Geochemical Quantification of Olivine Minerals by Atom Probe Tomography

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The ability of atom probe tomography (APT) to interrogate small sample volumes with high efficiency makes it uniquely useful in the study of small mineral grains or domains. Although it is frequently employed in the analysis of geological materials [1], particularly in the characterisation of nanoscale chemical heterogeneities [2], the degree of quantitative accuracy achieved by APT can be difficult to determine.

Deficiencies in nitrogen and oxygen, for example, have been documented in the analysis of semiconductors and other engineered materials [3,4]. In geomaterials, measured chemical compositions have been found to be deficient in oxygen, and also in silicon for some silicate minerals [5]. While these discrepancies may not affect the measurement of cation or interstitial chemistry, which is often of interest, the extent to which these chemical measurements can be relied upon is an open question. Some studies have made comparisons with reference materials for both chemical and isotopic analysis [6,7], and these have generally demonstrated good accuracy in the APT measurements [8,9]. However, similar comparisons have not been made for many oxides, silicates, sulphides and other classes of commonly studied minerals.

Challenges to accurate quantification include equivalent sampling (ranging) of mass peaks in the APT mass spectrum, baseline and background correction to deal with spectrum noise and peak tails, and accurate deconvolution of mass peak overlaps. Ideally, these should be addressed using systematic or algorithmic methods of analysis and quantification before comparisons with standard reference materials (characterised by well-established analytical methods) can be used to evaluate any intrinsic biases that may be present in the data.

To study small olivine mineral grains in extraterrestrial materials, and to gain a better understanding of quantification of trace and minor elements in silicate minerals in general, we have developed algorithmic methods for quantification of APT mass spectra from olivine. This approach uses corrected time-of-flight data [9], equivalent peak sampling, background correction methods, and peak identification and deconvolution to produce robust results independent of subjective decisions made by the analyst. Analyses of a well-characterised olivine sample [10] are used to test and tune the effectiveness of this approach and to characterise the achievable accuracy for this mineral system.

Our efforts to better determine the accuracy of APT data from mineral grains are motivated by a desire to characterise small volumes of material within samples returned from the asteroid Bennu [11] that may otherwise be difficult to isolate from a surrounding matrix. Accurate quantification within such small sample volumes has the potential to address many challenges in geochemical analysis, and in particular

within the study of extraterrestrial materials, where chemical and isotopic anomalies can yield highly significant information relating to events and processes in the early Solar System.
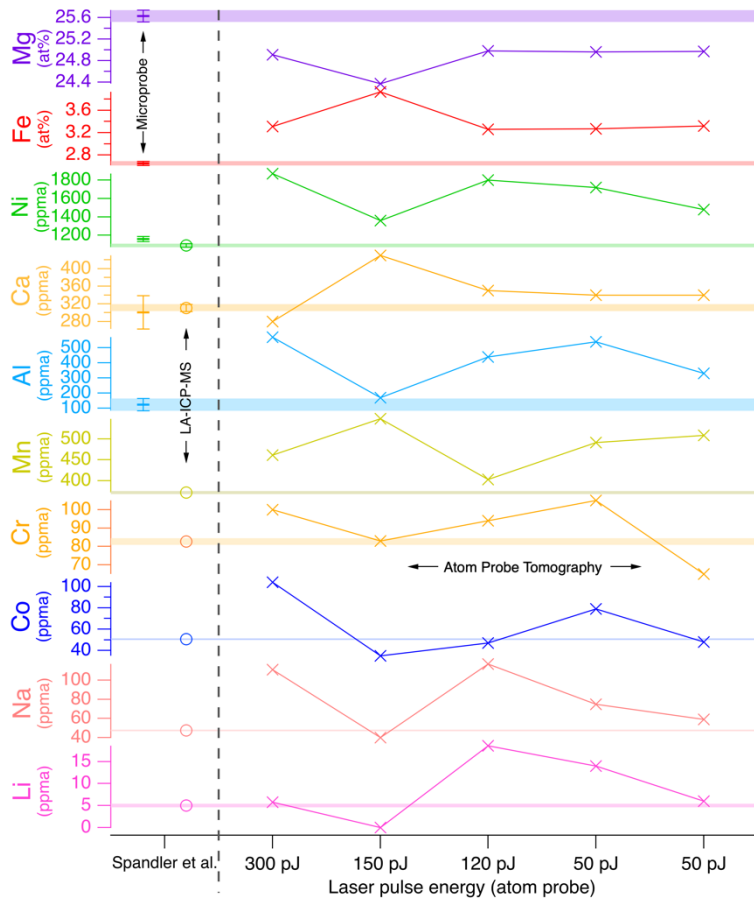
Fig. (1). Comparison between microprobe and laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) results with those from APT, for major, minor and trace element concentrations. APT datasets were collected under a range of different operating conditions.

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