

Rare-earth element fractionation in uranium ore and its U(VI) alteration minerals

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ABSTRACT

A cation exchange chromatography method employing sulfonated polystyrene cation resin (DOWEX AG50-X8) was developed in order to separate rare-earth elements (REEs) from uranium-rich materials. The chemical separation scheme is designed to reduce matrix effects and consequently yield enhanced ionization efficiencies for concentration determinations of REEs without significant fractionation using solution mode-inductively coupled plasma mass spectrometry (ICP-MS) analysis. The method was applied to determine REE abundances in four uraninite (ideally UO_2) samples and their associated U(VI) alteration minerals. In three of the samples analyzed, the concentration of REEs for primary uraninite are higher than those for their corresponding secondary uranium alteration phases. The results for U(VI) alteration minerals of two samples indicate enrichment of the light REEs (LREEs) over the heavy REEs (HREEs). This differential mobilization is attributed to differences in the mineralogical composition of the U(VI) alteration. There is a lack of fractionation of the LREEs in the uraninite alteration rind that is composed of U(VI) minerals containing Ca^{2+} as the interlayer cation (uranophane and bequerelite); contrarily, U(VI) alteration minerals containing K^+ and Pb^{2+} as interlayer cations (fourmarierite, dumontite) indicate fractionation (enrichment) of the LREEs. Our results have implications for nuclear forensic analyses since a comparison is reported between the REE abundances for the CUP-2 (processed uranium ore) certified reference material and previously determined values for uranium ore concentrate (UOC) produced from the same U deposit (Blind River/Elliott Lake, Canada). UOCs represent the most common form of interdicted nuclear material and consequently is material frequently targeted for forensic analysis. The comparison reveals similar chondrite normalized REE signatures but variable absolute abundances. Based on the results reported here, the latter may be attributed to the differing REE abundances between primary ore and associated alteration phases, and/or is related to varying fabrication processes adopted during production of UOC.

1. Introduction

Uraninite is the most common U^{4+} mineral species and is the main ore mineral in many uranium deposits. It has an ideal formula of UO_2 , but is typically $\text{U}_{1-x-y-z}^{4+}\text{U}_x^{6+}\text{REE}_y^{3+}\text{M}_z^{2+}\text{O}_{2+x-(0.5)-z}$ (Janeczek and Ewing, 1992) and crystallizes in the fluorite structure. The latter can host many elements with ionic radii similar to U^{4+} in eightfold coordination. This applies particularly to Th^{4+} , the rare-earth elements (REEs^{3+}), and Y^{3+} (Frimmel et al., 2014; Mercadier et al., 2011; Burns and Finch, 1999). The incorporation of these elements into the structure is mainly a function of temperature and element availability (Frimmel et al., 2014; Burns and Finch, 1999). For example, old (> 1-2 billion years) uraninite may contain 7-10 wt % PbO due to radioactive

disintegration of U, and samples of uraninite containing up to 11 wt % CaO and 12 wt % REE_2O_3 have been found (Burns and Finch, 1999). Under oxidizing conditions, uraninite dissolves slowly in aqueous solution by oxidation of U(IV) to UO_2^{2+} uranyl ions, which can be complexed by inorganic and organic species promoting the formation of insoluble uranyl minerals around the U(IV) mineral grains (Finch et al., 1999; Wronkiewicz et al., 1992, 1996). The uranyl minerals that form depend on the water chemistry surrounding the UO_2 matrix, and include uranyl oxyhydrates (schoepite and studtite), silicates (uranophane and soddyite), phosphates (autunite), and vanadates (carnotite) (Finch et al., 1999).

In this study, we seek to determine if fractionation, i.e., relative enrichment of the REEs, occurs during the alteration of uranium ore.

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REEs overall exhibit very similar chemical properties and are generally considered to be resistant to fractionation in supracrustal environments. These characteristics, coupled with their low solubilities, allow REE distributions to be used as a fingerprinting tool to help identify the parental material of altered surficial crustal rocks (Nance and Taylor, 1977; Wildeman and Condie, 1973). However, mobilization and fractionation of the REEs can occur during surface alteration of rocks (Nesbitt, 1979).

In the fields of nuclear science and nuclear forensics, there is significant interest to trace the origin of uranium ore concentrate (UOC) as these materials represent the most common form of interdicted nuclear material (Orlov, 2004). Tracing the source of an unknown UOC is a complicated task (Keegan et al., 2012), however, several studies have successfully attributed uranium ores and uranium ore concentrates (UOCs) to specific mining areas via elemental and isotopic fingerprinting (Keegan et al., 2008, 2012, 2014; Varga et al., 2009, 2010a,b; Han et al., 2013; Svedkauskaitė-LeGore et al., 2007). Rare-earth element signatures have been described as the most effective tool for defining the geologic provenance of uraninite (UO_2+x), because of their tendency to fractionate within uranium oxides (Mercadier et al., 2011). However, few examples are reported in the literature in which uranium ore and UOC produced from the same geographic area/deposit are compared directly (Balboni et al., 2016).

Several mass spectrometry analytical techniques can be applied to measure REE abundances in uranium-rich samples. However, the most accurate and precise data for elements in low abundances (i.e., close or at the instrumental detection limit) is typically achieved with the removal of uranium from the matrix prior to analysis (Hou et al., 2005). Additional factors that may hinder determination of low abundances of lanthanides in uraninite include isobaric interferences, which result from oxide and hydroxide ions of barium, and matrix suppression of ion signal intensity (Watkins and Nolan, 1990; Rucandio, 1997). Most frequently, solvent extraction, extraction chromatography or ion exchange techniques are used to pre-concentrate the lanthanides (Lee et al., 2001; Flavelle and Westland, 1986; Premadas and Srivastava, 2002; Malhotra and Satyanarayana, 1999). Solvent extraction methods however efficient, employ and generate high amounts of organic and/or radioactive waste (Lee et al., 2001; Flavelle and Westland, 1986; Premadas and Srivastava, 2002; Malhotra and Satyanarayana, 1999). Extraction chromatography and ion exchange techniques are advantageous and widespread in the field of actinide and lanthanide separation as they provide effective REE removal and ease of use (Varga et al., 2010a,b; Rucandio, 1997; Desideri et al., 2004; Bertaux et al., 1999). Chemical separation involving ion exchange is an efficient method for pre-concentrating the pertinent analyte(s) (increase sensitivity, reduce interferences), and to protect the instrument from ion signal saturation associated with the most abundant elements in the sample (e.g., U in uraninite) (Varga et al., 2010a,b; Watkins and Nolan, 1990; Rucandio, 1997). In this work, we have chosen cation exchange chromatography using sulfonated polystyrene cation resin (DOWEX AG50-X8) to isolate REEs from the U-dominated matrix of uraninite and associated alteration products. This resin has been proven effective in REE separation from geological matrices (Watkins and Nolan, 1990; Rucandio, 1997) relative to other applications (Rucandio, 1997; Buzon et al., 2007; Simonetti et al., 2008), and involves inorganic acids as eluents. Therefore, the final solution is a suitable media for analysis by mass spectrometry (Watkins and Nolan, 1990; Rucandio, 1997; Juras et al., 1987; Strelow, 1980, 1984). The AG50-X8 resin retains lanthanides in 1–2 M hydrochloric acid media (distribution coefficient greater than a 1000 (Strelow, 1984)), and REEs are separated from Ba and U(VI), amongst other metals, by eluting these elements with 2M HNO_3 (Strelow, 1980).

