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Separation and Measurement of Pa, Th, and U Isotopes in Marine Sediments by Microwave-Assisted Digestion and Multiple Collector Inductively Coupled Plasma Mass Spectrometry

Cesar Negre*, Alexander L. Thomas, Jose Luis Mas, Jordi Garcia-Orellana, Gideon M. Henderson, Pere Masque and Rainer Zahn

*Corresponding Author.

Separation and measurement of Pa, Th and U isotopes in marine sediments by microwave-assisted digestion and MC-ICP-MS

César Negre^{*1}, Alexander L. Thomas², José Luis Mas³, Jordi Garcia-Orellana^{1,4}, Gideon M. Henderson²,
Pere Masqué^{1,4}, Rainer Zahn^{1,5,6}

¹ Institut de Ciència i Tecnologia Ambientals (ICTA), Universitat Autònoma de Barcelona, 08193
Bellaterra, Spain.

² Department of Earth Sciences, Oxford University, Parks Road, Oxford, OX1 3PR, United Kingdom.

³ Departamento de Física Aplicada I. Escuela Universitaria Politécnica (Universidad de Sevilla), Virgen
de Africa 7, 41012 Sevilla, Spain.

⁴ Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain.

⁵ Institució Catalana de Recerca i Estudis Avançats (ICREA), Lluís Companys 23, 08010 Barcelona,
Spain

⁶ Departament de Geologia, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

cesar@negre.us, alexander.thomas@earth.ox.ac.uk, ppmasb@us.es, jordi.garcia@uab.cat,
gideon.henderson@earth.ox.ac.uk, pere.masque@uab.cat, rainer.zahn@uab.cat

*Corresponding author: Tel +34-935811191. Fax +34-935813331. E-Mail: cesar@negre.us

This manuscript describes a new protocol for determination of Pa/Th/U in marine sediments. Based on microwave-assisted digestion, it represents an important reduction of working time over conventional hot-plate digestion methods, and the use of HClO₄ is avoided. While Th and U are completely dissolved with a first microwave step, around 40% of ²³¹Pa remains un-dissolved and a short hot-plate step with reverse *aqua regia* is required to achieve total digestion and spike equilibration. Next, the method involves a separation of these elements and a further purification of the Pa fraction using Dowex AG1-X8 resin. Separation with Bio-Rad and Sigma-Aldrich resins was compared; while both perform similarly for Th and U, Pa yields are higher with Bio-Rad. Finally, samples are measured using a Nu instruments Multiple Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS). Overall chemical yields range around 50% for Pa, 60% for Th and 70% for U.

Keywords: protactinium, uranium series, sediment microwave digestion, anion exchange separation, MC-ICP-MS

INTRODUCTION

The development of Pa, Th, U geochemistry in Earth Sciences research as tracers and chronometers of natural processes, such as magma genesis ^[1], carbonate dating ^[2], ocean circulation and past export productivity ^[3], has relied on the improvement of analytical techniques. Analysis of such radiogenic elements in deep-sea sediments has been performed for many years ^[4], together with the development of alpha and beta spectrometry, which have been the traditional analytical tools. The appearance of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and more specifically of MC-ICP-MS in recent years offers great advantages such as an improvement of detection limits and greater precision, coupled with a rapid sample throughput ^[5,6].

In line with ICP development, microwave-assisted digestion has been used as a sediment pre-treatment method for an increasing number of applications ^[7]. However, application for Pa/Th/U analysis is limited ^[8,9] and microwave protocols have not been published. This manuscript provides full

details of a new microwave-assisted digestion protocol for Pa/Th/U determination in marine sediments. Conventional digestion techniques use open vessels or Teflon bombs applying hot plate heating with HCl, HNO₃, HClO₄, HF and/or H₃BO₃ in a sequence of multiple addition-heating steps [4,8,10]. Microwave, in turn, enables to directly and rapidly heat the sample solvent mixture, and allows a precise control of temperature and pressure, making total dissolution faster. Total dissolution is essential to quantify and differentiate between detrital, authigenic and scavenged components of Pa, Th and U in sediments, necessary for their use as tracers of natural processes. With microwave assistance, temperature is not limited to the boiling point of the reagents, thus making it easier to achieve complete digestion without HClO₄, which requires specially adapted facilities (e.g. fume hood wash-down equipment). In addition, volumes of solvents are typically reduced by a factor up to 10 contributing to blank minimization and reducing the time spent for sample dry-down.

