Reference materials mapping: spatial geochemical heterogeneity characterization

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Reference materials (RM) are mandatory to produce high quality analytical results, and therefore must be well characterized with respect to heterogeneity. Microbeam techniques use very small sample masses, which can make representativity a difficult goal to achieve. Characterization of RM has mainly been done by computing statistics on numerous replicate determinations (microbeam and bulk samples; mg to g). Such studies do not take into account the systematic spatial relationships between determinations and may hence not necesarily arrive at a representative heterogeneity estimate. In the case of glasses (NIST-600s, GSD-1, etc.) and some pressed pellets (MASS-1, MACS-1 and MASS-3), anomalous "hot pots" can sometimes be larger than beam size, and can be clustered or segregated along a spatial trend. Such information is critical to determine optimal beam size or for locating optimal transects for calibration. Improved heterogeneity characterisations will lead to improved constraints on precision and accuracy of RM in general and specifically for microbeam RM.

A set of systematic experiments has been carried out to map RM with LA-ICP-MS and microXRF, to determine concentration variations in the widest possible field of view regimen. The first step is instrumental optimization of mapping to control instrumental drift. MicroXRF mapping of pulverized RM (precious metal bearing: WMS-1, CHR-Pt+, MASS-1 and MASS-3) were used to delineate precious metals nuggets, which are indeed present in many instances. This has been used to demonstrate that large sample masses are often necessary for many sulfide RM. Precipitated materials (such as MASS-1) are devoid of nuggets while most powdered RM showed nuggets. LA-ICP-MS mapping of glasses typically used to calibrate analysis, e.g. NIST-600 series, also show heterogeneities, especially for precious metals. Elemental maps have been computed to show visually heterogeneities and their locations. Variographic analysis has been undertaken to visualize variability as a function of the spatial scales.

Spatial information is an important contribution in characterizing many RM (glass and powders). Such information was previously difficult or expensive to acquire. Now spatially resolved geochemical data for RM are rapidly becomming easily accessible; this type of characterisation is the next step in RM characterization.

Volatile transfer from magma sources in the Taupo Volcanic Zone

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The Taupo Volcanic Zone (TVZ) is a rifted arc where dominantly silicic magmatism and volcanism has evolved intimately with tectonic. Two distinct rhyolite magma types (dry-reducing and wet-oxidizing) have erupted from the central TVZ over the past ~550kyrs [1]. We measured major, trace, and volatile element concentrations (including B isotopes) in quartz-hosted melt inclusions from several large, rhyolitic eruptions representing these distinct types in an effort to: 1) determine if the magma was vapour saturated, and 2) identify disparities in the volatile contributions to the overlying hydrothermal systems. Dry magma in the upper crust may not be volatile saturated and, therefore, would contribute very little to the overlying hydrothermal system.

Melt inclusions from the dry type Ohakuri and Mamaku eruptions (~240 ka) have high chlorine values ranging from 0.25 to 0.36wt%, and show a positive correlation between chlorine, fluorine, Rb/Sr ratio and other incompatible elements, suggesting that no vapour phase was exsolved prior to eruption. In comparison, volatile data from the wet type Kaharoa eruption (~1314AD) show vapour saturation and exsolution of a volatile phase during crystallisation [2].

The combination of boron and boron isotopes is an effective tracer of the volatile contribution from slab-derived fluids. Measured B and δ^{11}B in these two different types of systems, reveal distinct signatures. The isotopic composition of the Kaharoa is homogeneous, with δ^{11}B of + 4‰, and boron contents range from 20-30 ppm. Because the Kaharoa was saturated, the boron preferentially partitions into the fluid phase ($D_B^{fluid/melt} >> 1$), which requires that a much higher bulk content of boron existed prior to eruption. The Mamaku and Ohakuri melts, on the other hand, have homogeneous boron contents around 15 ppm, but isotopic ratios ranging from – 3 to + 3‰. These two different signatures can be linked to variable contributions of fluid from the subducting slab, and we attribute this to a decrease in slab-derived fluid flux across the TVZ.

Geochemical heterogeneities and the generation of wet vs. dry rhyolites in the TVZ can be directly linked to the input of slab-derived fluids. As such, boron could potentially be a very useful tracer for volatile transfer processes where magmas are saturated. Our methodology can determine if a magmatic system is volatile saturated, and hence, could help identify areas in the upper crust where there is a maximum potential for heat transfer to the overlying geothermal system.

[1] Deering (2008) *Journal of Petrology* **49**, 2245-2276. [2] Johnson (2011) *Geology* **39**, 311-314.