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Secondary ion mass spectrometry for the measurement of ^{232}Th/^{230}Th in volcanic rocks

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Abstract

A technique is presented for the determination of ^{232}Th/^{230}Th in volcanic rocks by secondary ion mass spectrometry (SIMS). The technique utilizes a large format high-resolution, high-transmission ion microprobe, the Cameca IMS 1270. Although samples of chemically separated Th are required, these samples demand no special treatment in addition to that already utilized in thermal ionization mass spectrometry. This SIMS technique has considerable advantages in terms of sample size requirement, ease of sample loading, and rapidity of analysis over existing techniques, while providing an overall reproducibility of 0.5%–1.0%. Replicates of standard reference materials and rock materials already characterized by other techniques show excellent agreement with established values, supporting the reliability and accuracy of this new method. (Int J Mass Spectrom 203 (2000) 187–198) © 2000 Elsevier Science B.V.

Keywords: Secondary ion mass spectrometry; Ion microprobe; Th isotopes; U-series; U-Th disequilibrium

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1. Introduction

The traditional α-particle counting techniques originally employed for ^{232}Th/^{230}Th analysis are severely limited by the α-decay count rates of ^{230}Th (and ^{232}Th) measurable in some geological samples. As a consequence, the precision of α-counting ^{232}Th/^{230}Th measurements on 1 μg Th samples derived from typical volcanic rocks are intrinsically limited, on the basis of counting statistics alone, to approximately $\pm 8\%(2\sigma)$ for a one week analysis [1,2].

Advances in thermal ionization mass spectrometry (TIMS) and high abundance sensitivity TIMS (HAS-TIMS) have dramatically improved capabilities in determining both Th and U isotopes for U-series disequilibria, leading to fundamental contributions in areas ranging from the chronology of climate change to mantle melting processes [3,4]. Secondary ion mass spectrometry (SIMS) offers further improvements for ^{232}Th/^{230}Th measurement in terms of smaller sample size, simplified sample mounting and shorter analytical time requirements—all of which are particularly valuable in studies of U-series disequilibria in young volcanic rocks.

TIMS techniques characteristically produce counting precisions no better than 0.3%–0.5% (2σ) for a typical 1.5 h analysis of a 300 ng Th load. When combined with systematic errors inherent to this type of mass spectrometry, long-term standard reproducibility is typically 1.5% (see, e.g. [1]). The fundamen-

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tal physical limit on TIMS is the high first ionization potential for Th and the consequently poor ionization efficiency of Th^+ by this technique, typically cited as 0.005%–0.05% in recent studies of volcanic rocks (see e.g., [1–3]).

New advances in inductively coupled plasma mass spectrometry (ICP-MS) have demonstrated ionization efficiencies for Th substantially superior to those for TIMS, but still only in the range 0.04%–0.2% [2,5]. Nonetheless, when coupled to state-of-the-art mass spectrometers ICP techniques also show considerable promise in the determination of $^{232}Th/^{230}Th$.

Secondary ion mass spectrometry (SIMS) is capable of producing Th ionization efficiencies in excess of 2% [6], an additional order of magnitude above even ICP techniques. This enables the use of very small ($<$50–100 ng) samples and short (45 min) analytical times, while still achieving an overall reproducibility of 0.5%–1%. The fundamental advantage of very high ionization efficiency by SIMS shows promise of even greater gains in all these respects, as sample loading procedures are refined for better efficiency in exposing the entire sample for sputtering.

The technique presented here is a “hybrid” application of the ion microprobe, an instrument primarily designed for in situ elemental and isotopic analysis of intact minerals and glasses [7]. Reid et al. [8] have already demonstrated some success in the use of SIMS for the in situ Th isotope dating of intact zircons. However, this technique, as applied to questions of the timing of zircon crystallization and consanguinity in large silicic magma systems, requires spot analyses of large populations of zircon grains to properly interpret the interrelationship of individual zircon model ages. Thus, although the application of SIMS to the analysis of chemical separates represents a departure from more traditional uses of the ion microprobe in geochemical analysis, the substantially higher yield of Th^+ under sputtering ionization, especially compared to TIMS, makes this an appropriate and important application for this instrument.

There are obvious advantages to any technique which can reduce the size of Th load required—less rock material needs to be processed and therefore considerable time and effort is saved in selecting clean grains of material and in digesting and processing the sample. England et al. [6] and Zindler [9] recognized the enhanced ionization efficiency of Th under sputtering by a primary ion beam and applied the Isolab 54 instrument to the determination of $^{232}Th/^{230}Th$ in volcanic rocks by SIMS [10]. We have subsequently extended and refined this application of SIMS by using the IMS 1270 instrument.

Critical to the success and quality of $^{232}Th/^{230}Th$ measurement by any form of mass spectrometry are those factors militated by the extreme dynamic range of this ratio in volcanic rocks ($0.4–2.0 \times 10^5$); (1) the provision of a Th ion signal of sufficient intensity, stability and duration to make a usefully precise measurement of $^{232}Th/^{230}Th$, (2) the capability to eliminate or correct for the abundance sensitivity effect of ^{232}Th on ^{230}Th signal, (3) stable quantitative detection of the radically disparate peak signals for ^{232}Th and ^{230}Th, and (4) the effective discrimination of any isobaric interferences on the analyte peaks. This article contains a detailed description of a $^{232}Th/^{230}Th$ measurement technique utilizing the IMS 1270 which not only fulfills these requirements but offers considerable advantages over other existing mass spectrometric techniques.

