A new procedure allowing the sequential extraction of Ra, Nd, Th, Pa and U from the same initial natural sample (sea or river waters, particles, sediments, rocks) is proposed. Extraction recoveries were better than 90%. Procedural blanks ranged from 80 pg (for Nd) to below 1 fg, the detection limit of the MC-ICP-MS used (for Pa); all were negligible compared with the amounts of elements currently determined. Based on classical anionic resins attached to a peristaltic pump allowing precise flow rate control, this procedure allowed a consequent reduction of the sample size, which improved the sampling resolution and reduced the sampling cost. It also ensured a better consistency of the samples for the five tracers.

Keywords: chemical extraction chromatography, isotopes, natural samples, marine geochemistry, radium, neodymium, thorium, protactinium, uranium.

Received 18 Nov 09 – Accepted 11 May 10
The ultimate goal of these extractions was the measurement of Nd and U isotopic compositions. Joannon and Pin (2001) present several methods, which include (a) a first elution with Dowex AG50W-X8 and 5 mol l⁻¹ HNO₃ followed by a second on Sr resin with 5 mol l⁻¹ HNO₃, a procedure directly inspired from the initial development of Chabaux et al. (1994). This procedure was also adopted by Foster et al. (2004) for seawater; these authors underlined the need to re-process the Sr resin step several times, to obtain the optimum Ba–Ra separation. (b) A single chromatographic step based on Dowex AG50W-X8, followed by elution of Ra with 9 mol l⁻¹ HClO₄. (c) The use of an Empore Ra-specific disk, further leached with 5% v/v HF and aqua regia containing 10% H₂O₂, in order to recover Ra. More recently, Yokoyama and Nakamura (2004) proposed a first extraction step based on a column made of a mixture of AG50W-X8 and AG50W-X12 and elution with 4 mol l⁻¹ HNO₃ (processed twice on the same column), followed by a purification of the Ra fraction following three steps: (a) Sr and Hf in addition to Ra, Nd, Th, Pa and U from less than 5 mg of solid material. These authors aimed at extracting these tracers from the same sample, a target similar to ours. However, their sample matrices (ice dust) together with the extremely small size of their samples required a different chemical procedure.

The purpose of the present paper is to describe a procedure that allowed the separation of the five tracers listed above into five distinct fractions, using a single chromatographic column. In most cases, Th and U fractions could be measured without further purification, whereas further purification steps were required in order to completely isolate Nd, Ra and Pa from the matrix of their respective fraction. The ultimate goal of these extractions was the measurement of Ra, Th, Pa and U concentrations by isotope dilution and the determination of Nd and U isotopic compositions. After a review of the existing procedures for these tracers, details of the protocol are outlined, the aim being to provide a useful tool for other research groups interested in geochemical studies based on these specific tracers, used simultaneously.

**Review of the existing procedures**

### ²²⁶Ra

Because of undesirable polyatomic interferences, the main issue related to the extraction of radium from natural samples is the removal of barium from the matrix, knowing that Ba is about 10⁹ times more abundant than Ra in natural environments (Larivière et al. 2003). The latter authors successfully used a combination of Eichrom Sr resin and UTEVA cartridges, followed by a final separation of Ra from the rare earth elements (REEs) using a Eichrom Ln cartridge. However, their sample matrices – U ores for example – were particularly complex and rich in many interfering elements. Joannon and Pin (2001) present several methods, which include (a) a first elution with Dowex AG50W-X8 and 5 mol l⁻¹ HNO₃, followed by a second on Sr resin with 5 mol l⁻¹ HNO₃, a procedure directly inspired from the initial development of Chabaux et al. (1994). This procedure was also adopted by Foster et al. (2004) for seawater; these authors underlined the need to re-process the Sr resin step several times, to obtain the optimum Ba–Ra separation. (b) A single chromatographic step based on Dowex AG50W-X8, followed by elution of Ra with 9 mol l⁻¹ HClO₄. (c) The use of an Empore Ra-specific disk, further leached with 5% v/v HF and aqua regia containing 10% H₂O₂, in order to recover Ra. More recently, Yokoyama and Nakamura (2004) proposed a first extraction step based on a column made of a mixture of AG50W-X8 and AG50W-X12 and elution with 4 mol l⁻¹ HNO₃ (processed twice on the same column), followed by a purification of the Ra fraction following three steps: (a) Sr and Hf in addition to Ra, Nd, Th, Pa and U from less than 5 mg of solid material. These authors aimed at extracting these tracers from the same sample, a target similar to ours. However, their sample matrices (ice dust) together with the extremely small size of their samples required a different chemical procedure.

