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# Measurement of Femtogram Quantities of Protactinium in Silicate Rock Samples by Multicollector Inductively Coupled Plasma Mass Spectrometry

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**We describe a new method for the chemical separation and analysis of Pa in silicate rock samples by isotope dilution. Our new technique has the following advantages over previous methods: (a) The initial separation of Pa from the rock matrix is carried out using anionic exchange resin and HCl–HF mixtures, avoiding the need to remove F<sup>−</sup> quantitatively from the sample solution prior to this step, (b) Efficient ionization of Pa is achieved using a multicollector inductively coupled plasma mass spectrometer, so that smaller sample sizes and shorter measurement times are required, compared to previous methods using thermal ionization mass spectrometry or alpha spectrometry. (c) Plasma ionization requires less efficient separation of the high field strength elements from Pa, thus reducing reagent volumes, blanks, and sample preparation times. Instrumental mass fractionation can be corrected for using admixed U of known isotopic composition. Using this method, Pa concentrations can be measured to a precision of ~0.5% and an accuracy of ~1% using only a few tens of femtograms of Pa.**

<sup>231</sup>Pa has a half-life of 32 760 years and is the longest-lived intermediate daughter of <sup>235</sup>U. Chemical fractionation of U and Pa during geological processes may result in significant isotopic disequilibrium between <sup>231</sup>Pa and <sup>235</sup>U, and measurements of Pa in geological materials have been used to date U-bearing materials and to examine the rates of geological processes on time scales of <150 ka, in palaeoclimatology, oceanography, palaeoanthropology, sedimentology, and volcanology.<sup>1,2</sup> In volcanology, <sup>231</sup>Pa–<sup>235</sup>U disequilibrium has potential both as a chronometer and as a constraint on the processes and timing of mantle melting and melt transport.<sup>3–14</sup>

Early studies of <sup>231</sup>Pa–<sup>235</sup>U disequilibrium in geological samples used radioactive decay counting techniques and required large sample sizes (typically >1 pg of <sup>231</sup>Pa) and long counting times (days to weeks) to obtain precisions of 5–10% (2σ). More recent studies have used thermal ionization mass spectrometry (TIMS), which allows more precise and rapid analysis of smaller samples;<sup>15,16</sup> nevertheless, the analysis of Pa in silicate rocks is difficult and time-consuming. Pa concentrations in basaltic rocks are typically <300 fg/g, the low ionization efficiency of Pa (<0.7%) means that 50–100 fg of Pa is required for an analysis by TIMS, and the small ion beam sizes obtained require long (1–2 h) measurement times to obtain a precision of ~1%. Analysis of Pa by TIMS also requires a good separation of Pa from elements such as Ti, Zr, and Nb, which inhibit the ionization of Pa. Zr/Pa ratios in silicate rocks are typically ~10<sup>9</sup> and must be reduced by at least 4 orders of magnitude.<sup>15</sup> Separation of Pa from rock samples is complicated by the fact that Pa tends to fall out of solution easily due to hydrolysis or particle reactivity. In addition, Pa is adsorbed as an anionic chloride complex on anionic exchange resin in strong HCl solutions only in the absence of fluoride ions,<sup>17,18</sup> which has

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required  $F^-$  to be removed quantitatively before each anionic exchange separation step in previous methods. Here we describe a new method for the chemical separation and isotope analysis of Pa from silicate rock samples using a modified ion-exchange procedure and multicollector inductively coupled plasma mass spectrometry (MC ICPMS), which avoids many of the difficulties listed above.

## EXPERIMENTAL SECTION

**Reagents and Materials.** Dissolutions and chemical separations were carried out using Teflon vessels that had been thoroughly cleaned in boiling 10 M  $HNO_3$  + 0.05 M HF prior to use. Pa shows a tendency to stick to Teflon and could not be entirely removed without the use of HF in the cleaning solution. High-purity HF and HCl (Rohm and Haas Super Purity) and trace analysis grade (Primar) acids ( $HNO_3$ ,  $H_3BO_3$ ,  $HClO_4$ ) were obtained from Fisher Scientific.  $HNO_3$  was further purified by sub-boiling distillation in a quartz still, and all dilutions were carried out using deionized (18.2 M $\Omega$ ) water from a Milli-Q system.

Silica gel used in spike preparation was obtained from Merck (extra pure, 70–230 mesh), and anionic exchange resin (Bio-Rad, AG1-X8, 200–400 mesh) and TRU Spec resin (Eichrom, 50–100  $\mu m$  size) were cleaned thoroughly before use, with several rinses of 6 M HCl + 0.05 M HF,  $H_2O$ , and 6 M HCl.