A good chemical separation of Pa, Th and U from one other and from other elements is essential to ensure an accurate quantification with MC-ICP-MS. To avoid organic contamination, separation using anion exchange resins has proved preferable over solvent extraction techniques [11]. Such methods are based on the different and variable resin affinity of these elements under changing acid media. Pa separation is especially complicated because of its tendency to be removed from solution by hydrolysis and the necessity to completely eliminate any fluorides generated during digestion. Resins used with success for Pa/Th/U separation include Dowex AG MP-1 [8], TRU-Spec [12], and Dowex AG1-X8 [13].

In this article we describe a new protocol for the extraction, separation and measurement of Pa, Th and U from marine sediments, performing microwave-assisted digestion with HNO₃, HF and HCl, using Dowex AG1-X8 anion exchange resin for element separation, and MC-ICP-MS for quantification. We also show and discuss results obtained from experiments carried out to test the suitability of key parts of the method: (1) microwave-assisted vs. hot-plate-based digestion methods (2) a reverse *aqua regia* step, and (3) Pa monitoring through the elemental separation.

EXPERIMENTAL SECTION

Samples. Sediment reference materials exist for ^{230}Th , ^{232}Th , and ^{238}U but not for ^{231}Pa . Hence we used a suite of marine sediment samples from cores MD02-2594 (34.71°S; 17.34°E; 2440 m water depth) and MD02-2588 (41.12°S; 25.30°E; 2907 m water depth) from the South Atlantic. 76 samples were analyzed, 28 of which were replicated 2 or 3 times with the aim to derive method precision and/or test the different parts of the protocol, among them: (a) 2 samples for microwave digestion validity (1 and 2, Tab. 1), (b) 7 samples for the reverse *aqua regia* clean-up step (2 to 8, Fig. 2), and (c) 4 samples for comparing Dowex AG1-X8 Bio-Rad and Sigma-Aldrich resins (9 to 12, Fig. 3).

Equipment. For sample dissolution we used a Microwave Sample Preparation System, Model MDS-2000 (CEM Corporation, Matthews, NC, USA). Maximum power output is 630 W at a frequency of 2450 MHz, programmable at 1% increments. The system is equipped with a Pressure Control System for controlled pressure conditions up to 1.38 MPa (200 psi) inside a single closed vessel during heating.

Isotope abundances were measured with a Nu Instruments Multiple Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) ^[14], coupled to a Nu Instruments DSN-100 desolvating nebulizer with a typical uptake rate of 100 μL per min. Beam voltage is measured across 10^{11} Ω resistors, and sensitivities were ~ 100 V/ppm. A retardation filter on the central ion counter (Tab. 1) reduces abundance sensitivity to 2×10^{-7} and 1×10^{-7} at 2 and 3 atomic mass units below ^{232}Th , respectively.

Pa yields were determined by gamma detection of ^{233}Pa with a CANBERRA model GCW3522 germanium semiconductor, connected to a preamplifier 2002CSL and an analogical-digital converter CANBERRA 8701. Total detection efficiency is 22.7% at 312 keV with 1.52 keV resolution (FWHM), assessed with a ^{237}Np standard solution. The detector is confined inside a 15 cm thick iron shielding to minimize background.

Reagents and materials. HCl 32% m/v PA Merck, HNO₃ 65% PA Merck, HF 40% PA-ISO Panreac and $18 \text{ M}\Omega\text{cm}^{-1}$ water (Milli-Q) were used in order to minimize sample contamination.

Dowex AG1-X8 anion exchange resin, chloride form, 100-200 mesh (80-150 μm particle size; Bio-Rad and Sigma-Aldrich Laboratories) was used for separation of Th, Pa and U, and further purification of Pa fractions. Silica gel 40-63 μm particle size (230-400 mesh ASTM; Sigma-Aldrich) was used for the preparation of the ^{233}Pa spike. As resin support, conical polypropylene columns with 2 mL bed volume (8 mm internal diameter) plus 10 mL reservoir (Bio-Rad Laboratories) were employed.

