

Methodology for Rare Earth Element Determinations of Uranium Oxides by Ion Microprobe

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A methodology for the determination of the rare earth elements in uranium oxides by ion microprobe has been set up on a Cameca ims-3f instrument. An uranium oxide reference material from a syn-metamorphic uranium deposit related to albitisation has also been developed for this type of analysis. Applications of the methodology are presented for a series of uranium oxides selected from some major uranium deposit types: from the world's highest grade unconformity-related uranium deposit from the Athabasca Basin (Saskatchewan, Canada; the Shea Creek and the McArthur River examples), a perigranitic vein-type deposit (Pen Ar Ran, Vendée, France) and a volcanic caldera-related deposit (Streltsovkoïe, Transbaïkalie, Russie). Each type of uranium deposit appears to have a specific REE signature. All REE patterns from the Shea Creek and the McArthur deposits are characterised by bell-shaped patterns centred on Tb-Dy and similar to those already published for uranium oxides from unconformity-related deposits from Australia. Such bell-shaped REE patterns centred on Tb-Dy may therefore be considered as a typical signature of uranium oxides from Mesoproterozoic unconformity-related deposits. A smoother bell shape pattern centred on Eu characterises the syn-metamorphic albitisation related deposit of Mistamisk selected for the reference material. The REE patterns from the Pen Ar Ran deposit show a fractionation from LREE to HREE with anomalously high abundances of Sm, Eu and Gd with respect to the other REEs, similar to the REE patterns of uranium oxides from the volcanic-related deposits of Streltsovkoïe.

Keywords: ion microprobe, rare earth elements, reference material, uranium oxide.

Une méthodologie d'analyse des Terres Rares dans les oxydes d'uranium par microsonde ionique (Cameca ims-3f) a été mise au point. Un oxyde d'uranium de référence a également été développé pour ce type d'analyse. Les applications et la méthodologie sont présentées sur une sélection d'oxydes d'uranium provenant de quelques-uns des plus importants types de gisements d'uranium : ceux associés à une discordance du Bassin Athabasca (Saskatchewan, Canada), les gisements les plus riches du monde avec les exemples de Shea Creek et de McArthur River, un gisement périgranitique de type filonien (Pen Ar Ran, Vendée, France), et un gisement associé à une caldera volcanique : Streltsovkoïe, (Transbaïkalie, Russie). Chaque type de gisement s'est révélé avoir une signature Terres Rares spécifique. Tous les spectres des gisements de Shea Creek et de McArthur River ont une forme en cloche centrée sur Tb-Dy, similaire à celle obtenue pour les oxydes d'uranium des gisements associés aux discordances australiens. Ces spectres Terres Rares en forme de cloche peuvent donc être considérés comme étant la signature typique des gisements d'uranium mésoprotérozoïques associés à une discordance. Les spectres des oxydes d'uranium du gisement d'uranium syn-métamorphe associé à une albitisation de Mistamisk ont également une courbe en cloche mais moins fractionnée et centrée sur l'euprimum. Les spectres Terres Rares des oxydes d'uranium de Pen Ar Ran montrent une décroissance des Terres Rares légères aux Terres Rares lourdes avec des teneurs anormalement élevées en Sm, Eu et Gd et sont similaires aux spectres Terres Rares des oxydes d'uranium de gisements associés au volcanisme à Streltsovkoïe.

Natural uranium oxides incorporate variable quantities of elements during their crystallisation, reflecting variations in their ionic radii, the physical-chemical conditions prevailing in the environment (temperature, nature of ligands in the mineralising fluids), and the composition of the rocks with which the mineralising fluid has been in contact. Furthermore, post-depositional re-equilibration with later fluids under different P-T conditions can modify the original composition. The fractionation of REEs is particularly interesting in uranium oxides, because their ionic radii (1.16 to 0.977 Å) are close to that of U^{4+} (1 Å) in eight-fold coordination, and most REEs are not sensitive to changes in redox conditions. Hence, they are much less mobile than radiogenic Pb, which has a much larger ionic radius (1.29 Å) than U^{4+} in eight-fold coordination and thus REE are likely to better preserve their primary distributions. A literature survey of available data on REE distribution in uranium oxides, although very limited, tends to show that each type of uranium deposit appears to be characterised by a specific REE signature (Fryer and Taylor 1987, Pagel *et al.* 1987, Hidaka *et al.* 1992, Hidaka and Gauthier Lafaye 2000), although strong variations occur within a specific type of uranium deposit (Fayek and Kyser 1997).

The purpose of the present paper is to present a methodology for the *in situ* determination of the rare earth elements in uranium oxides. Some applications of the methodology are presented for uranium oxides from various types of deposits from various parts of the world and from different uranium oxide generations within a single deposit. These samples have also been carefully dated by *in situ* isotopic U-Pb determinations at the same scale, both types of analysis being performed by secondary ion mass spectrometry (SIMS) on a CAMECA IMS-3f ion microprobe.

REE determination methodology

Most uranium ore bearing samples tend to be highly heterogeneous with several generations of uranium oxides resulting from several episodes of uranium deposition and/or post-depositional alteration. These different uranium oxide generations can be mixed at a sub-millimetre scale, as shown by reflected light microscopy and by back scattered electron (BSE) images

from scanning electron microscopy and by variations in composition revealed by electron microprobe analysis. Therefore, the selection of homogeneous areas with only one generation of uranium oxide for trace element or isotopic determinations is frequently difficult to achieve even using microchip sampling for analysis by thermal ionisation mass spectrometry (TIMS). As the REE are present in most occurrences in trace amounts ($< 10^4 \mu\text{g g}^{-1}$) in uranium oxides, *in situ* analysis by ion microprobe represents one of the most promising techniques for the determination of their concentration, as well as U and Pb isotopic compositions for age dating with a space resolution of about 20–40 μm .

BSE methodology

BSE images were adjusted to give the highest contrast in order to detect the slightest variations of average atomic number in the uranium oxides, to reveal the presence of any internal structure. The revealed structure reflects either primary growth features, such as zoning of the mineral during its deposition, or more or less complex alteration features produced by post-depositional fluid circulation that generally introduces elements such as Si, Ca and Fe with lower ionic radii and atomic weight than U or Pb. Consequently, such substitutions confer to the altered zones a lower average atomic number (LAZ), which appears as darker grey domains in BSE images. In contrast, the un- or less-altered zones with the highest uranium and lead contents, and thus the highest average atomic number (HAZ), will appear brighter in BSEM images.