### Nd isotopes

Although Nd isotopes have been used since the 1960s in deep Earth geochemistry, the first seawater Nd isotope data were measured by Piepgras et al. (1979) following an extraction procedure directly inspired from research in the Earth sciences (DePaolo and Wasserburg 1976, Richard et al. 1976). The pre-concentration procedures vary from FeOx or MnOx co-precipitations to online cartridge extraction (Piepgras and Wasserburg 1987, Jeandel et al. 1998). The following Nd purification required first a cationic column (typically AG50W-X8) with an elution in 6 mol l⁻¹ HCl in order to separate the REE from the remaining matrix, followed by a selective extraction of the Nd from the other REE in dilute HCl with a Ln resin or equivalent (Jeandel 1993).

### Protactinium

Because protactinium is a highly refractory element that easily adsorbs onto any surface, the use of HF is often required to ensure maximum recoveries. Another important issue constraining this tracer’s chemistry is that its spectrometric determination requires a deposit (or solution) completely cleared of its neighbour ²³⁵Th, the crustal abundance of which is about 10⁷ times higher than that of
The procedures published to extract $^{231}\text{Pa}$ from various matrices recommend the separation of Pa from the matrix using AG1X-8 resin with an elution of $^{231}\text{Pa}$ using a concentrated HCl + diluted HF mixture, followed by a purification on TRU resin with an elution in 2 mol l$^{-1}$ HCl or 3 mol l$^{-1}$ HCl + 2 mol l$^{-1}$ HF (Bourdon et al. 1999, Pichat et al. 2004, Regelous et al. 2004). The Th/Pa ratio is often reduced by a second TRU resin elution.

Uranium

Uranium is usually separated from the matrix using AG1X-8 in a diluted nitric acid medium (or water) and purified with the same resin but using dilute HCl (Chen and Wasserburg 1981). Recently, the use of TEVA resin has been proposed, with an elution in 1 mol l$^{-1}$ HCl (Tagami and Uchida 2004).

More interesting for our purpose, are the procedures allowing the extraction of two or three tracers together. Depending on the author’s scientific objectives, these concern the couples Th/U or Ra/Th/U for Earth science research, or the Pa/Th couple for the marine sciences, neglecting simultaneous Nd extraction. However, none of these procedures allow a reliable extraction of the five tracers sequentially from a single voluminous sample.

U and Th

The most common procedures are based on AG1X-8 anionic resin, both U and Th being retained in 7 mol l$^{-1}$ HNO$_3$ and then eluted using H$_2$O or diluted HNO$_3$. The separation of U from Th has been performed by a second step using 6 mol l$^{-1}$ HCl for Th and H$_2$O for U (Joannon et al. 1997).

Th and Pa

Choi et al. (2001) suggest that both tracers be fixed on an AG1X-8 resin and elute Th with 9 mol l$^{-1}$ HCl and Pa with a mixture of 9 mol l$^{-1}$ HCl and 0.14 mol l$^{-1}$ HF. The Th fraction is further purified on another AG1X-8 column in a nitric acid medium, whereas the Pa fraction is passed through a further AG1X-8 column and again eluted with 9 mol l$^{-1}$ HCl and 0.14 mol l$^{-1}$ HF.

