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A simple-rapid method to separate uranium, thorium, and protactinium for U-series age-dating of materials

Andrew W. Knight^{a,1}, Eric S. Eitrheim^{a,2}, Andrew W. Nelson^{b,3}, Steven Nelson^{c,4}, and Michael K. Schultz^{d,*}

^aDepartment of Chemistry, E373 CB, The University of Iowa, Iowa City, IA 52246, USA

^bInterdisciplinary Human Toxicology Program, E373 CB, The University of Iowa, IA 52246, USA

^cDepartment of Geological Sciences, Brigham Young University, S389 ESC, Provo, UT 84602, USA

^dDepartments of Radiology and Radiation Oncology, Free Radical and Radiation Biology Program, Interdisciplinary Human Toxicology Program, The University of Iowa, ML B180 FRRB, 500 Newton Road, Iowa City, IA 52246, USA

Abstract

Uranium-series dating techniques require the isolation of radionuclides in high yields and in fractions free of impurities. Within this context, we describe a novel-rapid method for the separation and purification of U, Th, and Pa. The method takes advantage of differences in the chemistry of U, Th, and Pa, utilizing a commercially-available extraction chromatographic resin (TEVA) and standard reagents. The elution behavior of U, Th, and Pa were optimized using liquid scintillation counting techniques and fractional purity was evaluated by alpha-spectrometry. The overall method was further assessed by isotope dilution alpha-spectrometry for the preliminary age determination of an ancient carbonate sample obtained from the Lake Bonneville site in western Utah (United States). Preliminary evaluations of the method produced elemental purity of greater than 99.99% and radiochemical recoveries exceeding 90% for U and Th and 85% for Pa. Excellent purity and yields (76% for U, 96% for Th and 55% for Pa) were also obtained for the analysis of the carbonate samples and the preliminary Pa and Th ages of about 39,000 years before present are consistent with ¹⁴C-derived age of the material.

Keywords

Uranium; Thorium; Protactinium; Age dating; Geochronology

*Corresponding author. Tel.: +1 319 335 8017.

¹Tel.: +1 651 233 7856.

²Tel.: +1 715 308 5704.

³Tel.: +1 303 261 2656.

⁴Tel.: +1 801 422 8688.

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1. Introduction

Radiometric age-dating techniques are powerful tools that are used often to understand geological events; describe geochemical processes; and more recently, to develop understanding of materials for nuclear forensic analysis. Because the nuclear half lives ($t_{1/2}$) of the radionuclides involved are well known, radiometric techniques have the potential to reveal precise information regarding the time (t_0) at which a parent and daughter were separated biogeochemically. For geochronology applications, precise knowledge of $t_{1/2}$ is combined with understanding of distinct differences in the geochemical behavior of radionuclides to establish assumptions that guide the selection of parent/daughter relationships that are relevant to answering the geochemical question at hand. Thus, known radioactive daughter-ingrowth can be used to extrapolate radiometric measurements (performed today) to a time in the past when parent/daughter radionuclide disequilibrium is likely to have occurred. For environmental science applications, this information can be used to estimate geomorphic growth rates (Sims et al., 2013) and sedimentation rates (Aller and Cochran, 1976); as well as to obtain information about the rates of weathering of geological formations (Chabaux et al., 2013). For nuclear forensic applications, this information represents a powerful tool that can be combined with other forensic evidence to develop a more detailed understanding of the process, time, and location from which the material may have originated (Morgenstern et al., 2002; Eppich et al., 2013).

A mainstay for the last four decades in age-dating materials for various geochronology applications involves the disequilibria and daughter ingrowth of radionuclides in the natural U and Th decay series (^{238}U , ^{235}U , ^{232}Th) (Bourdon et al., 2003). With $t_{1/2}$'s ranging from billions of years to microseconds, U-series radionuclide disequilibria enable observers to obtain temporal information for a variety of chronometric uses (Ivanovich et al., 1992). Several excellent reviews provide detailed descriptions of the underlying assumptions that form the foundation for various time-dependent phenomena that can be described, and the time frame within which specific parent–daughter relationships can be most effectively employed. For timescales between approximately 10 k–375 k years before present, two of the most commonly used disequilibria employed are $^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ (Ivanovich et al., 1992; Bourdon et al., 2003; Peate and Hawkesworth, 2005; Martínez-Aguirre and Alcaraz Pelegrina, 2013). Because Th and Pa ages can be confirmatory, radioanalytical methods developed for U-series radiochronometry applications have sought to combine the analysis of Th, Pa, and U in a single analytical run. Methods of analytical quantification for these analyses include isotope dilution alpha-spectrometry and (more recently) mass spectrometry (Mola et al., 2014; Pickett et al., 1994).

Numerous approaches to radiochemical separations have been established for U-series radiochronometry (Morgenstern et al., 2002; Regelous et al., 2004; El-Sweify et al., 2009). Early methods using standard ion-exchange technologies and liquid–liquid extraction were effective, but often suffered from relatively low radiochemical yields in the analysis of more complex matrices. Low radiochemical yields potentially increase the detection limits of the approach, which can be particularly detrimental to Pa dating, due the relatively low natural abundance of Pa in terrestrial samples (<300 fg/g, <0.03 dpm/g) (Regelous et al., 2004; Negre et al., 2009; Koornneef et al., 2010; Jeandel et al., 2011). In addition, relatively large

quantities of acid and mixed organic/acid waste prompted the development of improved approaches. While more recent methods have improved radiochemical yields, in general, two or more columns are usually employed, which complicates the process and can result in relatively large volumes of chemical waste (Koornneef et al., 2010). Within this context, we explored the potential to develop a new method, which might combine improved elemental purity of U, Th, and Pa fractions, with fewer steps, and less waste. In this paper, we describe this new method and present the application of the approach for the isotope dilution alpha-spectrometry analysis and preliminary age determination of an ancient carbonate sample obtained from the Lake Bonneville site in western Utah (Makarova et al., 1983; Oviatt, 1997). The method is relatively rapid; produces only small amounts of chemical waste; utilizes a commercially-available extraction chromatographic resin (TEVA; Eichrom Technologies, Inc.); and employs standard laboratory reagents.

