Determination of REE and Water Content in Volcanic Glasses Using Tandem LA - LIBS

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Introduction

Major advancement in laser ablation sampling has been realized for the analysis of geological samples for their elemental and volatile concentrations. This ground-breaking technology is called Tandem LA – LIBS that combines the capabilities of Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and Laser Induced Breakdown Spectroscopy (LIBS). LIBS is based on 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) with Applied Spectra J200 213nm Tandem LA-LIBS instrument. Thermo X-Series 2 ICP-MS was coupled to J200 Tandem LA – LIBS instrument for LA-ICP-MS analysis.
- Standard bracketing using NIST 612 in 2 batches was performed 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 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) analysis.
- To check consistency of LA-ICP-MS analyses, we have also analyzed 3 of the same samples using LA-ICP-MS facility at UNH (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 H measurements with LIBS, 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 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.

J200 Tandem LA – LIBS Instrument

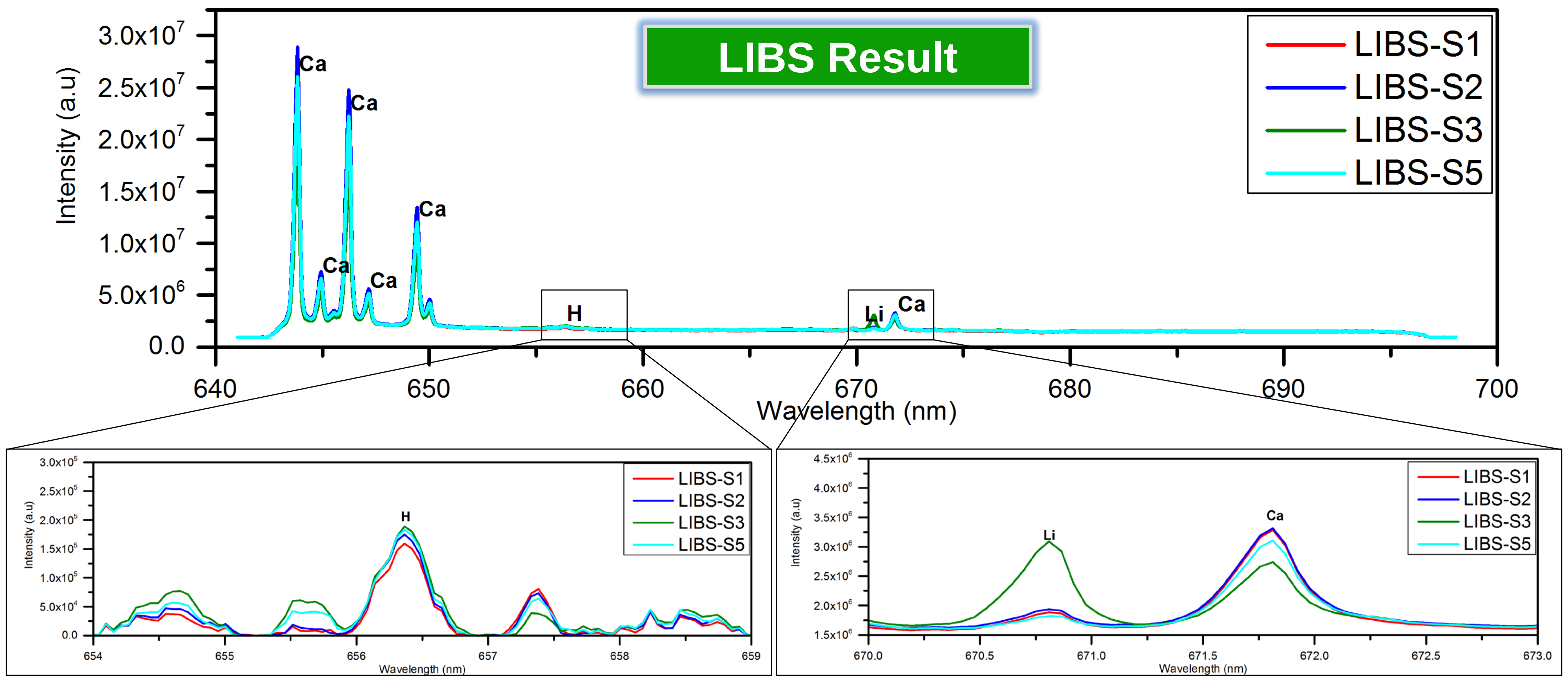
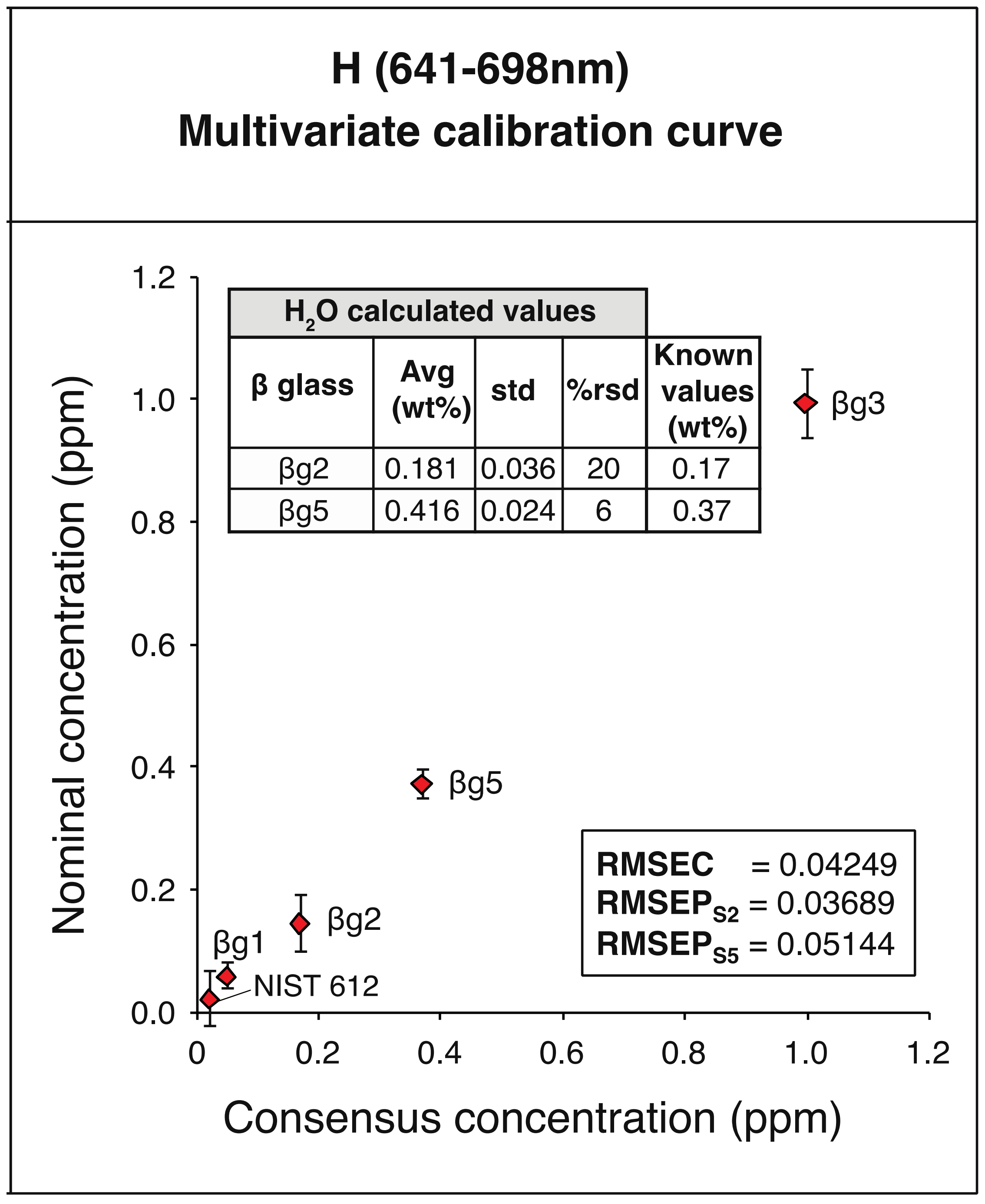


Figure 1: LIBS emission spectrum of the basaltic glasses from 641 to 698 nm. Ca peaks are particularly visible. The lower figures correspond to zoom in over the H and Li signals.