**Special Safety Considerations.** Solutions containing perchloric acid should be evaporated in a fume hood certified for such use, and recommended procedures for safe handling of this and other reagents should be followed. Levels of radioactivity due to the  $\beta$ -decaying  $^{233}Pa$  spike used in sample analysis are small, but the preparation of the  $^{233}Pa$  spike from  $^{237}Np$  involves higher levels of  $\alpha$  activity and should be carried out in a laboratory designed for such purposes.

**Spike Preparation.** A  $^{233}Pa$  tracer (half-life  $26.967 \pm 0.004$  days) was prepared by “milking” a solution of its parent  $^{237}Np$ . Our milking method takes advantage of the affinity of Pa for silica in the absence of  $F^-$  (R. Anderson, personal communication 1993). The Np solution ( $\sim 20$  kBq), which was stored in  $\sim 3$  mL of 7 M  $HNO_3$  + 0.05 M HF, was fumed twice with 0.5 mL of concentrated perchloric acid to remove  $F^-$ , taken up in 2 mL of 7 M  $HNO_3$ , and loaded onto a polypropylene column containing 5 mL of silica gel, which had been washed several times with 7 M  $HNO_3$ . The column was then rinsed with  $3 \times 1$  mL of 7 M  $HNO_3$ , before passing  $2 \times 5$  column volumes (cv) of 7 M  $HNO_3$ . All eluants, including the load solution, were collected in the original Np beaker. Pa was then stripped from the column with  $2 \times 4$  cv of 7 M  $HNO_3$  + 0.05 M HF. The column was rinsed three times with 3 cv of 7 M  $HNO_3$  to remove  $F^-$ , and these rinses were added to the Np fraction. The Pa fraction was evaporated to near dryness, fumed twice with perchloric acid, taken up in 7 M  $HNO_3$ , and passed again through the silica gel column. All 7 M  $HNO_3$  washes were added to the Np fraction from the first column. A small aliquot of the Pa fraction was diluted with water, and the approximate Np/Pa ratio determined by MC ICPMS. Generally three or four passes through the silica gel column were required to obtain a Np–Pa separation factor of  $> 10^6$ , corresponding to a  $^{237}Np/^{233}Pa$  ratio of  $< 30$ , in order that the effect of Np decay on the  $^{233}Pa$  concentration of the spike solution over several half-lives of  $^{233}Pa$  was insignificant. The Np solution had previously been milked several times for Pa, and the  $^{231}Pa$  content of  $^{233}Pa$

spike solutions was below detection limits ( $< 0.2$  fg/g). The purified  $^{233}Pa$  spike was diluted to a concentration of  $\sim 300$  fg/g with 7 M  $HNO_3$  + 1 M HF and stored in a sealed Teflon dropper bottle.

**Chemical Separation of Pa.** For Pa analysis by MC ICPMS, it is not essential to separate Pa from the high field strength elements (HFSE), as shown below, whereas the presence of significant amounts of HFSE inhibits Pa ionization during TIMS analysis. However, it is important to obtain a Pa fraction that is free of Th and U. Tailing of a large  $^{232}Th$  peak onto masses 231 and 233 can be a problem (see below), and  $^{232}ThH^+$  is a potential interference on mass 233.  $^{233}U$  (decay product of  $^{233}Pa$ ) must be removed because U and Pa are ionized with similar (but not identical) efficiency in the plasma source, so that unlike TIMS,  $^{233}U$  cannot be removed by slow filament warmup.<sup>15</sup> In addition, a clean Pa fraction is required in order to avoid possible molecular interferences and matrix effects.

Sample powders (between 0.1 and 2.5 g) were weighed out and spiked with  $^{233}Pa$  to obtain a  $^{231}Pa/^{233}Pa$  ratio of  $\sim 3$ . If U concentrations were to be determined on the same aliquot, a  $^{236}U$  spike was used. This avoids potential problems with ingrown  $^{233}U$  from the Pa spike that may arise when using a  $^{233}U$  spike<sup>15</sup> and also allows the efficiency of the U–Pa separation to be checked by monitoring mass 236 in the final Pa fraction.<sup>19</sup> In our method, natural U is added to the sample prior to analysis in order to correct for instrumental mass fractionation, as described below, and so an enriched  $^{235}U$  spike could not be used.

