Validation of LA-ICP-MS fluid inclusion analysis with synthetic fluid inclusions

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ABSTRACT

Laser ablation—inductively coupled plasma—mass spectrometry (LA-ICP-MS) has become recognized as a sensitive, efficient, and cost-effective approach to measuring the major-, minor-, and trace-solute compositions of individual fluid inclusions in minerals. As a prerequisite for the routine analysis of natural inclusions in our laboratory, the precision and accuracy of the technique was assessed using sets of multi-element synthetic fluid inclusions. Five multi-element standard solutions were prepared, and incorporated as fluid inclusions in quartz crystals at 750 °C and 7 kbar. Fluid inclusions were ablated with a 193 nm ArF excimer laser and analyzed with a quadrupole ICP-MS, equipped with an octopole reaction cell for the removal of Ar-based interferences. The internal standard used in all cases was Na. Analytical precision for K, Rb, and Cs is typically better than 15% RSD, whereas Li, Mg, Ca, Sr, Ba, Mn, Fe, Cu, Zn, and Cl analyses are typically reproducible within 30% RSD. Measured concentrations approximate a Gaussian distribution, suggesting that analytical errors are random. Analyses for most elements are accurate within 15%. Limits of detection vary widely according to inclusion volume, but are 1 to 100 µg/g for most elements. These figures of merit are in excellent agreement with previous studies. We also demonstrate that, over the range investigated, precision and accuracy are insensitive to inclusion size and depth. Finally, the combination of our LA-ICP-MS analyses with microthermometric data shows that charge-balancing to NaCl-H2O equivalent chloride molality is the most valid approach to LA-ICP-MS data reduction, where chloride-dominated fluid inclusions are concerned.

INTRODUCTION

Laser ablation—inductively coupled plasma—mass spectrometry (LA-ICP-MS) combines the high spatial resolution of laser probes with the high sensitivity, low detection limits, and multi-element capabilities of ICP-MS analysis. For these reasons, LA-ICP-MS is ideally suited to the in situ chemical analysis of geological materials, and offers the additional benefit of minimal sample preparation (e.g., Durrant 1999; Fryer et al. 1995; Heinrich et al. 2003; Jackson et al. 1992; Norman et al. 1998). The technique has been widely applied to mineral, glass, and melt-inclusion analysis, and has become increasingly popular for individual fluid inclusion analysis a result of its trace-element capabilities. Recent fluid inclusion studies using LA-ICP-MS have provided important constraints on fluid processes in the crust, especially concerning ore genesis (Appold et al. 2004; Audétat et al. 2000a, 2000b; Audétat and Petitte 2003; Gagnon et al. 2004; Muller et al. 2001; Rusk et al. 2004; Stoffell et al. 2004; Ulrich et al. 1999, 2001, 2002). However, some uncertainties in analytical procedure and data quality remain, a few of which we address in this study.

The perceived analytical difficulties with LA-ICP-MS fluid inclusion analysis, mainly the availability of matrix-matched calibration materials and element fractionation caused by heating or particle condensation during ablation, can be circumvented with: (1) the use of a 193 nm ArF laser with beam homogenization optics (Günther et al. 1997a; Günther and Heinrich 1999a); (2) an appropriate choice of laser irradiance and pulse rate; (3) the use of He as a carrier gas (Eggins et al. 1998; Günther et al. 1998; Günther and Heinrich 1999b); and (4) premixing of the He aerosol with Ar upstream of the inductively coupled plasma (Günther and Heinrich 1999b). These aspects of LA-ICP-MS analysis are summarized in a comprehensive review by Heinrich et al. (2003).

Despite these analytical advancements, the precision of single fluid-inclusion analyses by LA-ICP-MS can be poor for some elements, arising from the low transient signal intensity. Therefore, a prerequisite for resolving heterogeneities among natural fluid inclusions beyond analytical uncertainty is an assessment of the technique. This study examines analytical precision, accuracy, and detection limits on an element-specific basis, using synthetic fluid inclusions spanning a wide variety of concentrations and inclusions dimensions.

Previous LA-ICP-MS studies on homogeneous populations of natural fluid inclusions report analytical precisions within 31% RSD for Sr and Rb (Ghaziz et al. 1996), within 20% for Na, Cl, K, Mn, Fe, Zn, As, Rb, Sr, Cs, W, Ph, and Bi, and within 30% for Ag, Sn, and Ce (Günther et al. 1998). Reported accuracies for K, Cs, and Rb are within 3% for synthetic fluid inclusions analyses (Günther et al. 1998). However, accuracy is rarely reported, mainly arising from the difficulty in obtaining multi-element fluid inclusion standards. Typical detection limits are reported...