SIMS methodology

The determination of REE abundance in natural uranium oxides by SIMS was performed for the first time using a SHRIMP (sensitive high-resolution ion microprobe) by Takahashi *et al.* (2002) and Horie *et al.* (2004). In the present work, new calculation procedures and the calibration of a new uranium oxide reference sample have been developed for the deconvolution of the raw signals obtained by low mass resolution SIMS and to quantify the rare earth element concentrations. All REE patterns were chondrite-normalised, using the values calculated by various research teams (Figure 1) (Evensen 1978, Anders and Grevesse

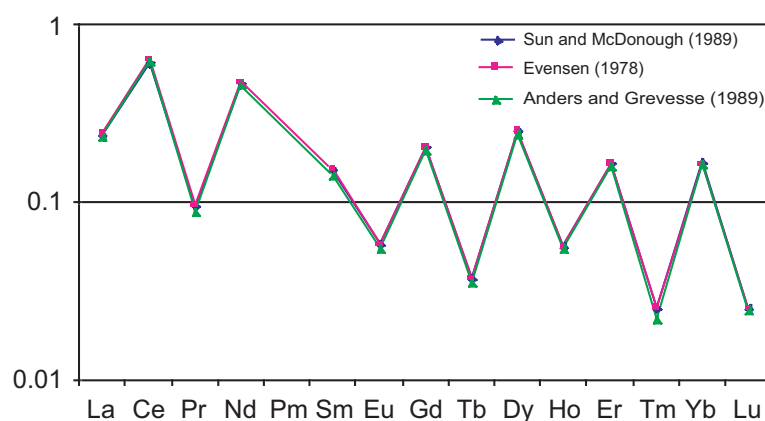


Figure 1. Concentration patterns of REE in chondrite, determined by Evensen (1978), Anders and Grevesse (1989) and Sun and McDonough (1989).

1989, Sun and McDonough 1989). Their results were comparable. For our study we used the values of Anders and Grevesse (1989).

The instrumental conditions used for REE analyses in uranium oxides with the CAMECA IMS 3f ion microprobe were similar to those described in Fahey *et al.* (1987) and Hinton (1990). Uranium oxide samples were prepared as gold-coated thin sections or sections of some millimetres in thickness. A 10 kV O^- primary beam of 10 nA current was focused to a spot of 30 μm in diameter. Secondary ions were accelerated to 4500 eV. The intensity of REE isotopes was measured at a mass resolution of 300, under conditions of energy filtering (80 eV) to reduce the contribution of LREE oxide isobaric interferences on the HREE masses (Fahey *et al.* 1987). The energy window was 40 eV. The magnet was cyclically peak-stepped through thirty-one masses between mass 89 ($^{89}Y^+$) and mass 251 ($^{235}UO^+$), including the background, mass 235 ($^{235}U^+$) and masses of all significant REE isotopes (Table 1). The counting time was 5 s on each peak at masses 89, 235 and 251, and 10 s on each peak at other masses. Sixteen successive measurement cycles were accumulated over a period of about two hours on each sample position, producing a counting statistical precision of better than 10% on most of the peaks. Isobaric interferences which remained between light REE oxides and heavy REE were eliminated by the deconvolution technique of Fahey *et al.* (1987).

The concentrations of Y and REE were then determined following a two-step procedure:

(1) deconvolution of the energy-filtered signals from masses 139 to 251 to separate the M^+ and MO^+ contribution, to determine the REE intensities. There are sixteen mono-atomic species (Y, La to Lu, and U) and

ten oxide species (LaO to DyO and UO), involved for thirty-one measured masses (several isotopes are measured for some species). The intensities were obtained after three iterations, realised using ExcelTM software and the equations of Fahey (1988):

(i) absREEdconvolution.xls to calculate absolute REE intensities and

(ii) errREEdconvolution.xls to calculate REE intensity errors.

The distribution of secondary ion intensities measured at different masses between the different mono-atomic and oxide species were calculated by inversion of the matrix of the isotopic abundance (Table 1), using the natural isotopic abundances data of Guthrie and Heath (1961). For example, the isotopes ^{151}Eu and ^{153}Eu represent 47.8% and 52.2% of total Eu respectively.

MO^+/M^+ ratios for each element were variable according to the sample surface electrostatic charge state, due to the different energy distributions of MO^+ and M^+ species. To take this phenomenon in account, the UO/U ratio was measured and used to calibrate every species. Thus, they were systematically determined for every analysis using the tool "Solver" in ExcelTM, to give rough values of MO^+/M^+ . However, the calculated HREE abundances do not depend strongly on this correction, because the use of energy filtering reduces considerably the influence of the molecular ions on the atomic ions' masses (Fahey *et al.* 1987). However, we note that Gd is an exception, because its isotopes interfere with those of four different LREE oxides (LaO, CeO, PrO, NdO) yielding intensities with more than 100% of bias: thus the Gd results were not taken into account. Also, the masses corresponding to Yb are connected with those of GdO; the results of

Table 1.
Natural abundance of REE and REE oxides, isotopes corresponding to the masses measured by SIMS (abundance data from Guthrie and Heath 1961)

	Y	La	Ce	Pr	Nd	Sm	Eu	LaO	CeO	PrO	Gd	Tb	NdO	Dy	Ho	SmO	Er	EuO	Tm	Yb	GdO	TbO	Lu	DyO	²³⁵ U	²³⁵ UO
89	1.0000	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
139	0	1.0000	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
140	0	0	0.8850	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
141	0	0	0	1.0000	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
142	0	0	0.1110	0	0.2710	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
143	0	0	0	0	0.1220	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
146	0	0	0	0	0.1720	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
147	0	0	0	0	0	0.1500	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
149	0	0	0	0	0	0.1380	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
151	0	0	0	0	0	0	0.4780	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
153	0	0	0	0	0	0	0.5220	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
154	0	0	0	0	0	0.2271	0	0.0009	0.0026	0	0.0215	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
155	0	0	0	0	0	0	0	0.9967	0	0	0.1473	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
156	0	0	0	0	0	0	0	0	0.8850	0	0.2047	0	0	0.0006	0	0	0	0	0	0	0	0	0	0	0	0
157	0	0	0	0	0	0	0	0	0	1.0000	0.1570	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
159	0	0	0	0	0	0	0	0	0	0	0	1.0000	0.1214	0	0	0	0	0	0	0	0	0	0	0	0	0
161	0	0	0	0	0	0	0	0	0	0	0	0	0.0830	0.1890	0	0	0	0	0	0	0	0	0	0	0	0
162	0	0	0	0	0	0	0	0	0	0	0	0	0.1720	0.2550	0	0	0.0014	0	0	0	0	0	0	0	0	0
163	0	0	0	0	0	0	0	0	0	0	0	0	0	0.2490	0	0.1500	0	0	0	0	0	0	0	0	0	0
165	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.0000	0.1380	0	0	0	0	0	0	0	0	0	0
166	0	0	0	0	0	0	0	0	0	0	0	0	0.0560	0	0	0.0740	0.3340	0	0	0	0	0	0	0	0	0
167	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.2290	0.4780	0	0	0	0	0	0	0	0
168	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.2670	0.2710	0	0	0.0014	0.0020	0	0	0	0	0
169	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.5205	1.0000	0	0	0	0	0	0	0
171	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.1430	0.1469	0	0	0	0	0
172	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.2190	0.2042	0	0	0.0005	0	0
173	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.1610	0.1564	0	0	0	0	0
174	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.3180	0.2481	0	0	0.0009	0	0
175	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.9976	0.9740	0	0	0
235	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.0000	0
251	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.0000