2. Materials and methods

2.1. General

Radioactivity standards were prepared in Aristar Ultra (Sigma-Aldrich) nitric acid (HNO_3 , metals grade, certified to parts per trillion metal, PPT, purity), which had been diluted to working concentrations using ultra-pure distilled-deionized water of similar certified metal content (Baseline[®], Seastar Chemicals, British Columbia, Canada). Tracers were prepared from Standard Reference Materials (SRM's) obtained from the United States (USA) National Institute of Standards and Technology (NIST, Gaithersburg, MD USA) or from NIST-traceable certified reference materials (CRM's, Eckert Ziegler Radioisotopes, Atlanta, GA USA). Analysis of U consisted of Natural-U (U-NAT, CRM 92564) and ^{232}U standards (CRM 92403), certified to be in secular equilibrium with ^{228}Th , which was used as a tracer for Th analysis. A control standard ^{230}Th (SRM 4342A) was purchased from NIST. Radiochemical yields for Pa analysis were achieved by isotope dilution techniques using ^{233}Pa tracer, prepared by solvent extraction from ^{237}Np (CRM 92566). Tracers were prepared within six months of studies presented here and tracer solutions were stored in double-sealed plastic bottles (certified for low metal content, Seastar Chemicals) and stored at 5 °C continuously to minimize potential evaporation effects. Acids and salts used for radiochemical separations included: HNO_3 ; hydrochloric acid (HCl); hydrofluoric acid (HF); perchloric acid (HClO_4); sulfuric acid (H_2SO_4); and ammonium bioxalate $[(\text{NH}_4)_2\text{C}_2\text{O}_4]$ and were ACS reagent grade purity (Fischer Scientific) or higher. Chemicals used for electrodeposition included: sodium sulfate (Na_2SO_4); sodium bisulfate (NaHSO_4); potassium hydroxide (KOH); and ammonium hydroxide (NH_4OH) and were reagent grade (Fisher Scientific). Half-lives and alpha-particle emission energies stated are values originating from the Evaluated Nuclear Structure Data File (ENSDF) and were obtained through United States National Nuclear Data Center (NNDC, Brookhaven National Laboratory, US Department of Energy). Unless otherwise stated explicitly, all uncertainties cited are "standard uncertainties," corresponding to a coverage factor $k=1$ (Currie, 1968). Acid dependencies of extraction chromatographic resins were identified from the manufacturer's website and can be found at www.eichrom.com.

2.2. Safety considerations

Solutions containing HF and HClO₄ are potentially dangerous and appropriate personal protective equipment should be used when using these acids. Similarly, use of radioactive materials is potentially hazardous and appropriate ALARA principals should be considered prior to conducting experiments using radioactive materials.

2.3. Radiotracer preparation

The isotopic tracers used for this study were ²³²U/²²⁸Th, and ²³³Pa. The ²³²U ($t_{1/2}$ = 68.81 years) tracer used is in radioactive equilibrium with daughter ²²⁸Th ($t_{1/2}$ = 1.9 years). Control spikes used for method validation were U-NAT and ²³⁰Th ($t_{1/2}$ = 7.5×10^4 years). The U-NAT standard solution contains natural U isotopes; ²³⁸U ($t_{1/2}$ = 4.5×10^9 years), ²³⁵U ($t_{1/2}$ = 7.0×10^8 years), and ²³⁴U ($t_{1/2}$ = 2.5×10^5 years) in natural abundances. Radioactive standard solutions were prepared by serial dilutions, which were performed volumetrically (with gravimetric and radiometric confirmations), with dilutions of 5- and 500-fold performed in 1.0 M Aristar Ultra HNO₃ to obtain final-working secondary-standard solutions. Volumetric dilution factors for standards were confirmed gravimetrically and radiometrically (*via* liquid scintillation counting (LSC) and alpha-spectrometry) to within 2% for all radiotracers employed, according to our quality control protocols. Radiotracers and control spikes were added using calibrated volumetric pipets according to our routine procedures.

