Sequential Separation of Uranium, Hafnium and Neodymium from Natural Waters Concentrated by Iron Coprecipitation

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A new ion exchange chromatography method is presented for the isolation of high field-strength elements (HFSE) from freshwater and seawater samples that have undergone iron coprecipitation. Large volumes of water can be condensed through the application of iron coprecipitation, but clean separation of elements from the precipitate proves difficult. The technique described is a five-column process designed to separate the HFSE, including rare earth elements such as neodymium and hafnium, before removing the iron and isolating uranium. Subsequent isolation of Nd and Hf was achieved using established ion exchange chromatography methods. The efficacy of our chemistry was verified by measurements of analytical reference materials – both reference solutions and seawater samples – subjected to the chemical separation methods described. Elution results indicate high yields (> 90%) determined by concentration measurements of a known reference material added to each column. Measurement results for isotopic compositions of seawater (U, Nd) and reference solutions (NIST SRM 960, U) were identical within uncertainty to previously published values. Compositions were identical between solutions (Spex CLMS3, Spex PLND2) that underwent different iron coprecipitation procedures. Isotopic determinations for reference materials JNdi-1 and NIST SRM 960 measured with the mass spectrometers used in this study were in agreement with universally accepted values for these materials, and indicate high precision.

Keywords: column chemistry, freshwater, seawater, iron coprecipitation, uranium isotopes, HFSE isotopes.

Une nouvelle méthode de chromatographie échangeuse d'ions est présentée pour la séparation des éléments à champ électrostatique élevé («HFSE») à partir d'échantillons d'eau douce et d'eau de mer ayant subi une co-précipitation du fer. De grandes quantités d'eau peuvent être condensées grâce à la co-précipitation du fer, mais une séparation nette des éléments du précipité se révèle difficile. La technique décrite est un procédé cinq colonnes destiné à séparer les «HFSE», y compris les terres rares tels que le néodyme et l'hafnium, avant d'enlever le fer et de séparer l'uranium. La séparation subséquente de Nd et Hf a été réalisée à l'aide deméthodes bien établies de chromatographie échangeused'ions. L'efficacité de notre chimie a été vérifiée par l'analyse de matériaux de référence –à la fois des solutions standards et des échantillons d'eau de mer - soumis aux procédés de séparation chimique décrits. Les résultats des élutions indiquent des rendements élevés (> 90%) déterminées par des mesures de concentration d'un matériau de référence connu ajoutédans chaque colonne. Les résultats des mesures de la composition isotopique de l'eau de mer (U, Nd), et des solutions standards (NIST SRM 960, U) sont identiques dans l'intervalle d'incertitude des valeurs précédemment publiées. Les compositions sont identiques entre les solutions (Spex CLMS3, Spex PLND2) ayant subi différentes procédures de co-précipitation du fer. Les déterminations isotopiques pour les matériaux de référence JNDI-1 et NIST SRM 960 mesurées avec les spectromètres de masse utilisés dans cette étude sont en accord avec les valeurs universellement acceptées pour ces matériaux, et indiquent en outre une grande précision.

Mots-clés : chimie sur colonne, eau douce, eau de mer, co-précipitation du fer, isotopes de l'uranium, isotopes des HFSE.

Isotopic compositions of high field-strength elements (HFSE), including the uranium series (U-series), neodymium and hafnium, in glacial melt-water, seawater and a mixture of the two can provide insight to the timescale of hydrological processes, source areas and the geographical extent of weathering processes. The application of U-series isotopic determination in natural aqueous systems is a powerful tool for quantifying rates of chemical and physical processes occurring at the surface of the Earth (Vigier *et al.* 2006, Andersen *et al.* 2007, Aciego *et al.* 2009, Owens *et al.* 2011). U-series radioactive decay chains have distinct advantages over other isotopic systems for determining timescales of processes due to the variable decay rates of radiogenic daughter products within the chains (Cheng *et al.* 2000). Neodymium and hafnium have been employed to determine the timescale and spatial extent of surface processes (Aciego *et al.* 2009), including determining the sources of dust and seawater (Van de Flierdt *et al.* 2004, Rickli *et al.* 2010, Persson *et al.* 2011, Huang *et al.* 2012, Aarons *et al.* 2013) and the geographic magnitude of weathering processes. A review of existing ion exchange column chemistry for the determination of Nd, U and Hf from natural samples can be found in Jeandel *et al.* (2011).

In natural water systems, the concentrations of these elements are low. Seawater concentrations for U are ~ 3.2 ng g^{-1} (Chen *et al.* 1986), ~ 50 pmol kg^{-1} for Nd (Piepgras and Wasserburg 1982) and ~ 1 pmol kg^{-1} for Hf (Rickli *et al.* 2010). Seawater has higher concentrations of these elements than glacial melt-water; therefore, large quantities of the latter are required for accurate isotopic measurements. One way to increase the sample size while minimising the amount of water that is returned to the laboratory is to use iron coprecipitation (Choi *et al.* 2001, Rickli *et al.* 2010). When iron changes oxidation state in water, due to changes in pH, the insoluble materials form precipitates out of solution as iron hydroxide; during precipitation and flocculation, the iron scavenges HFSE out of solution. Using this method, 20-litre water samples can be reduced to < 200 g of iron slurry containing more than 90% of the HFSE, thus greatly reducing the material and financial resources required to transport large volumes of water from the field to laboratory for analysis.