The box represents the REE area and the figures indicate masses of each element.

calculated intensities of this REE thus cannot be taken into account.

(2) conversion of elemental count rate, resulting from the first step, to $\mu\text{g g}^{-1}$ by comparing the REE^+/U^+ ratios in the sample with the ratio measured in a reference sample, a uraninite from Mistamisk (Kish and Cuney 1981), for which the calibration is described below. The drift of REE^+/U^+ ratio with respect to UO^+/U^+ during the analytical sessions was modelled by a least squares regression line, and conversion calculated according to equation 1:

$$\text{REE}/^{235}\text{U}_{\text{sample}} = \frac{(\text{REE}^+/\text{U}^+)_{\text{sample}}}{A \cdot (\text{UO}^+/\text{U}^+)_{\text{sample}} + B} \cdot (\text{REE}/^{235}\text{U})_{\text{reference}} \quad (1)$$

where A and B are the coefficients of the least squares regression line used to model the evolution of the REE^+/U^+ ratio with respect to UO^+/U^+ during the analytical sessions. This equation was calculated in an Excel[™] calculation sheet ("REEquantification.xls"). The precision obtained on the REE compositions were calculated using the equations of Fitzsimons *et al.* (2000).

The ^{235}U isotope was employed to measure U concentration rather than ^{238}U , because its intensity was large enough to be counted during the same scan as the REE^+ ions, when the ^{238}U intensity would be too large. $(\text{REE}/\text{U})_{\text{reference}}$ refers to the known composition of the Mistamisk reference sample. Uranium concentration at the point of each SIMS analysis, which was needed to obtain absolute REE concentrations, was determined by electron micro-probe using the same conditions as described by Kister (2003).

However, this technique presents instrumental limitations: (i) precision is limited at the small scale of analysis due to the limited amount of analysed material, and (ii) complex matrix effects of the concomitant element, spectroscopic interference on HREE from oxides of LREE and instrumental fractionation occur with SIMS. A specific calibration has to be undertaken for each type of matrix using a reference sample with a composition as closely matched as possible to that of the analysed sample.

Calibration

Mistamisk uraninite geological setting

The reference sample was a massive uraninite taken from the Mistamisk uraninite-albite veins (Kish

and Cuney 1981). The Mistamisk deposit is located in the Labrador Palaeoproterozoic trough, which extends over 800 km in northern Québec. This basin is bounded by Archaean gneisses (2.5 to 2.4 Ga) of the Rae Province to the west, by the Grenville Province (1.1 to 0.9 Ga) to the south and by Proterozoic and Archaean gneisses to the east. The western part of the trough is mainly composed of epicontinental sediments deposited on Archaean gneisses, whereas the eastern part mainly consists of basaltic and gabbroic rocks. All these rocks were metamorphosed, during the Hudson orogeny at about 1.80 Ga (Dimroth 1978).

The Mistamisk series comprise basalts and gabbros, overlying clastic (arkoses and siltstones, black shales) and chemical sedimentary rocks (stromatolitic dolomites). The volcanic rocks were thrust over the sedimentary rocks during the Hudson orogeny (Dimroth 1978).

The Mistamisk sediments were metamorphosed at low grade (300 °C, 2 kbar; Kish and Cuney 1981). Mudstones are composed of quartz, phengite, albite, small amounts of chlorite and, locally, monazite and allanite.

The Mistamisk Valley uranium showings are located in the metasediments of the western part of the trough. Two sets of uranium veins were highlighted ("K" and "B" veins, Kish and Cuney 1981). The mineralogy of the "K" and "B" veins is similar, except that "B" veins are more altered. The principal vein components are: albite, uraninite, dolomite, Mg-rich chlorite, hematite, quartz, Ni and Pb tellurides (melonite and altaite). Uraninite is heterogeneously distributed, in general concentrated in the axial part of the veins. It is often fractured and re-cemented by albite and carbonates. Locally, pitchblende veinlets are observed. Weak alteration to hexavalent uranium minerals is observed in outcropping samples.

U-Pb measurements define a discordia with an upper intercept at 1.8 Ga and a lower intercept at 0.4 Ga (Kish and Cuney 1981). The upper intercept corresponds to uraninite crystallisation, which fits well with the age of the Hudson orogeny. The other characteristics of the veins are also consistent with a syn-metamorphic formation of uraninite in conjunction with albitisation (Kish and Cuney 1981). The lower intercept may correspond to a remobilisation of uraninite as pitchblende.

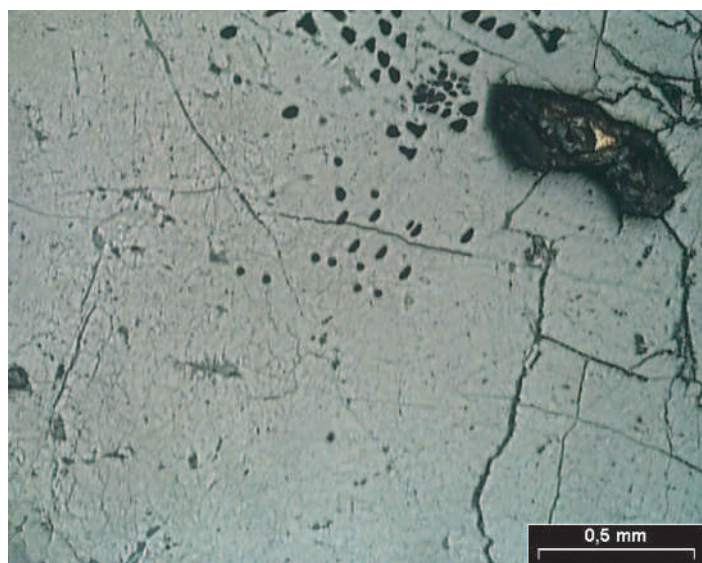


Figure 2. Optical image in reflected light microscopy of a large surface of a uraninite from the Mistamisk sample. At the top, the black spots correspond to the craters produced during ion microprobe analyses.