Samples were digested in concentrated HF– $HNO_3$ – $HClO_4$  overnight. The solution was evaporated to incipient dryness and then twice evaporated to complete dryness with concentrated  $HNO_3$ . The sample was then treated with 6 M HCl, dried down, redissolved completely in 5–30 mL of 6 M HCl and 0.5 mL of saturated boric acid solution, and left on a hot plate for at least 10 h. It is essential that the sample is completely in solution at this stage to ensure sample/spike equilibration. If any solid residue was observed, the sample was treated again with 15 M  $HNO_3$  and 6 M HCl. After evaporating to dryness, the sample was converted to fluoride form with concentrated HF and placed in an ultrasonic bath until any solid residue had a jellylike appearance. The solution was then evaporated to near dryness, 3–5 mL of 4 M HF added, and transferred to a 15-mL centrifuge tube. After centrifuging at 4000 rpm for 5 min, the supernatant was transferred to a clean centrifuge tube, and the solid residue was broken up and leached a further 3 times with 4 M HF. Pa is strongly partitioned into the liquid fraction, together with the high field strength elements and some transition elements and actinides.<sup>20,21</sup> This step therefore results in an initial separation of Pa from the rock matrix. The solid residue was checked for  $^{233}Pa$  activity by  $\gamma$ -counting before discarding (this fraction contains much of the Ra, Th, and rare-earth elements.<sup>20</sup>

The first column separation took advantage of the fact that Pa is strongly adsorbed onto anionic exchange resin in strong ( $> 2$  M) HF as fluoride complexes.<sup>18</sup> The sample in  $\sim 9$  mL of 4 M HF

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was loaded onto a disposable polypropylene ion-exchange column containing ~4 mL of AG1-X8 (200–400 mesh) resin in F<sup>−</sup> form, previously conditioned with 4 M HF. Most matrix elements were washed off the resin with 15 cv of 4 M HF, followed by 1 cv of 1 M HCl + 0.5 M HF. Pa, together with the HFSE, some transition elements, and actinides were then collected in a further 1 cv of 1 M HCl + 0.5 M HF.

Initially, we planned to use TEVA Spec resin for the purification of protactinium,<sup>5</sup> because this resin should provide an efficient separation of Pa from both U and Th as well as the HFSE.<sup>22</sup> However, we found that Pa would not stick on the TEVA resin in either HCl or HNO<sub>3</sub>. Instead, we used TRU Spec resin for Pa purification.<sup>7,23,24</sup>

A 0.1-mL aliquot of perchloric acid was added to the Pa fraction from the anionic columns, which was evaporated, fumed at 170 °C, but not allowed to dry. A 1.5-mL aliquot of 10 M HCl was added to the sample, together with 0.5 mL of saturated boric acid solution, to complex any remaining fluoride ions. The sample solution was then loaded onto a Teflon column containing 0.15 mL of TRU Spec resin, conditioned with 10 M HCl. The resin was washed sequentially with 1 mL of 10 M HCl, 1 mL of 6 M HCl, and 1 mL of 4 M HCl to remove Ti, Zr, Nb, and most other remaining cations. Any remaining Th was then eluted in 2 mL of 1 M HCl. The resin was then washed with 0.5 mL of 6 M HCl, before collecting Pa in 2 × 0.5 mL of 3 M HCl + 2 M HF. U remained on the resin and could be recovered with 0.01 M HNO<sub>3</sub> + 0.1 M HF.

We found that a second pass through TRU Spec resin was necessary in order to reduce further the Th/Pa ratio and avoid “tailing” of the <sup>232</sup>Th peak onto masses 231 and 233 during mass spectrometric analysis. The Pa fraction from the TRU Spec column was therefore evaporated to near dryness with 2–3 drops of concentrated perchloric acid, taken up in 10 M HCl and boric acid, and passed a second time through a 0.15-mL TRU Spec column. At this stage, the <sup>232</sup>Th/<sup>231</sup>Pa and <sup>238</sup>U/<sup>231</sup>Pa ratios of the Pa fraction were typically <100 and <3, respectively, corresponding to Th–Pa and U–Pa separation factors of about 10<sup>5</sup> and 10<sup>6</sup>. The clean Pa fraction was evaporated to near dryness, taken up in 1.0–1.5 mL of 0.6 M HCl + 0.02 M HF, and spiked with U of known isotopic composition (NBS U112a was used) in order to obtain a <sup>238</sup>U signal of ~3 V in the mass spectrometer. The Pa yield was determined by passing an unspiked solution of a rock powder of known <sup>231</sup>Pa content through the chemistry procedure, which was then spiked with <sup>233</sup>Pa and passed through a final 50-μL column of TRU Spec resin in 6 M HCl + 0.1 M HF immediately prior to analysis in order to remove <sup>233</sup>U. Yields for the entire procedure was usually >90%; lower and variable yields in the early stages of this study were found to result from loss of hydrolyzed Pa complexes to the walls of the Teflon beakers between column passes. This could be avoided by reusing the beakers used for the collection of the Pa fraction from the anionic columns and by warming the final Pa fraction in 0.6 M HCl + 0.02 M HF in sealed beakers before mass spectrometric analysis.<sup>19</sup>