Internal tracers used were ^{233}Pa , ^{229}Th and ^{236}U . ^{233}Pa spikes were prepared by milking a ^{237}Np solution of 100.2 kBq, (Eckert & Ziegler Isotope Products, Valencia, CA, USA) adapting the protocol described in Regelous et al. [15]. ^{231}Pa impurities in the ^{233}Pa spike, stemming from the ^{237}Np solution, were quantified during a preliminary calibration soon after milking and therefore before decay of ^{233}Pa to ^{233}U . After a 6 months waiting period to allow nearly total decay to ^{233}U , ^{233}Pa spikes were calibrated by MC-ICP-MS against a well known ^{236}U standard [16]. This approach allows the ^{233}Pa concentration to be measured from a $^{233}\text{U}/^{236}\text{U}$ ratio and the ^{231}Pa from a $^{231}\text{Pa}/^{233}\text{Pa}$ ratio, therefore eliminating the effect of elemental fractionation within the mass spectrometer. ^{229}Th and ^{236}U sources were prepared at the Universitat Autònoma de Barcelona by dilution of certified reference solutions (^{229}Th , 73473-759, Analytcs, Atlanta, GA, USA; and ^{236}U , 1168-70, Isotope Products Europe, CA, USA). For MC-ICP-MS measurement corrections, uranium (CRM-145, New Brunswick Laboratory, NJ, USA) and thorium (Cat # 100059-1, High-Purity Standards, Charleston, SC, USA) standards were used.

To avoid deposition of Pa on the walls of glassware [17], polypropylene (PP) or polytetrafluoroethylene (PTFE) material was used.

Method. The analytical procedure for the measurement of Pa, Th, and U in sediments consists of three steps: sample digestion, element separation with anion exchange resin and MC-ICP-MS measurement (Fig. 1). Prior to digestion, samples were freeze dried and ground to a fine powder and homogenized with a ceramic mortar. Immediately before weighing, samples were heated at 60 °C to a constant weight to completely remove moisture.

Aliquots of about 0.20 g of sediment were placed in 100 mL microwave PTFE liners and weighed with a microbalance (to 1×10^{-4} g precision). Samples were covered with 2 mL of Milli-Q water and

traced with ^{236}U (36 mBq), ^{229}Th (0.32 Bq) and ^{233}Pa (~4 Bq) spikes. Next, a mixture of concentrated $\text{HNO}_3\text{:HCl:HF}$ (10:4:6 mL) was added to dissolve CaCO_3 and break down aluminosilicates. After 12 hours for tracer homogenization, samples were run in the microwave at 0.69 MPa for 5 min and at 0.90 MPa for an additional 30 min ^[18]. Samples were left to cool and transferred to PTFE beakers. To minimize the loss of sample by adsorption onto the microwave liner, the interior of each vial was rinsed with about 2 mL of HNO_3 . Beakers were heated at 140 °C to reduce solution volume to incipient desiccation. As an additional clean-up step, 9 mL of reverse *aqua regia* (6 mL HNO_3 + 3 mL HCl) were added to remove remaining organic matter from the solution. Samples were dried once more at 140 °C and redissolved in 6 mL of HNO_3 . This operation was repeated twice in order to remove fluorides. Samples were finally dissolved in 4 mL of HNO_3 7.5M, ready for anion exchange.

Pa, Th and U were separated adapting the procedure described in Edwards et al. ^[19]. This involves (1) washing of 2 mL of Dowex AG1-X8 anion exchange resin per column with 10 mL Milli-Q, 10 mL HCl 6M, 10 mL Milli-Q and pre-conditioning with 10 mL HNO_3 7.5 M; (2) loading samples onto the resin; (3) washing columns with additional 4mL of HNO_3 7.5 M and converting to chloride form with 1.5mL HCl 6M; (4) eluting Th, Pa, and U with 6 mL of HCl 6 M, 6mL HCl 6 M + HF 0.05 M, and 6 mL Milli-Q water, respectively; (5) drying Pa fractions and subsequent recovery with 4 mL of HNO_3 7.5M; (6) purification of these Pa fractions in a second ion exchange separation, repeating steps 1-4. The second Pa purification is required to improve Pa:Th separation so as to reduce the interference of ^{232}Th hydrides to the ^{233}Pa beam during measurement.