Uraninite chemistry

In reflected light, the uraninite appears as massive, variably micro-fractured crystals (Figure 2). Hexavalent uranium minerals are locally developed at the margin of the crystals. BSE images revealed variations in the concentration of secondary elements in the structure of the mineral. The lighter grey domains correspond to compositions having the highest average atomic number - highest U and Pb contents - and thus represent the best preserved parts of the uraninite crystal. The darker grey domains correspond to uraninite which has lost variable amounts of radiogenic lead and which is slightly enriched in lighter elements, mainly Si with 1.4% m/m SiO_2 in altered area and less than 0.1% m/m in the best preserved areas. Lighter grey domains are predominant in the sample. On average, the Mistamisk uraninite contains $77.0 \pm 1.4\%$ m/m UO_2 and $13.5 \pm 1.5\%$ m/m PbO as determined by CAMECA SX100 electron microprobe analyses (Table 2). Calcium, with about 1.2 to 1.4% m/m, seems to have been incorporated during the growth of the crystal because it is distributed relatively homogeneously in the lighter grey domains (P1 and P3 profiles) and at slightly decreased

concentrations in the darker grey domains richer in silica (P2 average). Y_2O_3 contents are rather elevated ranging from 6 to 8000 $\mu\text{g g}^{-1}$. ThO_2 contents vary from some hundreds to some thousands of $\mu\text{g g}^{-1}$. FeO and P_2O_5 contents are relatively constant between 2000 and 3000 $\mu\text{g g}^{-1}$. Aluminium content varies from less than 100 $\mu\text{g g}^{-1}$ to a few thousands of $\mu\text{g g}^{-1}$. REE contents will be discussed below. In conclusion, apart from lead and to a lesser extent silicon, most elements show only limited variations in concentration in the selected Mistamisk uraninite sample.

REE analytical results: The first REE analyses of the Mistamisk by ICP-MS were published by Takahashi *et al.* (2002). Bulk REE and Y compositions of the Mistamisk uraninite (Table 3) have been determined independently by ICP-MS in two laboratories: IGEM-RAS (Moscow) and CRPG - CNRS (Nancy) on two chips extracted from the sample.

The two analyses made in Nancy and Moscow gave comparable results, with about the same bulk REE contents. (Figure 3). The maximum difference between the two sets of results was 26% for lutetium, but for

Table 2.
Results of average chemical determinations made along three different profiles in the Mistamisk uraninite

Profile	SiO_2	$\pm$	Y_2O_3	$\pm$	PbO	$\pm$	UO_2	$\pm$	P_2O_5	$\pm$	CaO	$\pm$	FeO	$\pm$	ThO_2	$\pm$	Al_2O_3
P1	0.11	0.02	0.64	0.09	11.90	3.43	78.52	2.73	0.07	0.01	1.37	0.71	0.40	0.17	0.48	0.27	< d.l.
P2-uraninite	0.80	1.23	0.63	0.25	14.01	2.84	76.83	2.89	0.06	0.00	1.10	0.51	0.34	0.10	0.53	0.19	< d.l.
P3	0.54	0.98	0.79	0.17	14.85	1.82	76.74	2.16	0.06	0.01	1.16	0.34	0.33	0.10	0.24	0.03	< d.l.

P1: 10 determinations, P2: 28 determinations, P3: 30 determinations.
Results in % m/m.

$\pm$ Standard deviation.

d.l. Detection limit.

Table 3.
REE composition ($\mu\text{g g}^{-1}$) of the Mistamisk uraninite
determined by ICP-MS at the CRPG-CNRS (Nancy, 2006)

Analysis	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Takahashi	1137	3168	1183	5194	1620	650	1500	450	2500	600	1291	200	776	70
CRPG	185	2130	435	2515	1220	260	1285	290	1885	335	865	110	565	55
IGEM	212	2374	507	3148	1452	238	1335	276	1788	332	796	94	447	41
% difference CRPG-IGEM	-14	-11	-16	-25	-19	8	-4	5	5	1	8	15	21	26

IGEM-RAS (Moscow 2006) are compared with the mean reported by Takahashi *et al.* (2002), see Figure 3.

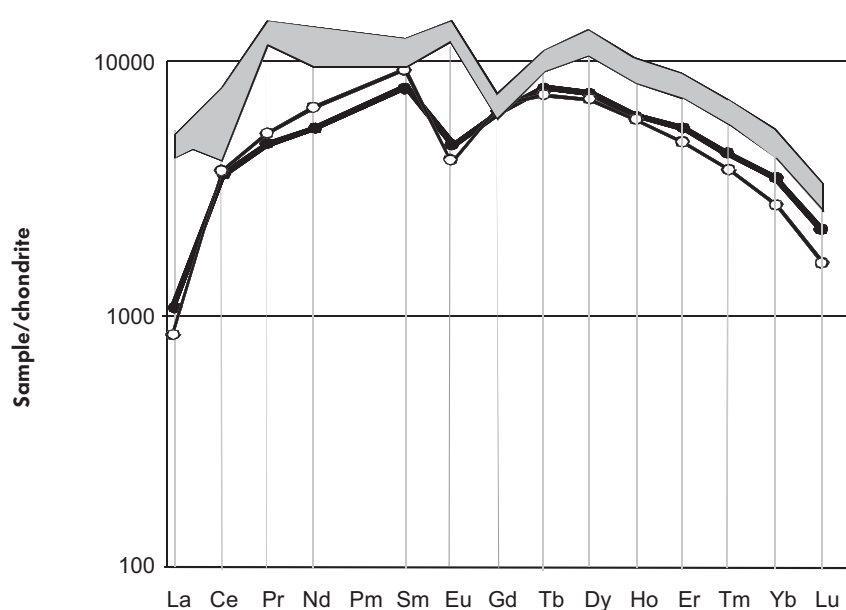


Figure 3. Rare earth element patterns in uranum oxide from Mistamisk, analysed by ICP-MS. The fine line (open circles) corresponds to the analyses carried out at the IGEM-RAS (Moscow, 2006), the thick line (filled circles) corresponds to those carried out at the CRPG-CNRS (Nancy, in 2006). In grey is the envelope of the results obtained by Takahashi *et al.* (2002).

