Determination of water concentration in volcanic glasses using Laser Induced Breakdown Spectroscopy (LIBS)

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Introduction

Improvements in laser-ablation for material sampling over the past few decades have led to the emergence of several applications of this in-situ technique to some important geochemical measurements. The technique is commonly used for both elemental [1] and isotopic [2] analyses, and has multiple advantages compared to dissolution techniques, notably higher spatial resolution, easier and faster sample preparation, and for many applications it is a non-destructive method. A significant advantage of this technique in geochemistry is full characterization of a sample (e.g., glass or mineral) using a single spot of limited size (i.e., 20-80 µm) to eliminate or minimize complexities due to potential chemical zonations. Major advancement is being realized in the analysis of volcanic glasses for their elemental and volatile concentrations using a new approach that combines the capabilities of the two most common laser-ablation techniques – Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and Laser Induced Breakdown Spectroscopy (LIBS). LIBS is based on direct measurement of the optical emission originating from the laser-induced plasma [3] whereas LA-ICP-MS involves transport and excitation of the ablated aerosol to a secondary source (ICP), before entering a mass spectrometer [4]. Here we present H_2O concentration data acquired with LIBS in tandem with LA-ICP-MS measurements of some major and trace elements in basaltic glasses.

Experiment details

- 4 basaltic glasses of known major oxide and H_2O content have been analyzed, in addition to NIST 612 (external standard and unknown), using an Applied Spectra tandem 213nm LIBS/LA-ICP-MS system (model J200) at Lawrence Berkeley National Laboratory (LBL). The instrument has a Czerny-Turner spectrometer with ICCD detector and an ICP-MS Thermo X-Series 2.
- We performed standard bracketing using NIST 612 in 2 batches done over 2 days. Each batch consisted of 25 successive analyses each for ~20 seconds.
- LIBS and LA-ICP-MS data have been acquired simultaneously. LIBS spectra are collected between 641 and 698nm, the range for Ca, H, and Li emission lines.
- Laser spot size was set to 60 µm and energy to 60 %. Ca has been used as an internal standard for LA-ICP-MS (i.e., ^{43}Ca) analyses.
- To check consistency of LA-ICP-MS analyses performed at LBL, we have also analyzed 3 of the same samples using LA-ICP-MS facility at UNH (New Wave Research 213 nm laser coupled with a Nu Attom ICP-MS). A similar bracketing procedure has been undertaken, except that this time one shot of 60s was performed for each sample within each batch. UNH data presented here have been processed according to the t_0 intercept method [5], and they are averages of 8 batches acquired using spot sizes of 30, 40, 65, and 80 µm).
- For LIBS H measurements, we have used a partial least squares regression (PLSR) routine [6,7] to match a spectrum of unknown samples to reference model spectra. We applied PLSR as a progressive approach to obtain multivariate calibration that takes into account all intensities at every pixel within a specific wavelength region. The prediction capability of the PLS model is based on cross-validation with a known standard. We performed PLSR to generate a calibration model plot using the 5 calibration samples with data collected on multiple days, and then the models were validated with 2 prediction samples (not included in the calibration model). Two statistical parameters were considered for model quality evaluations or as figure of merits; root mean square error of calibration (RMSEC) and root mean square error of prediction (RMSEP) [8,9].

LIBS Results

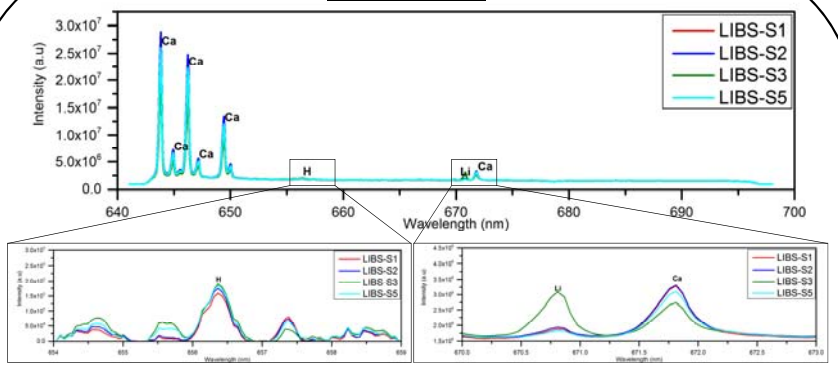

Figure 1: LIBS emission spectrum of the basaltic glasses from 641 to 698 nm. Ca peaks are particularly visible. The lower figures correspond to zoom in over the H and Li signals.

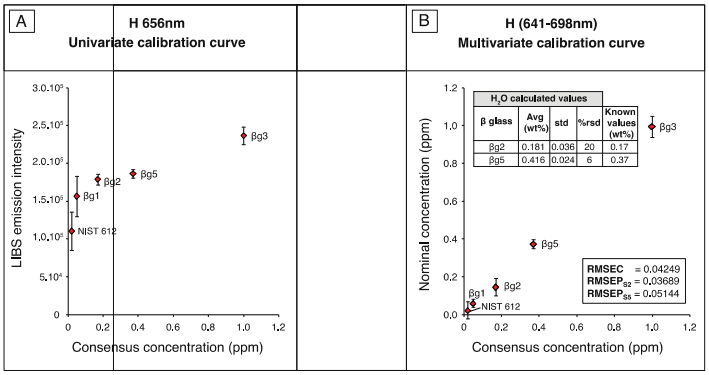

Figure 2: A) H_2O concentration univariate calibration curve using H LIBS emission intensity. B) H_2O concentration multivariate calibration with results for sample 2 and 5 in the Table inset. Note the better fit and precision achieved with multivariate analysis. See the experiment details section for more information.

LA-ICP-MS results

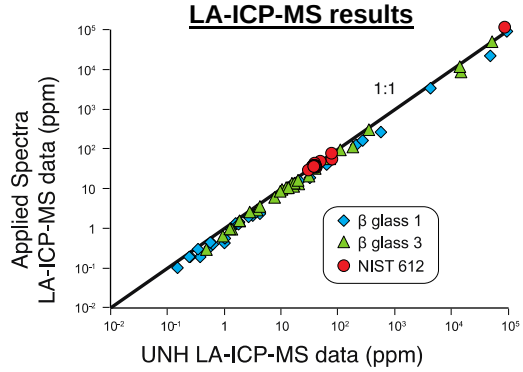

Figure 3: Comparison of selected major and trace element concentrations obtained using UNH LA-ICP-MS facility (New Wave Research 213 nm laser with Nu Attom ICP-MS) and Applied Spectra Tandem J200 (213 nm laser with Thermo X-Series 2). Chemical elements analyzed are Li, Mg, Ca, Sc, Ti, V, Cr, Ni, Sr, Y, Zr, Nb, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, and Pb.

Discussion and conclusion

The results presented here illustrate that the H_2O concentrations of volcanic glass can be determined precisely, and simultaneously with major and trace elements, using the LIBS/LA-ICP-MS tandem technique. We also show that the best approach to obtain precise and accurate H_2O concentrations is by applying multivariate analysis to the H measurements.

These results represent a step forward in the quest towards full *in-situ* characterization of a sample using a single laser run.

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