The day prior to MC-ICP-MS measurement, Pa, Th and U fractions were reduced to a single drop and recovered in 1 mL of distilled 2% HNO_3 . Small and diluted aliquots of the Th and U fractions were used for a rapid concentration check of ^{238}U and ^{232}Th in the multi-collector to optimize their intensities in the final measurements at ~4V. U, Th and Pa isotope abundances were then measured by MC-ICP-MS at Oxford University following standard protocols ^[16] (Tab. 2). Uranium was measured statically with ^{234}U in an ion counter, correcting for machine biases by bracketing each sample with a measurement of CRM-145 uranium standard. Thorium was measured in a two-step dynamic routine, correcting for

intensity variation by normalising to ^{235}U measured in each step. In cases where the sample ^{235}U signal in the diluted Th fractions was below 5 mV (i.e. ~50ppt solution concentrations of ^{235}U), CRM-145 U standard was added to the Th solutions to increase the beam size to ~10 mV to facilitate this correction. While the 230/229 measurement does not require correction for ion counter efficiency the 232/229 mass ratio is corrected using the standardised $^{235}\text{U}/^{234}\text{U}$ ratio of CRM-145 measured with ^{234}U in the ion counter. Protactinium analyses were made using multiple ion counting channels. Typical ^{231}Pa beam sizes were 10^{-7} - 10^{-6} V. Ion-counter gain and mass bias were measured by preceding each sample analysis with a CRM-145 U standard measurement. Abundance sensitivity and molecular interferences were assessed by measuring a ^{232}Th standard solution, as if it was a Pa sample, monitoring the ^{232}Th hydride and tailing contributions at the masses of interest. After corrections, $^{231}\text{Pa}/^{232}\text{Th}$ ratios in the Pa fraction were in the order of 3×10^{-5} . Abundance sensitivity originating from U isotopes is negligible because of the good separation of U from Pa in the two-step anion exchange, typical $^{231}\text{Pa}/^{238}\text{U}$ ratios measured in the Pa fraction were around 6×10^{-3} .

RESULTS AND DISCUSSION

Microwave-assisted digestion with reverse *aqua regia* clean-up step. The suitability of the additional clean-up step was assessed by processing 7 samples (2-8, Fig. 2) with and without reverse *aqua regia*. For reference, sample 2 was also analysed following the hot-plate methodology described by Thomas et al. [20]. While both techniques produced equivalent Th and U specific activities, Pa was systematically lower by an average of 40% in samples not exposed to reverse *aqua regia*. Results indicate that microwave-assisted digestion achieves a complete extraction of Th and U, but ^{231}Pa becomes only partially extracted and full spike equilibration is not achieved. Incomplete digestion leads in some ^{231}Pa either passing through the resin too quickly or being retained on the columns. This loss is reflected in the low $^{231}\text{Pa}/^{233}\text{Pa}$ measured in Pa fractions. Total Pa spike equilibration requires the more aggressive chemical treatment with the additional reverse *aqua regia* step that removes organic matter

as a potential binder of non-extracted ^{231}Pa . Using reverse *aqua regia*, ^{231}Pa results reproduce those achieved with hot-plate digestion (Tab. 1) suggesting that microwave-assisted digestion enables adequate dissolution of all Pa, Th and U isotopes as long as the reverse *aqua regia* step is used.

Anion exchange separation. Very low concentrations of ^{231}Pa in marine sediments require optimizing Pa recoveries hence making ion exchange elemental separation particularly critical. Pa behaviour was studied in 2 batches of 11 samples (4 replicates, shown in Fig. 3) and a procedural blank each, that were processed with Dowex AG1-X8 provided by two different manufacturers, Bio-Rad and Sigma-Aldrich Laboratories. ^{233}Pa content in each fraction after the first ion exchange separation was monitored by gamma spectrometry (Fig. 3a). Results show higher Pa yields using the Bio-Rad Laboratories resin, with $(61 \pm 8)\%$ of Pa being recovered in the Pa fraction (at a rate of 10% per mL) when pouring HCl 6M with HF traces through the resin. With Sigma-Aldrich resin only a $(12 \pm 14)\%$ of Pa was recovered in the Pa fraction, likely due to some matrix effect affecting Sigma-Aldrich resin more than Bio-Rad. This conclusion is supported by optimum Pa behaviour in (a) both procedural blanks, (b) the second Pa purification step, and (c) the improvement of Pa recoveries up to 80% when smaller amounts of sediment (~ 0.1 g) were processed. Using Bio-Rad, more Pa was eluted with the Load and Washing fraction than with Sigma-Aldrich (3.8 against 2.5% per mL), but very little was lost into the Th fraction (0.6% per mL) compared to Sigma-Aldrich (10% per mL). Loss of Pa into the Load and Wash fraction was likely a consequence of competition with other anions in the sample dissolution. In order to maximize Pa recoveries resin volumes shall be increased, or less sediment processed.