**Mass Spectrometry.** Pa isotope measurements were carried out using a Finnigan Neptune double-focusing MC ICPMS,

Table 1. Electron Multiplier and Faraday Cup Arrangement Used for Pa Isotope Measurements

| detector | SEM | H1  | H2  | H3  | H4  |
|----------|-----|-----|-----|-----|-----|
| cycle 1  | 231 | 232 |     |     | 238 |
| cycle 2  | 233 |     | 235 | 238 |     |

equipped with electrostatic analyzer, secondary electron multiplier (SEM), and retarding potential quadrupole for high abundance sensitivity. The instrument has nine Faraday detectors: one fixed in the central position, and four additional detectors on both the low-mass (L1–L4) and high-mass (H1–H4) sides. Samples were aspirated through a Cetac Aridus microconcentric nebulizer and desolvating system, at an uptake rate of between 50 and 100 μL/min, using a sample Ar gas flow rate of ~0.9 L/min. Most analyses were carried out using a standard PTFE Aridus nebulizer and spray chamber, but for later measurements, we used a PFA unit that decreased the sample washout time by a factor of ~2. The spray chamber was maintained at a temperature of 70 (PTFE) or 105 °C (PFA) and the desolvator at 160 °C. Typical Ar (sweep gas) and N<sub>2</sub> flows were 3 L/min and 20 mL/min, respectively.

At the start of each analytical session, the instrument was tuned and peak shapes on both Faraday cups and the SEM were optimized using a solution of natural U. The typical sensitivity was 8–15 V <sup>238</sup>U for a 20 ppb solution of U and a sample uptake rate of 80 μL/min. Cup positions were optimized using a solution of natural U, to which <sup>231</sup>Pa, <sup>232</sup>Th, and <sup>233</sup>U had been added. The Pa measurement routine consisted of two cycles of 8-s integrations; in the first cycle, <sup>231</sup>Pa was measured on the SEM and <sup>238</sup>U on Faraday H4, and <sup>232</sup>Th was monitored on H1. In the second cycle, <sup>233</sup>Pa was measured on the SEM and <sup>235</sup>U and <sup>238</sup>U were measured on Faraday cups H2 and H3 (Table 1). An exponential mass bias correction was applied to the <sup>231</sup>Pa/<sup>233</sup>Pa ratio using the <sup>238</sup>U and <sup>235</sup>U measurements from the second cycle and assuming a <sup>238</sup>U/<sup>235</sup>U ratio of 137.88. The mass bias correction was in the range 0.3–0.4%/amu. This approach assumes that the mass biases of U and Pa are the same, which is likely at the 0.1–0.2% level.<sup>25–27</sup> The <sup>238</sup>U measurements on each cycle were combined to eliminate the effects of beam instability and SEM–Faraday gain.<sup>26,28</sup> Each measurement consisted of 30–50 <sup>231</sup>Pa/<sup>233</sup>Pa ratios, took 15–20 min, and consumed between 20 and 100 fg of Pa. A wash solution of 0.6 M HCl + 0.02 M HF was used to flush Pa from the system between analyses. Wash solutions of dilute HCl or HNO<sub>3</sub> (containing no HF) were not as efficient at removing Pa from the inlet system. The wash solution was aspirated until count rates on masses 231 and 233 had returned to background (<4 counts/s) levels; the washout time between samples was typically 10 (using a PFA spray chamber) to 20 min (for the PTFE spray chamber). The total analysis time of ~30 min is significantly shorter than