2. Sample preparation

2.1. Chemical separation of Th

Our techniques for separation and purification of U and Th from volcanic rocks are similar to those used at Los Alamos National Laboratory [3,11] and other laboratories measuring U-series isotopes and concentrations [4]. Rock samples are initially dissolved using a combination of hydrochloric, hydrofluoric, perchloric, and boric acid. Two chemistries have been successfully used for the subsequent separation and purification of Th for SIMS analysis of $^{232}Th/^{230}Th$.

One uses simple anion exchange resin, the other uses a combination of anion exchange resin and Eichrom TRUSpec resin (Eichrom Technologies, Inc., Darien, IL, USA).

The simple anion exchange method involves three sequential columns. (1) A large volume HNO_3 anion column used to separate U and Th from most other major and trace elements, including Ra. Th concentrations ([Th]) in volcanic rocks vary widely; e.g. in typical mid-ocean ridge basalts (MORB) [Th] is approximately 0.1 μg/g, whereas in Mt. Erebus phonolites [Th] is approximately 30 μg/g. Therefore, the exact volume of this initial anion column is scaled according to the total sample weight to be processed (i.e., 0.1–1 g of sample, designed to yield $>$100 ng of total Th). 1 ml of resin is used for each 100 mg of rock. (2) A small volume ($\sim$1 ml of resin) HCl anion column to separate U from Th and purify U. (3) An HNO_3 microanion column ($\sim$0.5 ml of resin) for final purification of Th.

The TRUSpec/anion exchange method also involves three columns (1) A small volume (2–5 ml) TRUSpec column to separate Th from other major and trace elements, including U, Pa, and Ra. A practical advantage of this initial TRUSpec column is that the sample can be loaded in up to 40 ml of 10 M HCl, rather than HNO_3. (2) A small volume ($\sim$1 mL of resin) HNO_3 anion column to purify Th. (3) A HNO_3 microanion column ($\sim$0.5 ml of resin) for final Th purification.

Using a short-lived radiotracer (^{234}Th ; $t^{1/2} = 24.1$ days), gamma counting and ICP-MS assay, the total chemical yields for separation and purification of U and Th are $>$95% for both Th extraction chemistries. Chemical blanks for these procedures are $<$0.01 pmol for U and $<$0.02 pmol for Th.

The SIMS technique thus requires no additional processing or special purification relative to conventional TIMS preparation. Although extremely small samples (10–50 ng) can be measured with the IMS 1270, we currently try to produce sample loads containing $>$100 ng of total Th whenever possible. This allows replicate analysis when deemed necessary to increase analytical precision.

2.2. Sample mounting

Once the Th has been chemically separated from the rock sample and dried down, it is picked up in 0.1 N HNO_3 and deposited onto a 25.4 mm diameter planchet of spectrographically pure carbon. Each individual sample is confined within a 200–1000 μm diameter ring of polyethylene, previously applied by touching the appropriate gauge of surgical plastic tubing to the planchet as it rests on a hot plate. The distribution of Th solution into the carbon is also improved by slight heating of the planchet during deposition. Precipitating the Th sample within the pores of the planchet in this manner is a simple way to integrate the sample with a spectrographically neutral electrical conductor. This integration prevents any excessive charging under subsequent ion bombardment and samples prepared in this manner produce a very intense, stable secondary Th ion signal when sputtered.

The primary column of the IMS 1270 allows a wide range of adjustment of primary beam size and location. The ion imaging capability of the IMS 1270 allows direct viewing and steering of the primary beam within the sample while monitoring the lateral distribution of Th signal. Therefore, the diameter of the polyethylene enclosures can be readily varied, based on the sample mass—and precision for larger samples can be increased by consuming a number of successive subareas of each load.

This loading procedure is inherently simpler than that used by Zindler and co-workers [9,10], which was designed to provide a final sample distribution as close as possible in size to the default 150 μm diameter primary beam produced by the ISOLAB 54.

Unlike the Bourdon et al. [10] procedure, our mounting technique requires no high temperature thermal pre-preparation to remove polymer containment material from the periphery of the load. Analytical trials show both the carbon and polyethylene we use to be spectroscopically clean with respect to ^{230}Th and ^{232}Th. In addition, the sample may be loaded without micromechanical assistance, in just a few aliquots.

Refinement of our simple deposition technique to limit the depth distribution of the Th within the carbon will further increase the efficiency of consumption of the loaded Th. Carbon coating of the planchet after loading may further improve ion yield and assist in the stable consumption of “excess” Th deposited on the immediate surface of the planchet.

3. Instrumentation and analysis

A useful overview of the IMS 1270 architecture is contained in the review article by Ireland [12]. Originally conceived and manufactured as an instrument for in situ U/Pb geochronology—the WHOI IMS 1270, since its delivery in 1996, has been used successfully in a variety of geochemical applications including Th isotopes [7], Pb isotopes [13,14], and the determination of trace element concentrations in a variety of geological materials [15].

3.1. Mass resolution

The mass spectrometer of the IMS 1270 maintains full transmission at a mass resolving power (MRP) of >2000 with a field of view on the sample of at least 75 μm × 75 μm. This MRP is sufficient for effective resolution of interferences for the purpose of ^{232}Th/^{230}Th determination (see Sec. 4). For other applications, MRP can readily be increased to values in excess of 12 000 while maintaining flat topped peaks, but this requires a concomitant compromise in both field of view and transmission.