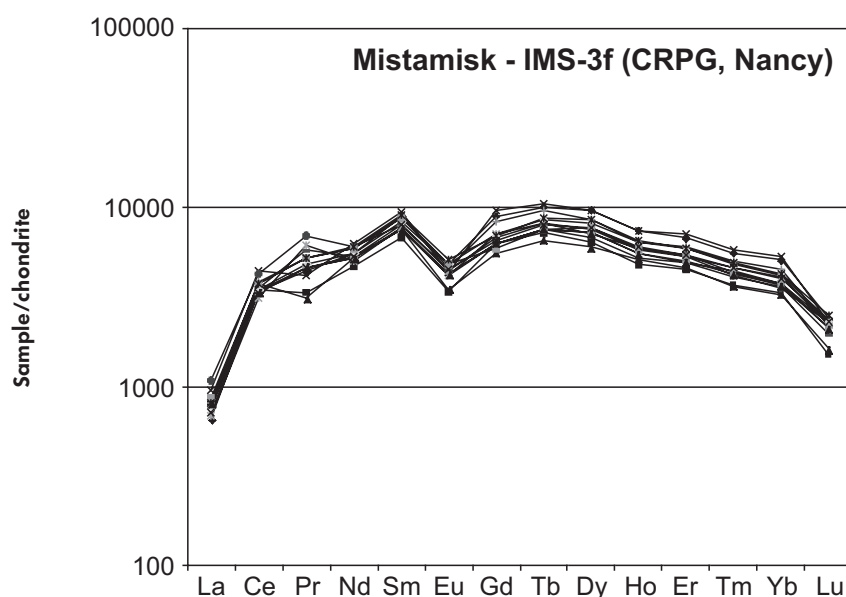


Figure 4. Rare earth element patterns normalised to chondrite from the Mistamisk uranum oxide measured with the Cameca IMS-3f ion microprobe at the CRPG (Nancy) during different analytical sessions.

most elements the difference was close to or better than 10% (Table 3). Although the heavy REE patterns of Takahashi *et al.* (2002) are nearly parallel to those of the CRPG and IGEM, REE abundances were 1.1 times higher for Gd to 5 times higher for La and a gadolinium anomaly was obtained instead of the classical europium anomaly. Such discrepancies cannot only result from analyses of different parts of the crystal with variable REE contents and fractionation. Hence, the data reported by Takahashi *et al.* (2002) appear to be questionable and will not be considered further in the present paper. The homogeneity of the REE distribution within a uraninite sample was also tested by comparing the REE patterns obtained during different analytical sessions using the ion IMS3f microprobe (Figure 4). The observed variations were of the same order of magnitude as those obtained between the two ICP-MS analyses made at the CRPG and IGEM-RAS. Note that the scatter of SIMS results can be linked to the sampling scale and a possible heterogeneity at this scale.

Applications to natural uranium deposits

REE signatures of uranium oxides from the Shea Creek and McArthur River deposits (Canada)

Geological setting: The McArthur River and the Shea Creek uranium deposits are located in eastern and western part of the Athabasca Basin (Saskatchewan, Canada), respectively. Both are unconformity-related uranium deposits (Kister 2003). The McArthur River deposit is the world's largest high-grade uranium deposit and is poor in associated arsenides-sulfides (monometallic type). It is dominantly hosted by the Wollaston belt graphitic schist, metamorphosed during the Hudson orogeny (1.85-1.75 Ga), but also extends partly into the overlying Manitou Falls sandstone. The Shea Creek deposit has a lower U grade and tonnage and it is associated with a complex Cu-Ni-Co arsenides-sulfides paragenesis (polymetallic type). It is mainly enclosed in the Manitou Falls sandstone at the unconformity, but the deposits also extend into a graphite-bearing metasedimentary slab located between two acidic granitic gneiss blocks (Lorilleux *et al.* 2002). Metamorphism of the sediments and granitic emplacement and deformation are coeval and occurred during the Talston orogeny (2.0-1.9 Ga, Brouand *et al.* 2003). The location of the ore deposits in both occurrences is controlled by reverse faults

rooted into structures in the basement. The cumulative displacement along the reverse faults reaches 80 m for the McArthur River deposit, but only 25 m for the Shea Creek deposit.

U-Pb isotopic ages: In the Athabasca Basin, previous U-Pb dating of uranium oxides revealed a great variety of ages: (i) the most common U-Pb ages fall within a time interval of 1330 to 1380 Ma (Cumming and Krstic 1992, Philippe *et al.* 1993); (ii) the most recent *in situ* analyses by SIMS of the uranium oxides from the McArthur River deposit revealed ages from 1460 to 1540 Ma (Fayek *et al.* 2002, Alexandre and Kyser 2003), more than 100 Ma older than the most common ages; (iii) numerous younger ages inferred from upper concordia intercepts are scattered between 800 and 1300 Ma, and generally attributed to remobilisation events; (iv) rare analyses of pitchblende have been dated between 200 and 570 Ma from upper intercepts (Fayek *et al.* 2002, Alexandre and Kyser 2003).

Most ages were inferred from highly discordant data, displaying non-zero lower intercepts scattered between 200 and 700 Ma, without systematic links to the geological context. These data show that Athabasca Basin uranium oxides have a complex history, marked by several stages of deposition and remobilisation of U and/or Pb. However, it is not possible at present to know if there were only one or several uranium deposition stages. Recent *in situ* U-Pb analyses using an ion microprobe (Kister 2003, Kister *et al.* 2007) indicate that the two uranium deposits have not recorded the same events. At least three stages of early uranium deposition or remobilisation have been identified for the McArthur River deposit, at ca. 1460 Ma, 1335 Ma and 1275 Ma, while only two have been recorded in the Shea Creek deposit, around 1340 and 1275 Ma. Conversely, in the Shea Creek deposit at least three recent remobilisation events have been found (ca. 400 Ma, 130 Ma and 60 Ma), while only one has been recorded in the McArthur River deposit (ca. 800 Ma).