The main goal of this work was the development of a simple and inexpensive methodology to remove lanthanides from uranium-rich matrices through cation exchange chromatography followed by concentration determination by high resolution-inductively coupled

plasma mass spectrometry (HR-ICP-MS). Validation of the proposed chemical separation technique was achieved via measurement of the REE abundances for the uranium ore concentrate reference material CUP2, and comparison of REE concentrations determined by both solution mode (SM) and laser ablation (LA- ICP-MS) techniques for the same uraninite samples. Finally, the chemical extraction method was applied to the determination of lanthanide abundances in four uranium ore samples (uraninite) and their U(VI) mineral alterations. Results from the latter comparison will provide insights into the fractionation behavior of REEs within uranium ore, and possible implications for nuclear forensic purposes are discussed.

2. Experimental

2.1. Instrumentation

All trace element analyses were performed within the MITERAC ICP-MS Facility at the University of Notre Dame. The solution mode (SM)-ICP-MS analysis of all samples, standards, and blanks was carried out using the Nu Atom (Nu Instruments) high resolution (HR)-ICP-MS. All measurements were conducted in medium mass resolution ($M/\Delta M \approx 3000$), and at the start of each analytical session the instrument was tuned and calibrated using a multi elemental solution (1 ng g^{-1}). Standard and spike solutions were prepared from 1000 mg g^{-1} elemental standard solutions (BDH® ARISTAR® Certified reference standards). The aliquots obtained during the optimization and calibration phase of the chemical separation protocol were prepared for SM-ICP-MS analysis using an external calibration method that involved In (1 ng g^{-1}) as the internal standard. The abundances of the trace elements investigated in samples with U-rich matrix were determined by a standard/spike addition method (Jenner et al., 1990), which includes correction for matrix effects and instrumental drift (Jenner et al., 1990).

In situ laser ablation measurements were carried out using a New Wave Research UP213 Nd:YAG laser ablation (LA) system coupled to a Thermo Finnigan Element 2 sector field high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS). Background ion signals were determined for 60 s with the laser on and shuttered. Sample ion signals were collected for 60 s subsequent to the start of the ablation. Concentrations were determined using the NIST SRM 610 glass wafer as the external standard using a “standard-sample” bracketing technique; CaO and ThO_2 wt.% contents (obtained by electron microprobe) were used as the internal standards. Analytical settings and conditions employed were similar to those reported by Chen and Simonetti, 2013 (Chen and Simonetti, 2013). Data reduction was performed offline using *Glitter* software (Van Achtenbergh et al., 2001), which yields concentrations, internal uncertainties, and limits of detection. The average relative uncertainty (2σ mean) for each elemental concentration determination is a function of the recorded ion signals (which depends on the absolute abundance of each trace element in the sample), and ranges from ~5 to 10% for most elements investigated here. The minimum detection limits were calculated using the *Glitter* software and is determined by Poisson counting statistics ($\text{MDL} = 2.3 \cdot \sqrt{(2B)}$, where B is the total counts in the background interval (Van Achtenbergh et al., 2001). In this work, the MDLs for the rare-earth elements range between 0.002 and 0.015 ppm. During each laser ablation analysis, no significant changes in ion signal intensities were observed in the time resolved spectra, further indicating the homogeneity and lack of inclusions present within uraninite (at the scale of 10s of μm).

2.2. Cation exchange separation

A stock solution containing U, La, Sm and Er was used for the optimization of the cation exchange separation. The solution was prepared from single element stock standard solutions (1000 mg L^{-1}) and diluted to the desired concentration of 900 ng g^{-1} . La, Sm and Er were

Table 1

Investigated uraninite samples, geographic location of origin, and uranium deposit type. Sample # refers to the catalog number of the samples obtained from the Rod Ewing sample collection, housed at the University of Notre Dame.

Sample Name	Sample #	Mine	Origin	Uranium deposit type
Yancey1	513	Unknown	Yancey Co, NC, USA	Pegmatite
Marshall Pass1	623	Marshall Pass	Colorado, USA	Hydrothermal vein
Great Bear Lake	626	Echo Mine	Great Bear Lake region	Metamorphite
Jefferson	637	Jefferson Country CO	Jefferson Country Co	Metasedimentary
Billiken Lode	522	Billiken Lode	Jefferson Co, CO, USA	Meta-sedimentary
Shinkolobwe	437	Shinkolobwe	Democratic Republic of Congo	Veni

considered in this study to represent light, middle and heavy rare-earth elements, respectively. The separation procedure was based on the method proposed by Rucandio (1997) (Rucandio, 1997), which involves a column extraction (Dowex 50W-X8 resin) procedure aimed at separating REEs from geologic materials (silicate rocks) for ICP-AES analysis. In this study, the volumes were modified with respect to the original method to maximize the separation of uranium from the elution of the REEs. Hydrochloric and nitric acids employed for sample preparation were purified using Savillex DST-1000 Acid Purification Systems (one for each acid).

2.3. Uranium ore samples

The uranium ore samples analyzed in this work are listed in Table 1 and were obtained from the “Ewing collection” of minerals and rocks housed at the University of Notre Dame (e.g., Fig. 1).