For ^{232}Th/^{230}Th determination, the planchet-loaded sample is bombarded by 100–250 nA of O^- produced in a duoplasmatron. The primary beam is initially set up as 50–75 μm diameter spot probe, but then rastered out into a 250 μm^2 patch on the sample for analysis. MRP is retained by utilizing the dynamic transfer optical system (DTOS) of the IMS 1270 secondary ion optics.

3.2. Instrumental fractionation

Instrumental fractionation of isotope ratios in SIMS can generally be considered as a combination of mass discrimination effects at the site of sample sputtering with those in the ion detectors themselves. Other, mass spectrometric or “ion optical,” effects are generally relatively insignificant in a properly aligned instrument.

At masses above 200 we expect instrumental fractionations of $\leqslant$0.1% per Da, based on the behavior of Pb in a wide variety of matrices [7]. This appears substantiated by externally calibrated measurements of synthetic ^{232}Th/^{230}Th standard material (see Sec. 5).Correction for instrumental fractionation therefore appears relatively insignificant when other factors contribute to an overall reproducibility of 0.5%–1% on ^{232}Th/^{230}Th. For practical purposes, even this minimal fractionation will be empirically removed (by inclusion in the detector gain correction) as long as detector gain calibration is done on a standard where ^{232}Th/^{230}Th has been characterized with sufficient accuracy.

3.3. Ionization efficiency

Typical sample behavior, in terms of Th signal during analysis, is illustrated in Fig. 1(A)–(C) for Th loads derived from AThO and Erebus rock samples, and for synthetic UCSC ThA standard. The gradual decline of Th^+ intensity with time as sputtering progresses is a direct reflection of the depth distribution of the Th load in the planchet.

Experiments to quantitatively determine the ionization efficiency—defined as the ratio of Th^+ ions produced to the total number of Th atoms removed by sputtering—are complicated by uncertainties in the actual mass of Th loaded (due to reliance on ion column yield estimates and other processing losses). More importantly, only a fraction of the Th originally loaded is consumed in an individual sputtered crater. This is evidenced in the rather consistent intensity of Th signal from Th loads of greatly varying weight (10–300 ng) in Fig.1(A) through (C). This is attributable to the fact that each sample analysis produces a generally consistent sputter crater size in a relatively uniformly porous carbon medium hosting the Th. Each of our sample analyses, therefore, consumes a

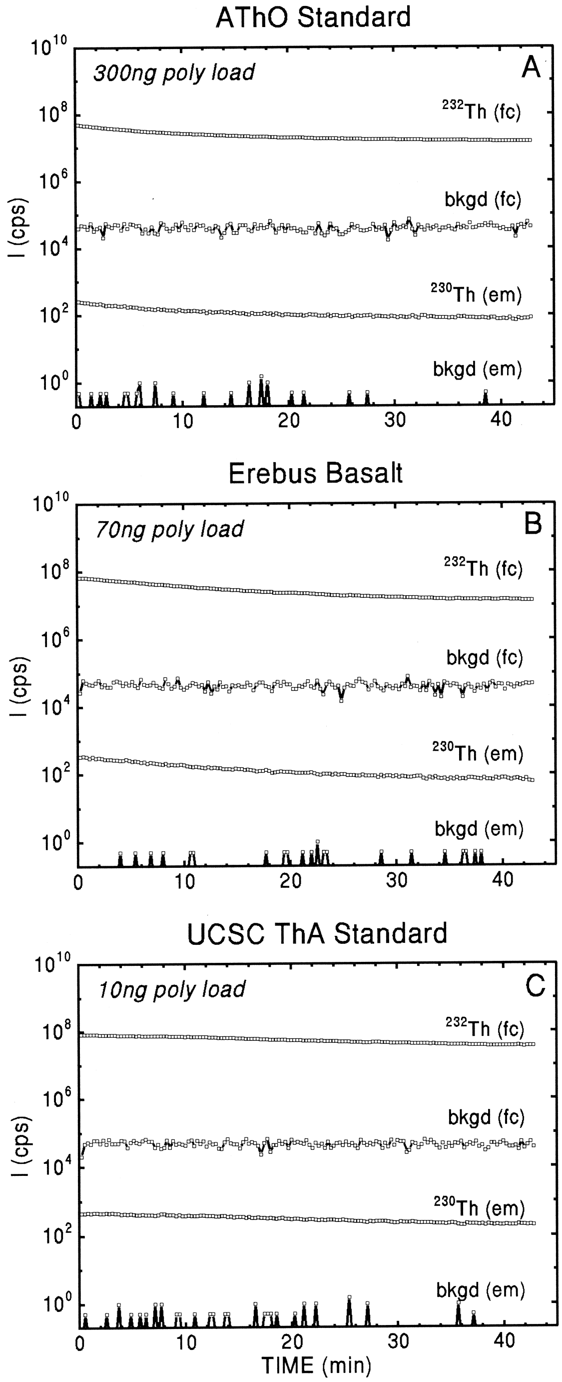

Fig. 1. Relative performance of polyethylene confined sample loads of; (A) AThO rock standard (300 ng total Th), (B) Erebus 84505 basalt sample (70 ng total Th), and (C) UCSC ThA synthetic standard (10 ng total Th). Signal intensity (*I*) is expressed in counts per second (cps) for each individual counting cycle. Both electron multiplier (EM) and Faraday Cup detectors (FC) were used. This set of data demonstrates the relative independence of I on total Th content of sample, implying instead that a rather consistent aliquot of Th is consumed in each analysis. This is attributed to the generation, for each sample analysis, of a generally consistent sputter crater size in a relatively uniformly porous carbon medium hosting the Th.

similar amount of total Th, independent of the total weight loaded.