REE analytical results: REE patterns from the Shea Creek (Figure 5, Table 4) and McArthur River (Figure 5, Table 5) deposits were determined for the different generations of uranium oxides and different degrees of hydrothermal alteration of the minerals. In both deposits, REE patterns mainly feature bell-shaped curves centred on Tb or Dy, which agree with the available REE data published on other unconformity-type

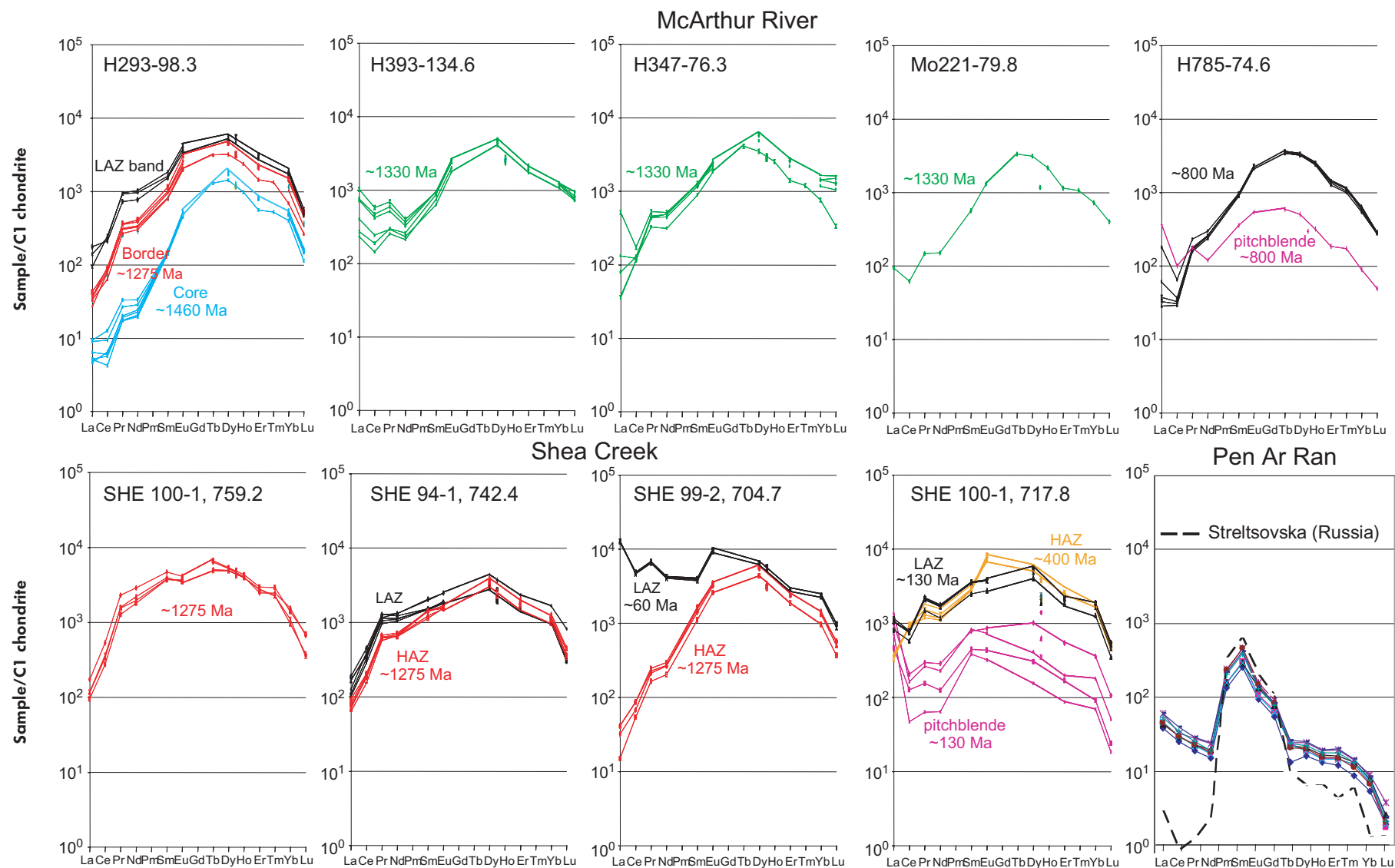


Figure 5. Chondrite-normalised REE patterns of uranium oxides from the McArthur River (top), Shea Creek (four bottom left) and Pen Ar Ran (bottom right) deposits.

Table 4.
SIMS determinations of REE in uranium oxides ($\mu\text{g g}^{-1}$) from the Shea Creek deposit

