In situ ^{238}U-^{234}U-^{230}Th isotopic analysis by laser ablation multiple-collector ICPMS

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We report preliminary *in situ* U-Th isotopic data at very high spatial resolution using laser ablation sampling, combined with multiple collector ICP magnetic sector mass spectrometry (MC-ICPMS). Although still in its developmental stages, our laser ablation technique offers significant potential in U-series disequilibrium studies requiring isotopic data at the micron scale, including magmatic zircon geochronology and applications in palaeohydrology. For example, U-Th dating by thermal ionization mass spectrometry (TIMS) has been used to examine the relationship between hydrological and climate variations at Yucca Mountain, Nevada (e.g. Paces *et al.*, 1995; 1996; 1998). However, it would be desirable to obtain such data at a finer scale than possible with conventional micro-sampling, combined with TIMS.

We have applied the laser ablation MC-ICPMS technique to certified glass standards and naturally occurring opal. Opal is well suited to U-series geochronology (Paces *et al.*, 1995; 1996; 1998); it has a large content of U (several hundred ppm), coupled with extremely low Th/U ratios, so that U-Th isotopic data can be acquired at a fine scale, with high precision, and without requiring corrections for initial Th. In addition, conventional dating by TIMS demonstrate that opal is not susceptible to diagenetic exchange of U and Th (Paces *et al.*, 1995; 1996; 1998). We have measured variations in $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ in opal on spatial scales of 50 μm, corresponding to sample sizes of less than 0.02 mg. For 80,000 year old samples, the technique is capable of resolving events separated in time by less than 10,000 years.

Standard glasses NIST SRM 611 and SRM 613, with independently known $\delta^{234}U$ values of $-828.8 \pm 0.1‰$ and $-827.2 \pm 0.2‰$ ($2\sigma_M$), respectively, were used to assess the precision and accuracy of our laser ablation technique, when applied to U isotope measurement. The former has a U concentration of 500 ppm and the latter a U content of 50 ppm. The ion beams are sufficiently large and persistent enough to enable Faraday/Daly gain and mass bias variations to be monitored internally, during the course of the measurement. Nineteen laser analyses on SRM 611 and seven measurements on SRM 613 give respective weighted mean $\delta^{234}U$ values of $-828.6 \pm 0.2‰$ and $-826.2 \pm 1.8‰$ ($2\sigma_M$), in excellent agreement with the conventional measurements, verifying the accuracy of the U measurement technique by laser ablation. For SRM 611 and 613, external reproducibility is 0.8‰ and 4.8‰ (2σ), respectively, and suggests that the within-run analytical uncertainty (typically 4‰ for SRM 611 and 18‰ for SRM 613) overestimates the true uncertainty by a factor of 4 to 5. The U measurement technique was also evaluated using an opal sample, known from TIMS analyses to be in secular equilibrium with respect to ^{238}U, ^{234}U and ^{230}Th (Paces *et al.*, 1995; 1996; 1998). To maximize data acquisition time for the opal analyses, we correct the measured ratios for Faraday/Daly gain and mass bias effects externally, based on bracketing measurements for the SRM 611 glass. Fourteen experiments on the secular equilibrium opal give reproducible $\delta^{234}U$ measurements that are slightly offset from the expected value of zero. This may be due to applying an external, rather than an internal mass bias correction to the measured ratios.

The measurement of $^{230}Th/^{238}U$, although reproducible, is more problematic and still in the investigative stage. Ten experiments on secular equilibrium opal yield $^{230}Th/^{238}U$ ratios that are identical within their uncertainties. However, elemental fractionation effects, as a result of introducing ablated particles to the plasma, lead to suppressed ion beams for Th relative to those for U, so that the measured $^{230}Th/^{238}U$ ratio, and consequently the ^{230}Th-age, are systematically lower than the true value. Both the SRM 611 glass and secular equilibrium opal show approximately the same depletion in ^{230}Th relative to the ^{238}U ion beam, implying that the fractionation is largely matrix-independent. The measured $^{230}Th/^{238}U$, corrected for this effect, and combined with $^{234}U/^{238}U$, provide ages for opals that are in good agreement with conventionally determined values.

References

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