Ra, Th and U–Pa (or U alone)

Several similar procedures have been proposed to separate Ra, Th and U–Pa from the same matrix (Luo et al. 1997, Pietruszka et al. 2002, Pin and Joannon 2002, Goldstein and Stirling 2003). These extractions require a 2–10 ml TRU resin column with a 0.5 ml Eichrom inert bed, from which Ra is eluted with 9 mol l$^{-1}$ HCl, Th with 4 mol l$^{-1}$ and 1.2 mol l$^{-1}$ HCl, and finally U–Pa with a mixture of 0.1 mol l$^{-1}$ HCl and 0.05 mol l$^{-1}$ HF. Uranium and Pa were further passed through a second column with a 0.5 ml Eichrom inert bed to remove the extractant (Goldstein and Stirling 2003). The procedure of Luo et al. (1997) is particularly interesting because one of the steps also allows REE extraction on a very small amount of resin (0.45 ml of TRU resin) allowing the elution of Ba with 1.5 mol l$^{-1}$ HNO$_3$. REE with 3 mol l$^{-1}$ HCl, Th with 0.2 mol l$^{-1}$ HCl and U with 0.1 mol l$^{-1}$ HCl + 0.3 mol l$^{-1}$ HF. However, these authors did not try to extract Ra and Pa, the less abundant radionuclides. Including these latter would increase the sample volume, and then the resin volume as demonstrated by Goldstein and Stirling (2003).

U, Th, Pa, Ra, Sr, Nd and HF

Aciego et al. (2009) had to extract these tracers from the same very small sample (5 mg). Therefore, they proposed an interesting detailed procedure based on the successive use of four primary ion exchange columns and two ‘clean up’ columns (TRU, Sr and Ln resins), allowing the extraction of these seven different tracers from a very small matrix. Their field constraint was the opposite to ours, which involved the extraction of the tracers from large volumes of a particularly rich matrix (seawater, for example). As detailed below, this yielded different working approaches.

This overview of the existing procedures leads to the following conclusions:

- None of the procedures described above allows the simultaneous extraction of Ra, Nd, Th, Pa and U from large natural samples, although many of them clearly contributed to the procedure proposed in this work.

- Two multi-purpose resins are sufficient to meet our requirements: the anionic AG1X-8 and the Eichrom TRU.

- Extracting tracers as scarce as Pa, Ra or Nd from certain matrices (e.g., basalt rocks, biogenic material or seawater) requires large sample volume and therefore large amounts of resin. Our aim being to increase the sampling resolution and the consequent number of analyses, the cost of the whole procedure was clearly an issue. As TRU resin is currently fifteen times more expensive than AG1X-8, we preferred to use the latter.
**Proposed procedure**

**Co-precipitation and digestion of the samples**

Before separating Pa, Th, Nd, Ra and U, these elements needed to be pre-concentrated (in the case of water samples) or solubilised (in the case of solid matrix).

**Water samples:** Because of the very low surface seawater Th, Pa and Nd contents, sample volumes of 20–30 l are required (Choi et al. 2001, Lacan and Jeandel 2001). Although Th, Nd, Pa and U are easily scavenged from seawater using either Fe or Mn oxides (Chen et al. 1987, Pippgras and Wasserburg 1987, Roy-Barman et al. 1996, Choi et al. 2001), Ra co-precipitation requires Mn oxide (Ghaleb et al. 2004, Bourquin et al. 2008). Therefore, Mn oxide only allows the simultaneous co-precipitation of the five elements. Volumes were less critical for river waters, but the same tracers were entrained by the same co-precipitation procedures (Chen and Wasserburg 1981).

**Particles, rocks and sediment:** Solid materials were digested using sequential hot concentrated acid attacks (Goldstein and Stirling 2003) with Th, Pa, Ra and U spike additions, either on a hot-plate or, more efficiently, using a microwave oven. All acids and reagents used for the digestion and further for the chemical separation were doubly distilled, except HF which was of ‘Suprapur’ quality. The resulting solutions were evaporated to dryness and re-dissolved in a final volume of 0.5 ml 7 mol l$^{-1}$ HNO$_3$. For instance, the gneiss sample used as a test sample for this study was first digested with a mixture of 5 ml of HF, 4 ml of HCl and 15 ml of HNO$_3$ at 80 °C (all concentrated acid), and then dried. The residue was re-dissolved in 10 ml of 7 mol l$^{-1}$ HNO$_3$ to convert the medium into soluble nitrates.