Here, we describe a chemical separation technique for isolating U, Hf and Nd from samples collected via iron coprecipitation. Previous methods involving the removal of the iron precipitate from the sample have separated either uranium (Vigier *et al.* 2006) or Hf-Nd (Rickli *et al.* 2010, Huang *et al.* 2012) from iron, but there are no published methods for the clean separation of all of these elements

from the same iron solution. This new five-step chromatographic procedure allows for the clean separation of U, Hf and Nd from a single sample. Separation of these individual elements makes it possible for a more comprehensive study of the sample and the environment from which it came (e.g., glacier, ocean, fjord, etc.).

The objectives of this study were: (a) to individually separate U, Hf and Nd from the iron used to condense bulk-water samples as well as other elements that interfere with mass spectrometry measurements; (b) to attain near 100% yield recovery while avoiding mass fractionation during ion exchange chromatography; (c) to minimise blank values throughout the procedure; and (d) to obtain the same separation results for both freshwater and seawater samples.

Experimental procedures

Laboratory conditions, reagents and laboratory ware

Chemical separations and sample preparation were performed in an ISO 4 (class 10) laminar flow hood inside an ISO 7 (class 10,000) clean room of the Glaciochemistry and Isotope Geochemistry Laboratory (GIGL) in the Department of Earth and Environmental Sciences at the University of Michigan (Ann Arbor, MI, USA).

Ultra-pure reagents were used for all chemical separations. Acids were double distilled at the GIGL site from reagent grade acid. Super de-ionised water was purified using a Super Q (SQ) Millipore purification system, which provided water with a resistivity of better than 18.2 MΩ cm.

Laboratory ware, including Teflon beakers and columns, was stringently cleaned via a multi-step acid cleaning regimen. The laboratory ware was wiped with clean methanol to remove organic residue, rinsed three times in SQ water before being submerged in a capped 2-l beaker filled with distilled 7 mol l^{-1} HNO_3 and left on a hot plate overnight. The laboratory ware was then rinsed another three times in SQ water and submerged in a capped 2-l beaker filled with distilled 6 mol l^{-1} HCl and left on a hot plate overnight. Again the laboratory ware was rinsed three times with SQ water and then each individual beaker was filled one-third of the way with concentrated HNO_3 and trace HF, capped and left on the hot plate for a minimum 3 days as a final step in the cleaning process before being rinsed an additional three times with SQ water and dried in a ProPlastic Technology Mojave-Single N_2 Dry Storage Cabinet (an enclosed metal-free drying rack system with

internal ULPA air filtration that is over-pressurised with respect to laboratory air).

Sample description

To test the elution scheme, samples were created to mimic those collected in subglacial melt-water streams and open ocean natural environments. The freshwater 'subglacial melt-water' sample was composed of 10 l of tap water from the city of Ann Arbor with multi-elemental reference material solutions added (including NIST SRM 960, Spex CLMS3 and Spex PLND2). The seawater 'open ocean' sample was composed of natural seawater, filtered and purified of organic contaminants with no additives. This seawater was procured from TopFin©, which collects seawater off the East Coast of Florida and thus should be representative of well-mixed mid-Atlantic surface seawater. Because the Hf concentration of seawater is low (0.4–1.1 pmol kg^{-1} (Godfrey et al. 1996)) and typically requires > 60 l of sample (Rickli et al. 2010), we added an aliquot of a pure Hf reference material to bring the concentration of Hf high enough to measure the yield and isotopic composition. We note that the seawater isotopic 'composition' with respect to Hf will be the composition of the added reference material rather than Atlantic seawater.

In addition to the 'seawater' and 'freshwater' samples created for elutions, iron coprecipitation experiments were run for isotopic fractionation with three reference solutions and one blank. The first consisted of 10 l of SQ water with aliquots of HFSE from Spex CLMS3, and NIST SRM 960 added. The second consisted of 10 l of TopFin© natural seawater with ~ 50 ng of Hf equivalent added from the Spex CLMS3 solution. The third consisted of 10 l of TopFin© natural seawater without additives, to assess the Nd composition. TopFin© natural seawater was used as a seawater reference material because the U composition of seawater is uniform within 1% throughout the global oceans (Esat and Yokoyama 2006) and the Nd composition is relatively constant within ocean water masses, specifically the North Atlantic, with discernable regional variations that are hard to quantify due to a lack of constraints on source compositions (Van de Flierdt et al. 2004, 2006). A blank was composed of 10 l of SQ water with single element spikes of U (^{236}U), Nd (^{150}Nd) and Hf (^{178}Hf) in accordance with previous studies that have used unnatural single-isotope spikes to measure concentrations by isotope dilution in ice (Aciego et al. 2009).

