LASER ABLATION ICP-MS: DATA REDUCTION

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Analysis and calculation of concentrations

Laser ablation analyses are done in time-resolved mode. A ~30 s background or blank signal is taken while the laser is off. This is followed immediately by turning on the laser and ablating the sample, generating a time-dependent signal (Fig. 1). Measurements are made for another 3-4 minutes unless the laser ablates entirely through the sample or the signal drops significantly due to beam defocusing with progressive ablation. Reference glass standards (BHVO2g, BIR1g, BCR2g, NIST610 and NIST612) are run before and after a sequence of samples.
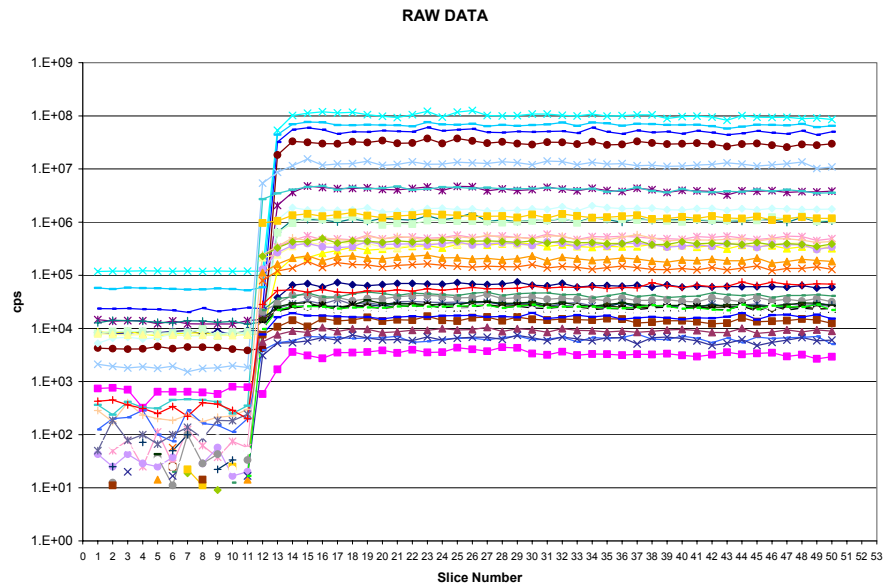

Figure 1. Typical time-resolved signal for an analysis of a glass reference standard (BHVO2g). Ablation of the sample begins at slice #14. Homogeneity of the glass is revealed by the parallel nature of the time-resolved signals.

Raw data for each analysis are each examined offline in order to pick out segments of time corresponding to when the laser was ablating through a homogeneous vertical section of a sample. The criterion used to identify a homogeneous section is that the time-resolved signals of all the elements are parallel (Figs. 1, 2a). This is equivalent to saying that the ratios of all elements analyzed are constant with time (Fig. 3). Cross-cutting time-resolved elemental curves can indicate a transition into a new material (such as ablating through the sample and into the underlying glass holder). If cross-cutting occurs at the onset of ablation, this may be due to surface contamination. In this case, the analyst should avoid the immediate signal after ablation starts and focus on the sections

having higher quality data. Once appropriate time-resolved sections are chosen for the background and the sample (or reference standard), the *average* background signal intensity is subtracted from the signal intensities of the sample.
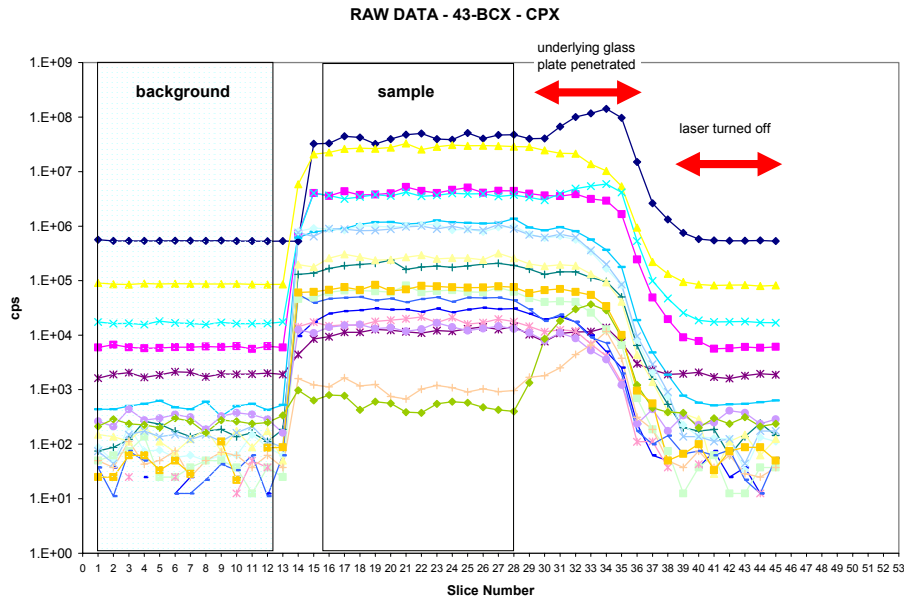