**Parameters of the chemical extraction**

**Resin volume and column geometry:** Based on the matrix charge, we estimated that 4 ml of conventional anion-exchange resin (Dowex AG1X-8, 200–400 mesh) would be necessary to allow the tracer extractions from the different matrices usually encountered in marine and continental environments. This amount of resin was loaded onto different column geometries. The first extractions were performed on a 6 mm internal diameter column, which was in-house made from thermo-retractable FEP (fluoro(ethylene-propylene)). This column yielded satisfactory separations and recoveries for Th, Pa and U, however, (a) the process lasted for 13 hr, and (b) the resolution of the Nd and Ra peaks was not satisfactory (Figure 1). Thinner columns were then tested to improve the elution stages. A column diameter of 4 mm provided the best result, as shown in Figure 2. However, such a geometry considerably lowered the elution flow rates, yielding work durations of more than 24 hr. The flow rates were increased by

![Figure 1. Elution peaks of the different tracers, using a fluoro ethylene-propylene column of 240 mm length and 6 mm internal diameter (ø), without flow rate control. The circle indicates the poor separation of the first fractions.](image-url)
mounting a high precision peristaltic pump at the base of the column (Figure 2). Contrastingly, the in-house FEP columns were no longer appropriate, because their geometry was affected by the pumping. These changes induced variation in the flow rates, precluding good control over the eluted volumes for each fraction. Finally, a quartz column of the same geometry was used: the quartz was easily cleaned and rigid enough to resist to the pressure variations induced by the pump. The total duration of the procedure was thereby reduced to 7 hr 30 min.

Separation procedure: Table 1 summarises the conditions allowing the successive extraction of the different tracers. Once the appropriate column geometry was established, the flow rates were adjusted at each step of the separation to yield satisfactory peak resolutions.

The column was pre-conditioned with 8 ml of 7 mol l\(^{-1}\) HNO\(_3\). The sample was then loaded in 7 mol l\(^{-1}\) HNO\(_3\) (0.5 ml). The beaker that contained the sample was rinsed three times with 0.5 ml 7 mol l\(^{-1}\) HNO\(_3\) and an additional 1 ml 7 mol l\(^{-1}\) HNO\(_3\) was loaded. This quantity (3 ml) corresponded to the elution of Ra together with the main matrix, which included Fe, Mn and Ba. The flow rate ranged between 0.05 and 0.055 ml min\(^{-1}\). An additional quantity (7 ml) of the same acid at exactly the same flow rate allowed the collection of the REE, including Nd. Recovering the Th fraction required 12 ml of 9 mol l\(^{-1}\) HCl, with a slightly higher flow rate of 0.08–0.09 ml min\(^{-1}\). Protactinium was then eluted with 12 ml of a mixture of 9 mol l\(^{-1}\) HCl + 0.14 mol l\(^{-1}\) HF, at a flow rate of 0.2–0.3 ml min\(^{-1}\). Finally, U was collected with 20 ml of diluted HCl at the highest flow rate (0.4 ml min\(^{-1}\)).

The most critical steps of this procedure were (a) the good resolution of the Ra vs. Nd peaks, strongly dependent on the control of flow rate, requiring precise peristaltic pumps, (b) the transition between the nitric and hydrochloric acid (between Nd and Th fractions), which required a dry front between both acids to avoid the formation of aqua regia and (c), as detailed below, prevention of any contribution (even very small) of Th or U into the Pa fraction.

A mixed standard solution made of 100 ng of Nd and Ba, 10 ng of Th and U, 60 pg of Ra and 2 pg of Pa was loaded onto the column described above. Note that since Ba can be easily measured by ICP-MS, most of the tests were made using Ba as a proxy for Ra.

Concentration determinations: This section recapitulates briefly the conditions of the spectrometric determinations, published elsewhere (Lacan and Jeandel 2005, Venchiarutti 2008, Venchiarutti et al. 2008). Neodymium and Ba (Ra) concentrations were measured using an inductively coupled plasma-mass spectrometer (Perkin Elmer ELAN 6000), with an external standard calibration and using In/Re as the internal standard. Due to the very low Th, and Pa concentrations in seawater and their high ionisation potential, Th, Pa and U concentrations were measured by isotope dilution using the more precise multi-collector inductively coupled plasma-mass spectrometer (Thermo-Finnigan Neptune at the Observatoire Midi-Pyrénées, Toulouse). Each fraction of Th, Pa and U was bracketed with a specific calibrator: IRMM-35 certified reference material spiked with \(^{229}\)Th, Amersham QSA\(^{\text{®}}\) synthetic standard (nominal activity 519 Bq ml\(^{-1}\)) spiked with \(^{233}\)Pa and NBS 960 spiked with \(^{236}\)U respectively. The fractions