Carboy containers were precleaned in the GIGL clean laboratory prior to sample collection to minimise blanks. The 10 l collap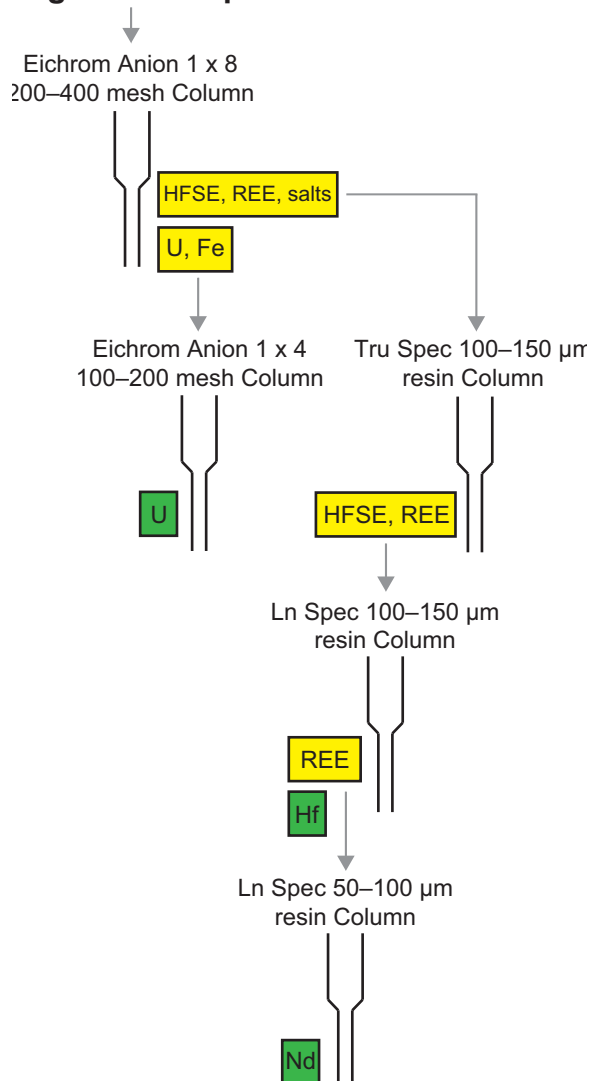sible polyethylene carboys (Thermo Fisher Scientific, Wayne, MI, USA) were triple rinsed with SQ water, leached for 48 hr in 10% reagent grade HNO$_3$, triple rinsed with SQ water, leached 48 hr in 10% double-distilled HCl and triple rinsed with SQ water. The carboys containing 10 l of 'sample' underwent iron coprecipitation, using precleaned Fisher brand I88–500 GSA/VA ferric chloride hexahydrate (FeCl$_3$•6H$_2$O) certified by the American chemical association at 97–102% assay, to reduce sample volume based on established cleaning and sampling procedures outlined in the supplementary material in Rickli et al. (2010). The pH of the samples was lowered to approximately 2–3 by adding 9 mol l^{-1} HCl and the samples were then shaken until they were homogenous. Next, a precleaned FeCl$_3$•6H$_2$O–3 mol l^{-1} HCl mixture was added to the sample. The sample was then shaken vigorously and left to sit so that it would reach chemical equilibrium. The last step consisted of adding and mixing [NH$_4^+$][OH$^-$] (ammonia hydroxide) to the sample to raise the pH to approximately 8–9. The high pH caused the iron to precipitate out of the solution along with the uranium over the course of a 2-day period. Once the settling period had elapsed, the sample was decanted. Final preconcentration of the iron precipitate was accomplished in the clean laboratory by centrifuging the samples, resulting in ~ 4 g of iron precipitate for digestion and column chemistry.

Prior to column chemistry, seawater samples were rinsed ten times with SQ water that had been buffered with ammonia hydroxide to a pH of 9 (Auro et al. 2012) after final centrifugation to remove excess salts prior to digestion. All samples were treated twice with 1 ml of aqua regia to remove any organic material that could compromise the ion exchange chromatography process.

Column chemistry

Our new ion exchange chromatography method is a multiple-column process (Figure 1). The first column was designed to separate cleanly most of the HFSE from the Fe and U. The first column had a 10 ml reservoir with a 13 cm-long column with a diameter of approximately 1.25 cm and was filled with 0.5 ml of Eichrom Anion prefilter 100–150 mesh resin and 5 ml of Eichrom Anion 1×8 100–200 mesh resin. This column was cleaned twice with a 5 ml, 12 mol l^{-1} HCl–0.13 mol l^{-1} HF mixture and twice with 10 ml of SQ water, and then preconditioned twice with 5 ml of 12 mol l^{-1} HCl. The coprecipitate samples were evaporated to dryness and digested in 10 ml of 12 mol l^{-1} HCl, which was then loaded onto the preconditioned columns and collected along with two rinses of 2 ml 12 mol l^{-1} HCl and 5 ml 12 mol l^{-1} HCl. This eluted volume contained cleanly separated HFSE (including Hf, Nd, Th). The remaining sample

Digested sample

Eichrom Anion 1 x 8
200–400 mesh Column

HFSE, REE, salts

U, Fe

Eichrom Anion 1 x 4
100–200 mesh Column

Tru Spec 100–150 μm
resin Column

U

HFSE, REE

Ln Spec 100–150 μm
resin Column

REE

Hf

Ln Spec 50–100 μm
resin Column

Nd

Figure 1. Summary of the chemical scheme for the clean separation of Ca, REE and HFSE (including Hf, Nd and Th), and U from water samples condensed via iron coprecipitation.

was then rinsed off the column and collected in four 2 ml 0.5 mol l^{-1} HCl eluted volumes. This U- and Fe-bearing portion was then dried and redissolved in the loading solution for the next set of columns (5 ml 7.5 mol l^{-1} HNO$_3$).

The second column was designed for the removal of iron from the remaining elements and the clean isolation of U. The second column had a 10-ml reservoir with a 13 cm-long column with a diameter of approximately 1.25 cm and was filled with 5 ml of Eichrom Anion 1 × 4 200–400 mesh resin. This column was preconditioned with 3 ml 0.25 mol l^{-1} HNO$_3$, twice with 5 ml 7.5 mol l^{-1} HNO$_3$ and again with 3 ml 0.25 mol l^{-1} HNO$_3$. The U–Fe eluted volume from the

previous column digested in 5 ml 7.5 mol l^{-1} HNO$_3$ was then loaded onto the second column. After rinsing the iron off with two additional 5 ml volumes and one 1 ml volume of 7.5 mol l^{-1} HNO$_3$, the clean uranium cut was eluted and collected in three 2 ml and one 1 ml volume of 0.25 mol l^{-1} HNO$_3$. These uranium-bearing portions were dried and redissolved in the analysing solution.