Yancey1 (Yancey Co, NC) - pegmatite-hosted uraninite is from the Spruce Pine pegmatite, North Carolina. The pegmatites in this area are of early Paleozoic age and cut mica and amphibole gneiss and schist rocks of Precambrian age (Brost, 1962). *Jefferson Co.*, CO - uranium ore veins are hosted in folded and faulted Precambrian meta-sedimentary rocks; the U-Pb age for the uranium ore is 69 ± 1.1 million years (Zhao and Ewing Rodney, 2000; Dahlkamp, 1991). *Marshall Pass* (Marshall Pass district, CO) - uranium mineralization in this area occurs in fault-controlled veins and breccia zones in limestone of the Pennsylvanian Belden Formation (320–300 million years). The uranium ore is located at the intersection of major faults with Tertiary (between 65 and 2 million years) erosion surfaces. These surfaces were buried by Early Tertiary siliceous tuffs, a likely source of uranium (Zhao and Ewing Rodney, 2000; Deditius et al., 2007). *Great Bear Lake* (*Great Bear Lake*, Echo Mine, Canada) – uranium mineralization consists of disseminated grains in veins associated with metamorphosed and fractured andesitic tuffs (1800 million years). *Shinkolobwe*, (Democratic Republic of Congo) uranium mineralization is hosted in dolomite, dolomitic shale, carbonaceous quartzite and quartz micashist. Age data indicates two types of mineralization, one unconformity-related (652 ± 7 Ma) and the other syn-orogenic during the Lufilian orogeny (~ 530 Ma) (Decree et al., 2011).

Amongst the uranium ore samples chosen for this work, those from *Yancey*, *Marshall Pass*, *Jefferson Co* and *Great Bear Lake* consist of both unaltered uraninite and alteration rinds (Fig. 1). Thus, they were selected to determine the REE fractionation between uranium ore and its U(VI) alterations. The *Shinkolobwe* sample was analyzed both by SM-

ICP-MS after chemical separation of REEs from the uranium matrix and LA-ICP-MS for comparative purposes so as to validate the methodology employed here (Frimmel et al., 2014; Balboni et al., 2016).

2.4. Preparation and characterization of solid samples

Pristine uraninite and associated alteration were separated by mechanical means using a mortar and pestle and separated visually with the aid of a binocular microscope. After mechanical grinding, the larger uraninite grains were selected. Grains were rinsed in $18 \text{ M}\Omega \text{ cm}^{-1}$ water then in 0.1M HCl for ~ 2 min to remove surface contamination.

2.4.1. U(VI) alterations

Powder X-ray diffraction data were collected for the uranium ore alteration samples (yellow-orange powders) to determine the crystalline nature of the alteration products. Data were collected using a Bruker Davinci automated diffractometer at room temperature over the angular range of $5\text{--}55^\circ$ (2θ , $\text{CuK}\alpha$) with a step width of 0.02° and a fixed counting time of 15 s/step.

2.4.2. Laser ablation

Samples were prepared as described in Balboni et al (2016) (Balboni et al., 2016). Briefly, for each sample of uranium ore, grains or chunks were separated or cut from the bulk material and fixed in 1-inch round epoxy filled mounts. The surface of each sample was polished and carbon coated. Prior to LA-ICP-MS, major element analyses were conducted for each sample using a Cameca SX-50 electron microprobe. An accelerating voltage of 15 KV was used, along with a beam size of $15 \mu\text{m}$, and a beam current of 100 nA. Standardization was performed using well-characterized in-house standards of uranium oxide (UO_2), thorium oxide (ThO_2), galena (PbO), anorthite glass (Al_2O_3 , CaO), titanium oxide (TiO_2), manganese metal (MnO), zircon (ZrO_2 , SiO_2), vanadium oxide (V_2O_5), yttrium aluminum garnet (Y_2O_3), and apatite (P_2O_5). Uncertainties (2σ mean) are based on counting statistics and are $\leq 2\%$ for TiO_2 , UO_2 , MnO and V_2O_5 ; $\leq 3\%$ for PbO ; $\leq 5\%$ for SiO_2 , Al_2O_3 , P_2O_5 , CaO , ZrO_2 and ThO_2 and $\leq 6\%$ for Y_2O_3 . For all samples, spots analyzed were homogeneous in relation to their major element composition ($75 \mu\text{m}$ diameter) based on their backscatter electron images also collected on the electron microprobe cited above.

2.5. Dissolution of CUP2 standard and uranium ore samples

0.01–0.05 g aliquots of CUP2 standard, uranium ore and respective



Fig. 1. Example of uranium ore samples and their associated alteration rinds (*Great Bear Lake* and *Jefferson Co*). X-ray fluorescence elemental maps of samples are reported in the supplementary information.

alterations were digested using concentrated DD HNO₃ in 15 mL capped Savillex® Teflon vials on a hotplate for 48 h in a clean room (class 1000) laboratory. After 48 h, for the ore and alteration samples, the solution was centrifuged and unreacted solid residue was separated from solution, dried, and weighed. Partial dissolution of these samples was considered desirable as to avoid digestion of the host rock minerals, especially the silicate matrix and refractory minerals, which may overprint the REE signature of the sample. All solutions were then retransferred in capped Savillex® Teflon beakers and evaporated to dryness. 2 mL of a 1:1 concentrated (DD)HNO₃: (DD) HCl acid mixture was added to each sample. After 24 h, the samples were uncapped and evaporated to almost complete dryness. At this point, 2 mL of concentrated DD HNO₃ was added to each sample and immediately brought to almost complete dryness. Finally, 2 mL of concentrated DD HNO₃ was added and then diluted gravimetrically to a final volume of ~100 mL with 18 MΩ cm⁻¹ water. Aliquots of samples were completely dried and prepared for chemical separation.

3. Results and discussion

3.1. Separation procedure optimization and method validation

To optimize the separation of the REEs from a uranium-bearing solution, a 900 ng g⁻¹ stock solution containing U, La, Sm and Er was prepared and its elution behavior on AG50-X8 was investigated. The procedure was optimized as follows: a) 10 cm tall columns were filled with 1.42 mL of wet 200-400 mesh AG50W-X8 resin; b) 8.52 mL of sample solution in 1.75M HCl was loaded onto the conditioned resin column; c) The uranium was washed out with 14 mL of 2M HNO₃; d) The REEs were eluted with 6 mL of 7M HNO₃. Final aliquots were brought to dryness overnight on a hotplate at 80 °C; samples were the re-dissolved in 2% DD HNO₃ for SM-ICP-MS analysis.