Radiochemical yield determinations for Pa were carried out using an isotopically-pure ²³³Pa ($t_{1/2}$ = 26.967 days) solution obtained *via* solvent extraction isolation from ²³⁷Np ($t_{1/2}$ = 2.14×10^6 years) based on procedures described previously with slight modifications (Fig. 1) (Sill, 1966; McCabe et al., 1992; Burnett and Yeh, 1995). Briefly, the glass ampoule containing the ²³⁷Np solution (in 0.5 M HNO₃) was opened and the contents were transferred and stored in a new Seastar Teflon bottle. At the time of preparation, this solution was transferred and taken to dryness in a Teflon beaker and redissolved in a minimum volume of 6 M HCl (Ultra-pure, Fluka). This process was repeated three times to ensure that the solution was fully converted to the chloride form and the ²³⁷Np was redissolved in 50 mL 6 M HCl (Ultrapure, Fluka) and transferred to a 250 mL glass-separatory funnel. Extraction of ²³³Pa was achieved by the addition of 50 mL octan-2-ol (pre-equilibrated in Xylenes). The funnel was shaken vigorously for 1 min and the aqueous and organic layers were allowed to separate (~5 min). The aqueous layer, containing ²³⁷Np, was collected and returned to the storage bottle for future ²³³Pa tracer preparations. The organic fraction, containing ²³³Pa, was washed with 50 mL of 6 M HCl and shaken for 1 min (to extract residual ²³⁷Np) and allowed to separate 5 min. Washings were repeated a total of three times to remove any residual ²³⁷Np. Each time, the aqueous-acid layer was discarded. Back-extraction of purified ²³³Pa into an aqueous solution that would be suitable for tracer additions, was accomplished by adding 50 mL of water containing 3 g Na₂SO₄ in 5 mL concentrated H₂SO₄ to the separatory funnel. Again the contents were shaken for 1 min and allowed to stand for 5 min. The aqueous layer, containing ²³³Pa, was transferred to a 250-mL Erlenmeyer flask and heated on a hot plate at medium heat. A few drops of concentrated HClO₄ and HNO₃ were added to oxidize any residual organic matter. This solution was then

taken to dryness, redissolved in 20 mL 20% H₂SO₄, and stored in a 30 mL Teflon bottle (Seastar Chemicals) to minimize adsorption of Pa to the walls during storage.

To confirm the purity of the ²³³Pa fraction (*i.e.*, absence of ²³⁷Np), a sampling ($n = 3$) of electrodeposited sources was analyzed by alpha-spectrometry and beta-counting. These sources were also used as standards for yield monitoring (by beta counting) of the Pa radiochemical yields for method evaluation as described previously (Sill, 1966; Burnett and Yeh, 1995). To confirm quantitative electrodeposition of Pa to the stainless steel planchettes (for use in yield determinations), the supernatant of the electrodeposited sources were also analyzed for residual ²³³Pa by High Purity Germanium (HPGe) gamma-spectrometry. No residual ²³³Pa could be detected in the supernatant solutions, based on examination of the count rate of ²³³Pa gamma emissions peaks (311.9, 98.4, and 94.6 keV peaks, 24 h count time), with a calculated limit of detection of 0.4 mBq. (Currie, 1968) Further, no ²³⁷Np could be detected by alpha-spectrometry (absence of 4.7 MeV peak, 168 h count time, data not shown), thus confirming the purity of the ²³³Pa standards and quantitative deposition on the surface of the disk.

2.4. Chemical separations

Development of the analytical method presented here was carried out using an extraction chromatographic resin, TEVA, which has been described in detail previously (Horwitz et al., 1995). Briefly, the material consists of Amberchrom CG-71 solid-phase support-resin beads that have been impregnated with a quaternary-mixed-aliphatic-chain (primarily $n = 8$ or $n = 10$) functionalized ammonium salt ($n = 8$, N-methyl-N,N-dioctyloctan-1-ammonium chloride; or $n = 10$, N-methyl-N,N-didecyldecan-1-ammonium chloride; specifically (C₈H₁₇)(CH₃) N⁺Cl⁻, 27%; (C₁₀H₂₁)(CH₃) N⁺Cl⁻, 47%; (C₁₀H₂₁)₂(C₈H₁₇)(CH₃) N⁺Cl⁻, 27%; (C₁₀H₂₁)(C₈H₁₇)₂(CH₃) N⁺Cl⁻, 2%), commonly known as Aliquat 336. Columns were prepared by slurrying the TEVA resin in water to a concentration of 0.66 g per 5 mL and transferring a vortexed-homogenized 5 mL aliquot of the stock slurry to empty columns and allowing the water to drain by gravity flow. Pre-manufactured frits (provided with the empty columns) were inserted on top and beneath the resin and a 25 mL reservoir (AC-120, Eichrom) was attached and the column (Fig. 2).

To arrive at the optimum separation strategy, the elution profiles for Th, Pa, and U were determined by step-wise elution of 1-mL aliquots of eluent solutions directly to 20-mL standard plastic or glass LS vials for direct counting by LSC. To prepare, ~75 Bq ²³²U/²²⁸Th and ~180 Bq ²³³Pa were taken to dryness and redissolved in 5–15 mL 4 M HCl. These experiments were undertaken to determine the elution peak maximum at test acid concentrations and no attempt was made in these experiments to assess or correct for scintillant quench or background contribution. Unlike alpha emitting radiotracers, ²³²U and ²²⁸Th, that have a LSC counting efficiency near 100%, the LSC counting efficiency for beta-particle emitter ²³³Pa is less than 100%. Nonetheless, because the signal is proportional to the activity of the samples, the LSC experiments provide the necessary information to determine the elution peak maximum values of Pa. Prior to separations, the TEVA column was preconditioned with 10 mL of 4 M HCl and the sample was loaded on the column in 1 mL aliquots using an autopipet. Each aliquot was collected into a separate LS vial

containing 15 mL of LS cocktail (Ecolite™, MP Biomedicals, Solon, OH USA). Once each 1-mL aliquot was collected (Fig. 3), vials were shaken, dark adapted, and counted by LSC for 30 min each for two cycles using routine counting parameters.