Subsequent isolation of Nd and Hf was achieved using previously established ion exchange chromatography methods (Fritz and Umbreit 1958, Münker *et al.* 2001, Aciego *et al.* 2009) and are summarised in Tables S3–S5 .

Mass spectrometry

Uranium and hafnium isotopic compositions were measured at the Wyoming High Precision Isotope Laboratory at the University of Wyoming on a Neptune PLUS ultra high-precision, high-sensitivity multi-collector inductively coupled plasma-mass spectrometer in 1 mol l^{-1} HNO$_3$ (Richter *et al.* 2001, Ball *et al.* 2008, Sims *et al.* 2008). Uranium measurements were obtained in ten cycles of 5 s integrations after 30 s of baseline measurements. Each uranium sample was bracketed with reference solution U010, diluted to a similar concentration as the samples (40 ng ml^{-1}) and a linear correction was applied for both mass fractionation and detector efficiency. NIST SRM 960 U reference material test portions were measured every five to ten samples. A total of fifty-eight measurement runs of NIST SRM 960 were completed alongside the $[^{234}U/^{238}U]_{ACT}$ sample measurements from August 2011 to March 2014, including four that underwent iron coprecipitation and column chemistry. The reproducibility of these runs is shown in Figure 2 with a long-term mean value of 0.9637 compared with the accepted $[^{234}U/^{238}U]_{ACT}$ value for NIST SRM 960 of 0.9631 (Cheng *et al.* 2000).

Hafnium measurements were obtained in twenty-five cycles of 10 s integrations, and baselines were measured by defocusing on peak before each sample. Hafnium isotopic compositions were corrected for mass fractionation using the accepted value of $^{179}Hf/^{177}Hf = 0.7325$, employing the exponential law. Calibration was achieved for Hf samples by sample-calibrator bracketing (Aciego *et al.* 2009, Rickli *et al.* 2010) using the Hf reference material JMC-475 (accepted $^{176}Hf/^{177}Hf = 0.28216$ (Vervoort and Blichert-Toft 1999)) with an average normalisation factor of 1.0004, and diluted to a similar concentration as the samples (25 ng ml^{-1}).

Neodymium isotopic compositions were measured on a Thermo Scientific Triton PLUS thermal ionisation mass
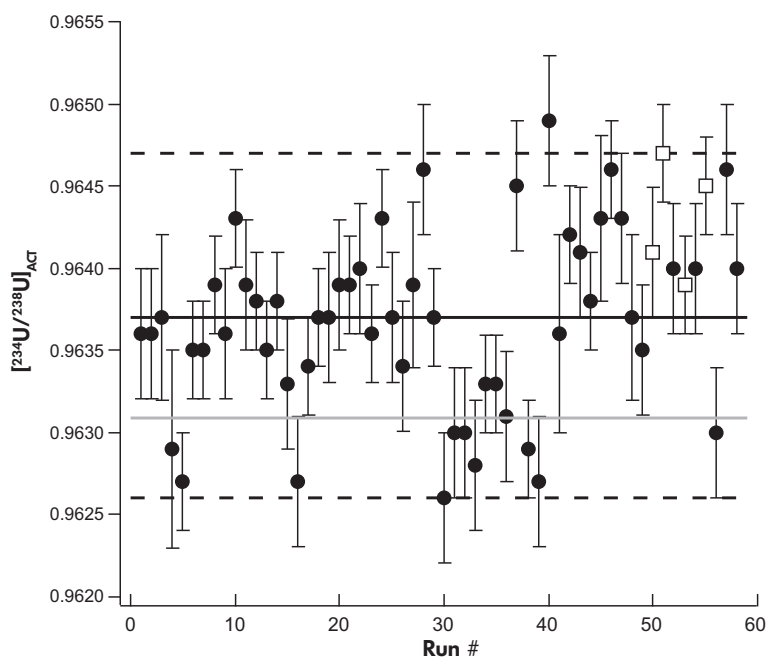
Figure 2. Plot of $[^{234}U/^{238}U]_{ACT}$ measurements of NIST SRM 960 obtained using the Neptune PLUS MC-ICP-MS over time. Black circles represent individual $[^{234}U/^{238}U]_{ACT}$ measurements of unprocessed NIST SRM 960; error bars are 2 *s* (measurement repeatability). Open squares represent individual $[^{234}U/^{238}U]_{ACT}$ measurements of NIST SRM 960 aliquots that were run through the ion exchange chromatography method described in the text. The solid black line denotes the long-term mean value, equal to 0.9637, of all of our $[^{234}U/^{238}U]_{ACT}$ measurements of NIST SRM 960 since 2011; dashed black lines represent 2 SE of the mean (measurement reproducibility). The accepted $[^{234}U/^{238}U]_{ACT}$ value of NIST SRM 960, equal to 0.9631 (Cheng *et al.* 2000), is indicated by the grey line. Measurements of NIST SRM 960 presented here are from a series of runs extending over 2 years from August 2011 to March 2014.

spectrometer (TIMS) at the University of Michigan. The Nd samples were evaporated to dryness and digested in a 3 mol l^{-1} HCl–3 mol l^{-1} HNO$_3$ mixture to achieve a 1 μg ml^{-1} solution and then loaded onto degassed double rhenium filaments. TIMS analyses began by slowly heating each filament until a stable and optimal signal was obtained before initiating measurements (once ^{144}Nd reached > 50 mV). Data measurements were acquired through 200 cycles of 4 s integrations; ^{143}Nd/^{144}Nd were normalised to ^{146}Nd/^{144}Nd to 0.7219 using the exponential law. Mass 150 was monitored and no Sm interferences were detected. A long-term record of measurements of 10 ng aliquots of the Nd isotopic reference material JNdi-1 made on the Thermo Scientific Triton PLUS thermal ionisation mass spectrometer has been kept since the machine was installed in January 2011 (Figure 3). JNdi-1 was measured as having a mean ^{143}Nd/^{144}Nd ratio of 0.512101, which is consistent with the accepted ^{143}Nd/^{144}Nd JNdi-1 value of 0.512115 (Tanaka *et al.* 2000).

