A comparison of modern mass spectrometric methods for Th isotope ratio measurement

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Since 1986, when the first measurements of Th isotope ratios in corals were published by Edwards *et al.* (1986/87), numerous advances have been made in the measurement of Th isotope ratios by mass spectrometry. As a result, new avenues for research using the U-Th disequilibrium system have been successfully exploited, including high-precision re-calibration of the Pleistocene sea-level curve (e.g. Bard *et al.*, 1990), the investigation of magma dynamics and the timing of eruptions in continental and oceanic settings (e.g. Goldstein *et al.*, 1989; Reid, 1995), and the use of U-Th disequilibrium as a 'tracer' for processes that affect mantle sources prior to and during magnetism (e.g. Bourdon *et al.*, 1996). Despite these advances, made possible by the smaller sample requirements and higher precision of mass spectrometry over the older alpha spectroscopy method, the dating of volcanic rocks and authigenic or biogenic sediments (other than corals) over the past 400 to 500 kyr. have yet to be established as routine methods. Because of the potential importance of these dating techniques to the fields of palaeoclimatology and volcanology, isotope geochemists have continued to focus on the development of newer and better techniques for the measurement of Th isotope ratios in even smaller samples.

The measurement of Th isotope ratios by TIMS has generally yielded ionization-plus-transmission efficiencies (hereafter, simply 'efficiencies') of about 5×10^{-5} to 10^{-4} in volcanic rocks, although an order of magnitude improvement can be achieved for corals, because of their relatively low $^{232}Th/^{230}Th$ ratios, and the resulting ability to analyse far smaller samples of total Th than is possible with volcanic rocks (thermal ionization efficiency increases as the total amount of Th in a sample decreases; Edwards *et al.*, 1986/87). While the TIMS method permits the analysis of most volcanic rocks, it is best suited to those which are relatively high in Th, because low-Th rocks such as MORBs still typically require the preparation of more that one gram of uncontaminated material, which is a non-trivial task at best. In contrast, the thermal technique is perfectly suited to coral analysis, due to high U concentrations and the ready availability of relatively large amounts of sample material.

The measurement of Th isotope ratios by SIMS, first achieved using the Lamont Isolab 54 mass spectrometer, afforded a routine increase in efficiency of about a factor of ten over TIMS (~0.1%), making the analysis of MORBs and medium- to high-Th content phenocrysts from volcanic rocks far easier (e.g. Bourdon *et al.*, 1996). Improvements to the SIMS Th technique using the Isolab, now situated at the NHMFL, show the promise of efficiencies in the range of 2 to 5% (though, to date, this has been demonstrated only for standards), a level at which low-Th phenocrysts, perhaps even in MORBs, and low-U marine carbonates, may become amenable to analysis.

The new Cameca 1270 Ion Microprobe at UCLA has been shown to permit in situ Th isotopic analysis of zircons and allanites, leading the way to entirely new applications in the study of magma system evolution and dynamics (Reid *et al.*, 1997). Furthermore, experiments with chemically separated Th, loaded using the technique developed for the Isolab, show that the 1270 and the Isolab yield similar ionization efficiencies. The addition of multi-collector capability to this instrument in the near future will undoubtedly lead to further improvement in its Th analysis capability.

Perhaps the most exciting of the new techniques for Th isotope ratio measurement has seemed to be the multi-collector ICP-MS (e.g. Luo *et al.*, 1997). Experiments with the Plasma 54 in Lyon have demonstrated the capability for ionization efficiencies in the 0.1 to 0.5% range, similar to the SIMS results. However, the ease of sample preparation for this type of analysis, especially compared to that required for SIMS, makes it a very attractive alternative for many applications. Contamination of the tubing in the sample inlet system is a concern, but can be overcome by sustained washing between samples or the addition of a carrier element to the Th sample solution.

A limitation for all of these techniques has been the accurate and precise intercalibration of the ion-counting and faraday detection systems, due to the high dynamic ratios characteristic of most Th samples. While precisions in the range of 0.1% 2σ for ^{230}Th/^{232}Th ratios are theoretically possible, this level of precision has never been obtained. Though in part due to detector intercalibration uncertainties, the problem has received less attention than it might have, due to the fact that, for most applications where increased precision would be desirable, sample size limitations more-or- less precluded attainment of precisions better than 0.5 to 1.0%. As we look now to the ability to analyse much smaller samples of Th, in part due, perhaps, to the ability to process much larger total samples for ICP-MS analysis, detector intercalibration will increasingly become a more important issue. We have developed a technique, similar to that discussed by Luo *et al.* (1997), which involves the addition of a specially prepared U standard to Th samples being readied for SIMS or ICP-MS analysis. The standard, which is similar to NBL U500, but with ^{234}U/^{238}U ratio of about 5×10^{-5}, can be used to obtain an interdetector calibration at the 0.1% level or better, without resorting to peak-switching intercalibration at relatively high intensities, or assuming a linear response for the ion-counting detection system over many orders of magnitude in count rate.

Experiments with all systems are currently underway, and new results will be presented at the meeting.

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