

Online Resource 6

S-type ignimbrites with polybaric crystallisation histories: the Tolmie Igneous Complex, Central Victoria, Australia

Contributions to Mineralogy and Petrology

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Analytical details

Major-element analyses of whole-rock samples and minerals

Representative rock samples from the TIC were selected to avoid alteration and crushed using standard methods for XRF analysis. Both Li-borate glass discs and powder mounts were used for the analyses, which involved several different laboratory facilities. Analyses obtained at the University of Melbourne used a Siemens sequential (SRS1) spectrometer, while those at Monash University used a Phillips 1520 XRF Spectrometer. Loss of volatile elements during XRF fusion was determined on many samples (those of Birch (1975), Clemens (1981) and unpublished by Dudley), as well as measurement of Fe^{2+} by titration with potassium dichromate solution. Microprobe analyses on selected minerals were obtained using a JEOL MK5 microprobe at the University of Melbourne and an ARL EMX microprobe fitted with a Microtrace EDS detector at Monash University.

REE analyses

Samples were analysed for rare earth elements by solution ICP-MS in the Department of Geological Sciences at the University of Cape Town, using a Thermo X-Series 2, and the following analytical procedure: 50 mg of 300# sample powder were dissolved in a 3:1 HF/HNO₃ acid mixture in sealed Savilex beakers on a hotplate for 48 h, followed by evaporation to incipient dryness and two treatments of 2 ml of concentrated HNO₃. The final dried product was then taken up in 5% HNO₃ solution containing 10 ppb Re, Rh, In and Bi as internal standards. Standardisation was against artificial multi-element standards. Replicate analyses of BHVO-1 typically gave an overall procedural error of better than 3% relative. The small grain sizes of zircons in rhyolitic rocks typically result in no residual, undissolved zircon being present after such dissolutions. Furthermore, analyses of international rhyolite standards (e.g. JR-1), in this laboratory, show no evidence of systematic error in REE analyses as a consequence of residual zircon. Thus, the REE analyses reported in the table of Online Resource 5 should be accurate.

Sr and Nd isotopes

Following HF-HNO₃ digestion of approximately 50 mg of sample material, Sr and Nd fractions were isolated using Sr.Spec, TRU.Spec and Ln.Spec resins (Eichrom) according to routines adapted from standard ion-exchange methods, after Pin and Zalduegui (1997) and Pin et al. (1994). Existing concentration data were used to obtain final solutions of 3 ml of 200 ppb Sr in 0.2% HNO₃ and 1.5 ml of 50 ppb Nd in 2% HNO₃. A single batch of 0.2% or 2% HNO₃ was used for each analytical session.

All isotope analyses were performed using a NuPlasma HR MC-ICP-MS (Nu Instruments, Wrexham, UK) in the Africa Earth Observatory Network, EarthLAB Facility in the Department of Geological Sciences at the University of Cape Town. For Sr isotope analysis, solutions were aspirated into the plasma via a microcyclonic spraychamber, while for Nd isotope analysis a Nu Instruments DSN-100 desolvating nebuliser was used.

Sr isotope analyses were corrected for background signals using an on-peak background measurement of the 0.2% HNO₃ solution. Instrumental mass fractionation was corrected using the exponential law and a fractionation factor based on the measured $^{86}\text{Sr}/^{88}\text{Sr}$ ratio and the accepted value of 0.1194. The ^{87}Rb contribution to the 87 amu signal was calculated and subtracted using this fractionation factor, the exponential law, the measured ^{85}Rb signal and a

$^{85}\text{Rb}/^{87}\text{Rb}$ ratio of 0.1194. NIST SRM987 was analysed as a bracketing standard, yielding an external, measured, 2σ reproducibility of 0.000019 ($n = 3$) on an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710277. All $^{87}\text{Sr}/^{86}\text{Sr}$ data were normalised to 0.710255, the in-house long-term average, which agrees with published results. The average $^{84}\text{Sr}/^{86}\text{Sr}$ ratio was 0.05643 ± 0.00012 , also in agreement with published values.

All Nd isotope measurements were corrected for Sm and Ce interferences and for instrumental mass fractionation, using the exponential law and a $^{146}\text{Nd}/^{144}\text{Nd}$ value of 0.7219. For further details of the analytical techniques see Will et al. (2007). JNdi-1 was used as bracketing standard, and all Nd isotope data presented are referenced to this standard, using a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.512115 (Tanaka et al. 2000).

The values of initial $^{87}\text{Sr}/^{86}\text{Sr}$ in Table 4 were calculated for an assumed age of 370 Ma. Quoted errors are 2σ values that result from propagation of the analytical uncertainties in Rb and Sr analyses and in the present-day $^{87}\text{Sr}/^{86}\text{Sr}$, through the equations.

Nd model ages were calculated using a linear $^{143}\text{Nd}/^{144}\text{Nd}$ evolution of the depleted mantle from $\epsilon\text{Nd} = 0$ at 4600Ma to a present-day ϵNd of +10 (Goldstein et al. 1984). The following algorithm was used: $T_{\text{DM Nd}} = (1/\lambda) \ln\{((^{143}\text{Nd}/^{144}\text{Nd}) - 0.51316) / ((^{147}\text{Sm}/^{144}\text{Nd}) - 0.214)\} + 1$, where $\lambda = 6.54 \times 10^{-12} \text{ yr}^{-1}$ (DePaolo 1981), 0.51316 is the present-day $^{143}\text{Nd}/^{144}\text{Nd}$ of the depleted mantle, 0.214 is the $^{147}\text{Sm}/^{144}\text{Nd}$ depleted mantle (McCulloch and Black 1984) and $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ are the measured and calculated present-day isotope ratios, respectively.

References

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