<table>
<thead>
<tr>
<th>Cumulative volumes (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
</tr>
<tr>
<td>Ba</td>
</tr>
<tr>
<td>Mn-Fe</td>
</tr>
<tr>
<td>Th</td>
</tr>
<tr>
<td>Nd</td>
</tr>
<tr>
<td>U</td>
</tr>
<tr>
<td>Ba</td>
</tr>
<tr>
<td>Mn-Fe</td>
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<tr>
<td>Th</td>
</tr>
<tr>
<td>Nd</td>
</tr>
<tr>
<td>U</td>
</tr>
<tr>
<td>Ba</td>
</tr>
<tr>
<td>Mn-Fe</td>
</tr>
<tr>
<td>Th</td>
</tr>
<tr>
<td>Nd</td>
</tr>
<tr>
<td>U</td>
</tr>
</tbody>
</table>

Figure 2. Elution peaks of the different tracers, using a quartz column ~ 340 mm in length and 4 mm in internal diameter (a), with a rigorous flow rate control using a peristaltic pump mounted at the base of the column. Note the different scale on the x-axis compared with Figure 1. Resulting elution duration was of 7 hr 30 min.
measured using the MC-ICP-MS were corrected for mass fractionation, gain calibration and, in the case of \(^{231}\)Pa and \(^{230}\)Th, for \(^{232}\)Th peak tailing.

**Close look at the different fractions**

The extraction recovery and purity of each fraction are compiled in Table 2. The results reported here were obtained from the mixed standard solution described above. The number \((n)\) of tests reported in Table 2 depended on the element: since the extraction of Th, Pa and U was rapidly solved, part of the tests focused on the ‘Ba–Nd’ separation, doubling the number of tests for these elements. This information on the quality of the fractions allowed us to decide whether an additional purification step was required before spectrometric determination. The final aim of this procedure was to determine Ra, Th and Pa by isotope dilution, and Nd and U isotopic compositions. In agreement with all known procedures based on reverse chromatography (presented above), the isotopic fractionations linked to the chemical separation may be considered as negligible for several reasons: (a) the recoveries of Nd, Th and Ra were close to 100%, preventing any isotopic fractionation, (b) the mass ratio of heavy elements is very low: for example, considering the worst recovery obtained when analysing natural particles for Pa (24%, see below) the kinetic fractionation between masses 231 and 233 was only 4‰, i.e., negligible compared with the analytical uncertainties on the \(^{231}\)Pa/\(^{233}\)Pa isotopic ratio and (c) for Nd, the lightest and then potentially most fractionated element, the use of the internal \(^{144}\)Nd/\(^{146}\)Nd ratio to correct the mass bias during Nd mass spectrometric isotopic determination corrected chemistry-induced fractionations.

**Ra fraction:** Table 2 shows that Ba was extracted with an average recovery of 96.8 ± 3.6% \((n = 5)\). This reveals the good elimination of Ba with the remaining matrix in the first fraction. We also performed some tests using a Ra reference solution with the same approach by comparing the elution efficiencies of Ra and Ba in the first fraction (Table 2, Figure 3). Two different tests were conducted: one by mixing Nd and Ra reference solutions and the other by mixing Ra with a multi-element standard solution containing sixty-five elements, from Li to U. Very similar results were obtained in both cases: the average recovery of the Ra extraction was 107.1 ± 1.9% and there was about 1% of Ra in the Nd fraction. The value slightly above 100% was probably due to a bias in the Ra standard solution calibration. The similar results obtained for Ra and Ba from the multi-element standard solutions confirmed that Ba is a relevant proxy for Ra in the separation test. The similarity of the two elements validates extrapolating the Ba results to Ra in natural sample tests. However, this also underlines that further steps are required to separate Ra from Ba.