This final separation procedure was optimized by minimizing the volume of the eluents without decreasing the effectiveness of the separation. 2 mL aliquots were collected separately and their uranium and lanthanide contents were determined by SM-ICP-MS, and their elution profiles are shown in Fig. 2. During the sample loading phase, ~7% of the U eluted from the column, whereas the abundances for the lanthanides in this fraction were below the ICP-MS instrument

detection limit. All of the remaining uranium can be quantitatively recovered by eluting with 14 mL of 2M HNO₃. The lanthanum, samarium and erbium completely eluted from the column with 6 mL of 7M HNO₃, and the uranium content in this fraction was below detection limit. The chemical recovery was 98% for La, 97% for Sm, 94% for Er and 96% for U.

To test if the chemical separation scheme reported here induces fractionation of the relative REE abundances in uranium-rich samples, the REE concentrations of CUP2, a certified reference material, was analyzed by SM-ICP-MS. In this work, the lanthanide concentrations for the dissolved CUP2 aliquots were determined after diluting the sample to approximately 100 ng g⁻¹, and were analyzed by SM-ICP-MS with and without chemical separation. Sample solutions were prepared for SM-ICP-MS analysis using a standard/spike addition method (Jenner et al., 1990).

The CUP2 material is processed uraninite from the Blind River/Elliot Lake area (Canada) (Jenner et al., 1990), and the deposit is a quartz pebble conglomerate (Ono and Fayek, 2011). Certification of the CUP2 standard is only available for major elements (Canada, 2016-05); however, Varga et al., 2010a,b (Varga et al., 2010a,b) characterized the REE signature of uranium ore concentrate from Blind River by SM-ICP-MS. The CUP2 standard and the UOC reported by Varga (Varga et al., 2010a,b) should have similar chemical signatures since both are uranium ore concentrate and are sourced from the same geographic and geologic area (Varga et al., 2010a,b; Ono and Fayek, 2011). Hence, Fig. 3 compares the chondrite normalized REE patterns for the UOC reported by Varga (Varga et al., 2010a,b) to that of the CUP2 standard obtained here. As expected, the concentrations of the REEs for CUP2 plot within the range of abundances reported for Blind River UOC by Varga et al. (Varga et al., 2010a,b; Ono and Fayek, 2011). The chondrite normalized REE patterns for both samples are relatively flat with a strong negative Eu anomaly, which is typical for uranium sourced from quartz pebble conglomerate, and thus consistent with the proposed geologic origin of the U ore (Varga et al., 2010a,b; Ono and Fayek, 2011). The REE abundances for the chemically processed CUP2 samples are three times higher than those recorded for samples that were strictly digested and analyzed without chemical separation (Fig. 3). This result is not surprising as the high uranium content of the CUP2 (75.42 ± 0.17 wt% (Canada, 2016-05)) most likely produces an

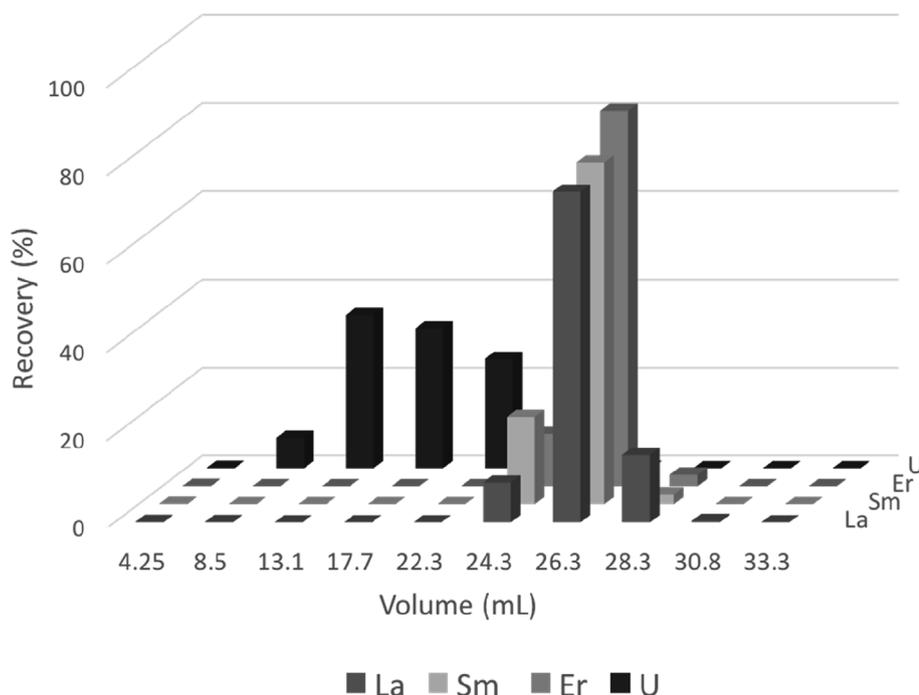


Fig. 2. Recovery (%) vs. elution volume of lanthanide and uranium eluted on AG50-X8 resin.

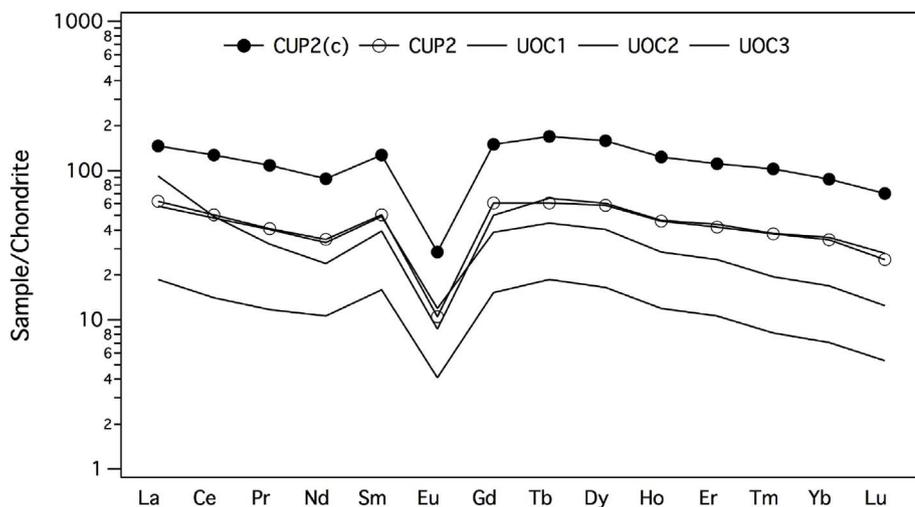


Fig. 3. Chondrite-normalized rare-earths plots for uranium ore concentrate standard before (CUP2) and after (CUP2(c)) chemical separation via extraction chromatography. Results are compared to REE signature from UOC samples originating from the geologic same area as CUP2, as reported by Varga et al., 2010a,b) (Varga et al., 2010a,b) (UOC1-UOC3).

enhanced matrix effect, and suppresses the ionization efficiencies of the remaining elements within the plasma/introduction region of the ICP-MS instrument.