The analysis of a 10 ng load of UCSC ThA standard plotted in Fig. 1(C) provides one reasonable estimate of ionization efficiency. This sample was delivered into a large, 1000 μm diameter, polyethylene confinement. Consequently, the 250 μm^2 rastered beam covered $<10\%$ of the total surface area of the planchet load. Therefore the maximum amount of Th sputtered was <1 ng ($2.60e^{12}$ atoms). From the data in Fig. 1(C) for $^{232}Th^+$ counts detected (^{232}Th represents 99.9994% of total Th in this load), and allowing for the time dilution of this monocollection mode analysis ($^{232}Th^+$ was counted for only 2.0 s of each 15.0 s cycle), approximately $6.23e^{10}$ atoms of Th^+ were sputtered. This produces a calculated ionization efficiency for Th^+ of 2.4%. This should, in fact, be taken as a minimum estimate. Since less than 50% of the total depth distribution of Th in the sample was likely consumed during this 45 min analysis, actual ionization efficiency may be closer to 5%.

An estimated ionization efficiency of $>2\%$ is in good agreement with the 2% value cited by England et al. [6] with the Isolab 54—particularly, given that the O^- primary beam used here is, in general, more efficient in producing positive secondary ions like Th^+ than the Ar^+ primary beam of the Isolab 54.

The previous example analysis underlines the fact that, although our current method of sample loading has the merit of simplicity, it is still difficult to maintain a balance between excessive penetration of the Th into the carbon planchet and loss of Th due to the efflorescence of excess material on the surface. Carbon coating of the sample after loading may increase utility of any excess material on the surface. However, anticipated improvements in the confinement of Th to the immediate volume sputtered by the primary beam will further reduce sample size requirement by reducing the percentage of residual unsputtered Th.

3.4. Ion detection

Ion detection for ^{230}Th, ^{232}Th, and background positions is accomplished dynamically by using magnetic peak switching. The ^{230}Th signal is collected by an ETP 133H multiple-dynode electron multiplier (EM) and processed through pulse-counting electronics with an overall dead time of 15 ns. Background measurement at nominal mass 227.5 is taken on each measurement cycle. It is difficult to find and maintain completely “clean” positions for background measurement in rock-derived Th loads at this sensitivity level. However, the electron multiplier background, as confirmed by measurements on synthetic standards, is routinely less than 0.05–0.1 counts per second.

The ^{232}Th signal is collected in a Faraday cup (FC) and processed through an industry standard Keithley 642LNFPA MOSFET-based electrometer operated as an ammeter with a 10^{11} gain. Typical backgrounds, as measured at 227.5 Da, are 8.0×10^{-3} pA (5.0×10^{4} cps). The uncertainty in determining and subtracting background for typical ^{232}Th signal levels greater than 3.2 pA (2×10^{7} cps) is thus $\leqslant 0.1\%$ for a 45 min analysis with 300 s counting time on background.

The gain match between Faraday cup and electron multiplier is calibrated periodically by measuring the ^{232}Th/^{230}Th ratio in a standard load of UCSC ThA or other synthetic standard. The relative efficiency of the electron multiplier is expected to decrease over the very long term in response to aging of the device and to the relative high voltage gain and pulse height discrimination threshold setting used. However, over periods of several days, the relative gain match is generally stable to better than 0.1%–0.15%. Any contribution from nonlinearity effects in the Faraday cup electrometer is limited by measuring the synthetic standards at similar signal levels to those of the samples.

Standard counting times and peak sequence used were; 2.0 s on background (FC) and 2.0 s on background (EM) at the 227.5 Da position, 6.0 s on ^{230}Th^{+} (EM) and 2.0 s on ^{232}Th^{+} (FC). Waiting times of 0.5 s were inserted before each EM counting position and 1.0 s before each FC counting position to allow for magnet and detector settling. The decline in ^{230}Th^{+} and ^{232}Th^{+} peak intensities with time, which is typically monotonic (see Fig.1), was corrected for using a standard double interpolation ratio algorithm common in TIMS analysis, with each ^{230}Th^{+} peak correlated to the time corrected interpolation of adjacent ^{232}Th^{+} peaks.

Spiking with ^{229}Th has been proposed or utilized by some labs to provide an internal gain match in each sample run. However, there are disadvantages in terms of isobaric interferences of ^{229}ThH^{+} on ^{230}Th^{+} (see Sec. 4) which are unnecessary if the gain match can be determined externally with the reproducibility discussed previously.

Future addition of dual collection capability to the multidetection focal plane of the IMS 1270 will allow simultaneous collection of ^{230}Th and ^{232}Th signals, with obvious advantages for reducing total analysis time and/or improving precision.

3.5. Abundance sensitivity

The IMS 1270 is a large radius magnetic sector mass spectrometer with abundance sensitivity enhanced by the use of off-axis detectors coupled by a single small detection electrostatic analyzer (ESA). (The EM is aligned directly on the optic axis of the detection ESA. The FC is adjacent to the EM and is selected by activating a simple electrostatic beam deflector.) All sectors of the mass spectrometer remain at $\leqslant 1 \times 10^{-8}$ Torr during analysis. The abundance sensitivity is better than 40 ppb at $\Delta m/m$ of 1/232. By extrapolation the contribution of ^{232}Th to ^{230}Th is thus expected to be <4 ppb ($\Delta m/m$ of 2/232), representing a $\leqslant 0.1\%$ contribution. Consequently, no explicit correction for this effect is currently made in our analyses.

