with the samples.

11. Results for Reference Glasses and Discussion

The mean and relative standard deviation (RSD) for replicate analyses of BCR-2G and VG-2 are listed Table S6, with preferred values for BCR-2G from GeoReM. The number of analyses of each reference material in each analytical routine are given in Table S3. The results for BCR-2G are from 17 independent sessions covering three years, which tests long-term reproducibility. With the exception of Zn, Ag, In and Sn our results for BCR-2G are all within 10% of the GeoReM preferred values [Jochum et al., 2005b]. With the exception of some elements with very low natural abundances, namely Se, Ag, Sb, Tl and Bi in BCR-2G and As, Mo, Ag, Sb, W, Tl and U in VG-2, the RSD are \( \leq 5\% \) and typically \( \leq 2\% \), demonstrating the high level of precision in the LA-ICP-MS technique over multiple analytical sessions undertaken over a two year period.

The MPI-DING glasses are a set of synthetic glasses prepared by melting of natural rocks; they therefore have trace element contents comparable to natural volcanic glasses, except for loss of volatile elements (cf. their low S contents [Jochum et al., 2006]), and loss or perhaps gain of siderophile elements into or out of the platinum crucibles during fusion. The vitrified komatiites GOR128-G and GOR132-G may be inhomogeneous because of quench olivine crystals detected in some aliquots [Jochum et al., 2006]. The mean and RSD for replicate analyses of the MPI-DING glasses and the percentage difference from the preferred values of Jochum et al. [2006] are listed in Table S7. There is generally good agreement (typically within 5%) for the commonly analyzed elements but discrepancies are often greater for low abundance elements, which are less commonly determined (Be, As, Mo, Ag, Cd, In, Sn, Sb, W, Tl and Bi). An important result is that the Se contents of the MPI-Ding glasses are consistent with those expected in the rocks from which they were made [e.g., Hamlyn et al., 1985; Jenner et al., 2010]. This indicates that Se is a less susceptible to loss by volatility than S, supporting its use as a proxy for S in degassed volcanic glasses [Jenner et al., 2010].

The results of applying the optimized analytical routine developed here to a large suite of Ocean Floor Basalt (OFB) glasses are given in a companion datafile [Jenner and O’Neill, 2012]. Polyatomic interferences have been identified and corrected for in this study (see section 7), but in case future work reveals overlooked interferences or related problems, these data may be corrected by referring to the values reported here for the reference glasses BCR-2G, VG-2 and the seven MIPI-DING glasses [Jochum et al., 2006]. Similarly, the values of NIST SRM 612 used for external calibration are given to permit recalibration of data presented here and in the work of Jenner and
O’Neill [2012] in anticipation of further improvement in the characterization of this material.

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