

U/Th dating by SHRIMP RG ion-microprobe mass spectrometry using single ion-exchange beads

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Abstract—We present a new analytical method for U-series isotopes using the SHRIMP RG (Sensitive High mass Resolution Ion MicroProbe) mass spectrometer that utilizes the preconcentration of the U-series isotopes from a sample onto a single ion-exchange bead. Ion-microprobe mass spectrometry is capable of producing Th ionization efficiencies in excess of 2%. Analytical precision is typically better than alpha spectroscopy, but not as good as thermal ionization mass spectroscopy (TIMS) and inductively coupled plasma multicollector mass spectrometry (ICP-MS). Like TIMS and ICP-MS the method allows analysis of small samples sizes, but also adds the advantage of rapidity of analysis. A major advantage of ion-microprobe analysis is that U and Th isotopes are analyzed in the same bead, simplifying the process of chemical separation. Analytical time on the instrument is ~60 min per sample, and a single instrument-loading can accommodate 15–20 samples to be analyzed in a 24-h day. An additional advantage is that the method allows multiple reanalyses of the same bead and that samples can be archived for reanalysis at a later time. Because the ion beam excavates a pit only a few μm deep, the mount can later be repolished and reanalyzed numerous times. The method described of preconcentrating a low concentration sample onto a small conductive substrate to allow ion-microprobe mass spectrometry is potentially applicable to many other systems.

1. INTRODUCTION

Isotopic disequilibrium between ^{230}Th and ^{234}U has been widely applied to the dating (U-series) of solids precipitated from aqueous solutions under a variety of conditions (Ku, 1976). Of late, U-series dating has been widely used in establishing the absolute chronology of Quaternary climate change, in calibrating the radiocarbon time scale, and in establishing milestones in human evolution. The technique works because U is relatively soluble in natural waters and is co-precipitated as a trace element in the precipitating solid whereas Th is insoluble and unavailable for co-precipitation. The dating is based on the decay of ^{238}U through two short-lived intermediate daughter isotopes to ^{234}U and decay of ^{234}U to ^{230}Th . The age equation (Broecker, 1963) includes terms for the activities of all three isotopes, so accurate and precise analyses of each isotope are essential for accurate age determination. Up until the mid 1980s, U-series analysis was typically done by decay-counting using alpha spectroscopy. Counting errors were generally $\sim 2\%$ and the technique required relatively large samples, generally 10 to 20 g, and counting times of several days. Thermal ionization mass spectroscopy (TIMS) as pioneered by Edwards et al. (1986) revolutionized the method by providing direct analysis of the isotopes on samples as small as a few tens of milligrams, and yielding individual run precisions typically 0.3–0.5%, but with long-term standard reproducibility of around 1% (McDermott et al., 1993). U and Th isotopes are separated from the sample and from each other and analyzed separately. Time for analysis is generally several

hours per sample for the Th isotopes alone, and the method is destructive; that is, all the separated isotopes are loaded on a filament that cannot be reanalyzed at a later time. Small sample size is a major advantage of TIMS for most geological materials, more so than the high precision. This is because most materials are subject to at least some open-system behavior, primarily U migration, that results in age errors much greater than the TIMS analytical error. The fundamental physical limit on TIMS is the poor ionization efficiency of Th^+ by this technique, typically 0.005% to 0.05% (McDermott et al., 1993). New advances in inductively coupled plasma multicollector mass spectrometry (ICP-MS) have demonstrated Th ionization, and therefore sensitivity, improved over TIMS, but still in the range of 0.04% to 0.2% (Luo et al., 1997, Shen et al., 2002).

Ion microprobe spectrometry is capable of producing Th ionization efficiencies in excess of 2%, an order of magnitude over ICP techniques (Layne and Sims, 2000). We present here a new analytical method for U-series isotopes using the SHRIMP RG (Sensitive High mass Resolution Ion MicroProbe) mass spectrometer, preconcentrating the U-series isotopes on a single ion-exchange bead. Although analytical precision is little better than alpha spectroscopy (ca. 2%), the method allows analysis of bulk sample sizes of a few tens of milligrams. The primary advantage of the technique is rapidity of analysis. U and Th isotopes are analyzed together, typically requiring only 60 min per analysis. Moreover, the method allows mounts accommodating tens of samples per

instrument loading, such that conceivably 20–40 samples could be analyzed per day. An additional advantage is that the method allows multiple reanalyses of the same bead and that samples can be archived for reanalysis at a later time.