Figure 2. A time-resolved signal for a sample (clinopyroxene). A window is selected for the background and for the sample. These windows are selected so as to correspond with near-parallel time-resolved signals. Note that at around slice # 30, the signals start to change in intensity and cross each other. This is due to a transition into the underlying glass plate after the laser ablated through the entire thin section.
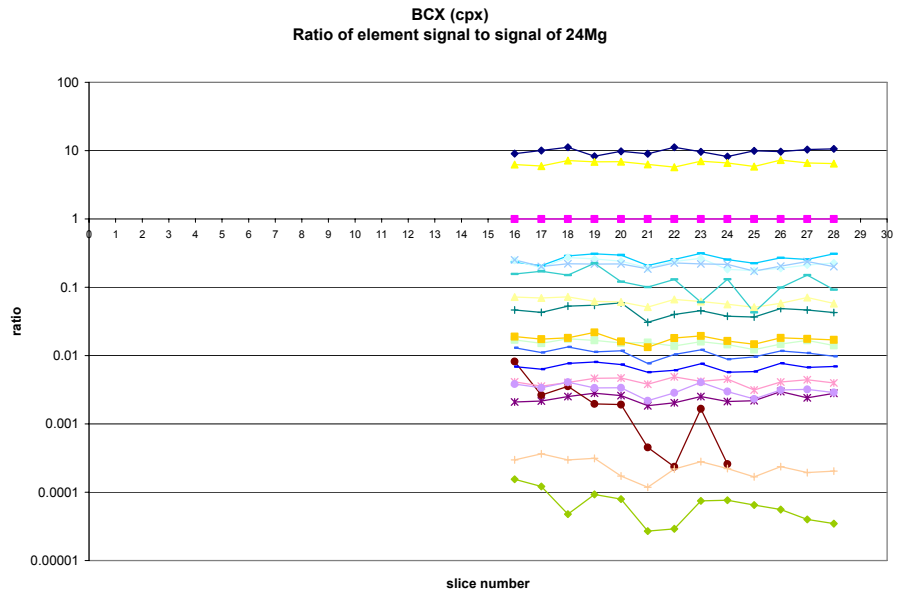

Figure 3. Same data as in Figure 2. Plotted are the ratios of various elements relative to a normalizing isotope (^{24}Mg), which is taken here to be the internal standard. Intensities of the sample signals have all been background corrected. The slices taken correspond to the slice window in Figure 2. Note that the ratios are relatively constant (even if the absolute signal intensities are varying).

Concentrations are determined as follows. Background-corrected intensities for a given element i are all normalized to an internal reference isotope IS, e.g., an internal standard. The internal standard is used to correct for variations in absolute signal intensities due to matrix effects and different ablation parameters (e.g., pit diameter) but not to variations in actual concentration in the sample. This means that the concentration of the internal standard must be known in all reference standards and sample unknowns. We typically take Mg (^{24}Mg or ^{25}Mg) or Ca (^{43}Ca) as internal standards. The weight concentration C_i^{Sa} of an element i in an unknown sample is then given by

$$C_i^{Sa} = C_{IS}^{Sa} \times \frac{I_i^{Sa}}{I_{IS}^{Sa}} \times \frac{C_i^{R}}{C_{IS}^{R}} \times \frac{I_{IS}^{R}}{I_i^{R}} \qquad \text{Eq. 1}$$

where C_{IS}^{Sa} is the concentration of the internal standard element in the sample, $\dfrac{I_i^{Sa}}{I_{IS}^{Sa}}$ is the ratio of background-corrected signal (cps) intensities of the element i to the internal standard element in the sample, $\dfrac{C_i^{R}}{C_{IS}^{R}}$ is the ratio of the concentrations of the element i to the concentration of the internal standard in the reference standard, and $\dfrac{I_{IS}^{R}}{I_i^{R}}$ is the ratio of the background-corrected signal (cps) intensities of the internal standard element to the element i in the reference standard.

The form of Eq. 1 allows us to deal with time-varying signal intensities. In many cases, the ablation signal slowly decays with time (occasionally even increasing) and this time-dependency differs from sample to sample. The measured quantity in Eq. 1 is $\dfrac{I_i^{Sa}}{I_{IS}^{Sa}}$. For example, if ^{24}Mg was our internal standard and we were interested in Li concentrations, we would work with the intensity ratio of ^{7}Li to ^{24}Mg rather than the absolute signal intensity of ^{7}Li.