For alpha-spectrometry analysis, TEVA columns were again assembled and preconditioned with 10 mL of 4 M HCl. The sample was loaded in 5 mL of 4 M HCl to the column *via* transfer pipette directly onto the frit at the top of the column. The eluent of the load solution was collected for Th and the remaining Th was collected in the same beaker with an additional 10 mL rinse with 4 M HCl (Fig. 2). Another rinse containing 25 mL of 4 M HCl eluted any residual Th prior to the elution of Pa, but was discarded (*i.e.*, this discarded fraction contains very little Th). Following the removal of residual Th, Pa was selectively stripped from the column (*i.e.*, U is retained) in 15 mL of 4 M HCl-0.1 M HF and this fraction was collected for Pa analysis. Finally, U was eluted from the column with 5 mL of 0.1 M HCl. Once fractions were collected, they were set aside for source preparation and analysis.

2.5. Source preparation

Instrumental methods employed for the studies presented here were carried out by LSC, alpha-spectrometry, and beta counting. Sources analyzed by alpha-spectrometry and beta counting were prepared *via* electrodeposition according to an approach developed previously (Kressin, 1977), using a model EP-4 electrodeposition module (Phoenix Scientific Sales, Roswell, GA USA). Briefly, following separation and purification the Th, Pa, U, each analyte fraction was slowly taken to dryness. For Th fractions, once the eluent reached a minimal volume (~ 3 mL), it was necessary to add 1 mL of concentrated HNO₃ and a few drops of 30% H₂O₂ to destroy possible organic resin material that co-eluted from the column bed of the TEVA column. The beaker was then covered with a watch glass and allowed to reflux for 20 min. Our experience indicated that neglecting the oxidation of organic matter step resulted in a visible cake on the Th planchettes that decreased yield and degraded spectral resolution. Once completely dry, all three fractions were redissolved in a buffer containing 5 mL 15% Na₂SO₄, 2.5 mL 5% NaHSO₄, and 2 mL of H₂O. The contents were transferred to plastic electrodeposition cells, which had been fitted with a stainless steel planchette (25 mm outer diameter, AF Murphy, Quincy, MA USA), with 3 rinses of 1 mL of H₂O. Once the module was assembled, a platinum electrode was inserted and the current was adjusted to 0.5 A for 5 min, and then kept at constant current (0.75 A) for 90 min. To terminate the deposition, 2 mL of 25% KOH was added (dropwise) with constant current for 1 min, followed by removal of the current and discarding of the solution. A final rinse of the inside wall of the cell was performed with 5% NH₄OH. The planchets were then removed from the cell and rinsed with minimal volumes of NH₄OH, ethanol, and acetone to clean and dry the counting source. Once dry, the sources could be analyzed by alpha-spectrometry and beta counting.

2.6. Source counting

Alpha-spectra were collected using vacuum-controlled alpha-spectrometers (Alpha Analyst, Canberra, Meridan, CT USA) equipped with 450 mm² passivated ion-implanted silicon detectors (PIPS, Canberra), with a source-to-detector distance of approximately 10 mm,

which resulted in a counting efficiency of approximately 20%. Thus, radiochemical yield determinations were obtained by standard calculations using efficiencies determined using standards prepared from NIST SRM 4342A (^{230}Th) in an identical geometry. Prevention of alpha-daughter recoil contamination of alpha-detectors was accomplished by use of thin films, prepared as described previously (using a mixture of iso-amyl acetate and collodion). These thin films have been demonstrated to have no effect on the alpha emission detection efficiency or spectra resolution. (Inn et al., 2008). Alpha-counting sources were counted for approximately 168 h, with a matched count-time background subtraction of each region of interest (ROI) applied to obtain background corrected integrated count rates. Standard isotope dilution techniques were used to calculate the apparent activity of added controls ^{230}Th and U-NAT radionuclides based on the ratio of control to added ^{232}U and ^{228}Th integrated counts (Makarova et al., 1983).

Beta counting for ^{233}Pa yield determinations was conducted using a Ludlum model 3030 Alpha Beta Radiation Sample Counter (Ludlum Measurements, Inc., Sweetwater, TX). Each Pa source was counted in triplicate for 10 min, with appropriate matched-count-time background subtraction. The count rate was compared to sources of ^{233}Pa with known activity to determine the radio-chemical yield. Purity of the ^{233}Pa tracer solution was confirmed by gamma-spectrometry using a P-Type HPGe detector (ORTEC, Oak Ridge, TN USA), which was calibrated for energy and efficiency using a NIST-traceable multi-line gamma-ray source obtained from Eckert Zeigler.

For the determination of elution peak maximum values for radiochemical separations, LS counting was carried out using a Packard (1600 CA Tri-Carb) LS counter using EcoLite LS cocktail in plastic LS vials with a water fraction of approximately 10%. The LS sources were counted so as to achieve at least 1000 total counts for a counting uncertainty of approximately 3% ($k = 1$).

2.7. Method evaluation

Preliminary evaluation was carried by validation runs in which control standards U-NAT and ^{230}Th were used to simulate the analysis of natural samples. For method evaluation experiments analyzed by alpha-spectrometry, Th, Pa, and U tracers and analytes were added to a Teflon beaker volumetrically (50 μL $^{232}\text{U}/^{228}\text{Th}$, ~ 0.07 Bq; 50 μL U-NAT, ~ 0.025 Bq; 100 μL ^{233}Pa , ~ 18 Bq; and 1 mL ^{230}Th , ~ 0.07 Bq), and taken to dryness. A nominal 5 mL volume of 4 M HCl was added and the process was repeated three times to convert the matrix to the chloride form for separations. After conversion of the carrier to the chloride form, the tracer and analyte radionuclides were redissolved in the load solution (5–15 mL 4 M HCl) for TEVA separation and purification (Fig. 2).