As an additional validation of the chemical separation scheme proposed in this study, SM-ICP-MS elemental abundance data obtained for uraninite samples processed by the chemical separation method are compared to those obtained by laser ablation for the same samples (Fig. 4). The chondrite normalized REE patterns of the samples analyzed by solution mode match those obtained by laser ablation,

therefore confirming that contamination from dissolved (non U-bearing) secondary minerals is not a concern.

Recent studies have shown that laser ablation-ICP-MS technique is a relatively quick and valid method to obtain accurate trace elements abundances in samples of interest to nuclear forensics (Balboni et al., 2016; Dustin et al., 2016; Bellucci et al., 2014), including U-rich materials ((Balboni et al., 2016) (Spano et al., 2017)). LA-ICP-MS analysis offers the advantage of spatial resolution that is lost during solution mode analysis. However, in this work we decided to conduct a chemical separation followed by SM-ICP-MS for reasons involving sample preparation and analysis. For a sample to be analyzed by LA-ICP-MS, it is desirable to prepare the sample as a thin section or polished epoxy mount. The uraninite samples are massive and crystalline in nature, whereas the U(VI) alteration are fine grained (nm size grained) and powdery. Although analysis of powder material by LA-ICP-MS has been proven successful, careful preparation is required to eliminate mineralogical effects and prepare highly homogeneous targets (Spano et al., 2017; Klemm and Bombach, 2001). Finally, to obtain accurate and precise laser ablation data it is necessary to obtain internal standard data for each sample, which we obtained by electron microprobe analysis. Uranyl minerals can be unstable during electron microprobe analysis, and this instability could lead to increased error in obtaining accurate and precise internal standard values (Graham et al., 1984). In this study all in situ analyses including electron microprobe (EMP) and laser ablation (LA)-ICP-MS were conducted on areas of UO₂ samples with no visible alteration.

Due to the high degree of heterogeneity within most samples, great care was taken to select spots that corresponded to uraninite, and not to alterations or secondary phases within the specimens. Many of the analysis totals for the elemental oxide concentrations are lower than 100 wt%, and typically range from 87 to 100 wt%. The lower calculated elemental oxide totals in uraninite may be attributed to either deviations from the ideal UO₂ formula, concentrations of elements not analyzed for by EMP, and/or partial hydration or alteration (coffinitization). For example, coffinitization and alteration of primary uraninite may lead to elevated contents of Si⁴⁺ (> 2.5% wt. SiO₂), Ca²⁺ (above 1.5% wt. CaO), and Al³⁺ (Frimmel et al., 2014). Hence, the spots analyzed by EMP that yielded elevated amounts of CaO and SiO₂ were not considered for LA-ICP-MS analysis.

For each sample, the average abundances derived from three to five ablation sites were compared with the concentrations obtained from one solution mode replicate analysis. The ion signals associated with LA-ICP-MS analyses are transient in nature and as such these may present an analytical challenge, and are therefore associated with slightly lower precision relative to SM-ICP-MS results for the same sample.

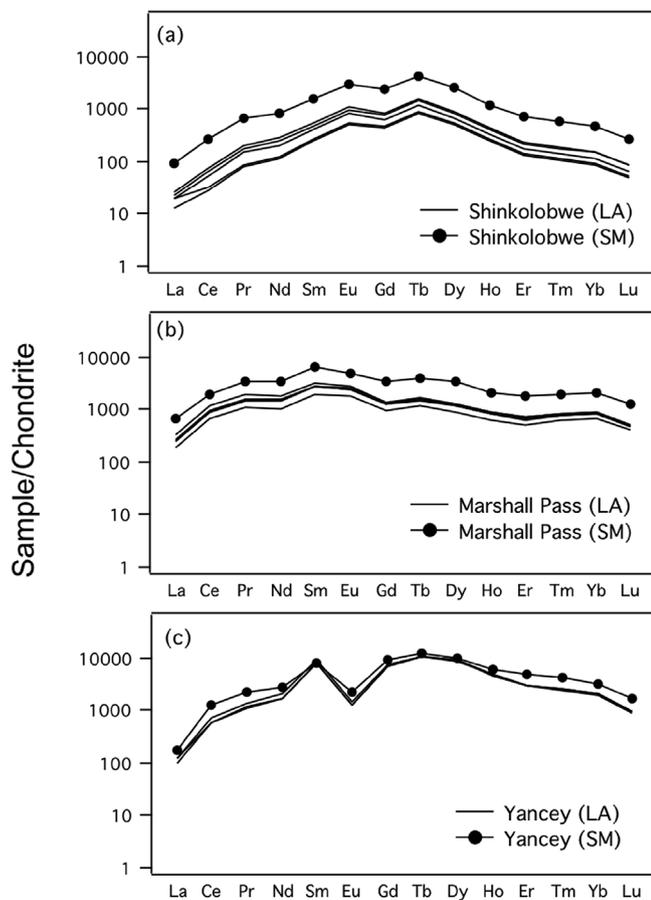


Fig. 4. SM-ICP-MS results compared to LA-ICP-MS analysis for the same uraninite samples. SM data were collected after REE separation from U-rich matrix using AG50-X8-based ion exchange columns.

Very good agreement exists between LA-ICP-MS results for all uranium ore samples and their corresponding SM-ICP-MS analyses for the same material after chemical separation (Fig. 4). For example, both LA and SM REE concentrations in the Shinkolobwe uraninite show enrichment of the middle REEs (Sm–Ho) centered at Tb - (Fig. 4a), which is consistent with the patterns for Shinkolobwe reported by both Frimmel et al., 2015 (Frimmel et al., 2014), and Mercadier et al., 2011 (Mercadier et al., 2011; Bonhoure et al., 2007).