Major and trace element concentrations were measured to ensure that our method had cleanly separated specific

elements of interest in the elution volumes expected. These determinations were performed at the University of Michigan Keck Elemental Geochemistry Laboratory using a Thermo-Scientific Element2 inductively coupled plasma-mass spectrometer operating in pulse-counting mode. The acidified 1 l water samples were aliquoted and 3 ml test portions of the solution was analysed. An acid blank, a reference solution of known concentration, and an additional acid blank were run in between every sample to measure the concentration accurately. Each sample was measured in triplicate; results obtained indicate the variability of the individual results were all lower than the reported uncertainty in the concentration of the reference solution.

Results

The percentage yields for Ca, Hf, Nd, Th, Ce, Lu, Fe and U from the elution scheme for columns 1 and 2 for both freshwater and seawater samples are summarised in Figure 4 and Figure S1. Yield percentages were calculated based on concentration measurements of a known amount of reference material added to each column. The elution
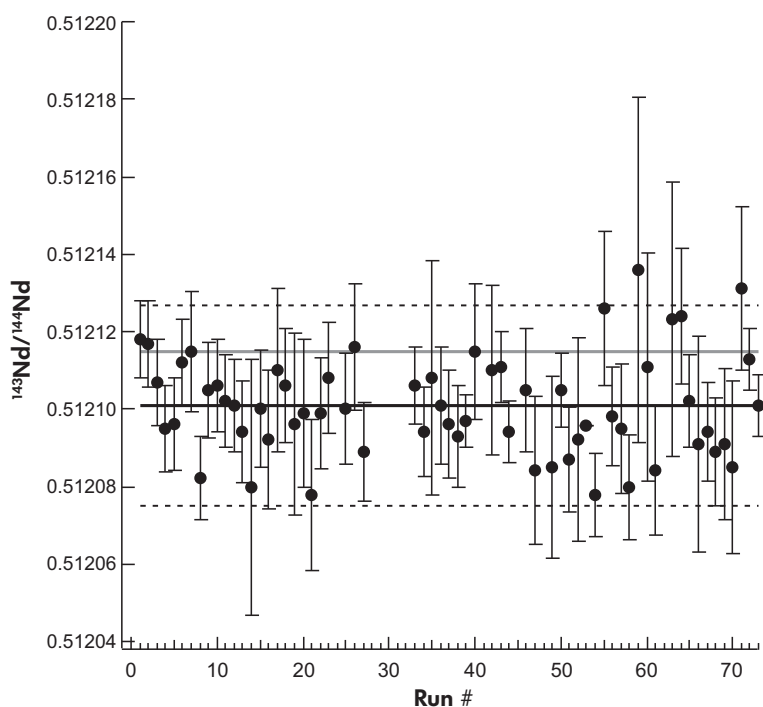
Figure 3. Plot of ^{143}Nd/^{144}Nd measurements of JNdi-1 (10 ng test portions) on the Triton PLUS TIMS over time. Black circles represent individual ^{143}Nd/^{144}Nd measurements of unprocessed JNdi-1 with 2 *s* uncertainties. The solid black line denotes the long-term mean value, equal to 0.512101, of all of our ^{143}Nd/^{144}Nd measurements of JNdi-1 since April of 2011; dashed black lines represent 2 *s* of the mean (measurement reproducibility). The solid grey line denotes the accepted ^{143}Nd/^{144}Nd value of JNdi-1, 0.512115 (Tanaka *et al.* 2000). Measurements of JNdi-1 presented here are from a series of runs extending over 2 years from August 2012 to May 2014.

profiles of the two columns indicate a yield of 94–100% for the elements of interest in their collection volumes (Figure 4 and Figure S1). Calcium was included as an indicator for the volumes that all major salt-forming cations would be eluted from the columns. In the first column, the majority (55–90%) of Ca (as well as other major salt-forming cations), HFSE including Hf, Nd, and Th and REE were removed by the initial 10 ml of 12 mol l^{-1} HCl; the subsequent 2 ml of 12 mol l^{-1} HCl eluted most of the residual volumes of these elements. Hafnium displayed unique behaviour as the seawater and freshwater samples did not follow the same trend, probably due to a seawater matrix effect (Figure 4). However, > 97% of the Hf was successfully separated in the HFSE-REE elution volume for both the freshwater and seawater samples. The Fe and U that remained on the columns were subsequently eluted in four volumes of 2 ml 0.5 mol l^{-1} HCl rinses. The bulk of U was recovered but ~ 6% was lost in the initial 12 mol l^{-1} HCl elution steps, leaving > 90% of the initial uranium to be loaded onto the second column. The second column removed the iron with 15 ml of 7.5 mol l^{-1} HNO$_3$ and subsequently separated the U remaining on the column cleanly with 0.25 mol l^{-1}

HNO$_3$ (Figure S1) in agreement with the work of Vigier *et al.* (2006).