Recoveries, validity, precision and uncertainties. Overall average recoveries at the time of measurement were $(53 \pm 12)\%$ with Bio-rad ($n=66$, 1σ) versus $(24 \pm 19)\%$ with Sigma-Aldrich ($n=44$, 1σ). Despite the low recoveries achieved with the Sigma-Aldrich resin, Pa was nonetheless quantified accurately (Fig. 3b) thanks to adequate spike equilibration during microwave digestion (including *aqua regia*) and a detection limit of the MC-ICP-MS of about 3×10^{-8} V ($\sim 3 \times 10^{-4}$ ppt) in the central ion counter. This is reflected in the ^{231}Pa concentration results, which are similar between the two resins (to

within a $\pm 2.7\%$ mean deviation) regardless of recovery efficiency. Both resins performed equally well for Th and U. Recoveries for Th were $\sim 60\%$ and for U $\sim 70\%$, resulting in concentrations exceeding by one order of magnitude those necessary for optimum MC-ICP-MS measurements.

Two samples were prepared by hot plate digestion, under ultra-clean laboratory conditions, following the protocol described in Thomas et al.^[20]. Results of this techniques agree well with those of microwave-assisted digestion for all isotopes; offsets between mean results were 2.2% for ^{231}Pa , 4.5% for ^{230}Th , 6.9% for ^{232}Th and 6.2% for ^{238}U (Tab. 1). Hot-plate-based Pa yields were $(59 \pm 12)\%$ ($n=11$, 1σ), similar to those achieved by the microwave-assisted protocol while digestion time was 3 times longer (6 days in total). No significant differences were observed in Th and U yields.

Method precision for the entire procedure from dissolution through to analysis (i.e. including any possible sample heterogeneity) was 7.0% (1σ) for ^{231}Pa (based on 15 samples with 2 or 3 replicates each, 36 replicates in total), 1.6% for ^{230}Th , 4.6% for ^{232}Th and 2.7% for ^{238}U (28 samples with 2 to 4 replicates each, 73 replicates). The worse precision for Pa compared to Th and U is likely due to (a) Pa being more difficult to extract from sediments; (b) production of ^{233}U from ^{233}Pa decay in the samples that produces different ionization at the time of measurement; (c) need for different – separately calibrated – sets of ^{233}Pa spikes for different batches (because the ^{233}Pa spike decays with a half life of 26.97 days); (d) relatively high abundance of Pa in blanks with respect to the natural ^{231}Pa concentrations in sediments.

In run uncertainties (1σ) of single measurements were on average $<2\%$ for all isotopes ($n=131$). In the case of Th and U, around 90% of the uncertainties were derived from concentration uncertainties of the internal ^{229}Th and ^{236}U tracers. For Pa, the spike concentration accounted for only 10% of overall uncertainties and, due to the low amounts of ^{231}Pa in the samples, most of the uncertainties were linked with the measurement of isotope ratios by MC-ICP-MS. Other minor contributors to the uncertainties were sample and spike weighing, and blanks. Total procedural blanks were $(17 \pm 12) \times 10^{-3}$ mBq of ^{231}Pa , $(22 \pm 3) \times 10^{-2}$ mBq ^{230}Th , $(7 \pm 3) \times 10^{-3}$ mBq ^{232}Th and $(13 \pm 6) \times 10^{-3}$ mBq ^{238}U ($n=10$).

CONCLUSIONS

Microwave-assisted pre-treatment with an additional clean-up step of reverse *aqua regia* permits a complete extraction of Pa, Th and U from sediments. A single microwave step with a mixture of HNO₃:HCl:HF is sufficient for a total extraction of Th and U isotopes, while a complete extraction of ²³¹Pa requires an additional hot-plate step with reverse *aqua regia*.

Elemental separation is more efficient using Dowex AG1-X8 Bio-Rad Laboratories resin, as indicated by superior Pa yields. A matrix effect further limits Pa attachment to the Sigma-Aldrich resin when eluting with HCl 6M so that most of it was lost before the Pa fraction elution. U and Th separation, however, is successful with both resins.

The complete procedure represents a measurable reduction of time over traditional protocols based on a pure hot-plate digestion. Hot-plate-based digestion requires about one week digestion time while microwave-assisted digestion produces the same results within two days.