For all samples analyzed here, the REE concentrations obtained by solution mode are two-to-four times higher than those measured by laser ablation (Fig. 4). The higher elemental concentrations measured by solution mode compared to laser ablation mode are not unexpected and could be the result of reduced ionization efficiencies during the LA-ICP-MS analyses due to the high uranium content of the matrix (U ~ 88 wt%).

The results reported in Figs. 3 and 4 suggest that the chemical separation scheme proposed here is an efficient method to obtain separation of the REEs from U-rich matrices. Moreover, this chemical separation procedure allows reduction of matrix effects and yields enhanced ion signals without significant relative fractionation of the REEs in uranium rich samples.

3.2. Method application: uranium ore and its alteration minerals

Samples *Great Bear Lake*, *Marshall Pass*, *Jefferson Co* and *Yancey* consist mainly of massive, black uraninite with a mantle of bright yellowish/orange alteration products (Fig. 1). Alteration minerals were identified by P-XRD analysis as corresponding to a combination of uranyl-oxyhydrate, silicate and phosphate minerals (Fig. 5). Details of the mineralogical compositions of the uranyl alteration minerals of each sample are reported in Table 2. In the following section, the elemental results for altered sections of each sample will be designated by an (a) after the locality's name (e.g., *Yancey (a)*). The concentration of REEs obtained for uranium ore samples (*Great Bear*, *Marshall Pass*, *Jefferson Co* and *Yancey*) are compared to those obtained for the associated uranyl alteration minerals of the respective ore subsequent chemical separation (Fig. 6).

REE abundances of the ore and alteration minerals for *Yancey* overlap, indicating that no REE fractionation occurs during alteration of this sample (Fig. 6). The *Marshall Pass(a)*, *Jefferson Co(a)* and *Great Bear Lake(a)* contain lower concentrations of REEs than their respective unaltered ore; additionally, the REE abundances in *Great Bear Lake (a)* and *Jefferson Co(a)* appear appreciably fractionated. Fig. 7 illustrates the ratio of REE abundances in the ore versus those in the corresponding alteration minerals. For the sample from *Yancey*, this ratio for most elements approaches unity; uraninite samples from *Marshall Pass(a)*, *Jefferson Co(a)* and *Great Bear Lake(a)*, are characterized by values > 1 and indicate that the REE abundances are greater in the ore than

Table 2
Characterization of alteration material by P-XRD for *Great Bear Lake*, *Marshall Pass*, *Jefferson Co* and *Yancey*.

Sample	Mineral name	Mineral formula
<i>Great Bear Lake</i>	soddyite	(UO ₂) ₂ (SiO ₄) (H ₂ O) ₂
	fourmarierite	Pb[(UO ₂) ₄ O ₃ (OH) ₄](H ₂ O) ₄]
<i>Marshall Pass</i>	becquerelite	Ca[(UO ₂) ₃ O ₂ (OH) ₃] ₂ (H ₂ O) ₈
	metaankoleite	K ₂ (UO ₂) ₂ (PO ₄) ₂ (H ₂ O) ₆
<i>Jefferson Co</i>	phosphuranylite	KCa(H ₃ O) ₃ (UO ₂)[(UO ₂) ₃ (PO ₄) ₂ O ₂ (H ₂ O) ₈
	dumontite	Pb ₂ [(UO ₂) ₃ (PO ₄) ₂ O ₂](H ₂ O) ₅
<i>Yancey</i>	clarkeite	(Na,Ca,Pb) (UO ₂)O(OH) (H ₂ O) _{0.1}
	uranophane	Ca[(UO ₂) ₂ (SiO ₃ OH)](H ₂ O) ₅
	curite	Pb ₃ [(UO ₂) ₈ O ₈ (OH) ₆](H ₂ O) ₃

associated alteration minerals (Fig. 7). Also, the slope of the line representing the ore/alteration ratio (La to Lu) can provide some insights into the behavior and possible fractionation of the REEs (Fig. 7). The slopes of the lines for *Yancey* and *Marshall Pass* show little to no fractionation since the values for these are 0.0023 and 0.0347, respectively; in contrast, those for *Jefferson Co* and *Great Bear Lake* yield slopes of 0.1243 and 0.457, respectively. The trend of *Jefferson Co* indicates that light REEs preferentially fractionate into the uranyl alteration rind associated with the sample.

The differential mobilization of the light vs heavy REEs may result from differences in mineral stabilities and their relative abundances as various minerals fractionate REEs differently since this changes the number of sites that can preferentially incorporate light vs. heavy REEs (Nesbitt, 1979). For these reasons, in order to better understand the fractionation of the light REEs in the *Jefferson Co(a)* sample, the mineralogy of the alterations for all samples should be fully investigated. Upon dissolution of uraninite, it is expected that the mobilized REEs would be incorporated into the structure of alteration minerals, due in part to the low solubility of the REEs. Sorption onto clay minerals may also occur (Chen and Simonetti, 2013); however, the alteration minerals investigated here by P-XRD did not reveal the presence of clay minerals. Considering crystal chemical constraints of uranyl mineral structures, such as ionic radii and cation coordination environments, we postulate that the REEs are more likely to substitute for the interlayer cation in the U(VI) mineral structure, rather than within interstices in the framework. *Yancey(a)* and *Marshall Pass(a)* contain uranyl layered minerals with Ca²⁺ in the interlayer (uranophane and bequerelite; Table 2). Ca²⁺ has an ionic radius of 1.12 Å, which is slightly larger than most of the REEs (1.16–0.97 Å); however, Ca²⁺ to REE³⁺ substitution is not implausible. For example, uranyl minerals with REEs as interlayer cations can be found in the minerals bijovite and kamotoite (Li et al., 2000); additionally reports of uranyl minerals in which REEs substitute for the interlayer Ca²⁺ site are known (Lu et al., 2007). REE³⁺ have also been shown to substitute for the Ca site within the

