

The School of Earth and Environmental Sciences Radiogenic Isotope Facility (RIF) standards and procedures

Elemental analysis

For trace element analysis of silicate samples by the quadrupole ICP-MS (Q-ICP-MS), we follow revised versions of a multi-isotope internal standardization analytical protocol described in Eggins et al. (1997). Details of the UQ revised versions were described subsequently in Kamber et al. (2003) and Li et al. (2005). The UQ protocol involves the use of USGS rock standard W-2 as the calibration standard, and other rock standards such as BHVO-2, BCR-2, BIR-1, AGV-1, G-2 etc. as independent standards of different rock types. With our multi-isotope internal standardization analytical protocol, typical external reproducibility in terms of relative standard deviations for the majority of the >40 elements routinely measured on our Q-ICP-MS is below 3%.

For trace element analysis of carbonate samples (e.g. corals, speleothems which have most trace element concentrations 2-3 orders of magnitudes lower than silicates), we used a protocol similar to that for silicates, but often these samples are measured on a dedicated Q-ICP-MS, where backgrounds are closely monitored. Apart from also using W-2 as the calibration standard, we also use a Japanese coral Jcp-1 as an independent standard and its recommended values for calibration of count rates for Ca and Sr (see Uysal et al. 2007; Nguyen et al. 2013).

For high-precision Element/Ca ratio analysis in coral skeletons, we use a tailored analytical protocol whereby Jcp-1 standard is used as the calibration standard, sample solutions are diluted to average 50,000 times to allow Ca, Sr and Mg signals to be measured on pulse-counting mode, and ^{45}Sc , ^{51}V , ^{115}In and ^{235}U are used as internal standards to calibrate mass response in their mass range for precise calibration and correction of drift in Sr/Ca and Mg/Ca ratios. This analytical protocol allows rapid ratio analysis (~150 samples/day) to precisions of 0.2%RSD for Sr/Ca, <0.5% for Mg/Ca, and ~1% for Ba/Ca and U/Ca. Detailed protocols are reported in Nguyen et al. (2013).

Isotope Analysis

For routine Sr-Nd-Pb-Hf isotope analysis, we use a tailored column separation protocol involving the use of Sr-spec, THRU-spec and LN-spec resins, allowing for a large number of samples to be processed in one batch without the need for evaporation in the intermediate stages. Upon screening of Sr-Nd-Pb-Hf concentrations in the final separates using the Q-ICP-MS, properly diluted aliquots of these elements are measured for their isotopic ratios on our Nu Plasma MC-ICP-MS fully automatically using a firmware-modified Cetex ASX-110 autosampler (although Sr samples, especially with highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$, are also routinely measured on our old VG Sector 54 TIMS). SRM-987 Sr standard, SRM-981 Pb standard, a laboratory-based Nd metal standard and a laboratory-based Hf standard are measured after measurements of every five unknown samples. This standard-sample-standard bracketing method is used for correction of minor drift that cannot be fully corrected using the

exponential mass fractionation law. Our laboratory-based Nd and Hf standards were calibrated against the JNdi-1 Nd and JMC-475 Hf international standards. Various rock standards (e.g. W-2, BCR-2, BHVO-2, BIR-1, G2, etc.) are often processed in the same batch of unknown samples for monitoring the reproducibility of our analytical protocols. Detailed analytical procedures were reported in Guo et al. (2014; 2016) and Wei et al. (2014a; 2014b).

For U-Th dating of carbonates on the MC-ICP-MS, we use a specially tailored protocol described in detail in Zhou et al. (2011) and Clark et al. (2014a). Using this protocol, each sample is spiked with a mixed ^{229}Th - ^{233}U tracer (calibrated against the secular-equilibrium HU-1 uraninite standard as well as our gravitationally-made U-metal standard CRM-112A or called SRM-960) and then completely dissolved in concentrated HNO_3 . After digestion, each sample is treated with H_2O_2 to decompose trace amounts of organic matter and to facilitate complete sample-tracer homogenisation. U and Th is separated using conventional anion-exchange column chemistry using Bio-Rad AG 1-X8 resin. After stripping off the matrix from the column using double-distilled 7N HNO_3 as eluent, 3.2 ml of 4N HNO_3 is used to elute U, and then 2.4 ml of a 2% HNO_3 solution mixed with 0.03% HF is used to elute residual U and Th into 3.5-ml pre-cleaned test tubes (here named Tube#1 and Tube#2, respectively). After column chemistry, solutions in Tubes #1 and 2 are first pre-screened for U and Th concentrations using a Thermo X-series II quadrupole ICP-MS. Based on the screened concentrations, a small amount of U is taken from Tube #1 (dried first if the liquid volume is too large) and mixed into Tube #2, targeting a final U