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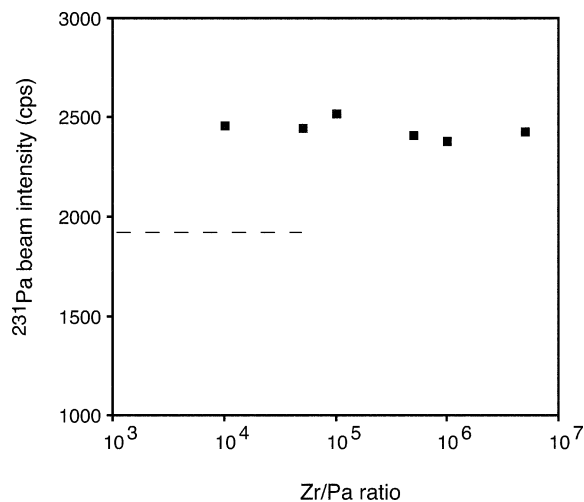


Figure 1. Intensity of the  $^{231}\text{Pa}^+$  beam measured in solutions of Pa to which had been added variable amounts of Zr, showing that the presence of HFSE in the Pa fraction do not significantly inhibit the ionization of Pa in the plasma source mass spectrometer. Dashed line shows the range in Zr/Pa ratio in the Pa fraction of silicate rock samples analyzed in this study, after having been purified by ion exchange.

that required for an analysis by TIMS (1–2 h, excluding filament preparation time).

The accuracy and linearity of the SEM used in this study (MasCom Cu–Be dynode multiplier, operating in ion-counting mode with a deadtime correction of 22 ns) had been characterized previously using NBS U isotopic standard solutions (D. Hoffmann, D. A. Richards, et al., in preparation). For the ion beam sizes (between 800 and  $10^4$  counts/s) and  $^{231}\text{Pa}/^{233}\text{Pa}$  ratios (between 0.8 and 6) measured in this study, there was negligible multiplier bias resulting from differences in beam intensity.

The  $^{232}\text{Th}$  peak was monitored during each sample analysis and was generally  $<2$  mV ( $<1.3 \times 10^5$  counts/s). The abundance sensitivity of our instrument is better than 0.3 ppm at 1 amu from  $^{232}\text{Th}$ , so that tailing of  $^{232}\text{Th}$  onto mass 231 was insignificant.

## RESULTS AND DISCUSSION

### Sensitivity, Blanks and Interferences, Detection Limits.

Using a Cetac Aridus microconcentric nebulizer and desolvating system, the sensitivity of our MC ICPMS for Pa is 500–600 V/ppm, and the ions detected/atoms consumed ratio of  $\sim 0.9\%$  is better than the best reported<sup>15,16</sup> TIMS analyses (0.5–0.7%). We found that the presence of moderate amounts of Zr, Nb, or Ti did not significantly inhibit ionization of Pa. This was determined by “spiking” different aliquots of a  $^{231}\text{Pa}$  solution with variable amounts of Zr, up to a Zr/Pa ratio of  $5 \times 10^6$  (Figure 1). After two passes through TRU Spec resin, the Zr/Pa ratio of rock sample solutions was always  $<10^5$ .

The background in the 228–239 mass range was examined at the start of each analytical session. Dark noise on the SEM was generally  $<1$  counts/s but increased significantly after a long measurement session. We therefore tried to introduce as little  $^{233}\text{Pa}$  into the instrument as possible and monitored the change in dark noise during each session. The background on masses 231 and 233 was generally  $<4$  counts/s, equivalent to Pa concentrations of  $<0.1$  fg/mL, for wash solutions prepared from

distilled acids. These interferences did not appear to be due to simple molecular species such as argides, oxides, or hydrides and, instead, may be caused by hydrocarbons.<sup>26</sup> These may be derived from the argon supply,<sup>26</sup> although the background could usually be decreased by using sample and skimmer cones that had been freshly cleaned in dilute  $\text{HNO}_3$  in an ultrasonic bath and by rinsing out the spray chamber, indicating that much of the background is derived from the cones and sample introduction system. Similar or only slightly higher ( $<7$  counts/s) count levels were present in unspiked blank solutions that had been passed through the entire Pa chemistry procedure, suggesting that interferences caused by hydrocarbons derived from the ion-exchange resins<sup>26</sup> were not significant. The 231/233 ratio of this background was variable for different wash solutions as well as unspiked blank solutions that had been passed through the same Pa chemistry procedure. Measurements of unspiked blank solutions could be used to correct for these interferences on masses 231 and 233; however, since most of these interferences are apparently derived from the cones and inlet system, we assessed backgrounds while aspirating an aliquot of the 0.6 M HCl + 0.02 M HF solution used to dissolve the samples. Any background correction was small (less than  $\sim 0.5\%$ ) compared to the  $^{231}\text{Pa}$  and  $^{233}\text{Pa}$  beams measured in this study (between 800 and 10 000 counts/s, for 20–250 fg/mL Pa solutions). Detection limits (estimated as blank plus  $3\sigma$  error of blank measurements) were  $\sim 200$  ag/mL for  $^{231}\text{Pa}$  and  $^{233}\text{Pa}$ .

