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Trace element characterization of USGS reference materials by HR-ICP-MS and Q-ICP-MS

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ABSTRACT

A trace-element characterization of United States Geological Survey (USGS) reference materials has been carried out using three different inductively coupled plasma mass spectrometer instruments: Nu Instruments AttoM, Thermo Scientific Element 2, and Agilent 7700x. The six USGS reference materials (BHVO-2, BCR-2, AGV-2, STM-2, RGM-2, and G-3) include both extrusive and intrusive rocks with compositions ranging from mafic to felsic that encompass a wide range of trace element concentrations and mineral phases. The prevalence of these 2nd (and 3rd) generation reference materials among geochemical laboratories and the added care that was taken during sample preparation make this generation of reference materials more suitable for characterization and use by the geochemical community.

The mafic-intermediate reference materials (BHVO-2, BCR-2, and AGV-2) had the most abundant published characterization prior to this study, which allowed for thorough and direct comparison with previous studies (and USGS certificates). Published data for these reference materials are relatively well constrained for most elements (i.e., not highly variable) and the results of this study generally correspond well with the literature. This can, at least partially, be attributed to the relatively simple matrices of these reference materials together with their overall smaller range of trace element concentrations.

Unlike the mafic-intermediate reference materials, STM-2 lacked any published trace element concentrations prior to this study and data for RGM-2 and G-3 were relatively sparse. Data for STM-2 and RGM-2 from this study are compared to preliminary USGS certificates, while data for G-3 are compared to the G-2 certificate values; for comparison with published data, RGM-1 and G-2 are included. Overall, the published data for RGM and G are variable across the entire suite of trace elements and display poorer agreement with the data from this study. This can be explained by the fact that, in addition to the comparison between generations that may add heterogeneity, the felsic reference materials have relatively complex matrices and larger ranges in trace element concentration. Given the new data that this study provides, the felsic reference materials can now be used by the geochemical community to produce more accurate trace element concentration analyses of felsic materials.

By using three instruments with different configurations, this study also serves as a comparison of the performance of each instrument in response to an array of geologic matrices. The data reveal that the tested instruments are all capable of producing accurate and precise trace element concentration data over a range of geologic matrices, provided that each instrument is carefully operated within its dynamic range. In many cases, this could be accomplished simply by ensuring proper dilution of samples; however, when matrices are more complex, the use of medium and high resolutions can be useful in reducing the amount of preparative chemistry that is required to manage highly variable trace element concentrations within a single sample as well as any potential isobaric interferences.

1. Introduction

The study and adequate characterization of geologic reference materials are essential for determining the accuracy of geochemical analyses and techniques. An experiment can yield results that are considered precise (i.e., with small standard deviation), however without reference materials that provide “known” values, it is impossible to determine if the results are accurate (i.e., close to the “true” value). Therefore, it is of critical importance that all reference materials are carefully prepared by manufacturers and fully characterized through precise, quantitative, and reproducible analyses (e.g., Chauvel et al., 2010; Jochum and Brueckner, 2008).

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This study reports the results of a series of trace element concentration analyses that were performed on a compositionally broad range of reference materials by inductively coupled plasma mass spectrometry (ICP-MS). The six reference materials, supplied by the United States Geologic Survey (USGS), are: BHVO-2, BCR-2, AGV-2, STM-2, RGM-2, and G-3 (Wilson, 1997a; Wilson, 1997b; Wilson, 1998; also see Flanagan, 1967 and 1976 for descriptions of previous STM, RGM, and G standards). This set of reference materials, which includes both intrusive and extrusive rocks with compositions ranging from mafic to felsic, encompasses a wide variety of geochemical characteristics and trace element concentrations. The second (and third) generation of USGS reference materials was selected for use in this study because it is more widely available and more care was taken to avoid contamination during sample preparation. These geochemical reference materials were recently analyzed in several high-precision isotopic (Pb, Sr, Nd, Hf) studies by Weis et al. (2005, 2006, 2007), Pretorius et al. (2006), and Chauvel et al. (2010, 2012) that also featured partial trace element characterization.

For comparison purposes, three different instruments are used in this study: the Nu Instruments AttoM (HR-ICP-MS), Thermo Scientific Element 2 (HR-ICP-MS), and Agilent 7700x (Q-ICP-MS). As a result of each instrument's unique method of separating ions according to their mass to charge (m/z) ratio, each instrument produces analyses with concomitant advantages and disadvantages. By characterizing a common set of reference materials, this study provides a robust evaluation of the precision and accuracy of each instrument. The trace element concentration analyses performed in the present study thus serve not only as reference values, but also as a tool by which each ICP-MS instrument is inter-calibrated and its relative performance can be assessed.

2. Analytical techniques

2.1. Sample preparation

The reference materials used in this study were prepared as powders by the United States Geologic Survey. For a complete description of sample collection and preparation methodology, refer to Flanagan (1967, 1976).