2. SHRIMP RG ION-MICROPROBE MASS SPECTROMETER

Secondary-ionization mass spectrometry (SIMS, or the ion-microprobe) has been applied to a wide variety of areas in the geosciences. A focused, or collimated beam of primary ions is

accelerated onto the polished sample surface, and the secondary ions that result from the sputtering of the sample are analyzed. For the SHRIMP RG, extracted secondary ions first pass through a magnetic sector and then through an electrostatic analyzer. The SHRIMP RG design has a large-radius secondary mass spectrometer that allows high transmission of secondary ions at high mass resolution (Williams, 1998).

The traditional strength of large-format ion-microprobe mass spectrometers, including the SHRIMP RG, is in the chemical and isotopic analyses of single crystals within rocks. The most common application is to U/Pb dating of single zircon crystals (100 s to 1000 s of ppm U), including the dating of individual growth bands. These zircons are common in igneous and high-grade metamorphic rocks and yield U/Pb ages in the range of 10^5 to 10^9 years (Williams, 1998). Direct dating of young zircons by U/Th using the ion-microprobe mass spectrometry has been reported by

Reid et al. (1997), Bacon et al. (2000), and Lowenstern et al. (2000). The direct U/Th dating of zircons is possible because most zircons have U concentrations of 100 s to 1000 s of ppm, making possible the direct detection of ^{230}Th (ca. 70 –100 ppb) as ^{246}ThO . Most materials, however, used in U/Th dating are low-temperature, water-deposited carbonates that contain only a few tenths of ppm U, with ^{234}U and ^{230}Th on the order of 0.01 ppb, too low for direct detection by the SHRIMP RG. Therefore, application of SHRIMP RG technology to these kinds of material requires some form of preconcentration of U and Th isotopes and deposition onto a substrate of a few 10 s to 100 s of square μm area. Layne and Sims (2000) analyzed ^{232}Th and ^{230}Th in volcanic rocks by preconcentration of Th isotopes and transfer to 200 –1000 μm -diameter corrals on carbon planchets. Surgical plastic tubing was used to make the corrals by touching the squarely-cut end of a piece of the tubing onto a heated graphite-planchet. ^{232}Th contents in the rocks ranged from 0.1 to 30 ppm (with corresponding ^{230}Th contents ranging from 0.01 to 0.1 ppb). Sample size of the rock (0.1 to 1 g) was adjusted to yield >100 ng of ^{232}Th . They obtained count rates of ^{230}Th on the order of 100 s of counts per second, and determined the Th ionization efficiency to be $\geq 2.4\%$.

For routine analyses of U/Th in 100 mg-sized samples of calcium carbonate, we found the corral area to be too large and the resultant isotope concentration too low for obtaining good analytical sensitivity.

Rather than corals on carbon planchets, we take the approach of absorbing the U and Th preconcentrate onto single ion-exchange beads of $\sim 100 \mu\text{m}$ diameter.

3. MATERIALS AND SPIKES

For calibration we analyzed an aliquot of a solution of Harwell uraninite (HU-1) which has been used as a secular-equilibrium standard in alpha counting and TIMS laboratories (Ivanovich et al., 1984, Ludwig et al., 1992, Cheng et al. 2000). For a dated sample, we analyzed a solid split of a coral from Barbados (Lamont coral #6) provided by W. G. Thompson of Lamont Doherty Earth Observatory, who performed four separate TIMS analyses on other solid splits that yielded an age of 123.4 ± 1.49 kyr (error based on standard deviation of replicate analyses, expressed as 2σ). After grinding and homogenization, an aliquot of our split was also analyzed at Lawrence Livermore Laboratory by the ISOPROBE ICP-multicollector mass spectrometer (by R.W.W.) using ^{233}U and ^{229}Th spikes.

For the SHRIMP RG analyses, we used ^{236}U and ^{229}Th spikes, both obtained from the National Institute of Standards and Technology, and calibrated them against elemental standards of U and Th in our laboratory. ^{233}U could not be used for double-spiking because of hydride interference on ^{234}U as discussed below.