To further evaluate the potential of the new method, the approach was applied for the age determination of a natural matrix geological material—an ancient carbonate sample (GC2 198'–205', Brigham Young University) obtained from the Lake Bonneville site in western Utah (Oviatt, 1997). A complete description of the material and its preparation will be described elsewhere. For these further evaluation runs, 0.5 g aliquots ($n = 3$) of GC2 198'–205' were added to Teflon beakers and dissolved in minimal 1 M HCl. To this slurry, the radiometric tracers were added (0.07 Bq $^{232}\text{U}/^{228}\text{Th}$, ~ 18 Bq ^{233}Pa). The slurry was

diluted to approximately 10 mL of concentrated HCl, covered with a Teflon watch glass, and refluxed under low heat over night. At the completion of the dissolution step, the remaining sand and other insoluble materials were separated via centrifugation at 3100 rpm for 30 min (IEC MediSpin, Thermo Scientific, Waltham, MA; USA). The pH was kept low to minimize adsorption of Pa and Th to the beaker or particulate matter. Following centrifugation, samples were transferred back to Teflon beakers and taken dry. Once completely dry, samples were redissolved in 2 M HNO₃. This process was repeated four times to ensure the complete conversion from the chloride to the nitrate form. As a precautionary step, the redissolved carbonate samples were centrifuged again for 30 min to remove any colloidal silica that could potentially interfere with the column separation steps. For these natural matrix samples, a pre-concentration step was included by the use of TRU resin (Eichrom Technologies, Lisle, IL) in a procedure previously described by Hull et al. (1992). Briefly, the sample was loaded to a preconditioned TRU column (1 mL column volume geometry as in TEVA separations) in 10 mL 2 M HNO₃. The column was rinsed with 30 mL of 2 M HNO₃ to remove commonions, followed by group-elution of the actinides with a rinse of 10 mL of 0.1 M ammonium bioxalate. The fraction containing ammonium bioxalate was sublimated to apparent completion in a glass beaker at moderate heat. Following complete removal of the ammonium bioxalate reagent, the sample matrix was converted to 4 M HCl, and separation of Th, Pa, and U was conducted according to the procedure described above using the TEVA resin (Fig. 2). Following the TEVA separation, electrodeposited sources were prepared and counted for 168 h in alpha-spectrometry chambers with known efficiencies. The ²³³Pa yield was determined as described above. Analysis of alpha-spectra allowed for the determination of a preliminary age of formation for the carbonates using U-series dating techniques (²³⁰Th/²³⁴U, ²³¹Pa/²³⁵U) to be described in detail in future publications.

3. Results and discussion

3.1. Results

We have developed a new method for separation and purification of Th, Pa, and U using the commercially-available extraction chromatography resin TEVA. Estimations of the elution peak maximum value for each element under conditions that achieved highly-pure fractions were determined by LS techniques. To further evaluate the method, a proof-of-concept isotope dilution alpha-spectrometry study was performed using a mixture of tracers (²²⁸Th, ²³³Pa, and ²³²U) and controls (²³⁸U, ²³⁵U, ²³⁴U, and ²³⁰Th) in a simple acid matrix. These experiments were designed to determine the radiochemical recovery, purity, and alpha-spectral resolution that could be achieved using the method. For this proof-of-concept study ($n = 3$), the mixture of radionuclides was loaded to preconditioned columns in 4 M HCl and elemental fractions were eluted separately. While Th passes directly through the column with the load solution and rinses, Pa and U are initially retained and can then be eluted sequentially from the column in 4 M HCl-0.1 M HF and 0.1 M HCl respectively. To further evaluate the new TEVA method, we performed an analysis of an ancient carbonate sample obtained from a relevant geological formation at the Lake Bonneville site in western Utah. These samples were weighed and acid digested by routine sample preparation

techniques and analyzed by isotope dilution alpha-spectrometry (Makarova et al., 1983; Tiessen et al., 1983; Oviatt, 1997).

While analysis of $^{231}\text{Pa}/^{235}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ ratios are considered powerful tools for age dating of materials, improved methods for obtaining elementally-pure fractions of all three elements in a single analytical run is desirable. Early assessments of available chromatography-based separations technologies led us to investigate extraction chromatographic resin TEVA (Eichrom Technologies), composed of Amberchrom resin beads impregnated with undiluted Aliquat 336. Aliquat 336 has been used previously as the organic layer in liquid-liquid extractions for the separation of actinides from complex environmental matrices and for nuclear fuel cycle applications (Sill et al., 1974; Eskandari Nasab, 2014). For efficient extraction using quarternary-amine-based extractants, radiometals must be present as anionic species (Eskandari Nasab, 2014). The anionic complex forms a stable cation-anion pair with the quarternary-amine, achieving extraction from the aqueous phase. For example, at low pH (*e.g.*, 4 M HCl), the predominate species are U(VI) and Pa(V), which are known to form strong anionic chloro-complexes (Kirby, 1959; Vandenhove and Payne, 2010), and are readily extracted into a solution of Aliquat 336 (Sill et al., 1974; Eskandari Nasab, 2014), presumably as cation-anion pairs. On the other hand, Th(IV) (the predominant redox state of Th) is weakly associated with Aliquat 336 due to the formation of a relatively weak-neutral $\text{ThCl}_4 \cdot 8\text{H}_2\text{O}$ complex in HCl (Cotton, 1999; Katz, 2006; Eskandari Nasab, 2014). This working hypothesis is supported by a subsequent study, which demonstrated low retention of Th on TEVA resin in all concentrations of HCl (Horwitz et al., 1995). Thus, we hypothesized that U(VI) and Pa(V) could be isolated from Th(IV) by reaction with the Aliquat 336-ligand-based TEVA in a strong acid solution of HCl. Experimentally, we observed little retention of Th on the TEVA column, with an observed elution peak maximum at 5 mL, resulting in radiochemical yields of $90 \pm 4\%$, and no observable radionuclidic impurity (Fig. 3; Table 1; Fig. 4).