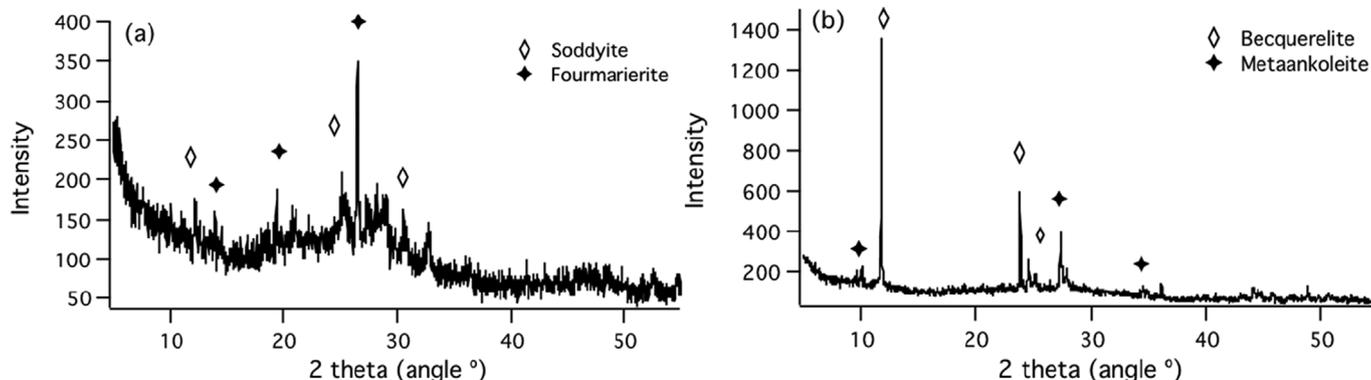


Fig. 5. Powder XRD pattern of *Great Bear Lake(a)* and *Marshall Pass(b)*. Strongest peaks are marked (◊◆) and are matched to PDF patterns for soddyite (00-053-0887), fourmarierite (04-012-9704), bequerelite (04-016-4479) and metaankoleite (04-011-5519).

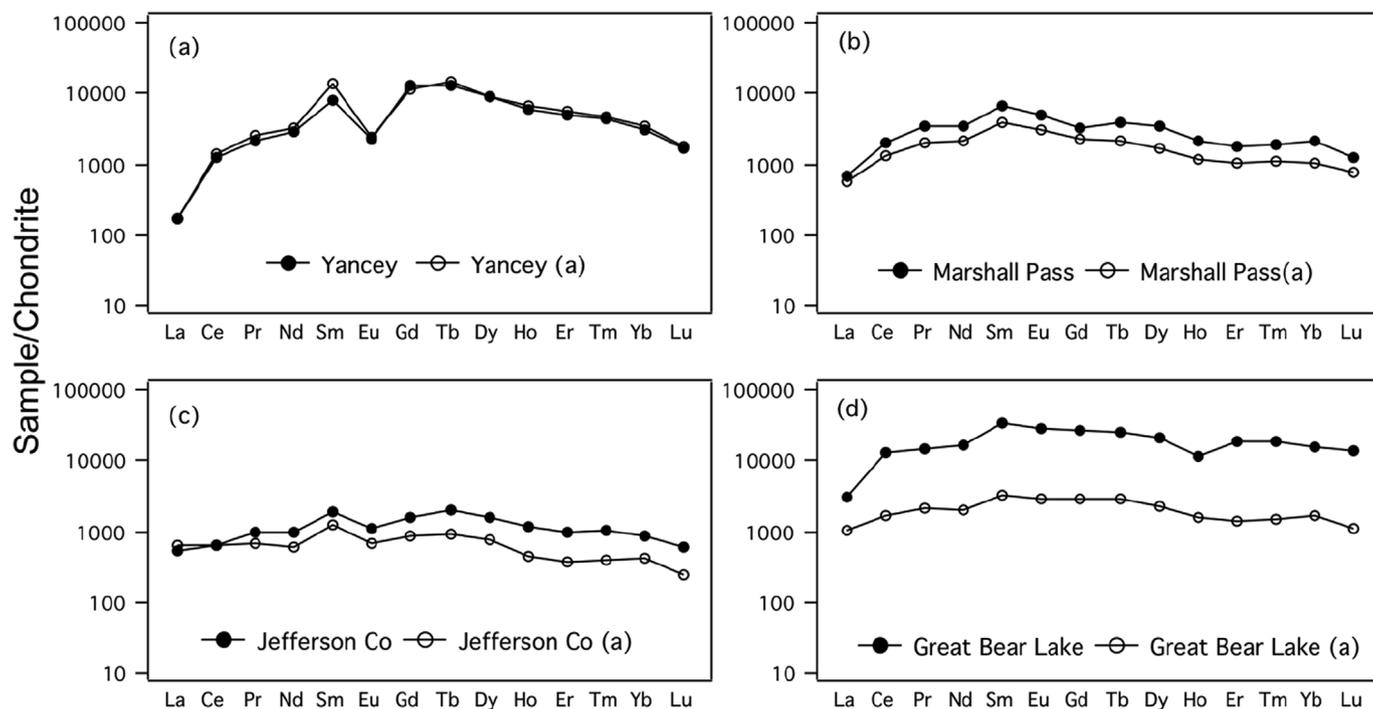


Fig. 6. Chondrite-normalized rare-earth patterns of uranium ore and their respective alteration for *Great Bear Lake*, *Marshall Pass*, *Jefferson Co* and *Yancey*.

carbonate minerals calcite (Curti, 1999; Fernandes et al., 2008) and aragonite (Schmidt et al., 2009). *Jefferson Co(a)* is composed of dumontite and phosphuranylite. Dumontite is a layered mineral with Pb^{2+} as the interlayer cation. The substitution in the crystal lattice of Pb^{2+} with the REEs is not favored due to large difference in ionic radii of Pb^{2+} (1.29 Å) compared to the REEs. Phosphuranylite is a layered uranyl oxyhydrate mineral with Ca^{2+} and K^+ cations located in the interlayer. The substitution of K^+ by REE^{3+} is unlikely due to large differences in ionic radii ($K^+ = 1.55$ Å) and charge. The large difference in charge of these cations would require substantial charge compensation mechanisms that may hinder substitution of REE^{3+} for K^+ .

Results indicate that some fractionation of REEs may occur as uranium ore alters to U(VI) minerals (Figs. 6 and 7) and abundances of the light REEs (LREE) appear fractionated over the heavy REE (HREE) in *Jefferson Co*. The LREEs have slightly larger ionic radii relative to the HREEs (lanthanide contraction), and this may explain the higher affinity for LREEs in the alteration rind for *Jefferson Co(a)* sample.