4. EXPERIMENTAL

4.1. Isolation of U and Th Isotopes

Samples (0.1 to 1 g) are dissolved in HNO₃, with sufficient H₂O₂ to remove organics. ~10 mg of Fe is added in the form of FeCl₃ solution to act as a carrier, and sufficient ²³⁶U and ²²⁹Th spikes are added such that ²³⁶U/²³⁵U and ²²⁹Th/²³⁰Th are close to unity. The solution is boiled to remove all H₂O₂ and allowed to sit overnight to allow equilibration between spike and natural isotopes. After dilution with ~100 mL H₂O, Fe(OH)₃ is precipitated by adding NH₄OH. The precipitate is isolated by centrifugation, and rinsed once in H₂O. The precipitate is dissolved with 1 mL of conc. HNO₃, and volume is adjusted to 7N HNO₃ (50%) for loading onto the ion-exchange column. Two mL of anion exchange resin (AG-1-X8, 100–200 mesh size, Bio-Rad Laboratories) is added to a 15-cm teflon column (5 mm I.D.) and the column is successively rinsed (3 column volumes [CVs], or 6 mL each) with 7N HNO₃, 6N HCl, combined solution of 1N HCl + 1N HF, and finally with 7N HNO₃. The sample is then loaded onto the column where U and Th are retained and Fe is eluted with 2 1/2 CVs of 7N HNO₃. Because U is not strongly held on the resin in nitrate form, elution of Fe with more than 2 1/2 CVs of 7N HNO₃ will result in leakage of some of the U. Thus, a second column-pass is necessary to completely separate out the Fe. U and Th are eluted together with 3 CVs of 1N HCl + 1N HF, and taken to dryness in a Teflon dish on a hotplate recycling with HNO₃ and H₂O₂ to remove any organics picked up from the resin. After reequilibrating the column with 3 CVs 7N HNO₃, the combined U + Th residue is loaded onto the column with ≤ 0.5 mL 7N HNO₃. The remaining trace amounts of Fe are

removed by 2 CV rinse with 7N HNO₃. Finally, U and Th are eluted together with 1N HCl + 1N HF and taken to dryness as above with HNO₃ and H₂O₂ until all organic impurities are eliminated.

4.2. Single Ion-exchange Beads

A 3-cm-square template was prepared from 0.25-mm-thick gold sheet on which 12 conical indentations were made, each with a volume of ~2 μ L (2.6 mm diameter by 1.2 mm depth). The final U and Th concentrates are each taken up in 2 μ L of 7N HNO₃ and transferred to one of the indentations. Using a binocular microscope and ultrafine camel-hair artists' brush, single ion-exchange beads of ~100 μ m diameter, preequilibrated with 7N HNO₃ and smeared on a glass slide to dry, are singly picked up and transferred to the indentations containing the concentrates of U and Th. For samples that are not size limited, such as corals, where larger amounts can be separated (~1 g), several beads can be added to the indentation allowing for user error in transferring beads. The gold sheet is then covered with a glass slide and allowed to sit overnight for equilibration. After removing the glass slide, the solutions are allowed to evaporate at air temperature, and the gold sheet is transferred to a muffle furnace for charring of the beads. Charring is necessary to remove most of the hydrogen contained in the beads. Hydrogen must be minimized because each isotope forms hydrides (AMU + 1) in the ionizing oxygen-beam, causing interferences (e.g., ²²⁹ThH interfering with ²³⁰Th and ²³⁵UH on ²³⁶U). The temperature in the muffle furnace is incremented in 100°C intervals of 30 min each to a final temperature of 400°C.

The beads cannot be heated in air above 400°C because of complete combustion and volatilization. Experiments heating the beads progressively to 600°C using a programmed reduction furnace (flushed with inert gas) resulted in only small improvements in the hydride interference, indicating that some C-H bonds remain intact. The simpler technique of charring in air is preferred given the minimal improvement in H removal and the additional problems with maintaining the integrity of the beads in the reduction furnace. The gold sheet is then cooled. The following procedure is analogous to the mounting of mineral grains for SHRIMP RG U-Th-Pb geochronology. Using a microscope and camel-hair brush, the beads are transferred to a sheet of double-sided transparent tape mounted on 6 x 6 cm glass plate. The beads are positioned near the center of a 2.5-cm-diameter circle inscribed on the glass plate, and their