The 'freshwater' and seawater samples that underwent iron coprecipitation and column chemistry showed similar elemental yield percentages eluted in specific volumes (Figure 4). $[^{234}$U/^{238}U]$_{ACT}$, ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf ratio measurements of both freshwater and seawater samples that underwent iron coprecipitation and were subject to multiple column ion exchange chromatography and are shown in Figures 5–7. All uncertainties in this study are reported as two standard deviations (2 *s*) from the mean. $[^{234}$U/^{238}U]$_{ACT}$ measurements of two separate TopFin© seawater aliquots that ran through different sets of ion exchange columns produced different values, with a mean of 1.1447, outside the 2 *s* uncertainty of the accepted $[^{234}$U/^{238}U]$_{ACT}$ value for global seawater of 1.1496 (Delanghe *et al.* 2002). The discrepancy between the TopFin© seawater $[^{234}$U/^{238}U]$_{ACT}$ measurements and the value of global seawater is probably due to differences in collection location, as TopFin© seawater was collected in the Atlantic. Table 1 displays ^{143}Nd/^{144}Nd values of two
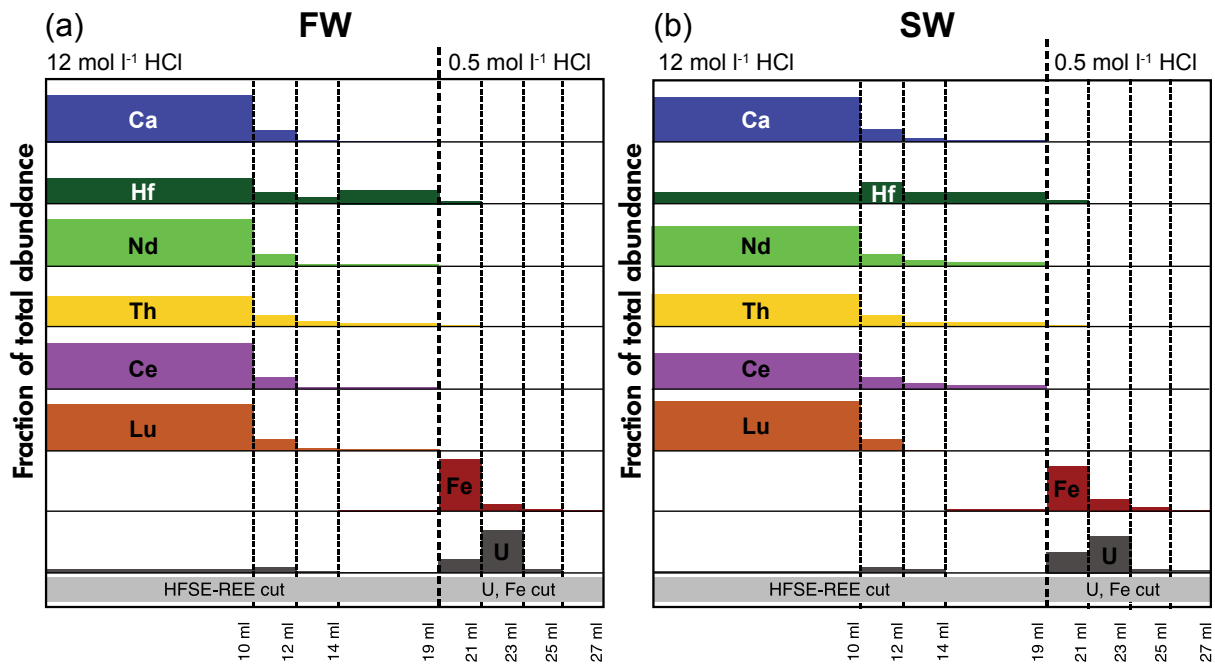
Figure 4. Histogram showing the elution scheme of HCl-based column 1 (Eichrom Anion 1 × 8 200–400 mesh) for the elemental separation of Ca, REE (including Ce and Lu) and HFSE (including Hf, Nd and Th) and U from freshwater (FW) and seawater (SW) samples condensed via iron coprecipitation.
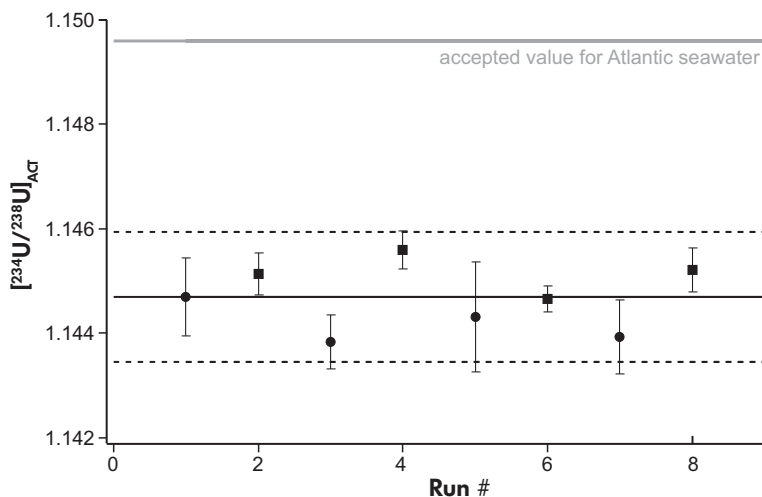

Figure 5. Multiple runs of $[^{234}U/^{238}U]_{ACT}$ measurements from the TopFin© seawater reference sample on the Neptune PLUS MC-ICP-MS. Circle and square symbols represent $[^{234}U/^{238}U]_{ACT}$ measurements of two different seawater aliquots run through separate sets of ion exchange columns; uncertainties are 2 *s* (measurement repeatability). The solid line denotes the overall seawater mean value, equal to 1.1447; dashed lines represent 2 *s* from the mean (measurement reproducibility). The solid grey line indicates the accepted $[^{234}U/^{238}U]_{ACT}$ value of Atlantic seawater (1.1496, Delanghe *et al.* 2002).