The high abundance sensitivity of the IMS 1270 results in a substantial advantage over simple TIMS instruments (1–2ppm at 2/232; [1]) and even double magnetic sector TIMS ($\approx$200ppb at 2/232; [3]). Further, it is comparable to the optimal operating value of current HAS-TIMS instruments (10–20 ppb at 1/237; [16]). It also provides an incremental advantage over the ISOLAB 54 SIMS [6] and Plasmaquad 54 ICP-MS instruments (40 ppb 2/232; [2]) which still require a modest abundance sensitivity correction (~1%).

4. Mass spectra

Critical to the success of any SIMS technique is the elimination of all significant isobaric interferences from the sputtered secondary ion signal. Due to the extreme magnitude of the ^{232}Th/^{230}Th ratio measured, potential interferences with ^{230}Th (rather than ^{232}Th) are the limiting factor in the analysis of chemically extracted Th. Table 1 shows the most likely isobaric interferences in samples of volcanic rock. Isobars involving Ti and Zr are easily resolved at the minimum working resolution of the IMS 1270 (MRP ≈2000, 10% definition), as are isobars involving Ba or rare earth elements (REE).

The high mass resolution capabilities of the IMS 1270 allow explicit examination of secondary ion spectra. Fig. 2 displays mass spectra of ^{230}Th at ≈2000 MRP for Th samples separated from basalt. Several isobars involving HfO_3^+ species require nominal MRP of ≈2350–2550 (Table 1). Although absolute separation of all interfering peaks (MRP >3000) can produce a more visually pleasing spectrum, 1800–2200 MRP provides the best balance of transmission and resolution—effectively reducing HfO_3^+ interferences to ≪0.1% level, provided Hf is kept at a modest level in the chemical separate.

Fig. 2(A) is the mass spectrum of an Erebus 84505 basalt processed by simple anion exchange and run at minimal MRP (1800). These conditions yielded ^{232}Th/^{230}Th analyses which agreed with the established value for this material from TIMS (see Table 2). All analyses in Table 2 were made on samples processed in this manner. Fig. 2(B) is the mass spectrum of a Samoa basalt run at an MRP of 2200, after processing by TRUSpec/anion exchange. This newer chemical separation procedure also yields accurate results, and appears to show some advantages in reducing the Zr/Th and Hf/Th ratios in the sample.

Table 1
Potential isobaric interferences on $^{230}Th^+$ in SIMS spectrum for Th loads

Ion species	Da	MRP
$^{46}Ti_5^+$	229.7632	−852
$^{90,92}Zr_2O_3^+$	229.7945	−964
$^{91}Zr_2O_3^+$	229.7960	−970
$^{90,92}Zr_2C_4^+$	229.8097	−1030
$^{90}Zr_2O_3H_2^+$	229.8098	−1030
$^{91}Zr_2C_4^+$	229.8113	−1037
$^{94}Zr_2N_3^+$	229.8219	−1089
$^{134}BaO_6^+$	229.8740	−1445
$^{150}SmO_5^+$	229.8919	−1628
$^{150}NdO_5^+$	229.8955	−1671
$^{166}ErO_4^+$	229.9100	−1868
$^{180}Hf^{16}O_2{}^{18}O^+$	229.9355	−2357
$^{178}Hf^{16}O^{18}O_2^+$	229.9369	−2391
$^{176}Hf^{18}O_3^+$	229.9389	−2441
$^{179}Hf^{16}O^{17}O^{18}O^+$	229.9390	−2445
$^{180}Hf^{16}O^{17}O_2^+$	229.9397	−2463
$^{177}Hf^{17}O^{18}O_2^+$	229.9407	−2488
$^{178}Hf^{17}O_2{}^{18}O^+$	229.9411	−2500
$^{179}Hf^{17}O_3^+$	229.9432	−2558
$^{182}W^{16}O_3^+$	229.9330	−2297
$^{184}WNO_2^+$	229.9439	−2577
$^{180}HfO_3H_2^+$	229.9470	−2669
$^{230}Th^+$	230.0331	
$^{229}ThH^+$	230.0396	35,658

In practice, analyses are now made routinely by using refined settings which provide a resolution of 2000–2200 while retaining maximum transmission of the IMS 1270 mass spectrometer. By comparison, SIMS analysis of ^{232}Th/^{230}Th with the ISOLAB 54 [6,9] is accomplished with MRP 1000 which produces a fourfold loss in intensity from the 400 MRP base of the instrument, and necessitates substantial removal of Zr (and presumably Hf) from the loads during chemical processing.