**REE fraction:** The elution sequence of REE was also examined in order to determine if this protocol, in particular the column configuration, fractionated the REE. The HREE (heavy REEs) were indeed eluted before the LREE (light REEs, Figure 4). The Nd fraction was eluted with an average recovery of 95 ± 6% \((n = 6)\). The REE fractionation yielded the elimination of about half of the Sm from the Nd fraction by this procedure, which may facilitate the further purification of Nd (Table 1, Figure 4).

**Pa fraction:** The purity of the Pa fraction regarding Th and U was essential. First, the \(^{232}\)Th peak tailing and the Th hydrides may interfere with both \(^{231}\)Pa and \(^{233}\)Pa peaks. Second, the gamma disintegration product of \(^{233}\)Pa, \(^{233}\)U, is an isobar of the \(^{233}\)Pa isotope. In this protocol, both residual U and Th were quantified. Protactinium was extracted with a recovery of 97.9 ± 0.7% \((n = 3, \text{Table 2})\). The residual amount of U in the Pa fraction – traced by the addition of \(^{236}\)U in the initial load – was less than 0.01% of the total U, which was negligible and would not affect the mass 233 measurements. The residual amount of Th (2.5 ± 1.6%) does not imply any purification.

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**Table 1.**

**Synthesis of the whole procedure proposed in this work**

<table>
<thead>
<tr>
<th>Elution steps</th>
<th>Reactants</th>
<th>Further purification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin conditioning</td>
<td>8 ml 7 mol l(^{-1}) HNO(_3)</td>
<td></td>
</tr>
<tr>
<td>Sample loading</td>
<td>0.5 ml 7 mol l(^{-1}) HNO(_3)</td>
<td></td>
</tr>
<tr>
<td>Ba, Ra, Fe, Mn elution (0.05–0.055)</td>
<td>2.5 ml 7 mol l(^{-1}) HNO(_3)</td>
<td></td>
</tr>
<tr>
<td>HREE, Nd elution (0.05–0.055)</td>
<td>7 ml 7 mol l(^{-1}) HNO(_3)</td>
<td>Yes</td>
</tr>
<tr>
<td>Th elution (0.08–0.09)</td>
<td>12 ml 9 mol l(^{-1}) HCl</td>
<td>Yes</td>
</tr>
<tr>
<td>Pa elution (0.2–0.3)</td>
<td>12 ml 9 mol l(^{-1}) HCl + 0.14 mol l(^{-1}) HF</td>
<td>Could be required</td>
</tr>
<tr>
<td>U elution (0.4)</td>
<td>20 ml 0.5 mol l(^{-1}) HCl</td>
<td>Could be required</td>
</tr>
</tbody>
</table>

The numbers in brackets are the imposed and strictly controlled flow rates, in ml min\(^{-1}\). For further details of when further purification steps are required to obtain extremely pure Ra, Nd or, in some circumstances Pa, refer to the text.
of the Pa fraction for marine samples. Nevertheless, for rock and sediment samples the resulting $^{232}$Th peak tailing may significantly influence the Pa isotopes measurement (see below).

**Th and U fractions:** Both of these tracers were particularly well purified, and were recovered with satisfactory yields. Th was collected with a recovery of $93 \pm 5.2\%$ ($n = 3$) and U with $99 \pm 0.8\%$ ($n = 4$). The $^{230}$Th measurements were made using a secondary electron multiplier, whilst $^{232}$Th was measured on a Faraday cup, based on the methods of Regelous et al. (2004).

**Blanks:** Blanks of the chemical procedure, including acid and column contributions, were determined by ICP-MS for Ra, Ba, Nd, $^{232}$Th and by MC-ICP-MS for $^{232}$Th, Pa and U. The average values and standard deviations of three blank determinations were $475 \pm 150$ pg for Ba, undetectable for Ra, $80 \pm 20$ pg for Nd, $21 \pm 2$ pg for $^{232}$Th, below the MC-ICP-MS detection limit of ~1 fg for Pa and less than 0.004 pg for U. All of these blank values may be considered negligible compared with the amounts of elements currently determined, i.e., a few ng for U and Nd, ng to l g for $^{232}$Th and 102 fg for Pa and Ra.