different TopFin© seawater aliquots run through separate sets of ion exchange columns and measured $^{143}Nd/^{144}Nd$ values of Atlantic seawater collected off the east coast of

Florida, ε_{Nd} = -9.6 ± 0.9 (Piepgras and Wasserburg 1987), which is slightly higher (although within uncertainty) of our measured 'reference solution' values (mean
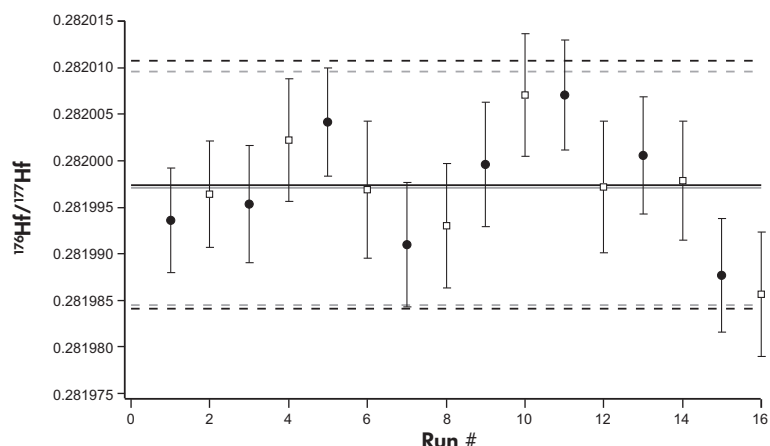
Figure 6. Multiple measurements of $^{176}Hf/^{177}Hf$ from an aliquot of a 10 ng ml^{-1} Elemental Scientific Hf reference solution Spex CLMS3, (black circles) and a mixture of TopFin© seawater reference material and Spex CLMS3 (open squares) using the Neptune PLUS MC-ICP-MS with 1s uncertainties. Both the Hf reference solution and the TopFin© seawater were run through the exchange chromatography method described in this study, with additional Tru Spec and Ln Spec ion exchange columns. The solid black line denotes the overall Hf reference solution mean value (0.2819974); the dashed black lines represent 2s about the mean (measurement reproducibility). The solid grey line denotes the overall seawater mean value (0.2819970); the dashed grey lines represent 2s of the seawater reference solution mean (measurement reproducibility). The $^{176}Hf/^{177}Hf$ measured reference solution values were normalised by bracketing with the accepted JMC-457 value (0.28216, Vervoort and Blichert-Toft 1999).

Table 1.
Compilation of reference material data

| | Reference materials | | | | |
	NIST SRM 960	Seawater	Spex CLMS3	Spex PLND2	JNdi-1
U (µg ml^{-1})		1.4–9.5			
n_t ; n_s		8; 1			
Literature*		3.213			
$(^{234}U/^{238}U)_{ACT}$	0.9637 ± 10	1.1447 ± 12			
n_t ; n_s	58; 10	8; 2			
Literature†	0.9631 ± 5	1.1462 ± 90			
$^{176}Hf/^{177}Hf$			0.281997 ± 7		
εHf			-27.28 ± 0.47		
n_t ; n_s			16; 2		
$^{143}Nd/^{144}Nd$		0.512230 ± 50		0.511542 ± 10	0.512101 ± 30
εNd		-8.4 ± 0.5		-21.39 ± 0.20	-10.48 ± 0.58
n_t ; n_s		1; 1		3; 8	61; 22
Literature‡,§		0.51195			0.512115 ± 7
εNd		-9.6 ± 0.9			-10.2

Uncertainties are reported as 2s. n_t is the total number of measurements, n_s is the number of individual solutions (dissolutions) for unknowns or run sessions in the case of the reference solutions, $_{ACT}$ identifies activity ratios, and ε represents epsilon notation. Seawater measured in this study was procured from TopFin©, and was collected from Atlantic surface water off the East coast of Florida. References for literature values: *Delanghe *et al.* (2002) (note the standard deviation represents the variability in ocean composition from samples from the Atlantic and Mediterranean Oceans); †Cheng *et al.* (2000); ‡Van de Flierdt *et al.* (2004) (note: this is the value for Atlantic surface water collected off the coast of Florida); §Tanaka *et al.* (2000). Literature values are given here with the reported 2s uncertainties.

ε$_{Nd}$ = 8.4 ± 0.5). The $^{143}Nd/^{144}Nd$ plotted in Figure 7 shows values for three sets of identical in-house reference solutions that were processed differently to test whether fractionation occurred during sample preparation and processing. The reference solution that underwent iron