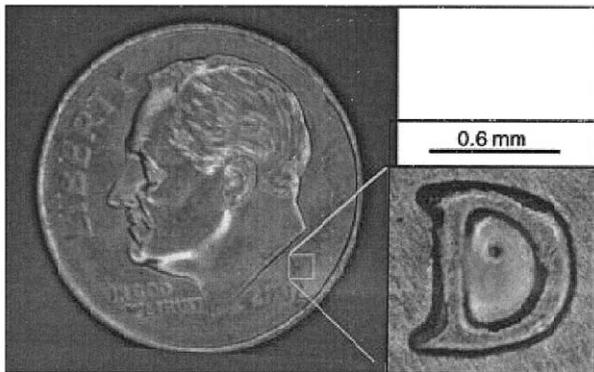
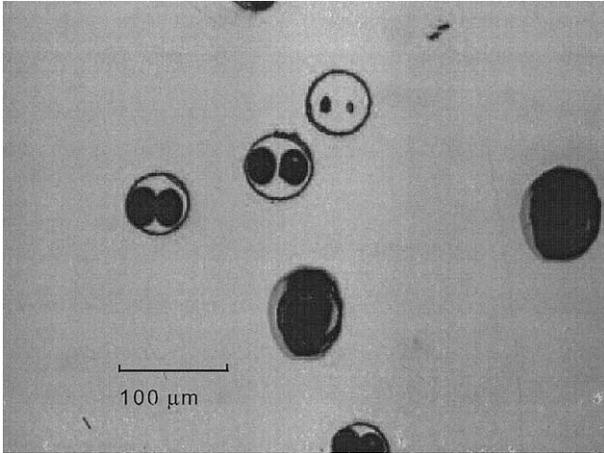


Fig. 1. Photomicrographs of ion-exchange beads in reflected light. Dark spots on upper photo are areas excavated by ion beam. Smaller spot areas ($\sim 50 \mu\text{m}$ diameter) were formed using Kohler focusing through a $200\text{-}\mu\text{m}$ Kohler aperture, allowing two to three spots on individual beads (beam currents 10 to 70 nA). Larger spot sizes ($100\text{--}120 \mu\text{m}$) were formed by taking out the Kohler aperture in the primary beam line. Spot areas were approximately equal to bead areas (beam currents up to 240 nA).

relative positions are noted in a laboratory notebook sketch. A 2.5-cm-diameter, 5-mm-thick plastic cylinder is then mounted over the circle on the tape, and epoxy is poured

over the beads to set overnight. The tape and glass plate are then removed, the beads being retained in the surface of the epoxy disk. The disk is then polished and the surface photographed using a reflected light microscope (Fig. 1). The polished surface is then coated with 100 nm of Au and placed in a steel holder and placed in the SHRIMP RG sample lock-chamber overnight to fully outgas (pressure to $\sim 5 \times 10^{-7}$ torr).

4.3. Analytical Technique and Data Reduction: U-Th Bead Experiments

During the process of testing the bead technique, a number of different primary ion beam configurations were tried.

The first experiments were done collimating the beam through a 200- μm Kohler aperture. This configuration produced spot sizes of $\sim 50 \mu\text{m}$ diameter, and two to three spots of this size could be analyzed on individual beads.

Both O_2^- and O^- primary beams were tested. Beam currents ranged from 10 to 70 nA on the bead, with the higher currents attained with O^- . Secondary count rates stayed linearly proportional to primary beam current. To provide stronger secondary-ion signals, a final experiment was carried out eliminating the Kohler aperture in the primary beam line (see Williams, 1998, and references therein for discussion of Kohler vs. “critical illumination” of the primary beam). Spot sizes were increased and were approximately equal to bead diameters (100 – 120 μm).

Beam currents up to 240 nA for O^- were obtained.

Secondary ion beams were increased by 40 – 50% which is not proportional to the increase in primary beam intensity

because the SHRIMP-RG transfer optics/mass analyzer is not designed to accept ions outside of a spot with a diameter much larger than 50 microns. However, the significant increase in secondary beam intensity generated within the area of acceptance justified the larger spot size as the amount of primary beam that could be focused through the largest available Kohler aperture had been maximized. Secondary ion count-rates for ^{235}U of over 100 K counts per second were produced with this primary beam technique. The beam excavates into the ion-exchange beads (a few μm deep) resulting in sputtering of $\sim 4\text{--}6$ ng of the carbonized bead, a small fraction of which is ionized as X^+ monoatoms of U and Th that are extracted into the mass spectrometer and subsequently counted. In preliminary experiments using the “defocused” beam, a few beads were analyzed a second time after the mount was ground and repolished to remove pits produced by the primary ion beam and to expose a fresh, flat surface. These data sets were reproducible at the analytical precision of this technique. Up to 50 cycles of peak switching, broken into blocks of 10 for data monitoring, were performed through the mass range (229 to 236 amu) completed on some beads. Secondary ion beams decreased significantly after 50 cycles, suggesting a limit caused by the crater-depth effect (for a discussion of this effect see [Valley and Graham, 1991](#)).