To conclude on these tests of standard solutions, the U and Th fractions were pure enough to be analysed by MC-ICP-MS without any further chromatographic step, whereas Ra, Nd and Pa fractions required further purifications: Ra had to be purified from Ba; Nd had to be purified from the remaining REE and Pa could have to be purified from Th, mostly when rocks or sediments are measured.

### Application to real samples

As no certified reference materials yet exist for the tracers considered in this work, we assessed the efficiency and reliability of our procedure by extracting and purifying Ra, Nd, Th and U (no spike of $^{233}$Pa available at that time) from two kinds of samples: (a) marine suspended particles, first digested in an acid medium on a hot plate (following Tachikawa et al. 1999) and (b) a gneiss digested as described above. For both samples, extraction recoveries were determined as follows. For Nd, Th and U, which are currently measured by ICP-MS (external standard calibration), eluted fraction concentrations were compared with those obtained from the mother solution derived from the acid-digested sample: a small aliquot (3%) of this solution was diluted in 2% v/v HNO$_3$ and measured by ICP-MS without chromatographic extraction, yielding the initial concentration for each element. Extraction recovery is the ratio between the eluted fraction concentration and the initial

### Table 2.

<table>
<thead>
<tr>
<th>Acid</th>
<th>$^{232}$Ra (%)</th>
<th>$^{232}$Nd (%)</th>
<th>$^{232}$Th (%)</th>
<th>$^{232}$Pa (%)</th>
<th>$^{232}$U (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO$_3$ 7 mol l$^{-1}$</td>
<td>98.8 ± 3.6</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>HNO$_3$ 7 mol l$^{-1}$</td>
<td>96.8 ± 3.6</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>HCl 9 mol l$^{-1}$</td>
<td>0.2 ± 0.2</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>HF 0.5 mol l$^{-1}$</td>
<td>0.8 ± 0.8</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
<td>0.0 ± 0.0</td>
</tr>
</tbody>
</table>

The major tracer eluted in the corresponding acid fraction is highlighted in dark grey. The remaining numbers reflect the abundance of any other tracer in the considered fraction (e.g., the abundance of Th is 2.5 ± 1.6% in the Pa fraction and 0.07 ± 0.1% in that of Nd).
concentration. For Ra, recoveries were determined by comparing the concentrations determined by isotope dilution using a thermal ionisation mass spectrometer (TIMS) in two aliquots – one aliquot spiked before the extraction (therefore not recovery dependent) and the other spiked after it. The additional purification step required before the spectroscopic analysis followed that published in Foster et al. (2004). First, most of the Ba was removed from a cationic

Figure 3. Comparison of the extraction of Ra with that of Ba, within a complex standard solution of sixty-five elements. The Nd peak only is shown here, illustrating the satisfactory separation of the tracers between the different fractions.

Figure 4. The rare earth element (REE) elution, showing that the HREE were eluted before the LREE, including Sm, which allowed a good pre-separation of Nd from the other REE (required before the mass spectrometric determination).
column (AG50W-X8 200–400 mesh) with 4 mol l$^{-1}$ HNO$_3$. This step was clearly not sufficient to remove all Ba and required two additional separations through Sr resin, Ra being extracted with 4 mol l$^{-1}$ HNO$_3$.

The flow rates recommended above were applied, which yielded good control on the volume of the fractions. For the marine suspended particles ($n = 3$) 98.5% of the Ra extracted during the procedure was collected in the first fraction, 97.8% of Nd in the second, 98.3% of Th in the third and 99.8% of U in the fifth, together with perfect peak separations. For the gneiss aliquots ($n = 2$) recoveries were: 99% for Ra, 94% for Nd, 88% for Th and 70% for U. No U was detected in the fractions prior to that for uranium, confirming the good separation of the peaks. This also suggests that the missing 30% were not eluted with 20 ml of acid only: rich samples might require larger volumes to achieve the U extraction.