The ultimate MRP of the IMS 1270, with flat-topped peaks, is well in excess of 12 000. Therefore, if necessary to cope with Hf-rich samples, MRP could easily be increased to 2500–3500 while maintaining the field of view required for the large current primary

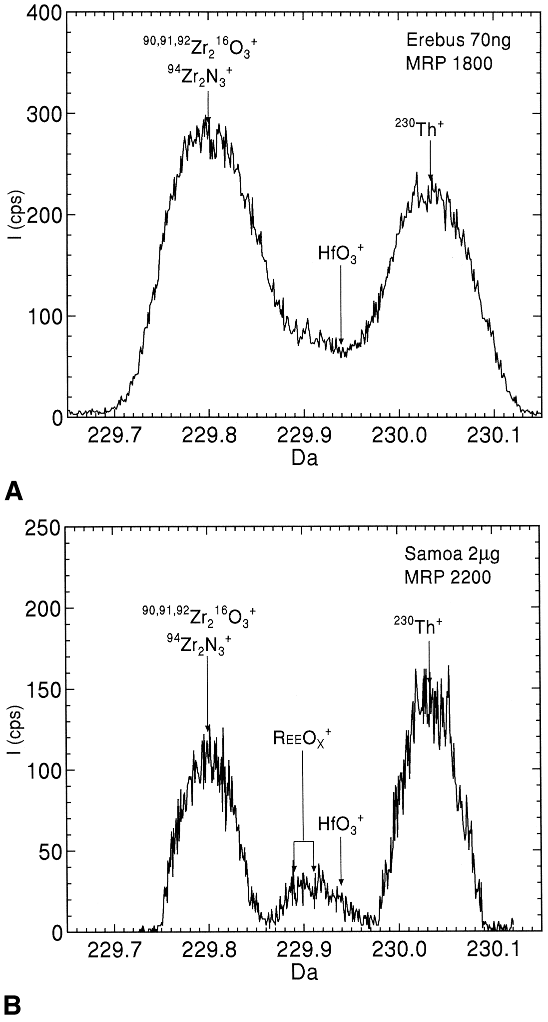

Fig. 2. (A) Mass spectrum of $^{230}Th^+$ and adjacent positive secondary ion peaks in a rock-derived Th load (Erebus 84505 basalt) processed by simple anion exchange. Mass resolving power of 1800 (10% definition) used here is the minimum normal instrument setting. Most analyses are now routinely performed with MRP of 2000–2200. (B) Mass spectrum of $^{230}Th^+$ and adjacent positive secondary ion peaks in a rock-derived Th load (Samoa basalt) processed by TRUSpec/Anion Exchange. MRP was 2200.

bombardment [13]. The concomitant loss in transmission would simply necessitate a modest compromise in either precision or analytical time. However, as detailed previously, the most sensible procedure seems to be the use of good chemical separation procedures to minimize the presence of Hf in the sample before measurement.

Spiking each sample with ^{229}Th at a concentration level intermediate between ^{230}Th and ^{232}Th has been proposed as a means of inherent detector gain matching (by counting with both detectors on the ^{229}Th peak during each sample analysis). However, $^{229}ThH^+$, which is produced at a level of approximately 1% of $^{229}Th^+$ under O^- sputtering, interferes with $^{230}Th^+$ and would only be eliminated at a nominal MRP of 38 000. Therefore, spiked loads require an extra peak measurement of $^{232}ThH^+$, and an empirical peak stripping at mass 230, based on the measured $^{232}ThH^+/^{232}Th^+$ ($= {}^{230}ThH^+/^{230}Th^+$). This introduces additional counting time and arithmetic uncertainties into the analysis, which compromise the ultimate precision and reproducibility to a greater degree than simply using an external Th standard such as UCSC ThA.

Other spikes comprising U masses [2] have also been proposed for internal gain matching in ICP-MS and SIMS techniques but, similarly, would seem to offer little advantage if detector matching stability can be maintained at a high level. ThO^+, rather than Th^+, offers some advantage in terms of signal intensity in the secondary ion spectrum under O^- bombardment. However, initial trials show an as yet unidentified low mass side peak at mass 230 which is only partially resolved at 2000 MRP. Further exploration of ThO^+ analyte peaks is planned and their use may provide an incremental advantage in future analyses. Blank levels, as measured in unloaded C planchets, and in procedural blanks of planchet loaded process reagents, were always <0.01% of the $^{230}Th^+$ signal from actual loads.

5. Accuracy and reproducibility

A well characterized standard for $^{232}Th/^{230}Th$ is essential for measurements of this type. Initial work, therefore, focused on the confirmation of an accurate $^{232}Th/^{230}Th$ value for the synthetic UCSC ThA standard. To this end, Faraday cup/electron multiplier gain matching was performed at the beginning and end of daily sessions using a $^{232}Th^+$ signal generated from Th metal at between 250 000 and 1 500 000 cps.

Table 2
Replicate data by IMS 1270 SIMS for rock standards and samples with existing accepted values from TIMS

Date	Load type	$^{232}Th/^{230}Th_{1270}$ /10E^5 (2σ)	$^{232}Th/^{230}Th_{TIMS}$ /10E^5 (2σ)	References (TIMS)
AThO Rhyolite standard				
10-23-98	300 ng poly 1/2	1.845 (0.6)		
10-23-98	300 ng poly 2/2	1.829 (0.7)		
10-23-98	740 ng poly 1/2	1.840 (0.7)		
10-23-98	740 ng poly 2/2	1.837 (0.7)		
10-26-98	350 ng poly	1.825 (0.7)		
Mean		**1.834**	**1.828** (0.4)	[18]
2σ%		0.7		
uncert.%		0.3		
Hualalai HU24 Basalt				
10-21-98	unconfined 1/2	1.822 (1.2)		
10-21-98	unconfined 2/2	1.827 (1.1)		
10-27-98	unconfined 1/2	1.823 (0.6)		
10-27-98	unconfined 2/2	1.820 (0.6)		
Mean		**1.823**	**1.816** (0.7)	K. Sims
2σ%		0.3		
uncert%		0.4		
Erebus 84505 Basalt				
10-23-98	70 ng poly	1.902 (0.7)		
02-24-99	poly 1/2	1.891 (0.5)		
02-27-99	poly 2/2	1.898 (0.5)		
02-27-99	poly	1.890 (0.5)		
03-11-99	poly	1.896 (0.6)		
Mean		**1.896**	**1.904** (1.0)	[19]
2σ%		0.3		
uncert%		0.2		
Table Mountain TML Latite				
10-15-99	poly 1/1	1.718 (0.8)		
10-15-99	poly 2/2	1.715 (0.7)		
Mean		**1.717**	**1.715** (0.5)	[3]
2σ%		···		
uncert%		0.5		