coprecipitation and complete column chemistry resulted in a mean $^{143}Nd/^{144}Nd$ value of 0.511546. The solution that did not go through iron coprecipitation but underwent complete column chemistry resulted in a mean $^{143}Nd/^{144}Nd$ value of 0.511541. The reference solution
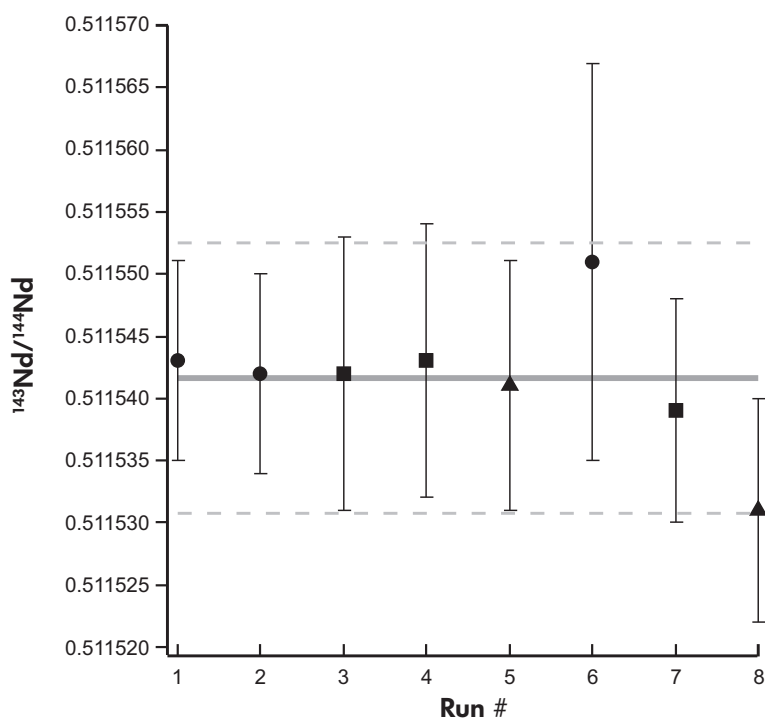
Figure 7. $^{143}Nd/^{144}Nd$ values for three identical sets of reference material solution Spex PLND2 that were processed differently to test sample preparation and processing. Samples represented by circles underwent iron coprecipitation and complete column chemistry and resulted in a mean $^{143}Nd/^{144}Nd$ value of 0.511546. Samples represented by squares did not go through iron coprecipitation but underwent complete column chemistry and resulted in a mean $^{143}Nd/^{144}Nd$ value of 0.511541. Samples represented by triangles did not go through iron coprecipitation and only underwent treatment by the final three columns (Tru Spec, Ln Spec and REE), resulting in a mean $^{143}Nd/^{144}Nd$ value of 0.511536. The solid grey line denotes the total $^{143}Nd/^{144}Nd$ mean value (0.511542); dashed grey lines represent 2 *s* from the mean. Uncertainties of individual measurements are expressed as 2 SE (measurement repeatability).

that did not go through iron coprecipitation and only underwent the final three columns (Tru Spec, Ln Spec and REE) resulted in a mean $^{143}Nd/^{144}Nd$ value of 0.511536. Measured blanks were 8 pg U, 10 pg Nd and 3 pg Hf.

$[^{234}U/^{238}U]_{ACT}$, $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$ measurements of the reference materials that were used are summarised and compared with accepted or published values in Table 1. We have demonstrated the long-term reproducibility of international reference materials on both the Neptune PLUS ICP-MS (U reference material NIST SRM 960 in Figure 2) and the Triton PLUS TIMS (Nd reference material JNdi-1 in Figure 3).

Analytical assessment

The ion exchange chromatography method described in this paper was successful in separating the HFSE (including REE and U) from the iron slurry for both freshwater and seawater samples. The per cent yields of HFSE from the

seawater and freshwater reference materials were high (> 90%) and the columns behaved comparably for both freshwater and seawater (Figure 4). There was a delayed effect in eluting the elements from seawater samples compared with the freshwater samples, with a slightly lower concentration in initial volumes passed and a slightly higher concentration in the subsequent volumes passed. However, each element of interest was predominantly eluted (94.8% U, 97.3% Hf and 99.6% Nd) and collected; thus, the discrepancies in small volumes did not lead to discrepancies in the total per cent yield of the elution volumes. Our measured values for reference materials were in good agreement with published values (Table 1), which demonstrates the validity of the sample measurements and the success of the new ion exchange chromatography method.

Determining U, Nd, Hf, and other trace and major element concentrations in each volume eluted from our columns is the best way to confirm high yields at specific steps and verify the absence of elutions at unexpected

volumes in the protocol. Measurement of the isotopic composition of reference solutions indicated that we obtained ~ 100% yields, as these solutions were subject to the same column chemistry as the samples. Verifying the known initial composition by the measurements ensured that no fractionation occurred during ion exchange chromatography. Measurement of uranium (NIST SRM 960) and Nd (Spex PLND2) in reference solutions prepared and processed to varying degrees of the complete methodology indicated that no fractionation took place during sample preparation and/or processing.

Conclusions

In this work a new five-column ion exchange chromatography method was designed for the clean separation of high field-strength elements, including the U-series, Nd and Hf, REE and U from freshwater and seawater samples that were subject to iron coprecipitation. The chemical elemental separation method presented here successfully performed clean, high-yield separations of U, REE and HFSE (including Nd, Hf) from bulk seawater and freshwater samples condensed via iron coprecipitation. Obtaining precise measurements of multiple radioactive and radiogenic isotopes from a single water sample that underwent iron coprecipitation minimises the material and financial expense of bulk-water radioactive and radiogenic isotopic determination and greatly shortens the time in which these analyses can be accomplished. Based on these results, it is now possible to measure HFSE, REE and U from a single freshwater and/or seawater sample that is concentrated using iron coprecipitation.

Acknowledgements

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Supporting information

Additional Supporting information may be found in the online version of this article:

Figure S1. Histogram showing the elution scheme of the HNO_3-based column 2.

Tables S1–S5. Details of sequential element separation employed in columns one to five.

Table S6. Cup configurations employed for MC-ICP-MS measurements of Hf and TIMS measurements of Nd.

Table S7. Operating conditions for MC-ICP-MS measurements of Hf and U.

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