Data were gathered in ~ 5 blocks per bead for ^{229}Th , ^{230}Th , ^{232}Th , ^{232}ThH (for hydride blank), ^{234}U , ^{235}U , and ^{236}U from 5 to 10 s for each peak. Signals for ThO_x^+ and UO_x^+ species were significantly smaller

than for the elements probably because of the carbon-rich and oxygen-poor composition of the beads. The high metal to oxide ratio in the beads is opposite to that observed in O-rich silicates. Because some hydrogen still remains in the beads after charring, a small correction for hydride formation is necessary. Preliminary tests counting ^{238}UH and ^{232}ThH showed that the hydride ratio to ^{238}U and ^{232}Th were within error of each other at our ability to measure. Thus, the relative amounts of hydride formation for ^{232}Th during sample analyses were monitored by counting on the ^{232}ThH peak, generally amounting to $\sim 1\%$ of the ^{232}Th count-rate. This factor was then applied to correct for the effect of ^{229}ThH on ^{230}Th , and for ^{236}U by ^{235}UH respectively. Because the amounts of ^{229}Th and ^{236}U spikes were added to approximate the abundances of ^{230}Th and ^{235}U in the samples, the corrections in the count rates of ^{230}Th and ^{236}U are $\leq 1\%$. Resolving power at 10% peak height is 6000.

Counts per second are generally in the low thousands for ^{230}Th and ^{234}U , tens to hundreds of thousands for ^{232}Th , and hundreds of thousands for ^{235}U . These count rates are somewhat independent of the sample size used, suggesting that the beads are generally at saturation with U and Th and perhaps are picking up only a fraction of the isotope yield. Therefore, count-rates are generally not improved with larger sample size. However, with larger sample sizes multiple beads can be used and accumulative precision can be improved by analysis of multiple beads from a single sample. Because the count rates of ^{238}U are in the millions,

which would overwhelm the ion-counter detector, the abundance of ^{238}U is calculated from the constant atomic ratio of $^{238}\text{U}/^{235}\text{U}$ of 137.88. Generally ~ 5 blocks (50 cycles) could be made on a single bead before count rates deteriorated due to deepening of the depression. Isotope ratios were calculated for each cycle, then averaged over the total number of cycles. Standard analysis and protocols followed those of Ireland (1995).

5. RESULTS

5.1. Uraninite

For the HU-1 uraninite analysis, we processed an aliquot representing $\sim 1 \mu\text{g}$ of ^{238}U (ca. 10^{-10} g ^{234}U and 10^{-11} g ^{230}Th). After column separation and transfer to the gold sheet, five ion-exchange beads were added. Analytical results for three of the beads are shown in Figure 2. Count

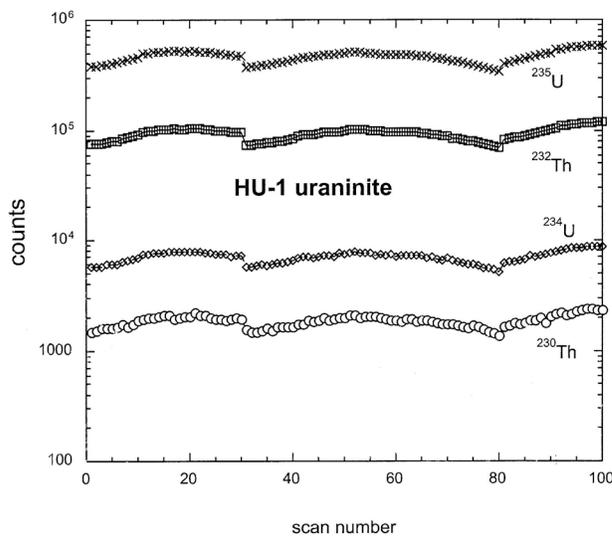


Fig. 2. Counts per cycle for ^{234}U (10 s), ^{235}U (5s), ^{230}Th (10 s), and ^{232}Th (5 s) on HU-1 uraninite on three different ion-

exchange beads equilibrated with the same solution. The first bead had three blocks of 10, the second five blocks of 10, and the third with two blocks of 10. The two discontinuities on the count plots indicate the point at which the shift from bead one to two and two to three occurred.

rates of the individual isotopes increased cyclically within each block. The counts for ^{234}U (ca. 7000) exceed those for ^{230}Th (ca. 1900) by a factor of 3.8 which compares with the abundance ratio of 3.29 in the original sample, indicating that yields of Th and U onto the beads are about equal. An estimate of the concentration of ^{238}U on a single bead is given by comparing the count rate of ^{235}U (ca. 9.4×10^4 c/s) with the count rate of ^{235}U in a zircon (ca. 600 c/s) containing 550 ppm of ^{238}U . Although sputter yields for beads and zircon might be quite different, the comparison suggests the individual beads may contain up to percent-levels of ^{238}U .