One drawback of Eq. 1 is that it only allows calibration against one external reference standard. This is the traditional approach. However, one drawback of this simplified approach would occur when the concentration of an element in a sample unknown is much larger or smaller than that in the reference standard. Ideally, one would like to have a reference standard whose concentrations are similar to that in a sample unknown because measurement uncertainties can propagate into very large uncertainties if extrapolated to concentrations too high or too low. When one does not know the concentration of an element in a sample, it is not always possible to match a sample to a reference standard. One way to improve on Eq. 1 is to use multiple external reference standards in the hopes that the sample concentration might be bracketed by two or more reference standards. To do this, several reference standards are analyzed. The quantity $\dfrac{C_i^{R}}{C_{IS}^{R}}$ is plotted versus $\dfrac{I_{IS}^{R}}{I_i^{R}}$ and a line (forced through the origin) is regressed through the scatter plot. The quality of the reference calibration can then be easily

assessed visually from the graph or by examining the regression statistics. The slope of this line is given by

$$m = \frac{C_i^R / C_{IS}^R}{I_i^R / I_{IS}^R} = \frac{C_i^R}{C_{IS}^R} \times \frac{I_{IS}^R}{I_i^R}$$

Eq. 2

and it follows that the concentration of the element i in the sample can be had from substitution of Eq. 2 into Eq. 1:

$$C_i^{Sa} = C_{IS}^{Sa} \times \frac{I_i^{Sa}}{I_{IS}^{Sa}} \times m$$

Eq. 3

External calibration (Mn)

$y = 0.0587x$
$R^2 = 0.9975$

(Ii/Iis) Si — y-axis
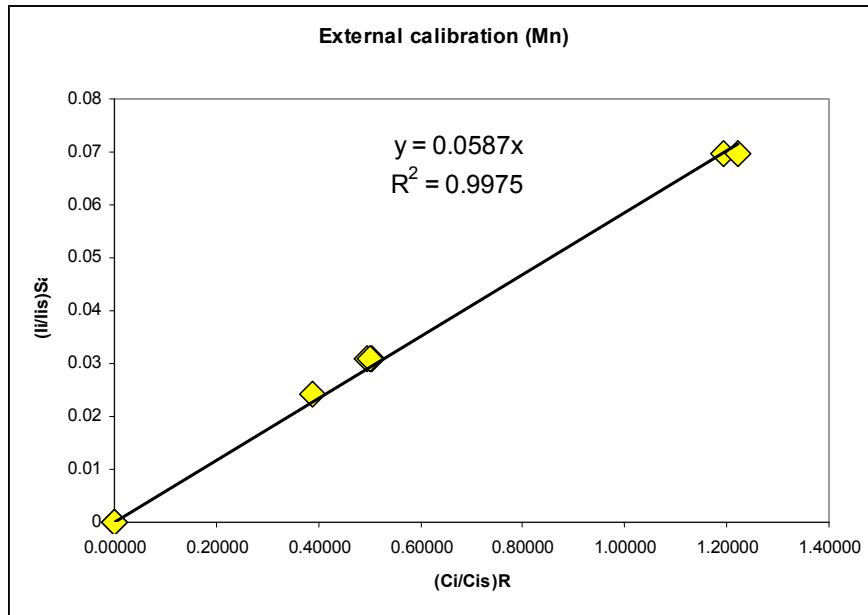(Ci/Cis)R — x-axis

Figure 4. An example of an external calibration using USGS glass standards, BHVO2g, BIR1g, and BCR2g.

Limit of Detection

The limit of detection (LOD) represents the minimum signal that can be resolved from the background signal. The definition taken here for the LOD is three times the standard deviation of the background signal $3 \times \sigma_i^{back}$ (cps). While the standard deviation of the background signal is unlikely to change significantly throughout most of the day, the actual LOD expressed in concentration will change if one changes the diameter of the ablation pit. To convert this to concentration, the quantity $3 \times \sigma_i^{back}$ normalized to the sensitivity of the instrument, which is expressed in signal per concentration unit (e.g, cps/ppm). The sensitivity of the instrument is unique to each ablation analysis. Thus, the following procedure must be adopted to estimate LOD in concentration unites. First, the quantity $3 \times \sigma_i^{back}$ is divided by the time-averaged signal intensity of the internal standard in the sample that was analyzed with the background, that is, $3 \times \sigma_i^{back} / \overline{I}_{IS}^{Sa}$, where the bar over the I is used to distinguish the time-average signal from each individual signal. The LOD for a given element i for a given sample analysis can then be expressed as

$$LOD_i^{Sa} = C_{IS}^{Sa} \times \frac{3 \times \sigma_i^{back}}{\bar{I}_{IS}^{Sa}} \times \frac{C_i^R}{C_{IS}^R} \times \frac{I_{IS}^R}{I_i^R} \qquad \text{Eq. 4}$$