Sample	Location	Y	La	Ce	Pr	Nd	Sm	Eu	Tb
SHE 100-1, 759.2									
1		7795 $\pm$ 1300	41 $\pm$ 9	322 $\pm$ 95	205 $\pm$ 44	1307 $\pm$ 296	694 $\pm$ 176	231 $\pm$ 61	230.7 $\pm$ 60.9
2		7646 $\pm$ 1440	22 $\pm$ 5	166 $\pm$ 52	114 $\pm$ 27	816 $\pm$ 201	545 $\pm$ 147	207 $\pm$ 59	242.1 $\pm$ 70.2
3		6836 $\pm$ 697	27 $\pm$ 4	206 $\pm$ 56	142 $\pm$ 26	1002 $\pm$ 179	586 $\pm$ 92	194 $\pm$ 27	183.6 $\pm$ 25.8
4		6527 $\pm$ 566	28 $\pm$ 3	221 $\pm$ 54	138 $\pm$ 18	888 $\pm$ 121	559 $\pm$ 73	200 $\pm$ 26	177.6 $\pm$ 18.6
SHE 94-1, 742.4									
1	HAZ	3857 $\pm$ 283	18 $\pm$ 2	110 $\pm$ 25	55 $\pm$ 5	296 $\pm$ 29	181 $\pm$ 14	85 $\pm$ 6	n.d.
2	HAZ	4171 $\pm$ 291	16 $\pm$ 1	112 $\pm$ 26	56 $\pm$ 5	310 $\pm$ 31	214 $\pm$ 17	86 $\pm$ 7	n.d.
3	HAZ	3868 $\pm$ 288	22 $\pm$ 2	124 $\pm$ 29	60 $\pm$ 6	326 $\pm$ 33	207 $\pm$ 16	89 $\pm$ 7	n.d.
4	HAZ	3493 $\pm$ 246	19 $\pm$ 2	119 $\pm$ 27	56 $\pm$ 5	291 $\pm$ 29	167 $\pm$ 13	87 $\pm$ 6	n.d.
5	HAZ	3953 $\pm$ 273	15 $\pm$ 1	93 $\pm$ 21	51 $\pm$ 5	300 $\pm$ 30	209 $\pm$ 16	94 $\pm$ 7	n.d.
6	LAZ	3786 $\pm$ 284	44 $\pm$ 4	272 $\pm$ 63	114 $\pm$ 10	555 $\pm$ 56	225 $\pm$ 18	100 $\pm$ 8	n.d.
7	LAZ	4180 $\pm$ 300	26 $\pm$ 2	199 $\pm$ 46	104 $\pm$ 9	597 $\pm$ 60	303 $\pm$ 24	140 $\pm$ 10	n.d.
8	LAZ	3773 $\pm$ 279	40 $\pm$ 3	213 $\pm$ 49	95 $\pm$ 9	498 $\pm$ 50	227 $\pm$ 18	102 $\pm$ 8	n.d.
9	LAZ	5769 $\pm$ 379	30 $\pm$ 3	237 $\pm$ 54	113 $\pm$ 10	599 $\pm$ 59	293 $\pm$ 22	140 $\pm$ 10	n.d.
10	LAZ	3977 $\pm$ 296	39 $\pm$ 3	226 $\pm$ 52	102 $\pm$ 9	512 $\pm$ 52	216 $\pm$ 17	101 $\pm$ 8	n.d.
11	LAZ	4304 $\pm$ 323	24 $\pm$ 2	173 $\pm$ 40	86 $\pm$ 8	472 $\pm$ 48	221 $\pm$ 18	108 $\pm$ 8	n.d.
SHE 99-2, 704.7									
1	LAZ	8941 $\pm$ 596	3017 $\pm$ 181	2880 $\pm$ 656	594 $\pm$ 51	1888 $\pm$ 185	572 $\pm$ 43	536 $\pm$ 38	n.d.
2	LAZ	9106 $\pm$ 625	3003 $\pm$ 181	2958 $\pm$ 674	608 $\pm$ 53	1931 $\pm$ 190	587 $\pm$ 44	552 $\pm$ 39	n.d.
3	LAZ	9405 $\pm$ 617	2867 $\pm$ 174	2931 $\pm$ 668	606 $\pm$ 52	1953 $\pm$ 191	602 $\pm$ 45	565 $\pm$ 40	n.d.
4	LAZ	8585 $\pm$ 586	2939 $\pm$ 182	2804 $\pm$ 639	572 $\pm$ 49	1820 $\pm$ 178	550 $\pm$ 42	513 $\pm$ 36	n.d.
5	HAZ	4692 $\pm$ 316	8 $\pm$ 1	41 $\pm$ 9	19 $\pm$ 2	120 $\pm$ 12	209 $\pm$ 16	179 $\pm$ 13	n.d.
6	HAZ	4552 $\pm$ 691	10 $\pm$ 2	53 $\pm$ 12	22 $\pm$ 3	134 $\pm$ 16	246 $\pm$ 23	195 $\pm$ 16	n.d.
7	HAZ	5360 $\pm$ 371	10 $\pm$ 1	52 $\pm$ 12	20 $\pm$ 2	122 $\pm$ 12	230 $\pm$ 18	189 $\pm$ 14	n.d.
8	HAZ	4876 $\pm$ 336	4 $\pm$ 1	33 $\pm$ 8	15 $\pm$ 1	91 $\pm$ 9	164 $\pm$ 13	145 $\pm$ 10	n.d.
SHE 100-1, 717.8									
1	Pitchblende	2179 $\pm$ 355	232 $\pm$ 62	124 $\pm$ 30	26 $\pm$ 4	130 $\pm$ 19	115 $\pm$ 18	48 $\pm$ 5	n.d.
2	Pitchblende	936 $\pm$ 75	109 $\pm$ 11	76 $\pm$ 18	14 $\pm$ 2	57 $\pm$ 7	65 $\pm$ 7	24 $\pm$ 2	n.d.
3	Pitchblende	978 $\pm$ 78	322 $\pm$ 25	98 $\pm$ 23	23 $\pm$ 2	104 $\pm$ 11	122 $\pm$ 11	41 $\pm$ 3	n.d.
4	Pitchblende	547 $\pm$ 43	170 $\pm$ 14	29 $\pm$ 7	6 $\pm$ 1	29 $\pm$ 4	56 $\pm$ 7	18 $\pm$ 2	n.d.
5	HAZ	6026 $\pm$ 479	77 $\pm$ 6	579 $\pm$ 134	136 $\pm$ 13	597 $\pm$ 61	429 $\pm$ 34	460 $\pm$ 35	n.d.
6	HAZ	5880 $\pm$ 457	85 $\pm$ 7	542 $\pm$ 125	115 $\pm$ 11	534 $\pm$ 55	414 $\pm$ 33	435 $\pm$ 33	n.d.
7	HAZ	6166 $\pm$ 484	84 $\pm$ 7	525 $\pm$ 122	106 $\pm$ 10	499 $\pm$ 53	408 $\pm$ 33	403 $\pm$ 31	n.d.
8	HAZ	6401 $\pm$ 512	91 $\pm$ 8	542 $\pm$ 126	161 $\pm$ 15	711 $\pm$ 73	485 $\pm$ 39	376 $\pm$ 29	n.d.
9	LAZ	3748 $\pm$ 312	252 $\pm$ 24	448 $\pm$ 106	189 $\pm$ 19	779 $\pm$ 83	513 $\pm$ 43	215 $\pm$ 18	n.d.
10	LAZ	3737 $\pm$ 312	245 $\pm$ 22	477 $\pm$ 113	197 $\pm$ 20	808 $\pm$ 87	533 $\pm$ 46	217 $\pm$ 18	n.d.
11	LAZ	3616 $\pm$ 322	242 $\pm$ 23	457 $\pm$ 108	191 $\pm$ 19	782 $\pm$ 83	524 $\pm$ 45	212 $\pm$ 18	n.d.
12	LAZ	2918 $\pm$ 246	192 $\pm$ 24	350 $\pm$ 82	133 $\pm$ 13	529 $\pm$ 57	367 $\pm$ 32	153 $\pm$ 13	n.d.
13	LAZ	3745 $\pm$ 325	248 $\pm$ 23	449 $\pm$ 106	185 $\pm$ 19	760 $\pm$ 81	516 $\pm$ 44	210 $\pm$ 18	n.d.
14	LAZ	3276 $\pm$ 279	272 $\pm$ 26	477 $\pm$ 113	189 $\pm$ 20	754 $\pm$ 82	526 $\pm$ 46	211 $\pm$ 18	n.d.