**Effect of  $^{233}\text{Pa}$  Decay.** The change in the  $^{231}\text{Pa}/^{233}\text{Pa}$  ratio resulting from decay of  $^{233}\text{Pa}$  to  $^{233}\text{U}$  is  $\sim 2.5\%$ /day. For Pa measurements by TIMS,  $^{233}\text{U}$  can be removed from the Pa sample by gentle heating of a filament.<sup>15</sup> This is not possible using MC ICPMS, but if Pa and U are ionized with identical efficiency in the plasma source,<sup>19</sup> then the measured 231/233 ratio of a spiked Pa sample will remain constant with time. However, we have found that, in our MC ICPMS, U is ionized significantly more readily than Pa. This was demonstrated by measuring the  $^{231}\text{Pa}/(^{233}\text{Pa} + ^{233}\text{U})$  ratio of a solution of Pa, prepared by mixing  $\sim 100$  fg of  $^{233}\text{Pa}$  spike solution and  $\sim 300$  fg of  $^{231}\text{Pa}$ , 3 times over the course of 3 months ( $\sim 3$  half-lives of  $^{233}\text{Pa}$ ). The measured 231/233 ratio of this solution was found to decrease with time as the  $^{233}\text{Pa}/^{233}\text{U}$  ratio decreased (Figure 2). This precluded the possibility of storing samples for long periods after the final chemical separation before analysis.<sup>19</sup> The change in the 231/233 ratio measured by MC ICPMS resulting from decay of  $^{233}\text{Pa}$  is estimated to be  $<0.6\%$ /day, which is smaller than the reproducibility of our measurements. All of our Pa analyses were in any case carried out within 24 h of the final U–Pa separation, to minimize the effect of  $^{233}\text{U}$  from the decay of  $^{233}\text{Pa}$  to the 233 signal, and before each measurement, we monitored mass 236 for those Pa samples that had been spiked with  $^{236}\text{U}$  in order to check that spike U (and by inference  $^{233}\text{U}$  from  $^{233}\text{Pa}$  decay) had been removed during column chemistry.<sup>19</sup>

An alternative explanation of the apparent change in the 231/233 ratio is that despite being stored in a solution containing HF, some Pa was lost to the beaker walls, so that decay of  $^{233}\text{Pa}$  to more soluble  $^{233}\text{U}$  decreased the 231/233 ratio of the solution over time. However, we believe that this is unlikely, because we have not observed any significant change in the Pa content of our spike solutions (beyond that due to decay) over similar periods of time,

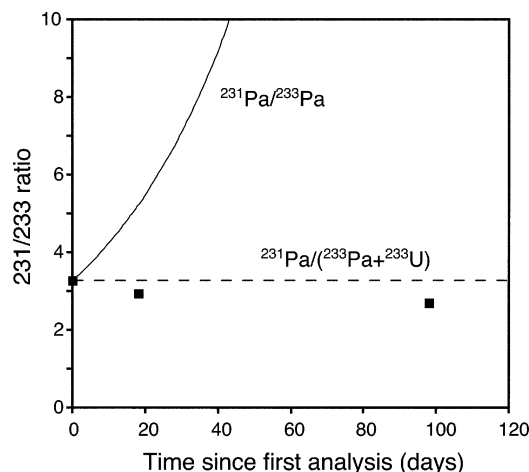


Figure 2. Change in the measured 231/233 ratio of a sample solution measured three times over a 98-day period. Immediately after passing through the TRU Spec column (day 0), the sample contained no  $^{233}\text{U}$ . Curve shows the calculated exponential evolution of the  $^{231}\text{Pa}/^{233}\text{Pa}$  ratio. The measured 231/233 ratio decreases as  $^{233}\text{Pa}/^{233}\text{U}$  decreases with time, probably due to more efficient ionization of U than Pa in the plasma source. Error bars on the 231/233 ratio measurements are smaller than symbol size.