A Th metal sample is a convenient means of producing a high intensity of $^{232}Th^+$ signal that is readily tunable to a consistent count rate for long periods of time. A typical counting cycle for these measurements was 2.0 s on each of EM background, FC background (both backgrounds counted at 227.33 Da), FC at $^{232}Th^+$, and EM at $^{232}Th^+$. Waiting times of 0.5 and 1.0 s, respectively, were allowed before each EM and FC peak to allow for magnet and detector settling times. Aliquots of UCSC ThA were then run as an unknown. In this manner, 20 measurements of UCSC ThA were made during a one month period. Fig. 3 represents a summary of these results. The measured $^{232}Th/^{230}Th$ value of UCSC ThA by IMS 1270 SIMS was $1.710 \times 10^5 \pm 1.2 \times 10^3$ (2σ). This is in excellent agreement with working value of UCSC ThA from replicate TIMS analysis [5] of $1.706 \times 10^5 \pm 1.4 \times 10^3$ (2σ), and also demonstrates the excellent reproducibility of these SIMS analyses (±0.7%) over an extended period.

UCSC ThA has subsequently been used as a standard to determine detector gain matching for each

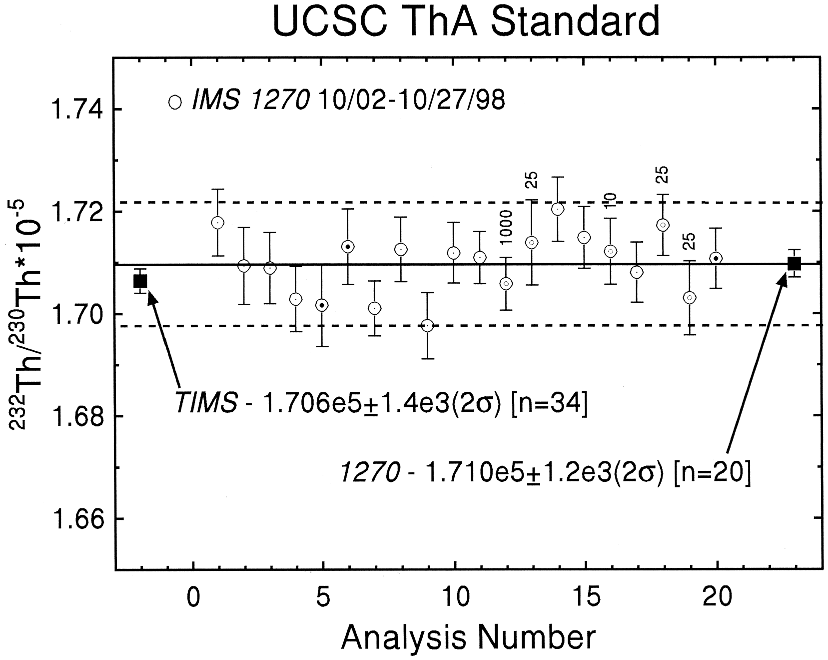

Fig. 3. Replicate ^{232}Th/^{230}Th analyses of UCSC ThA standard run with IMS 1270 SIMS in October 1998. All analyses were externally standardized by careful gain matching of FC and EM detectors with ^{232}Th^{+} signal from pure Th metal. Most SIMS analyses were performed on large unconfined loads in carbon. Loads that were confined by polyethylene rings are marked with their load weight in ng adjacent to each symbol. Twenty replicates by SIMS over a 25 day period gave a value of $1.710 \times 10^5 \pm 1.2 \times 10^3$ (2σ). Also plotted is an independent analysis of UCSC ThA by TIMS ($1.706 \times 10^5 \pm 1.4 \times 10^3$ (2σ; $n = 34$); [5]). Other available independent analysis of UCSC ThA include replicate TIMS analyses by Rubin ($1.709 \times 10^5 \pm 1.6 \times 10^3$ ($2\sigma\ n = 149$); [17]) and ICP-MS ($1.708 \times 10^5 \pm 2.6 \times 10^3$ ($2\sigma\ n = 5$); [5]).All three of these independent analyses agree with the IMS 1270 determination, and with each other, within their stated uncertainties. All tabled standard and rock sample data in this article are referenced to the previously derived SIMS value for UCSC ThA.

daily analytical session. This procedure has clear advantages over continuing to use Th metal gain matching routinely. First, the dead time of the electron multiplier has to be known extremely accurately for Th metal gain matching—when running with signals of 1×10^6 cps, the knowledge of EM dead time (15 ± 1 ns) automatically introduces an uncertainty of 0.1% into the gain match calculation. With standards of near natural ^{232}Th/^{230}Th, like UCSC ThA, the ^{230}Th^{+} count rate is $\leqslant 10^3$ cps—so the uncertainty in dead time stated above becomes an unimportant contribution to overall error when making normal ^{232}Th/^{230}Th measurements on samples. Second, running the electron multiplier at such high count rates caused de facto aging on the order of 0.1% per determination, so additional time-consuming interday calibrations and interpolations are needed.

