

First magmatism in the New England Batholith, Australia: Forearc and arc-backarc components in the Bakers Creek Suite gabbros

Supplement 5: Expanded Analytical Methods

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Major and Trace Element Geochemistry

Bulk-rock samples were crushed in a tungsten-carbide mill to a coarse powder from which a representative split was taken and further crushed for several minutes. Powders were prepared for major oxide analysis by dilution with a lithium borate flux and fusion at 1050°C to produce a glass disc, and for trace element analysis by pressing into a solid pellet with a small amount of PVA binder. Major element oxides (Na₂O, MgO, Al₂O₃, SiO₂, P₂O₅, K₂O, CaO, TiO₂, MnO and FeO) were analysed in the glasses by X-ray fluorescence (XRF) at the UoN using a Spectro X'Lab 2000 Energy Dispersive XRF system equipped with a Pb anode tube and using a polarised beam and multiple targets. All Fe is reported as FeO. Pressed powder pellets were analysed for many elements (S, Cl, Sc, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pr, Nd, Hf, Ta, W, Hg, Tl, Pb, Bi, Th, and U); of these, we report Pb, P, Ti, V, Mn, Zn, and Cr because many of these elements were not usefully detected and most were used only as a check and were superseded by the following round of trace elements (next paragraph).

Glass XRF discs from this study and from Jenkins et al. (2002) were then mounted in epoxy resin, bisected and progressively polished to a final grade of 0.2 µm. These samples were subjected to further trace element analysis (Cs, Rb, Ba, Th, U, Nb, Ta, Sr, Zr, Hf, Ga, Y, Sc, Co, Ni, and the rare earth elements La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, and Yb) by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Research School of Earth Sciences, Australian National University (ANU), using a quadrupole Agilent 7500s coupled to a 193 nm ArF Excimer laser (Eggins 2003). Samples were analysed in parallel with NIST 612 (primary normalisation standard) and BCR-2g (secondary external standard) glasses and isotope masses of either ⁴³Ca or ²⁹Si were used as internal standards depending on bulk silica content (using CaO or SiO₂ from XRF). Following from Eggins (2003), for the LA-system we used profile (raster) mode across samples using a circular laser ablation spot ~103 µm diameter with pulse frequency of 10 Hz and energy to the sample of ~10 J cm⁻². The ICP-MS was tuned to minimise oxide production, monitoring Th and maintaining ThO⁺/Th⁺ <0.3% (e.g. Jackson et al. 1992). Counts were collected by single collector peak hopping from one isotope to the next, using

pulse counting mode at each peak, with a sweep time for the entire elemental run table of 1.1 s. This resulted in ~50-150 sweeps per lithium borate disc depending on their sectioned thickness. Following established methodology of Eggins (2003), we used NIST 612 as the internal standard with the concentrations reported by Pearce et al. (1997). Data reduction is conducted according to Longerich et al. (1996). Limits of detection are typically much better than 1 ppm, and generally improve from $\sim 10^{-1}$ to $\sim 10^{-3}$ ppm with increasing element mass over the range from Sc to U (Eggins 2003 Geostandards Newsletter 27, 147-162).

XRF and LA-ICP-MS data are very well correlated for all elements above ~ 10 ppm; below this, the detection limit of XRF does not permit good assessment. Figure 1 in this supplement shows correlations between XRF and LA-ICP-MS data and the deviation for most elements from the 1:1 line below ~ 10 ppm.