Once isolated from Th(IV) (in the organic-extractant phase of the TEVA resin), we further hypothesized that differences in the chemistries of U(VI) and Pa(V) could be exploited to achieve separation and elemental purification. At this step, U(VI) and Pa(V) remain adsorbed to the TEVA column. For the isolation of U(VI) from Pa(V) a stripping agent was necessary because elution curves on TEVA for U(VI) and Pa(V) were very similar in dilute HCl solutions – thus difficult to separate (Horwitz et al., 1995; Mendes et al., 2013). Potential stripping agents to remove Pa(V) from an organic phase or extraction chromatographic resin has been previously examined. These studies demonstrated that stripping agents such as; HF, HClO_4 , and Na_2SO_4 are effective in the quantitative elution of Pa(V) (Kirby, 1959; Sill et al., 1974, 1979). For our purpose, the addition of a stripping agent must not only elute the Pa(V), but also it must leave the U(VI) adsorbed to the column. The most promising of these studies indicated that the introduction of a low concentration of HF would result in the formation of strong inner-sphere-soluble Pa fluoride species (presumably PaF_7^{2-}), which should effectively remove Pa quantitatively (Burnett and Yeh, 1995; Regelous et al., 2004; Negre et al., 2009; Koornneef et al., 2010). As a starting point, we chose a low concentration of HF (0.1 M) in combination with the same HCl concentration (4 M) as was used to elute Th(IV), which we hypothesized would maintain the adsorption of U(VI). While recent published efforts to develop similar methodologies were unsuccessful

in establishing an effective separation step for Pa, these attempts did demonstrate that even very low concentrations of HF were sufficient to abrogate binding of Pa to Aliquot 336-quarternary-amine-based TEVA resin (Kirby, 1959; Regelous et al., 2004). Thus, we applied a solution of 4 M HCl –0.1 M HF, which we expected would remove Pa(V) while the adsorbed U(VI) species, presumably of the form $R_3CH_3NUO_2Cl_3$, would remain immobilized (Kirby, 1959; Eskandari Nasab, 2014). Fortuitously, experimental results validated that adding 15 mL of 4 M HCl –0.1 M HF successfully removed Pa(V) from the column with an observed elution peak maximum of approximately 3 mL (Fig. 2). LSC data shows all of the activity was accounted for in the first 5 mL of the solvent added. Radiochemical recovery of $85 \pm 12\%$ was determined by beta counting, and elemental purity in excess of 99.99% was quantified by alpha-spectrometry (Table 1).

Interestingly, early experiments showed the presence of observable-residual adsorption of Th(IV) in the alpha-spectrum, which was removed with the Pa fraction. Modifications were made to fully rinse the TEVA column until LSC data showed the Th(IV) activity dropped to background levels. Notably, a secondary broad elution peak (Fig. 2) characterized the elution of Th(IV) and at least 25 mL of added 4 M HCl rinse was required for complete removal of Th(IV). These results suggest: (1) the potential existence of a low-concentration of contaminant extractant of unknown composition in the resin bed with an affinity for Th(IV); (2) the incomplete conversion of the resin bed to the Cl^- form at the preconditioning step; or potentially (3) that Th adsorbed to the beads or other column materials may contribute to the ultimate shape of the elution profile and create the need for significant rinsing to remove residual Th(IV).

Following elution of Pa(V), sequential elution of U(VI) from the column was achieved by elution with 10 mL of 0.1 M HCl as described in Section 2.4 (Fig. 2) (Horwitz et al., 1995). Electro-deposited sources revealed overall process radiochemical yields of $93 \pm 3\%$, with apparent radiochemical purity of 100% confirmed by beta counting, alpha spectrometry, and high-resolution gamma spectrometry (Table 1, Fig. 5).

3.2. Control method evaluation

We further evaluated the new radiochemical separation approach for purification of Th, Pa, and U by preparing acid solutions with control spikes (^{238}U , ^{235}U , ^{234}U and ^{230}Th) — and analyzing them by isotope dilution alpha-spectrometry using tracers ($^{232}U/^{228}Th$ and ^{233}Pa). We evaluated the method based on critical metrics: achievable radiochemical yield of the tracers; the impurities in each alpha-spectra; and control-spike recovery (Table 1) (Makarova et al., 1983). Radiochemical tracer yields were >90% for U and Th for these experiments, while Pa yields were slightly lower (Table 1). Spike recoveries for ^{230}Th and U-NAT were calculated to be in excellent agreement with the expected values (Table 1). It should be noted that the recoveries determined by alpha-spectrometry were lower than those observed by LS counting, suggesting that some loss of analyte occurs at the electrode-position step. Further optimization of source preparation is ongoing in our laboratory and will be presented in a future manuscript. It is also recognized that the activity concentration of our available solutions did not include a test matrix with a sufficiently high concentration of ^{231}Pa to collect sufficient counts for statistical evaluation of a control spike recovery. Rather, our

results here are focused on radionuclide purity of the Pa fraction through alpha-spectrometry and radiochemical recovery based on beta-counting. Future experiments will include testing of matrices with higher concentrations of alpha-emitting ^{231}Pa to enable a statistical evaluation of ^{231}Pa control spike recovery (Currie, 1968).