concentration of around 10-15 ppb in the mixed solution. This mixed solution is then injected into the MC-ICP-MS through a DSN-100 desolvation nebuliser system with an uptake rate of around 0.12 ml per minute. U-Th isotopic ratio measurements are performed on the MC-ICP-MS using a detector configuration to allow simultaneous measurements of both U and Th isotopes. The $^{230}\text{Th}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ activity ratios of the samples are calculated using the decay constants given in Cheng et al. (2000). The non-radiogenic ^{230}Th is corrected using an assumed bulk-Earth atomic $^{230}\text{Th}/^{232}\text{Th}$ ratio of $4.4 \pm 2.2 \times 10^{-6}$. For corals from the Great Barrier Reef, non-radiogenic ^{230}Th is corrected using site specific $^{230}\text{Th}/^{232}\text{Th}$ values determined for detrital and hydrogenous end-members and corrected using a two-component mixing equation described in Clark et al. (2014b). U-Th ages are calculated using the Isoplot/Ex 3.75 Program (Ludwig, 2012).

Contact

For further information, please contact the RIF Manager, Prof. Jian-xin Zhao (Tel: +61 7 3346 9754; Email: j.zhao@uq.edu.au).

References

- Cheng et al. 2000 The half-lives of uranium-234 and thorium-230. *Chem. Geol.* 169, 17-33.
- Clark et al. 2014a Discerning the timing and cause of historical mortality events in modern *Porites* from the Great Barrier Reef. *Geochim. Cosmochim. Acta* 138, 57-80.
- Clark et al. 2014b Testing the precision and accuracy of the U-Th chronometer for dating coral mortality events in the last 100 years. *Quat. Geochronol.* 23, 35-45.
- Eggins et al. 1997 A simple method for the precise determination of ≥ 40 trace elements in geological samples by ICPMS using enriched isotope internal standardisation. *Chem. Geol.* 134, 311-326.
- Guo et al. 2014 Lithosphere thinning beneath west North China Craton: Evidence from geochemical and Sr-Nd-Hf isotope compositions of Jining basalts. *Lithos* 202-203, 37-54.
- Guo et al. 2016 The origin of Cenozoic basalts from central Inner Mongolia, East China: The

- consequence of recent mantle metasomatism genetically associated with seismically observed paleo-Pacific slab in the mantle transition zone. *Lithos* 240–243, 104-118.
- Kamber et al. 2003 A refined solution to Earth's hidden niobium: implications for evolution of continental crust and mode of core formation. *Precambrian Research* 126, 289-308.
- Li et al. 2005 ICP-MS trace element analysis of Song dynasty porcelains from Ding, Jiexiu and Guantai kilns, north China. *Journal of Archaeological Science* 32, 251-259.
- Ludwig, 2012 Isoplot 3.75, A Geochronological Toolkit for Excel. 5, Berkeley Geochronology Center Special Publication.
- Nguyen et al. 2013 Impact of recent coastal development and human activities on Nha Trang Bay, Vietnam: evidence from a *Porites lutea* geochemical record. *Coral Reefs* 32, 181-193.
- Uysal et al. 2007 U-series dating and geochemical tracing of late Quaternary travertine in co-seismic fissures. *Earth Planet. Sci. Lett.* 257, 450-462.
- Wei et al. 2014a Petrology and Sr–Nd Isotopic Disequilibrium of the Xiaohaizi Intrusion, NW China: Genesis of Layered Intrusions in the Tarim Large Igneous Province. *J. Petrology* 55, 2567-2598.
- Wei et al. 2014b, Plume-lithosphere interaction in the generation of the Tarim large igneous province, NW China: Geochronological and geochemical constraints. *Am J Science* 314, 314-356.
- Zhou et al. 2011 Speleothem-derived Asian summer monsoon variations in Central China, 54–46 ka. *Journal of Quaternary Science* 26, 781-790.