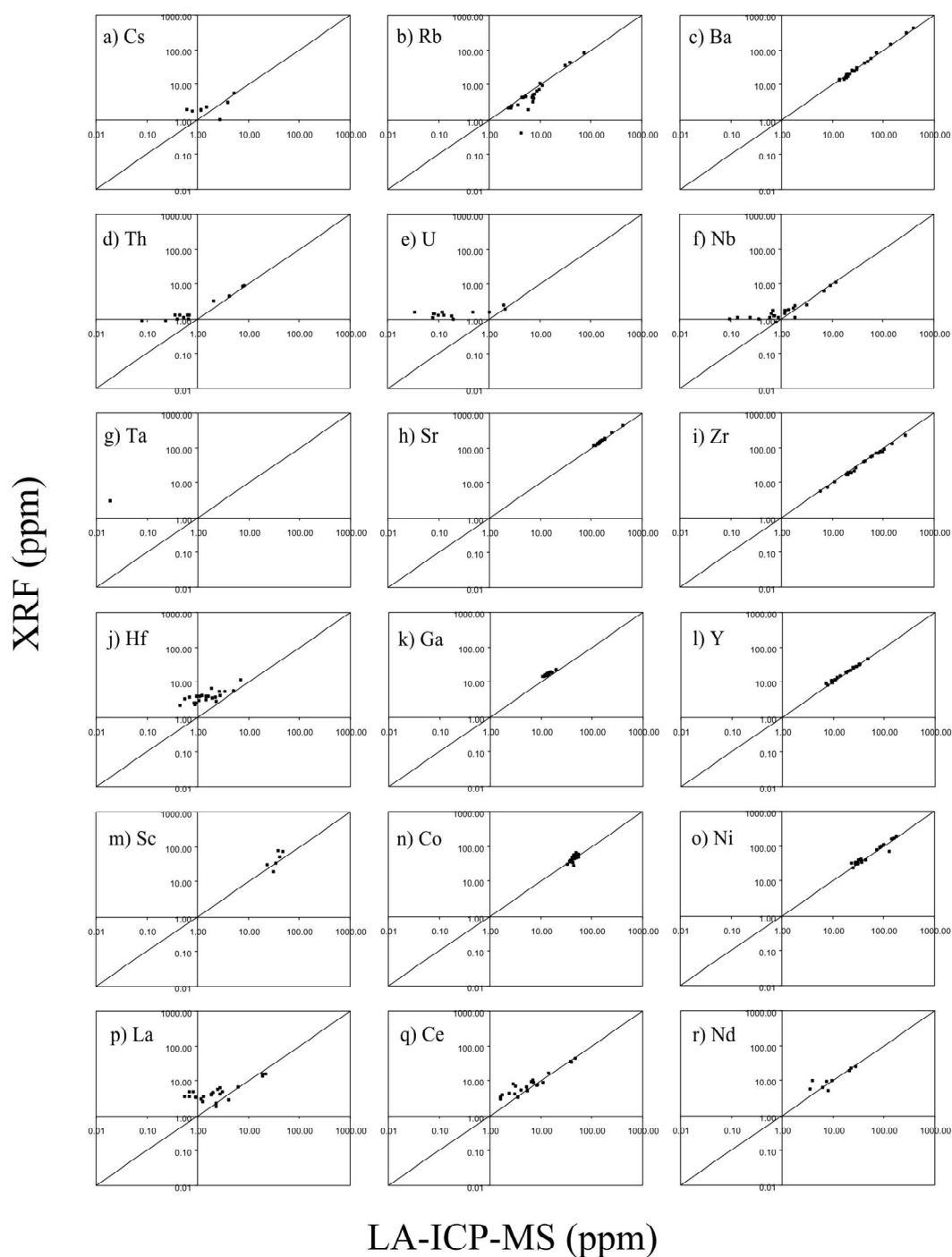


Figure 1. Comparison of LA-ICP-MS and XRF analyses (where detected) for samples of this study.

We analysed the natural glass BCR2g in parallel with NIST 612 glass to check final trace element concentrations across the mass range, and are able to make a detailed comparison for a selection of elements with the classic study of BCR2g (Rocholl 1998) and works discussed therein. We present below in Figure 2 of this supplement the USGS (1996)-normalised values for Ca, Sc, V, Co, Ni, Sr, Y, Zr, Cs, Ba, La, Nd, and Lu from the two analytical session of this study and from Seufert and Jochum (1997) and Rocholl (1998).