The resulting alpha-spectra for Th, Pa, and U from this present study were also analyzed for radiochemical purity. Inspection of the alpha-spectra from the Pa fraction revealed no observable contamination of U for the optimized column separation. Early evaluation of the method pointed to the potential for Th contamination of Pa sources as a possible confounding metric. To mitigate the presence of Th in the Pa fraction, we optimized the method by increasing the rinse volume (4 M HCl; following elution of the Th fraction) to desorb all residual Th from the column prior to the Pa elution. Our results indicate that a total volume of 40 mL of 4 M HCl is required to quantitatively remove residual Th. Based on an examination of counts in the ^{230}Th ROI in the Pa spectra, the increase in rinse volume decreased cross-contamination of ^{230}Th to levels that approach the limit of detection. Thus, in Pa spectra, we observed an upper limit of $<0.1\%$ ^{230}Th added, based on an average net count rate of 2.3×10^{-6} cpm in the ^{230}Th region of interest and a 100 h count time and alpha-detector counting efficiencies of approximately 20% (Currie, 1968; Gabriels, 1970). The Th and U α -spectra were analyzed for contamination by quantification of counts in the ^{238}U and the ^{230}Th ROI's, respectively. No indication of early elution of U from the TEVA column was observed in Th spectra, nor was the presence of any residual Th observed in U spectra. Expected presence of the decay products of ^{228}Th in the alpha-spectrum could be attributed to ^{232}U -daughter ingrowth (sample count time was 168 h; Fig. 4).

3.3. Lake Bonneville carbonate method evaluation

As a final proof-of-concept evaluation of the new method for radiochemical separations for U-series age determination of natural materials, we analyzed carbonate samples obtained from the Lake Bonneville site in western Utah (USA). In our first attempt, samples (0.5 g) were digested to dissolve the carbonate material according to established procedures (Tiessen et al., 1983) and analyzed by isotope dilution alpha-spectrometry (Makarova et al., 1983). Using standard Bateman equation-based dating techniques, our preliminary estimate of the formation of the deposit is approximately 39,500 ($^{230}\text{Th}/^{234}\text{U}$) and 40,000 ($^{231}\text{Pa}/^{235}\text{U}$) years before present. These ages compare favorably with preliminary ^{14}C ages of roughly 37,000 years (obtained with appropriate corrections). These ages should only be considered nominal, and no statistical conclusions can be made regarding concordance because the estimated detection limit of this separation protocol (TRU/ TEVA) (3 mBq per g sample, counted for 168 h) is greater than the decay rate determined for Pa and the estimation of the detection limit was based on a single count (Currie, 1968) Future investigations will established a more rigorous understanding of achievable detection limits and focus on techniques to improve the Pa measurement to minimize the uncertainties associated with the age determinations. Although the uncertainties associated with the measurements are large, calculated ages correspond well with the ^{14}C derived ages, radiochemical yields for tracers were less than expected — $62 \pm 12\%$, $24 \pm 9\%$ and $37 \pm 9\%$ for ^{232}U , ^{228}Th , and ^{233}Pa respectively. Control experiments demonstrated that losses associated with the TRU and TEVA column separations were negligible (see above) and it

was determined that losses could be attributed to sample preparation and source preparation steps. Modifications were made to improve the overall yields associated with these steps; including substitution of the electrodeposition source preparation with microprecipitated rare-earth-fluoride based filtered source preparation. It was also found that a digestion procedure in 25 mL of 2 M HNO₃ (1 h), followed by filtration of the sample to remove residual silicate residue (instead of centrifugation), prior to loading onto the TRU column improved the overall radiochemical yields for this carbonate sample. These modifications improved the overall radiochemical yields being $76 \pm 11\%$, $96 \pm 10\%$ and $55 \pm 12\%$ for tracers ²³²U, ²²⁸Th, and ²³³Pa respectively ($n = 4$). Future studies will include a more comprehensive optimization of the sample preparation and source preparation for these carbonate samples and a complete examination of the age of the material based on both ²³⁰Th/²³⁴U and ²³¹Pa/²³⁵U disequilibria. Alpha-spectral results of the U content in the carbonate samples revealed isotopic enrichment of ²³⁴U relative to parent ²³⁸U, which will be further examined also in these future studies.

4. Conclusion

Here we described a new simple method for the separation of Th, Pa, and U, using extraction chromatography resin TEVA, that can be applied for age-dating or radioanalytical analysis applications by isotope dilution alpha spectrometry or mass spectral techniques. The separation procedure can be performed in less than 3 h using a standard gravity-flow ion-exchange-type column arrangement and results in less than 50 mL of acid waste. The method provides acceptable to excellent radiochemical yields that are comparable to the other methods, with virtually 100% radiochemical counting source purity. Ongoing studies are underway to examine the potential to improve the overall speed of the approach by vacuum-based rapid chromatography approaches and the development of a column chromatography approach to preparation of ²³³Pa tracer working standards.

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Fig. 1.