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Figure 1. Protocol summary scheme.

Figure 2. Results of the experiment for the suitability of the reverse *aqua regia* clean-up step for (a) ^{231}Pa ; (b) ^{238}U ; (c) ^{230}Th ; (d) ^{232}Th . Open triangles represent results applying reverse *aqua regia* after the first microwave step; light grey squares are results without using this reagent; as reference, closed circles show results obtained following the methodology described in Thomas et al. ^[20], performing hot plate digestion with open vessels and using HClO_4 .

Figure 3. Pa behaviour through the anion-exchange separation process. (a) Pa contents in the different column eluate fractions. Comparison using Dowex AG1-X8 Sigma-Aldrich and Bio-rad for 4 duplicate samples (9-12) and procedural blanks (Bk). Pa content was quantified by gamma counting (represented as % of the spiked ^{233}Pa) in all the output fractions: sample load and washing in HNO_3 7.5M, conversion to HCl 6M, Th (in HCl 6M), Pa (HCl 6M + HF 0.05M), U (Milli-Q water) and column remainder. For Sample 9 Bio-rad, load & wash, conversion and column fractions could not be measured. In the procedural blanks, no ^{233}Pa was detected in fractions other than Pa. Divergences of total measured ^{233}Pa with respect to the total 100% initially spiked is due to measurement uncertainties and possible losses during beaker transfers at pre-treatment. (b) ^{231}Pa specific activities obtained after MC-ICP-MS measurements of the Pa fraction in these same samples, after performing an additional Pa purification step. Closed diamonds represent separation using Bio-rad resin and white circles, Sigma-Aldrich. See text for details.

Table 1. Results obtained for ^{231}Pa , ^{238}U , ^{230}Th and ^{232}Th with the microwave-assisted digestion method proposed in this paper and following a hot plate based digestion method described in Thomas et al. ^[20]. Units are Bqkg^{-1} .

Table 2. MC-ICP-MS configuration for U, Th and Pa measurements showing all detectors and masses collected (F: Faraday collector; IC: Ion Counter). Adapted from Thomas et al. ^[16].

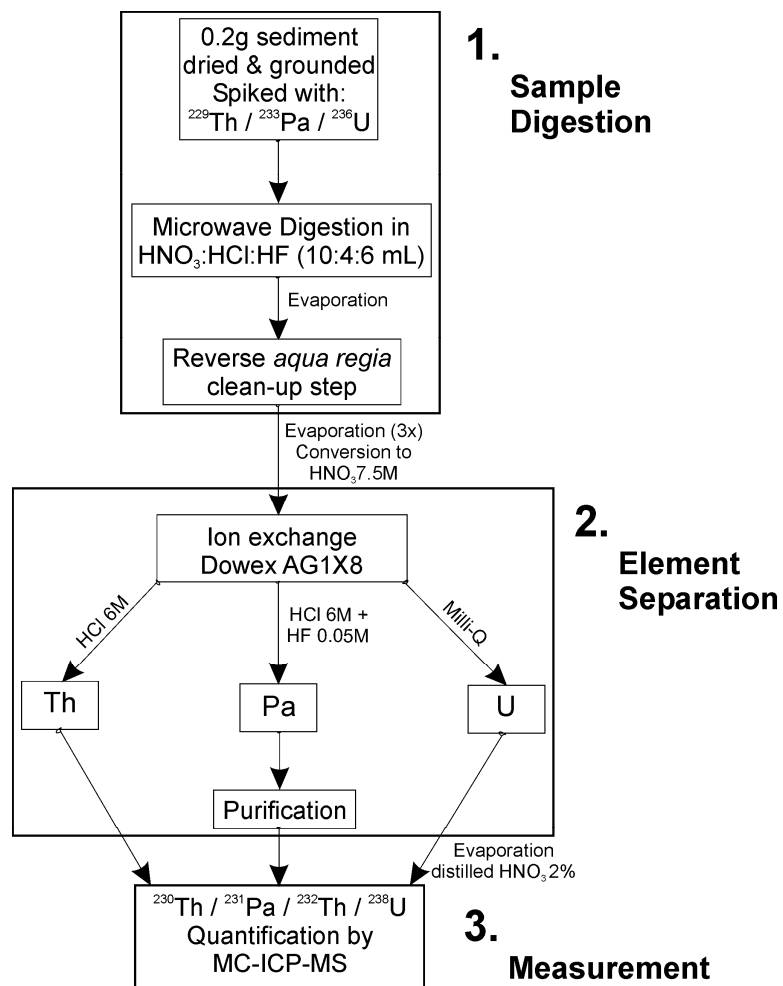


Figure 1.