Figure 3 shows the accumulated mean for the mass ratio of $^{235}\text{U}/^{234}\text{U}$, which is within counting error of the true value for blocks 3 through 10. Counting was continued for ca. 136 min (10 blocks accumulated from three different beads) to determine ultimately attainable precision. The accumulated standard error of the mean after 10 blocks is 0.26% (2σ), beyond which the precision did not improve. In fact, after the first six blocks (80 min of counting), probably the point of diminishing returns, the standard error of the mean was 0.32% (2σ). The analyzed $^{235}\text{U}/^{234}\text{U}$ was found to be 132.98 ± 0.35 in comparison to the true

value of 132.7. The progressive $^{230}\text{Th}/^{234}\text{U}$ activity ratio plotted against blocks is shown in [Figure 4](#), showing a final value of 0.998 ± 0.007 (0.2%, 2 σ), a value within error of unity. Precision does not appear to improve significantly beyond ~ 6 blocks of counting. This limit in precision is probably due to the instability of the excitation environment and to the fact that detection is via peak-hopping on a single electron-multiplier detector.

5.2. Lamont Coral #6

For the coral analysis, we used a half-gram of sample and isolated the uranium and thorium isotopes onto two ion-exchange beads. Count rates ([Fig. 5](#)) for ^{230}Th and for ^{234}U are similar to those for the uraninite. Four blocks were counted on the first bead and two on the second. The similarity of the count rates from bead to bead and from sample to sample suggests the beads are at saturation with U and Th. Error was little improved after approximately four blocks of counting ([Fig. 6](#)). The calculated age from the SHRIMP RG data of 120.0 ± 1.8 kyr (2 σ) is within counting-error of the age determined by TIMS of 123.2 ± 1.49 kyr (2 σ replicate-analysis error) and close to the age determined by ISOPROBE of 123.0 ± 0.5 kyr. The $^{234}\text{U}/^{238}\text{U}$ activity ratio of 1.120 ± 0.007 is slightly higher than the replicate-analyses error of the TIMS value of 1.1062 ± 0.0044 , but within error of the ISOPROBE value of 1.116 ± 0.0009 . The $^{230}\text{Th}/^{234}\text{U}$ activity ratio of 0.680 ± 0.0056 is slightly lower than the replicate-analyses error of the TIMS value of 0.689 ± 0.0052 and of ISOPROBE value of 0.689 ± 0.0015 . Inasmuch as the SHRIMP RG analysis of the uraninite yielded the correct value for the $^{235}\text{U}/^{234}\text{U}$ ratio

(Fig. 3) and, by implication the correct $^{234}\text{U}/^{238}\text{U}$ activity ratio of unity, the differences between the SHRIMP RG and TIMS value for the coral might be due to some $^{234}\text{U}/^{238}\text{U}$ heterogeneity among the coral aliquots, as they did not represent a homogenized powder but individual pieces of the coral.

6. DISCUSSION AND CONCLUSION

6.1. Sensitivity, Accuracy, and Precision

Based on the analysis of the uraninite and the coral, the SHRIMP RG method appears to yield high count rates of the isotopes of interest, with sensitivity perhaps superior to TIMS, and with accuracy comparable to TIMS.

Instrumental fractionation of mass during analysis seems to be insignificant at least for the range of uranium isotopes from 233 to 235. Analytical error, however, is at least a factor of 2 poorer than for replicate