Protactinium extraction was validated by the measurements of more than one hundred seawater and particle samples in the scope of the KEOPS project, see http://www.obs-vlfr.fr/prod/vt/op/ec/keops/keo.html (Venchiarutti 2008, Venchiarutti et al. 2008). Protactinium is classically determined by isotope dilution, using $^{233}$Pa as a spike. During Venchiarutti’s work, Pa extraction was achieved on a FEP column (as described for the first extractions in this article) using the same reactants, elution volumes and the same volume of AG1X-8 anion-exchange resin. Only the column geometry and the used material (from FEP to quartz) were later changed to improve the elution stages of Ra and Nd. However, the tests performed with multi-element standard solutions showed that the geometry change did not modify the Pa extraction efficiency, thereby confirming the good extraction of Pa when using the quartz column instead of the FEP column.

The obtained average Pa recoveries from these natural samples were 57.5 ± 4.4% for the seawater (the highest recoveries reaching 97%) and 23.7 ± 4.6% for the particles – values in agreement with those resulting from other Pa analytical procedures on the same matrix (Choi et al. 2001, Thomas et al. 2006). These relatively low recoveries were probably due to the presence of abundant silica in the seawater matrix that forms gels during sample preparation, probably preventing an efficient Pa extraction.

In addition, good quality Pa determinations required particularly pure Pa fractions because of the possible mass interferences with its abundant neighbour $^{232}$Th, the content of which in seawater varies from 3 to 500 pg l$^{-1}$, corresponding to a $^{232}$Th/$^{231}$Pa ratio of 3000 to $5 \times 10^5$.

For KEOPS samples, the Pa fractions were free of significant amounts of $^{229}$Th and $^{236}$U (added to detect any presence of Th and U elements in the Pa fraction), indicating a good separation of Pa from these two elements. Therefore, the corrections from $^{232}$Th peak tailing applied for the determination of the $^{231}$Pa concentrations were low, up to 7% for the dissolved samples, and slightly higher for the particulate samples with an average tailing of ~ 20%. For most of the Pa fractions, the $^{233}$U bleeding was insignificant (≤ 0.01%; Venchiarutti 2008, Venchiarutti et al. 2008).

The situation is different when rocks or sediments are analysed, in which the $^{232}$Th/$^{231}$Pa ratio is about $10^7$ in the initial sample. Therefore, even a contribution of 2.5% (Table 2) of $^{232}$Th in the Pa fraction could dramatically bias the Pa measurement, with tailing of the $^{232}$Th peak and Th hydrides interfering on both $^{231}$Pa and $^{233}$Pa. In such a case, the first Pa fraction may be purified by one or two additional elution steps on the same resin but with smaller columns, loading the sample in HNO$_3$ and eluting it in diluted HCl + HF (Pichat et al. 2004).

Conclusions

Radium, Nd, Th, Pa and U were separated from the same initial matrix, either seawater, particles or rocks. Such a strategy had the following benefits: (a) reducing the sample size, and consequently, (b) improving the sampling resolution, (c) ensuring the homogeneity of the sample for those five tracers and (d) keeping a reasonable cost for large sampling coverage, such as those planned in marine campaigns such as GEOTRACES. After a preliminary step, either by co-precipitation or by strong acid digestion, samples were loaded in 7 mol l$^{-1}$ HNO$_3$ on a thin quartz column made of AG1X-8 anionic resin (4 mm diameter, 4 ml resin) equipped with a high precision peristaltic pump. Results show that (a) the extraction recoveries were usually above 95% for all the tracers, for standard solutions as well as for natural samples, (b) the blanks were negligible and (c) this unique extraction step allowed the direct spectrometric determination of Th and U isotopes, and often Pa, at least for marine samples. Because of the high Th/Pa ratio of crustal material, Pa purification from rocks or sediments required additional steps. Radium and Nd fractions were eluted at the beginning of the procedure, although their final purification also required at least one additional step (for Nd), and two or three steps for Ra (for removing all Ba from the Ra fraction). One of the most important recommendations of our procedure is the precise control of the flow rates, calibrated to thoroughly separate each tracer from the other.
Acknowledgements

The authors are grateful to M. Polvé, G. Manhes and J.-L. Birck for their helpful advice. They also thank P. Brunet, F. Candaudap and R. Freydier for their technical assistance with TIMS, ICP-MS and MC-ICP-MS instruments, respectively. Two anonymous reviewers are deeply thanked for their detailed comments. This work was supported by a grant of the University of Toulouse (BQR) and by the ANR-Blanc NT05-3. 43160 (AMANDES).

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