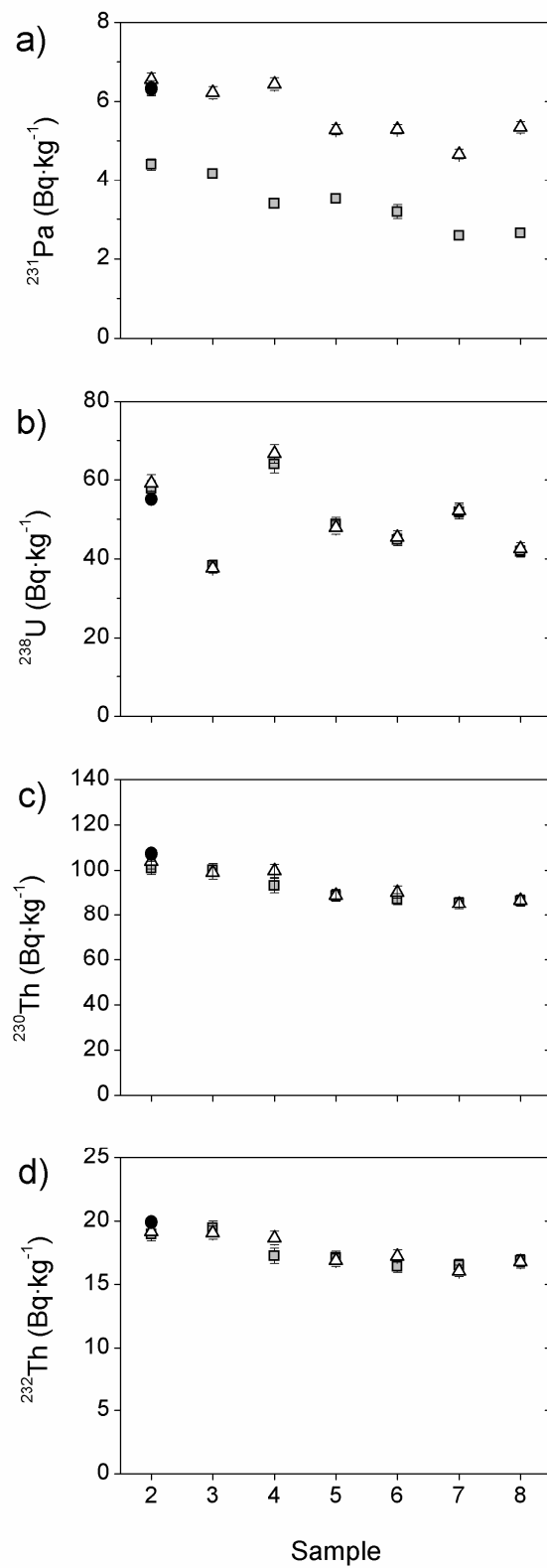


Figure 2.