Great Bear Lake(a) is composed of soddyite, a neutral uranyl silicate framework structure with no monovalent or divalent cations, and fourmarierite, a layered mineral with Pb^{2+} as the interlayer cation. The mineralogy of *Great Bear Lake(a)* and the positive slope (0.457, Fig. 7) may seem to suggest a similar LREE fractionation behavior as discussed for *Jefferson Co*. The REEs patterns of the alteration and ore for the *Great Bear Lake* are smooth (Fig. 6); however, the ore/alteration pattern displays spikes in the heavy rare-earths (Fig. 7). These spikes cannot be explained solely by simple light rare-earth fractionation into U(VI) secondary minerals. Various factors could be affecting the HREE spikes and fractionation including but not limited to, the presence of minor mineral phases that were not detected by P-XRD analysis (poorly crystalline phase, low abundance), or inter-mine REEs composition variations (Keatley et al., 2015).

Finally, the trace element contents of primary uraninite in samples from *Jefferson Co*, *Great Bear Lake* and *Marshall Pass* are higher than those for secondary uranium phases, suggesting that primary uraninite

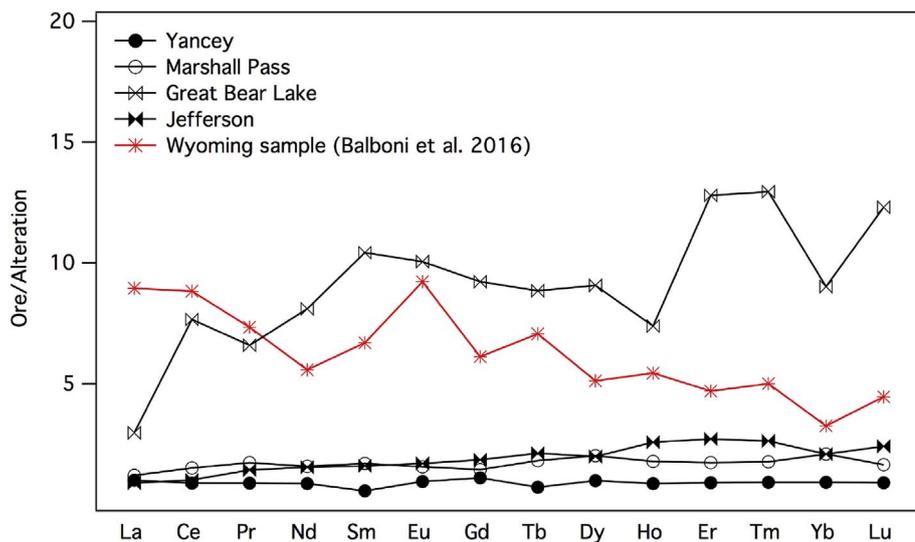


Fig. 7. SM-ICP-MS elemental abundance of uranium ore vs. respective alteration *Yancey*, *Marshall Pass*, *Great Bear Lake* and *Jefferson Co*. Data were collected after REE separation from U-rich matrix using AG50-X8. The “Wyoming sample” data set represents the REE ratios of a uranium ore and a UOC sample sourced from the same location in Wyoming (data from Balboni et al., 2016) (Balboni et al., 2016).

has higher capacity for incorporating trace elements than its associated secondary mineralization.

Understanding REE behavior during uranium ore oxidative alteration may provide valuable insights into fractionation processes that may occur in the production of UOC. At the early stages of the nuclear fuel cycle after dissolution of the ore (acid or in situ leaching through oxygenation), the uranium is commonly precipitated from solutions to produce UOC using one of five reagents: ammonium hydroxide, hydrogen peroxide, ammonium carbonate, magnesia, and sodium hydroxide (Plaue et al., 2013). Use of various precipitation agents will promote formation of slightly different uranium products. For example, the use of ammonium hydroxide will promote formation of ammonium uranate $(\text{NH}_4)_2\text{U}_2\text{O}_7$, whereas use of peroxide will favor the formation of studtite (or metastudtite) $[(\text{UO}_2)_2\text{O}_2(\text{H}_2\text{O})_2] \cdot 2(\text{H}_2\text{O})$ (Clegg et al., 2001; Cahill and Burkhart, 1990; Gayer and Thompson, 1958; Cordfunke and Loopstra, 1971). Therefore, in order to accurately identify any correlation between the REE pattern of UOC and that of the respective ore, it is of primary importance to investigate the effect of the manufacturing process on the relative distribution of the REEs (Varga et al., 2011). Although several studies have successfully attributed uranium ores and uranium ore concentrates (UOCs) to specific mining areas (Keegan et al., 2008, 2012, 2014; Varga et al., 2010a,b; Han et al., 2013; Svedkauskaite-LeGore et al., 2007), few examples are reported in the literature in which uranium ore and UOC processed from the same geographic area are directly compared. Balboni et al., 2016 (Balboni et al., 2016) reported a direct comparison between the REE signature of a uranium ore sourced from a roll front deposit in Wyoming and a sample of UOC from the same geographic area. Fig. 7 illustrates the ratios between REE abundances (La–Lu) in the Wyoming ore sample versus those from the UOC using the data in Balboni et al. (2016). In general, the chondrite normalized REE pattern is maintained between the ore and the UOC (Balboni et al., 2016); however, the data in Fig. 7 show a slight enrichment in the HREEs for the UOC compared to the ore sample, which is confirmed by a calculated, negative (-0.3618) slope for the line. Factors that could contribute to the observed REEs fractionation in this sample include: i) the type of processing employed to produce the UOC; ii) the crystalline nature and composition of the final product and its ability to accommodate REEs in its structure; iii) an incomplete extraction from the deposit; iv) intermine variations; iv) dissolution of secondary alteration phases.

The results reported here indicate that fractionation of the REEs may occur between uranium ore and its associated alteration products, and may be controlled by the nature of the secondary minerals present. Although REEs signatures are usually maintained between the ore and the UOC, slight REEs fractionation processes may occur. Future work should focus on understanding how different chemical precipitations of leached ore may fractionate the REEs. This knowledge could help to better understand how process and chemical history of samples affect the REE signature of UOC, which is fundamental information for attribution studies.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apgeochem.2017.10.007>.

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