Table 2. Repeat Measurements of the  $^{231}\text{Pa}$  Concentration of a Pa Solution<sup>a</sup>

|      | $^{231}\text{Pa}$ (fg/g) |
|------|--------------------------|
| mix1 | $3305.8 \pm 11.9$        |
| mix2 | $3335.9 \pm 19.2$        |
| mix3 | $3329.2 \pm 7.7$         |
| mix4 | $3303.0 \pm 18.9$        |
| mean | $3318.5 \pm 33$ (2 SD)   |

<sup>a</sup> Uncertainties are  $2\sigma$  errors on each measurement. The concentration of the  $^{231}\text{Pa}$  solution was determined using a  $^{233}\text{Pa}$  spike solution that had been calibrated against the rock standard TML, indicating a reproducibility for Pa measurements in standard solutions of  $\sim 1\%$ . Total Pa used in each analysis was 100–500 fg.

as determined by repeated analysis of the TML rock standard.

**Precision and Accuracy.** The internal precision on analyses of solutions containing  $\sim 100$  fg of total Pa was generally 0.4–0.7% ( $2\sigma$ ), using the  $^{238}\text{U}$  beam measurement to correct for variations in beam intensity between cycles. Without this correction (i.e., simple peak hopping), internal precision was limited to 1.0–1.5%, due to changes in signal intensity caused by plasma flicker and by variations in the supply rate of sample solution from the nebulizer to the ion source.

Mixtures of a  $^{231}\text{Pa}$  solution, diluted from a stock provided by K. Sims (Woods Hole Oceanographic Institution), with a  $^{233}\text{Pa}$  spike solution, which had been passed through TRU Spec resin to remove  $^{233}\text{U}$ , were reproducible to 1.0% (Table 2), using 100–500 fg of total Pa. Similar reproducibility was obtained for rock samples; seven digestions of the rock standard TML spiked with  $^{233}\text{Pa}$  gave an external error of 1.2% (2 SD) using 20–150 fg of Pa (Table 3). Duplicate analyses of a young (1000 y) basaltic andesite from the Lesser Antilles (sample RW35), using two different batches of  $^{233}\text{Pa}$  spike agreed to within 1.0% (Table 4).

Each batch of  $^{233}\text{Pa}$  spike prepared was calibrated against the rock standard TML (jar 3), which was assumed to be in U–Pa equilibrium. This Pliocene lava from Sonora, CA, is widely used

Table 3. Calibration of a  $^{233}\text{Pa}$  Spike Solution against the Rock Standard TML<sup>a</sup>

| analysis no. | $^{233}\text{Pa}$ (fg/g) | $\pm 2\sigma$ | Pa (fg) <sup>b</sup> |
|--------------|--------------------------|---------------|----------------------|
| T1           | 503.3                    | 4.1           | 50                   |
| T2           | 497.2                    | 3.4           | 50                   |
| T3           | 508.5                    | 2.9           | 100                  |
| Ts           | 499.8                    | 3.2           | 150                  |
| T4           | 502.5                    | 5.7           | 20                   |
| T5           | 503.6                    | 2.6           | 100                  |
| T6           | 501.9                    | 2.1           | 150                  |
| mean         | $502.4 \pm 6.5$ (2 SD)   |               |                      |

<sup>a</sup> Each analysis represents a separate dissolution of the TML rock standard mixed with a  $^{233}\text{Pa}$  spike, indicating a reproducibility for Pa determinations in silicate rock samples of 1.2%. <sup>b</sup> approximate total Pa used for the analysis.

Table 4.  $^{231}\text{Pa}$  Concentrations and ( $^{231}\text{Pa}/^{235}\text{U}$ ) Ratios of Silicate Rock Samples<sup>a</sup>

|                      | $^{231}\text{Pa}$ (fg/g) | U (ppm)    | ( $^{231}\text{Pa}/^{235}\text{U}$ ) | ( $^{234}\text{U}/^{238}\text{U}$ ) |
|----------------------|--------------------------|------------|--------------------------------------|-------------------------------------|
| RW35                 | $509.2 \pm 6.2$          | $0.679^b$  | 2.222                                | nd <sup>f</sup>                     |
| RW35 <sup>e</sup>    | $504.8 \pm 3.6$          | 0.679      | 2.202                                | nd                                  |
| FON39                | $131.1 \pm 1.6$          | $0.472^c$  | 0.823                                | 1.009                               |
| LV18a                | $3459.5 \pm 29$          | $10.365^d$ | 0.989                                | nd                                  |
| LV18b <sup>e</sup>   | $3514.2 \pm 23$          | $10.508^d$ | 0.991                                | nd                                  |
| LV18(2) <sup>e</sup> | $3589.4 \pm 25$          | $10.549^d$ | 1.008                                | 1.010                               |
| LP96–36              | $297.5 \pm 2.1$          | $0.8778^d$ | 1.004                                | 1.000                               |
| LP96–36 <sup>e</sup> | $298.0 \pm 1.8$          |            |                                      |                                     |