Schematic illustrating the liquid-liquid extraction of ^{233}Pa from ^{237}Np liquid-standard (CRM 92566) for use as a radiometric tracer. A ^{237}Np standard in 50 mL of 6 M HCl was transferred to a 250 mL separation funnel containing 50 mL of octan-2-ol (preequilibrated in xylenes). The contents were shaken for 2 min, and then the phases were allowed to separate for 5 min. Once separated the aqueous phase was collected for ^{237}Np , and an additional 50 mL of 6 M HCl was added to the separation funnel. To remove any residual ^{237}Np , the funnel was shaken for 2 min, and then allowed to separate for 5 min. The aqueous layer was discarded and two more washes of 6 M HCl were added. The ^{233}Pa was back extracted into the aqueous phase using a solution containing 3 g Na_2SO_4 in 5 mL H_2SO_4 diluted with 50 mL H_2O . The contents were shaken for 2 min, separated for 5 min, and the aqueous phase was collected for ^{233}Pa . Contents were taken dry on medium heat with 1-2 drops of a solution containing 1:1 of concentrated HClO_4 : HNO_3 to remove any potential organic. The final solution was stored in 20 mL of 20% H_2SO_4 in a Teflon bottle.

Fig. 2.

The new column separation protocol using TEVA for separation and purification of Th, Pa, and U. The column is preconditioned (4 M HCl). In step 2, the sample is loaded to the column (5 mL 4 M HCl) and collected for Th activity. In step 3, the remaining Th is collected (10 mL 4 M HCl) and combined with the previous fraction to account for Th activity in the sample. To prevent any potential Th cross contamination in the Pa or U fraction, an additional rinse (25 mL 4 M HCl) is added to the column and is discarded. In

step 5, Pa is stripped from the column and collected (4 M HCl-0.1 M HF) quantitatively. The final rinse (5 mL 0.1 M) allows for the collection of U.

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Fig. 3.

Elution curves that describe the final separation procedure as a function of elution volume.

The procedure for the separation of U, Th, and Pa was performed in 1 mL aliquots. Each mL added to the column was collected in a 20 mL LS vial containing 15 mL of Ecolite LS cocktail. In the 4 M HCl load solution, Th reaches an elution maximum (~5 mL) and returns to near background activity in ~20 mL. The final 15 mL were needed to remove residual Th in the Pa fraction observed in early experiments. The next 15 mL 4 M HCl-0.1 M HF removed Pa from the column, while U remained adsorbed. A final 5 mL 0.1 M HCl desorbed the U for collection and counting.

Fig. 4.

Alpha-spectra of the Th fraction obtained in the analysis of carbonate samples from Lake Bonneville. The carbonates were acid digested to allow leaching of the actinides. Electrodeposited sources were made and counted via alpha-spectroscopy for 168 h. The resulting spectrum shows natural Th (^{232}Th , 3.9 MeV; ^{230}Th , 4.6 MeV) and tracer (^{228}Th , 5.4 MeV) isotopes with a resolution FWHM of 31 keV. Over the course of this time frame, ^{228}Th decay products approached secular equilibrium due to their short half lives. The arrow shows the absence of a peak at 4.2 MeV corresponding to ^{238}U , further demonstrating the absence of U contamination. The ^{230}Th activity was used for age determination of the samples by isotope dilution alpha-spectroscopic principles.

Fig. 5.

Alpha-spectra of the resulting U fraction obtained by analysis of carbonate samples from Lake Bonneville. The carbonates were acid digested to allow leaching of the actinides. A pre-concentration step of the actinides was performed using TRU resin to remove matrix interferences (*i.e.*, calcium). The actinides were removed from the TRU column in 0.1 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$. Elementally pure fractions of U were obtained from the TEVA column using the method described in this paper. Electrodeposited sources were made and counted *via* alpha-spectroscopy for 168 h. The resulting spectrum shows natural U (^{238}U , 4.1 MeV; ^{235}U , 4.5 MeV; ^{234}U , 4.7 MeV) and the tracer (^{232}U , 4.2 MeV) with a resolution FWHM of 31 keV. The arrow shows the absence of a peak at 5.4 MeV corresponding to ^{228}Th , further demonstrating the absence of Th contamination in the U fraction. The ^{234}U and ^{235}U activities were used to calculate the age of the carbonate samples.

Table 1

Radiochemical yield, spike recovery, observable impurities, and spectral resolution for U, Th and Pa *via* alpha-spectroscopy and beta counting. Yields were determined using efficiencies determined using standard source prepared from a NIST SRM. The radiochemical yield for Pa was determined from beta counting.

Element	Radiochemical yield ^a (%)	Spike recovery ^b (%)	Impurity ^c (%)	Resolution ^d (keV)
Th	90 ± 4	97 ± 3	ND	31
Pa	85 ± 12	NA	~0.1%	NA
U	93 ± 3	98 ± 1	ND	31

^aRadiochemical yield was determined from alpha spectroscopy as the average integrated count rate for each isotope divided by the total activity added.

^bSpike recovery was calculated using isotope dilution α -spectroscopic techniques for the recovery of each control using the isotopic ratio (control/tracer) multiplied by the tracer activity added.

^cImpurity was calculated by integrating approximate regions of interest for potential contaminants and calculating the percentage of (alleged) cross contamination based on the known added activity of the radionuclide of interest.

^dResolution was obtained from the full width half max (FWHM) of peaks in the α -spectra as generated by Genie 2000 Software (Canberra).