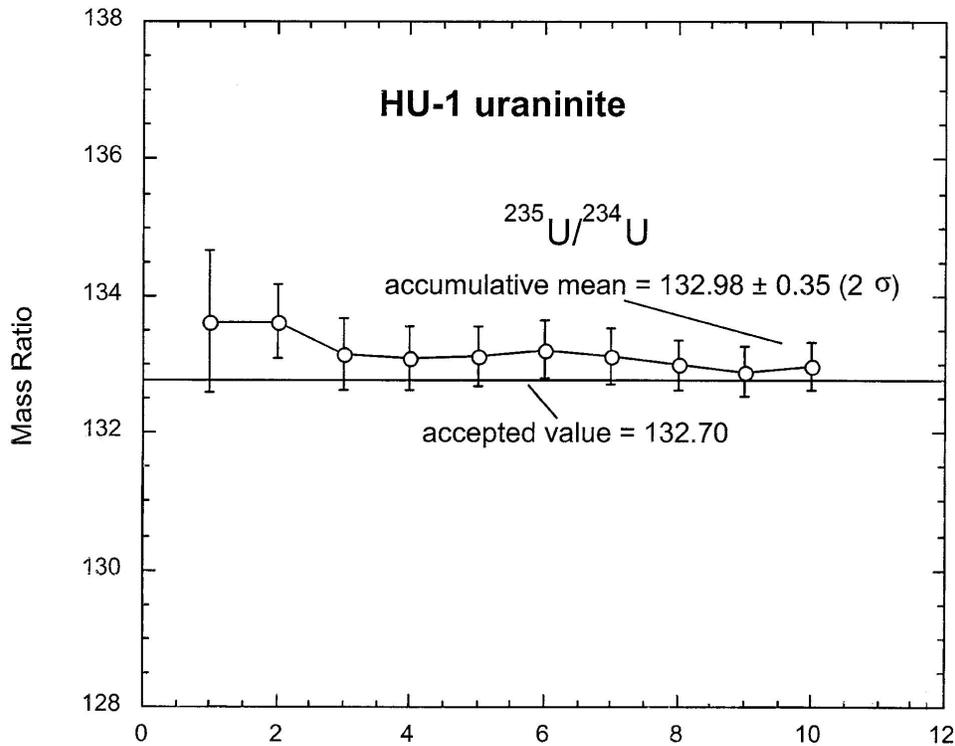


Fig. 3. Mass ratio of $^{235}\text{U}/^{234}\text{U}$ and accumulated error for HU-1 uraninite as analyzed by SHRIMP RG ion-probe. Accumulative mean of 132.98 ± 0.35 (2σ) is in agreement with known value of 132.7 calculated from $^{234}\text{U}/^{238}\text{U}$ activity ratio of unity and constant $^{238}\text{U}/^{235}\text{U}$ atomic ratio of 137.88 (Cheng et al., 2000). Accumulated error of $\sim 0.3\%$ is little improved after six blocks, or 60 scans.

U/Th dating by ion-microprobe

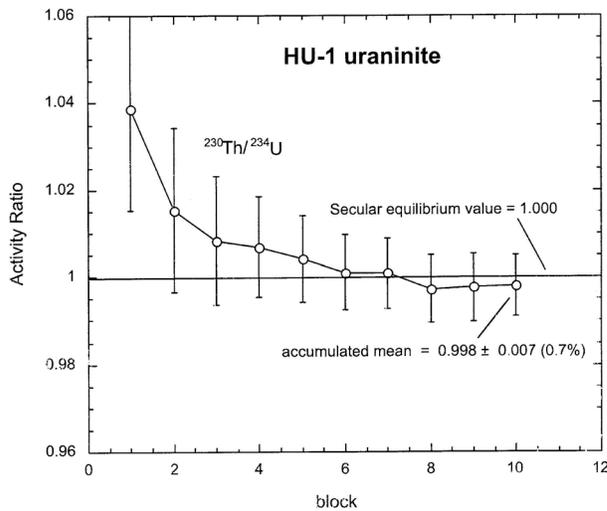


Fig. 4. ($^{230}\text{Th}/^{234}\text{U}$) activity ratio and accumulated error of HU-1 uraninite as analyzed by SHRIMP RG ion-probe. Accumulative mean of 0.998 ± 0.007 (2σ) is in agreement with TIMS value of 1.0026 ± 0.0016 (2σ) (Cheng et al., 2000).

analyses by TIMS, but better than by α -spectroscopy.

Counting error seems to be little improved by prolonging counting beyond ~ 4 – 6 blocks, or 40 to 60 min of counting.

6.2. Advantages of Ion Microprobe Analysis

A major advantage of the SHRIMP RG is that isotopes of both U and Th can be determined by a single peak-hopping acquisition sequence on a single sample, eliminating the need for tedious chemical separation, thereby shortening the processing time. Also, counting times per sample are relatively short, and multiple samples can be placed on a single mount for a single analytical session. Moreover, after isolation of the iso-