<sup>a</sup> Uncertainties are  $2\sigma$  errors of the mean. Analyses were carried out using between 20 and 150 fg  $^{231}\text{Pa}$ . U concentrations were measured by isotope dilution. <sup>b</sup> Reference 29. <sup>c</sup> Reference 8. <sup>d</sup> this study. <sup>e</sup> Repeat analysis of a separate sample dissolution, using different batch of spike. Activity ratios calculated assuming  $\lambda_{^{231}\text{Pa}} = 2.116 \times 10^{-5} \text{ y}^{-1}$ ,  $\lambda_{^{235}\text{U}} = 9.8485 \times 10^{-10} \text{ y}^{-1}$ , and  $^{238}\text{U}/^{235}\text{U} = 137.88$ . <sup>f</sup>nd, not determined.

as an equilibrium standard for U-series nuclides, including the  $^{235}\text{U}$ – $^{231}\text{Pa}$  pair.<sup>4,5,13,15</sup> To evaluate the accuracy of this method of calibration, we determined  $^{235}\text{U}$  and  $^{231}\text{Pa}$  concentrations in two samples known to be  $>0.8$  Ma in age (unless alteration has mobilized U, these samples will be in  $^{231}\text{Pa}$ – $^{235}\text{U}$  equilibrium). Three separate dissolutions of a 1 Ma-old fresh rhyolitic glass from Long Valley (sample LV18) yielded ( $^{231}\text{Pa}/^{235}\text{U}$ ) values that were within 1.2% of equilibrium (Table 4), even though significantly different Pa and U concentrations were obtained for each dissolution due to heterogeneity in this coarsely crushed sample. A basaltic lava from La Palma, Canary Islands (sample LP96-36), which has a magmatic Rb/Ba ratio,  $^{234}\text{U}/^{238}\text{U}$  ratio within error of equilibrium, and is reversely magnetized (i.e., older than  $\sim 800$  ka), yielded  $^{231}\text{Pa}$  and U concentrations of 297.5 fg/g and 0.878 ppm, respectively, corresponding to a ( $^{231}\text{Pa}/^{235}\text{U}$ ) ratio of 1.004 (Table 4). These results suggest that we are able to measure Pa concentrations with an accuracy that is within the reproducibility of the measurements ( $\sim 1.2\%$ ). Based on these measurements, the precision and accuracy of Pa determinations using our method are similar to those obtained by TIMS on comparable or slightly larger sample sizes.<sup>15,16</sup> We also measured the  $^{231}\text{Pa}$  concentration of a young dacite (FON 39) from Tonga, which was previously analyzed by Bourdon et al.<sup>8</sup> The two determinations differ by  $\sim 6\%$ ; the reason for this discrepancy is not clear, although we note that our laboratories have used different secular equilibrium rock standards to calibrate  $^{233}\text{Pa}$  spike solutions.

## CONCLUSIONS

Our new method for the chemical separation and isotope analysis of Pa has several advantages over previous methods. The initial separation of Pa from the rock matrix is carried out using anionic exchange resin in HF, which is an advantage when analyzing silicate rocks, which must first be digested in HF–HCl–HNO<sub>3</sub>. Previous methods have required F<sup>−</sup> to be completely removed from the sample solution prior to each column step, which is difficult when dealing with large samples. Isotope measurements are carried out by multicollector inductively coupled plasma mass spectrometry, so that complete separation of Pa from the high field strength elements (which inhibit ionization of Pa by TIMS) is not necessary. Only three ion-exchange column steps are required, in contrast to previous methods for silicate samples that have used four or more,<sup>5,7,15</sup> thus reducing reagent volumes, blanks, and sample preparation time. Only 0.3 mL of TRU Spec resin is required per sample.

Using our method, the <sup>231</sup>Pa/<sup>233</sup>Pa ratio can be measured with a precision of ~0.5%, and a reproducibility (for rock samples) of ~1.2%, on as little as 20 fg of Pa. Further reduction in sample

size and analysis time could be achieved by using multiple ion counting to measure the 231 and 233 ion beams simultaneously. Detection limits could be decreased to <200 ag/mL by eliminating background hydrocarbon interferences on masses 231 and 233, thus allowing the measurement of attogram quantities of Pa, for example, in mineral separates from volcanic rocks.

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