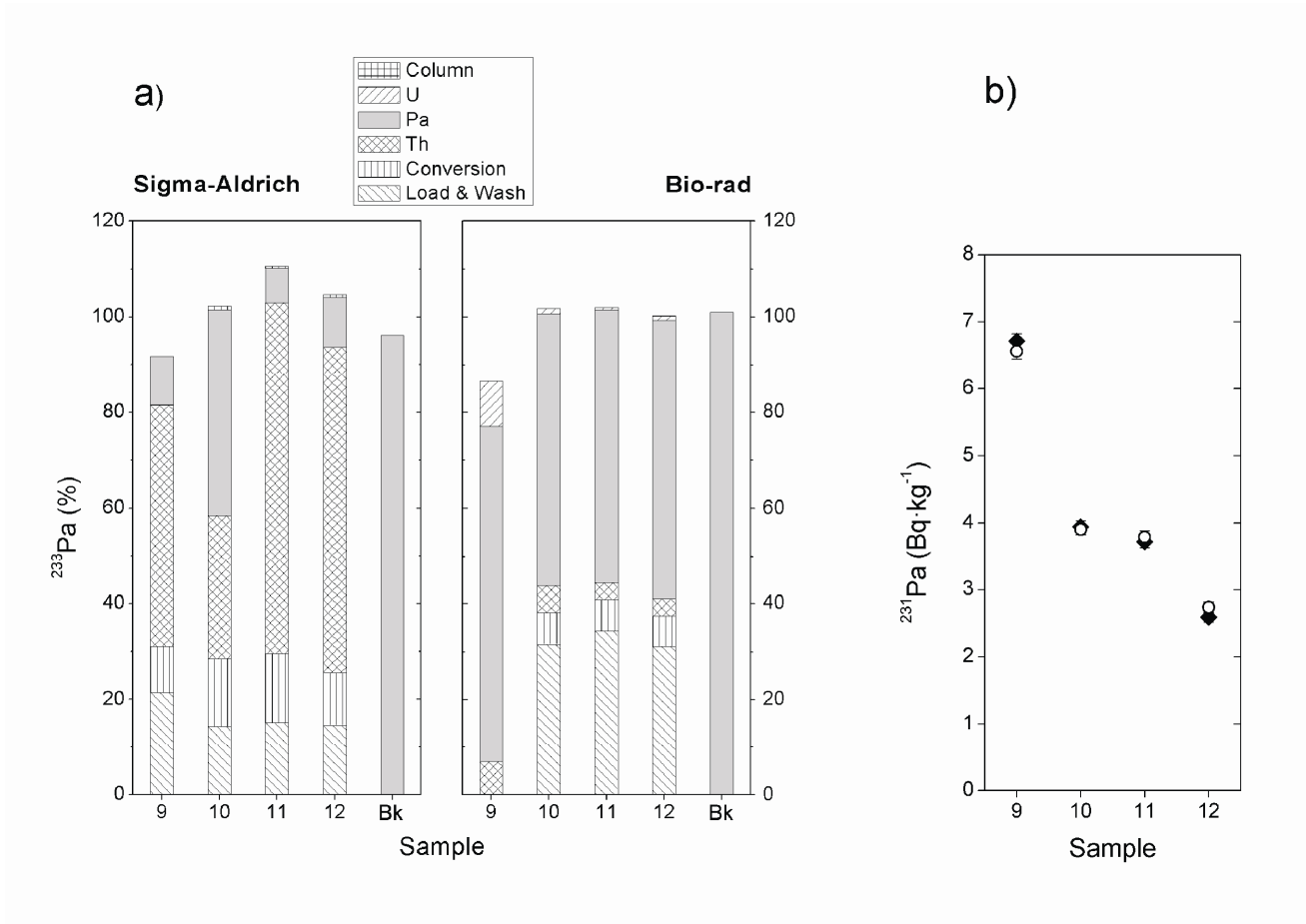


Figure 3.

Sample	Microwave-assisted digestion method				Hot plate digestion method			
	^{231}Pa	^{238}U	^{230}Th	^{232}Th	^{231}Pa	^{238}U	^{230}Th	^{232}Th
1	2.57 ± 0.08	56 ± 2	65 ± 2	11.1 ± 0.4	2.73 ± 0.13	52.18 ± 0.10	67.1 ± 0.6	12.68 ± 0.16
	2.57 ± 0.09	-	65 ± 3	11.0 ± 0.4	2.54 ± 0.13	53.18 ± 0.10	68.7 ± 0.7	11.09 ± 0.17
2	6.56 ± 0.15	59 ± 2	104 ± 3	19.2 ± 0.5	6.35 ± 0.18	55.21 ± 0.11	107.6 ± 0.9	19.9 ± 0.2
	6.78 ± 0.11	59 ± 2	103 ± 5	18.4 ± 0.7	6.31 ± 0.17	55.02 ± 0.11	107.0 ± 1.3	19.9 ± 0.3
	5.99 ± 0.11	58 ± 2	101 ± 4	18.7 ± 0.7	-	-	-	-

Table 1.

		STEP	F(+7)	F(+5)	F(+3)	F(+2)	F(+1)	AXIAL	F(-1)	F(-2)	IC(-3)	F(-4)	IC(-5)	F(-6)	IC(-7)	F(-8)
Bracketing CRM 145 standard	Pa	1					238			235	234					
		2							238			235	234			
	Th	3							238			235	234			
Uranium		4					238		236	235	234					
Thorium		5					235			232		230	229			
		6			238			235					230	229		
Protactinium		7				238		236	235		233	232	231		229	

Table 2.