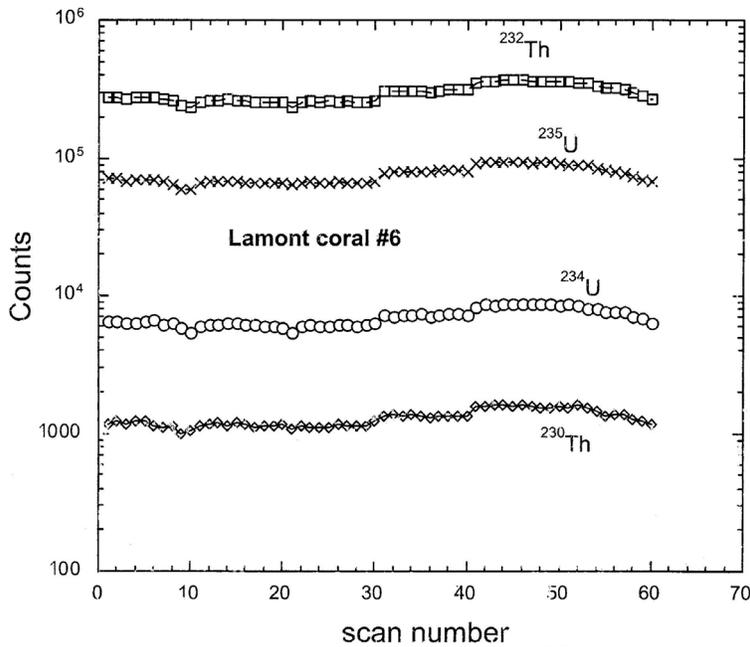


Fig. 5. Counts per cycle for ^{234}U (10 s), ^{235}U (5s), ^{230}Th (10 s), and ^{232}Th (5 s) of a solid aliquot of Lamont Barbados coral #6 with four blocks of 10 on one bead and two blocks of 10 on a second. Count rates are comparable to those of HU-1.

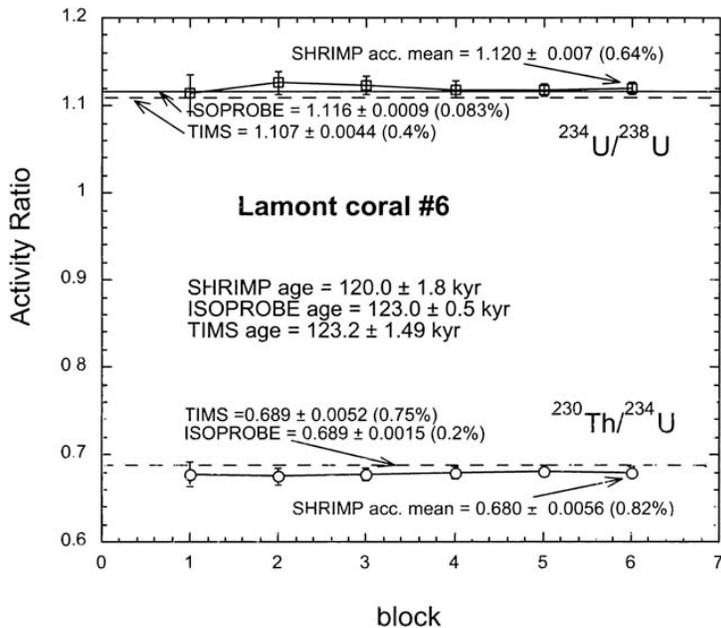


Fig. 6. ($^{230}\text{Th}/^{234}\text{U}$) and ($^{234}\text{U}/^{238}\text{U}$) activity ratios of a solid aliquot of Lamont Barbados coral #6 compared with TIMS and ISOPROBE analyses. The SHRIMP RG– determined ($^{234}\text{U}/^{238}\text{U}$) activity ratio is $\sim 1.2\%$ higher than the TIMS determination but within error of the ISOPROBE value. The age and accumulative error calculated from accumulated mean values of 120.0 ± 1.8 (2σ) kyr agrees with the TIMS age of 123.2 ± 1.49 (2σ) and is close to the age determined by ISOPROBE of 123.0 ± 0.5 kyr. We calculated the TIMS age and error from four analyses of a different piece of the coral by W. G. Thompson of Lamont Doherty Earth Observatory. The differences between the SHRIMP RG and TIMS $^{234}\text{U}/^{238}\text{U}$ value might be due to some ($^{234}\text{U}/^{238}\text{U}$) heterogeneity among the coral aliquots. topes on the beads, the SHRIMP RG analysis allows multiple reanalysis. Because the ion beam excavates a pit only a few μm deep, the mount can later be repolished and reanalyzed numerous times.

Apparently in the method described above, only a portion of the chemically isolated isotopes are picked up on the single beads and analyzed in the instrument. It is clear that singular and fundamental improvements in sensitivity and precision could be achieved if the entire isotope yield of a sample could be analyzed. Current and future work in this laboratory is devoted to finding a method to isolate the entire sample yields onto a solid with an area of $<100\ \mu\text{m}$. *Acknowledgments*— We thank W. G. Thompson of Lamont Doherty Earth Observatory who generously supplied us with a solid aliquot of his Barbados coral #6 and his unpublished TIMS analytical results. We are grateful to

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