Since determination of gain matching using UCSC ThA is insensitive to the electron multiplier dead time, a gain match efficiency is simply calculated to yield the correct ratio for the standard after running a ^{232}Th/^{230}Th measurement in the same manner as for samples. Nor is there substantial short term aging of the electron multiplier at count rates typically less than 1000 cps on ^{230}Th^{+}. Replicate analyses of ThA are performed at the beginning of each session and after each 2–3 samples to maintain a check on analytical quality and instrument stability.

Table 2 summarizes results for replicate analyses of rock standards and other volcanic rock samples with ^{232}Th/^{230}Th known from TIMS. The routine in run precision for typical 43 min (150 cycles) measurements on basalt-derived samples loaded in polyethylene confinements is 0.5%–0.7% (2σ). Therefore, as expected, precision is improved (where desired) by running one or more additional spot analyses on the same load, and such replicate analyses routinely overlap within analytical error. All sample determinations in Table 2 show excellent agreement with those values previously established by TIMS.

The in run precision of analyses of rock-derived samples already closely approaches the limits of counting statistics. Dual collection capability would allow an incremental gain in this respect, while simultaneously reducing accumulation time for each analysis to less than 20 min.

The expected overall reproducibility from typical in run precision combined with uncertainties in detector matching and drift (0.1%–0.2%) is already well below 1%. This is empirically supported by the long term reproducibility of synthetic standard UCSC ThA (Fig. 3) and replicates of rock-derived standards such as AThO and TML (Table 2). Absolute accuracy of these analyses is then closely determined by the availability of very well characterized standards.

6. Discussion and conclusions

SIMS determination of ^{232}Th/^{230}Th by using the IMS 1270 offers clear advantages in terms of initial rock sample size, simplicity of sample preparation and total instrumental time per analysis, while providing a reproducibility of better than 1%. The technique presented here is currently being successfully applied to Th isotope determination in MORB basalts, whose intrinsically low Th contents have severely limited the application of TIMS analysis in the past. This technique could also readily be extended to other applications beside volcanic rocks (e.g. corals or other marine biomineralization).

Installation of dual detection capability will eliminate the modest loss in precision due to short term variations in sample signal and allow the same number of total ion counts to be accumulated in less than half the time. Current precisions will thus be achieved in less than 20 min of instrument time. More substantial revolutions, such as the application of resonant postionization of the sputtered material by laser excitation might benefit the technique by increasing ionization efficiency further toward 100%.

More sophisticated means of integrating the Th sample with carbon are being developed which we hope will preserve simplicity of sample mounting while enhancing the percentage of the Th load that is readily accessible to sputtering. A realistic goal is to enable the routine use of 10 ng samples of rock-derived Th to produce analyses with overall accuracy of better than 1%.

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References

[1] F. McDermott, T.R. Elliot, P. van Calsteren, C.J. Hawkesworth, Chem. Geol. (Isotope Geoscience Section), 103 (1993) 283.

[2] X. Luo, M. Rehkamper, D.-C. Lee, A.N. Halliday, Int. J. Mass Spectrom. Ion Processes 171 (1997) 105.

[3] S.J. Goldstein, M.T. Murrell, D.R. Janecky, Earth Planet. Sci. Lett. 96 (1989) 134.

[4] R.L.Edwards, J.H. Chen, G.J. Wasserburg, Earth Planet. Sci. Lett. 81 (1987) 175.

[5] K.D. Collerson, Z. Palacz, P.J. Turner, EOS 78 (1997) F788.

[6] J.G. England, A. Zindler, L.C. Reisberg, J.L. Rubenstone, V. Salters, F. Marcantonio, B. Bourdon, H. Brueckner, P.J. Turner, S. Weraver, P. Read, Int. J. Mass Spectrom. Ion Processes 121 (1992) 201.

[7] G.D. Layne, N.Shimizu, K. Sims, EOS 79 (1998) F955.

[8] M.R. Reid, C.D. Coath, T.M. Harrison, K.D. McKeegan, Earth Planet. Sci. Lett.150 (1997) 27.

[9] A.Zindler, personal communication, 1998.

[10] B. Bourdon, C.H. Langmuir, A. Zindler, Earth Planet. Sci. Lett. 142 (1996) 175.

[11] S.J. Goldstein, M.T. Murrell, R.W. Williams, Earth Planet. Sci. Lett. 115 (1993) 151.

[12] T. Ireland, Advances in Analytical Geochemistry, JAI Press, Greenwich, CT, 1995, Vol. 2 (ISBN 1-55938-785-8) pp. 1–118.

[13] G.D. Layne, N. Shimizu, Secondary Ion Mass Spectrometry SIMS XI, G. Gillen et al. (Eds.), Wiley, New York, 1998, pp. 63–65.

[14] A.E. Saal, S.R. Hart, N. Shimizu, E.H. Hauri, G.D. Layne, Science 282 (1998) 1481.

[15] G.D. Layne, N. Shimizu, Ninth Annual V.M. Goldschmidt Conference, LPI Contribution No. 971, Lunar and Planetary Institute, Houston, TX, 1999, p. 167.

[16] J. Schwieters, personal communication, 2000.

[17] K. Rubin, personal communication, 1999.

[18] O. Sigmarsson, personal communication, 1998.

[19] M.K. Reagan, A.M. Volpe, K.V. Cashman, Geochim. Cosmochim. Acta, 56 (1992) 1401.