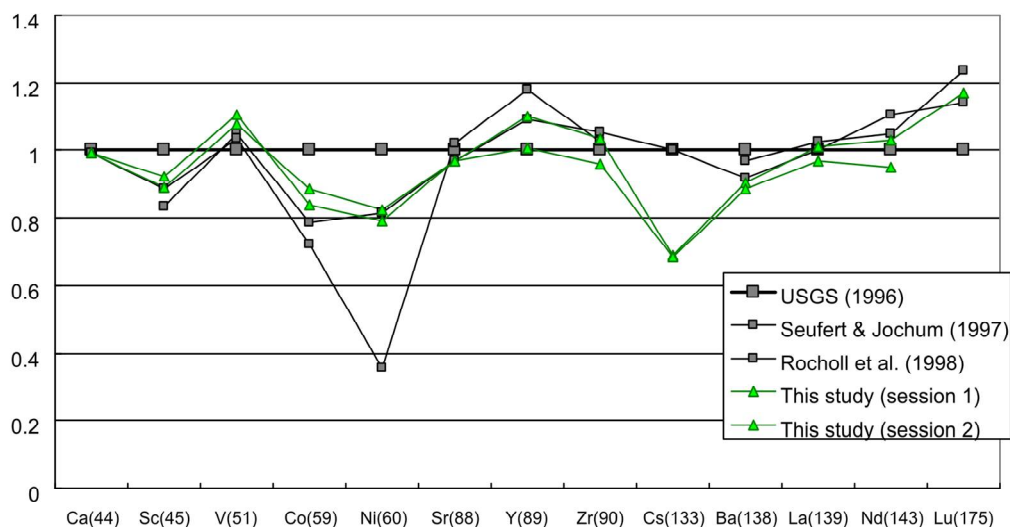


Figure 2. Behaviour of secondary standard natural glass BCR2g over two analytical sessions (in green), normalised to the USGS (1996) values and compared to important literature assessments by Seufert and Jochum (1997) and Rocholl (1998).

Most of our reported values are within ~10% of either those given by the USGS (1996) or those of Seufert and Jochum (1997) or Rocholl (1998). The internal standard Ca was within 0.6% of the USGS (1996) reported value. For trace elements, there are some variations from the USGS composition for our analyses and those in the literature. For Ni, there are wide variations in concentrations reported for BCR2g; our results are in the middle of the range and we therefore consider this element reliable. Cs is another potentially problematic element; it is noted in Rocholl (1998) that Cs may have been enriched by a factor of 1.4 in BCR2g. We obtained much lower values for Cs but this is entirely consistent with the suggested enrichment not affecting our piece of BCR2g (our values are ~0.96 times the BCR1 value discussed in Rocholl 1998). We therefore consider our Cs results reliable. For our analyses, V was ~7-10% higher due to possible ArB interference and we therefore report V values from XRF rather than LA-ICP-MS in our Supplement 1 Bulk rock geochemistry. It should be noted that our data, where seemingly different from USGS values, deviates in the same direction and by nearly the same amount as the other studies (Seufert and Jochum 1997 and Rocholl 1998).

Zircon U-Pb Chronology

Zircon U-Pb ages were determined at the Australian National University on SHRIMP I and SHRIMP RG. Zircon grains were obtained from geochemical samples BH30, DC15, A279 and CCD. Mineral separation was performed using standard crushing, washing, heavy liquid (Sp. Gr. 2.96 and 3.3), and paramagnetic procedures. Hand selected zircon grains were placed onto double-sided tape, mounted in epoxy together with grains of the reference zircons (AS3, SL13 and TEMORA), sectioned approximately in half, and polished. Reflected and transmitted light photomicrographs were prepared for all zircons, as were cathodoluminescence (CL) and Scanning Electron Microscope (SEM) images. These CL images were used to

decipher the internal structures of the sectioned grains and to ensure that the ~30 μ m SHRIMP spot was placed in such a way as to avoid crystal irregularities.

The U-Pb analyses were made following procedures given in Williams (1998, and references therein). Zircons separated from A279 and CCD were run on SHRIMP I, and each analysis consisted of 6 scans through the mass range, with the AS3 (Duluth Gabbro) reference zircon grains analysed after every three unknown analyses. Zircons from BH30 and DC15 were run on SHRIMP RG using a mass-unfiltered primary beam, with each analysis consisting of 5 scans through the mass range and the TEMORA (Middledale Gabbroic Diorite) reference zircon grains being analysed after every two unknowns. An unfiltered primary beam was used to ascertain whether mass-filtering affects primary or secondary beam stability, and the counting statistics suggest that it does not. The strength of the secondary (sputtered positive ion) beam varied by typically less than 2% during each SHRIMP RG analysis, and often by only 0.5-1.0%.

Data were reduced using the SQUID Excel Macro of Ludwig (2001). For the SHRIMP I session, Pb/U ratios were normalised relative to a value of 0.1859 for the AS3 reference zircon, equivalent to an age of 1099 Ma (Paces and Millar, 1993). Uncertainty in the U-Pb calibration for this session was 0.68%. For the SHRIMP RG session, Pb/U ratios have been normalised relative to a value of 0.0668 for the TEMORA reference zircon, equivalent to an age of 417 Ma (Black et al. 2003). Uncertainty in the U-Pb calibration for this session was 0.42%.

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