H_2O calculated values				
β glass	Avg (wt%)	std	%rsd	Known values (wt%)
βg2	0.181	0.036	20	0.17
βg5	0.416	0.024	6	0.37

RMSEC = 0.04249
$\mathbf{RMSEP_{S2}}$ = 0.03689
$\mathbf{RMSEP_{S5}}$ = 0.05144

Figure 2: *H_2O concentration multivariate calibration with results for sample 2 and 5 in the Table inset*

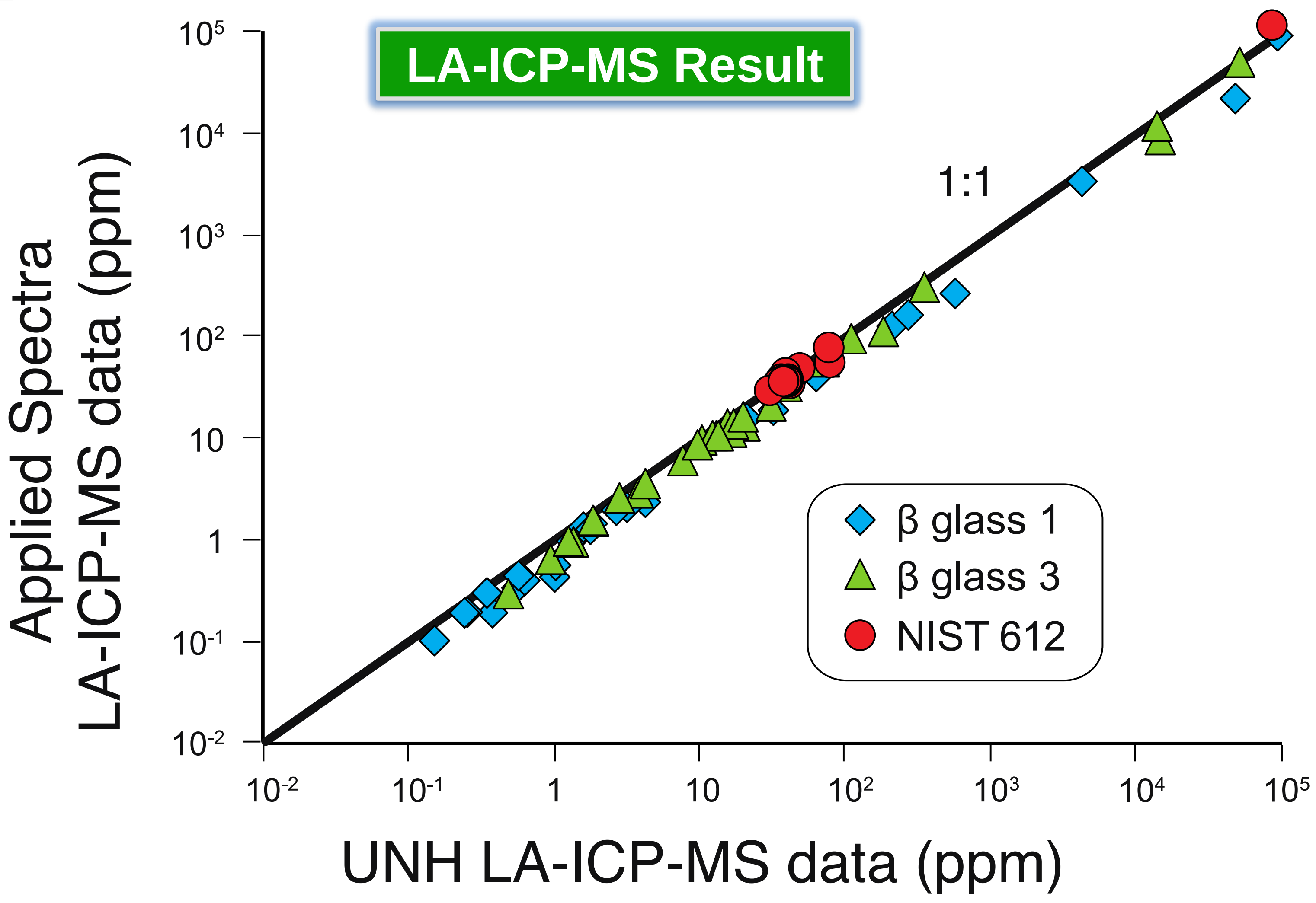


***Figure 3**: Comparison of selected major and trace element concentrations obtained using UNH LA-ICP-MS facility (Nu Attom ICP-MS) and Applied Spectra J200 Tandem (213 nm laser with Thermo X-Series 2). Chemical elements analyzed are Li, Mg, Ca, Sc, Ti, V, Cr, Ni, Sr, Y, Zr, Nb, La, Pr, Nd, Sm, Eu,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

Discussion and Conclusion

The results presented illustrates that the H_2O concentrations of volcanic glass can be determined precisely, and simultaneously with major and trace elements, using the Tandem LA - LIBS 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 sampling.

References

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