Concentration determination in the absence of a known internal standard

Under some circumstances, an internal standard with known concentration may not be available. However, the composition of an unknown can be still determined. This can be done by analyzing nearly all (>98%) of the major (>1 wt. %) and minor (~0.2-1 wt. %) cations in an unknown. For most minerals, this typically requires measuring Si, Ti, Al, Fe, Mg, Mn, Ca, Na, K, P and Cr. Many of these isotopes can only be determined in medium to high mass resolutions due to various isobaric molecular interferences (for example, ^{28}Si and ^{30}Si are loaded with interferences in low mass resolution mode). This means that this approach can only be done with sector field ICP-MS's with high mass resolution capabilities (e.g., the ThermoFinnigan Element 2). Quadrupole instruments cannot resolve these isotopes from interferences (although hexapole collision cell technology may help to eliminate some of the interferences).

Denoting the cation weight fraction in the sample as X_i^{Sa}, the following condition must hold:

$$\sum_{i=1}^{N} X_i^{Sa} = 1 \qquad \text{Eq. 5}$$

Dividing Eq. 5 by a reference cation X_r^{Sa} (for example by an isotope of Mg) and re-arranging gives the following expression for X_r^{Sa}

$$X_r^{Sa} = \frac{1}{1 + \sum_{i,i \neq r}^{N} \left(X_i^{Sa} / X_r^{Sa} \right)} \qquad \text{Eq. 6}$$

where the summation is over all cations *except* that of the reference cation X_r^{Sa}. Once X_r^{Sa} is known, the remaining cation fractions are determined by multiplying X_i^{Sa} / X_r^{Sa} by X_r^{Sa}. The quantity X_i^{Sa} / X_r^{Sa} is itself determined from the following equation

$$\frac{X_i^{Sa}}{X_r^{Sa}} = \frac{I_i^{Sa}}{I_r^{Sa}} \times \frac{C_i^R}{C_r^R} \times \frac{I_r^R}{I_i^R} \qquad \text{Eq. 7}$$

which has an identical form to Eq. 1 except that the internal standard subscripts (*"IS"*) have been replaced by the reference mass subscript (*"r"*).

Once cation fractions are known, the cation fractions can be converted into oxide fractions and then re-normalized to 100%. In the figure below, we show that for volatile-poor materials (such as a dry basalt), this approach is very robust. Once the major element composition of a material is determined, any one of these elements can be chosen as an internal standard for the subsequent determination of trace elements in low mass resolution mode. Uncertainties of course arise if the valence state of Fe is not known very well (e.g., FeO or Fe_2O_3) and if there are other volatiles besides oxygen that are not accounted for. We emphasize that this approach is only robust when all major and minor cations are determined.
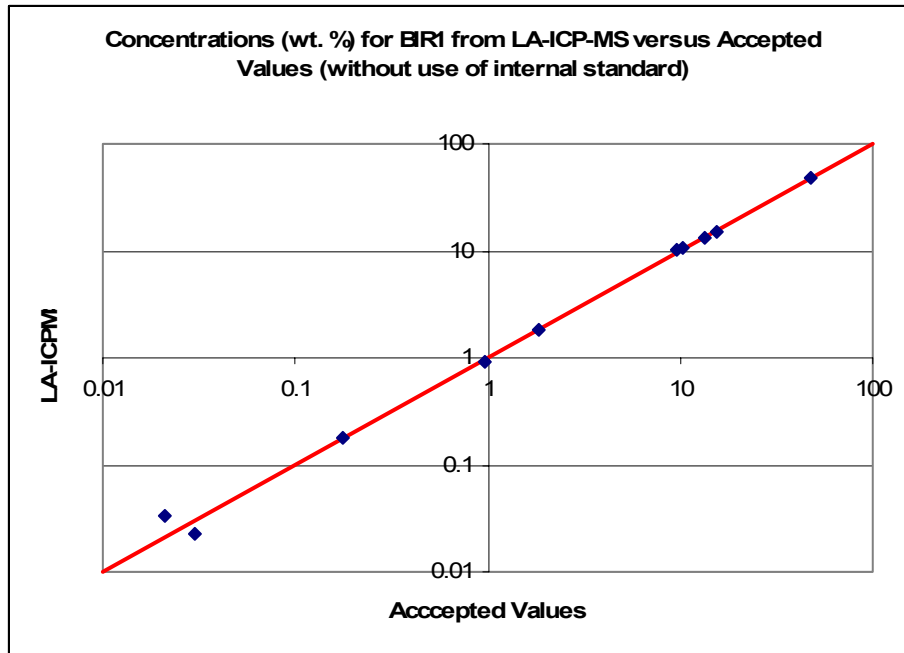
Figure 5. Oxide concentrations of major and minor elements in BIR1g glass standard determined by laser ablation ICP-MS (medium resolution mode) without an internal normalization standard versus accepted values.