2.2. Sample digestion

As noted by Pretorius et al. (2006), multiple factors can interfere with the complete digestion of geologic samples. Specifically, the presence of high bulk-rock concentrations of calcium and/or highly refractory phases such as zircon and tourmaline in granitoid samples can become problematic if the samples are not digested properly.

Rocks such as anorthosite, andesite, limestone, and carbonatite are among the most challenging geologic samples to digest due to their calcium-rich matrix (Pretorius et al., 2006). Such samples are especially prone to the incomplete recovery of the high field strength elements (i.e. Nb, Ta, Zr, & Hf) due to their strong tendency to hydrolyze and form insoluble compounds (Cotta and Enzweiler, 2012; Tanaka et al., 2003). These compounds are commonly avoided through the addition of hydrofluoric acid (HF), which promotes the formation of stable, soluble HFSE fluoro-complexes (Tanaka et al., 2003). To prevent the precipitation of HFSEs, a sufficient amount of F^- must be present in solution. In this HF media, however, Mg and Ca tend to react with F^- to form the minerals fluorite (CaF_2) and selliate (MgF). Inherent in this process is the coprecipitation of HFSEs that can lead to decreased recovery of these elements (Pretorius et al., 2006; Tanaka et al., 2003). Mafic and ultramafic samples undergo a similar coprecipitation process, however more typically in the structures of the minerals ralstonite ($Na_xMg_xA_{l2-x}F_{6-y}(OH)_y \cdot nH_2O$) and selliate (Pretorius et al., 2006; Rosenberg, 2006). Completely drying samples after digestion with HF will ensure the removal of fluorine from soluble HFSE-fluorocomplexes through volatilization (Chao and Sanzolone, 1992).

Digesting granitoids can be problematic because these rocks tend to include highly refractory phases such as zircon and tourmaline. These phases are systematically enriched in many trace elements, particularly Zr, Hf, Li, and the rare earth elements, making complete digestion essential for a quantitative trace element analysis. Yokoyama et al. (1999) have demonstrated that the consistency of trace element recovery can be improved by performing an extended digestion with perchloric acid, under high pressure conditions.

Digestion of samples (~100 mg) in this study was modeled after Pretorius et al. (2006) and Weis et al. (2006) Samples were digested in triplicate following one of two schemes depending upon bulk-rock composition:

Hotplate digestion — used for mafic samples (BHVO-2 and BCR-2). This scheme uses HF and HNO_3 as the primary digestion acids and uses HCl to ensure the complete removal of volatiles and precipitates. Additionally, in the case of an isotopic analysis, the step of HCl digestion ensures that samples will match the medium required for column chemistry. Hotplate digestion scheme is described in detail as the digestion method for mafic samples in Weis et al. (2006).

High-pressure PTFE bomb digestion — used for intermediate and felsic samples (AGV-2, STM-2, RGM-2, G-3). High-pressure digestion scheme is described in detail as the HF-HNO_3-$HClO_4$ digestion method in Pretorius et al. (2006). The addition of perchloric acid ensures that a high enough temperature may be reached for all of the fluorine to be driven off without drying down the solution completely over the extended (five day) digestion period.

2.3. Instrumentation

Two double-focusing (high-resolution) sector field instruments, the Thermo Scientific Element 2 and the Nu Instruments AttoM; and one quadrupole ICP-MS, the Agilent 7700x, were used to perform trace element analyses at the Pacific Centre for Isotopic and Geochemical Research at the University of British Columbia. Typical parameters for each instrument (Supplementary Table 1) and a more detailed discussion of how concentrations are calculated for each instrument can be found in Supplementary Material.

2.3.1. Thermo Scientific Element 2

The Element 2 is oriented in a reverse Nier–Johnson geometry; in this design only ions of the desired mass will be subjected to energy focusing because the ions have already been separated by mass (Batey et al., 2005). This design presents advantages over traditional geometry devices in terms of improved abundance sensitivity and reduced noise (Batey et al., 2005). Furthermore, reverse geometry devices do not face the challenge of having a dispersed beam of ions in the detector region. Instead, the electrostatic analyzer focuses the ion beam straight into a single collector. The Element 2 has a dynamic range spanning 9 orders of magnitude.

On the Element 2, concentrations (in ppm) are determined by a one-point calibration curve that is automatically generated for each element based on the accepted concentration values for a chosen standard solution that is analyzed at the beginning of each set of analyses. Samples were analyzed in groups of five to six and each group was bracketed on either side by a blank solution and the calibration standard. Felsic and intermediate samples (AGV-2, STM-2, RGM-2, and G-3) were grouped together and calibrated with the reference material AGV-2,

Table 1
Composition of interference solutions.

Solution	Matrix	AttoM (ppb)	7700x (ppb)
Ba		10	100
Ce	1% v/v HNO_3	2	10
Pr–Nd	0.05% v/v HF	2	10
Sm—Eu—Gd—Tm		2	10