Table 4 (continued).
SIMS determinations of REE in uranium oxides ($\mu\text{g g}^{-1}$) from the Shea Creek deposit

Sample	Location	Dy	Ho	Er	Tm	Yb	Lu	REE	LREE	HREE
SHE 100-1, 759.2										
1		1269 $\pm$ 317	225 $\pm$ 57	393 $\pm$ 106	60 $\pm$ 18	252 $\pm$ 107	16 $\pm$ 6	6291	2799	1914
2		1305 $\pm$ 351	240 $\pm$ 65	471 $\pm$ 138	71 $\pm$ 24	227 $\pm$ 108	17 $\pm$ 7	5544	1870	2003
3		1196 $\pm$ 163	221 $\pm$ 31	440 $\pm$ 62	55 $\pm$ 7	155 $\pm$ 29	9 $\pm$ 1	4630	2157	1791
4		1184 $\pm$ 142	220 $\pm$ 25	434 $\pm$ 51	55 $\pm$ 6	178 $\pm$ 27	8 $\pm$ 1	4472	2033	1797
SHE 94-1, 742.4										
1	HAZ	846 $\pm$ 67	n.d.	273 $\pm$ 18	n.d.	175 $\pm$ 13	9 $\pm$ 1	3896	745	1294
2	HAZ	976 $\pm$ 76	n.d.	327 $\pm$ 22	n.d.	209 $\pm$ 15	11 $\pm$ 1	4268	796	1512
3	HAZ	833 $\pm$ 67	n.d.	280 $\pm$ 23	n.d.	185 $\pm$ 14	9 $\pm$ 1	4395	828	1299
4	HAZ	762 $\pm$ 59	n.d.	244 $\pm$ 16	n.d.	159 $\pm$ 12	8 $\pm$ 1	3430	739	1166
5	HAZ	897 $\pm$ 69	n.d.	286 $\pm$ 19	n.d.	190 $\pm$ 14	10 $\pm$ 1	3956	763	1373
6	LAZ	704 $\pm$ 57	n.d.	234 $\pm$ 16	n.d.	160 $\pm$ 12	7 $\pm$ 1	4355	1311	1099
7	LAZ	752 $\pm$ 59	n.d.	245 $\pm$ 17	n.d.	182 $\pm$ 14	9 $\pm$ 1	4900	1369	1179
8	LAZ	718 $\pm$ 58	n.d.	238 $\pm$ 16	n.d.	160 $\pm$ 12	8 $\pm$ 1	4110	1174	1115
9	LAZ	1059 $\pm$ 80	n.d.	371 $\pm$ 24	n.d.	270 $\pm$ 19	20 $\pm$ 1	4623	1411	1701
10	LAZ	716 $\pm$ 57	n.d.	239 $\pm$ 16	n.d.	164 $\pm$ 12	7 $\pm$ 0	4132	1196	1119
11	LAZ	754 $\pm$ 61	n.d.	254 $\pm$ 18	n.d.	171 $\pm$ 13	8 $\pm$ 1	4420	1084	1179
SHE 99-2, 704.7										
1	LAZ	1480 $\pm$ 122	n.d.	391 $\pm$ 25	n.d.	377 $\pm$ 27	24 $\pm$ 1	16323	9488	2248
2	LAZ	1588 $\pm$ 121	n.d.	452 $\pm$ 30	n.d.	390 $\pm$ 28	24 $\pm$ 2	17018	9638	2430
3	LAZ	1627 $\pm$ 123	n.d.	446 $\pm$ 28	n.d.	406 $\pm$ 29	24 $\pm$ 1	16856	9525	2479
4	LAZ	1459 $\pm$ 111	n.d.	400 $\pm$ 26	n.d.	368 $\pm$ 26	21 $\pm$ 1	16510	9198	2227
5	HAZ	1317 $\pm$ 99	n.d.	377 $\pm$ 24	n.d.	214 $\pm$ 15	14 $\pm$ 1	5122	575	1908
6	HAZ	1378 $\pm$ 108	n.d.	397 $\pm$ 28	n.d.	234 $\pm$ 21	14 $\pm$ 1	6203	659	2010
7	HAZ	1377 $\pm$ 106	n.d.	385 $\pm$ 25	n.d.	215 $\pm$ 16	12 $\pm$ 1	5851	623	1978
8	HAZ	1054 $\pm$ 82	n.d.	296 $\pm$ 19	n.d.	157 $\pm$ 11	9 $\pm$ 1	4316	451	1507
SHE 100-1, 717.8										
1	Pitchblende	245 $\pm$ 24	n.d.	86 $\pm$ 9	n.d.	58 $\pm$ 7	3 $\pm$ 0	2756	675	389
2	Pitchblende	74 $\pm$ 7	n.d.	27 $\pm$ 2	n.d.	15 $\pm$ 1	1 $\pm$ 0	1302	345	115
3	Pitchblende	100 $\pm$ 8	n.d.	32 $\pm$ 3	n.d.	29 $\pm$ 2	1 $\pm$ 0	2124	711	161
4	Pitchblende	37 $\pm$ 4	n.d.	14 $\pm$ 1	n.d.	11 $\pm$ 1	0 $\pm$ 0	925	308	63
5	HAZ	1318 $\pm$ 108	n.d.	414 $\pm$ 30	n.d.	281 $\pm$ 22	12 $\pm$ 1	10952	2277	2013
6	HAZ	1295 $\pm$ 106	n.d.	399 $\pm$ 28	n.d.	277 $\pm$ 21	12 $\pm$ 1	10385	2124	1970
7	HAZ	1291 $\pm$ 107	n.d.	407 $\pm$ 29	n.d.	260 $\pm$ 20	11 $\pm$ 1	11039	2026	1958
8	HAZ	1509 $\pm$ 126	n.d.	493 $\pm$ 36	n.d.	305 $\pm$ 24	12 $\pm$ 1	11779	2365	2307
9	LAZ	1333 $\pm$ 115	n.d.	343 $\pm$ 26	n.d.	305 $\pm$ 25	13 $\pm$ 1	13275	2396	1981
10	LAZ	1346 $\pm$ 118	n.d.	356 $\pm$ 28	n.d.	307 $\pm$ 25	13 $\pm$ 1	13958	2477	2008
11	LAZ	1317 $\pm$ 115	n.d.	350 $\pm$ 28	n.d.	298 $\pm$ 25	13 $\pm$ 1	14465	2408	1965
12	LAZ	980 $\pm$ 85	n.d.	290 $\pm$ 23	n.d.	206 $\pm$ 18	9 $\pm$ 1	9994	1723	1476
13	LAZ	1286 $\pm$ 114	n.d.	337 $\pm$ 27	n.d.	301 $\pm$ 25	12 $\pm$ 1	15509	2368	1924
14	LAZ	1177 $\pm$ 105	n.d.	308 $\pm$ 25	n.d.	267 $\pm$ 22	11 $\pm$ 1	14876	2427	1752

HAZ = high average atomic number zones and LAZ = low average atomic number zones according to SEM observations.
All uncertainties are 95% confidence limits. Gd could not be analytically determined. n.d. no data.

Table 5.
SIMS determinations of REE in uranium oxides ($\mu\text{g g}^{-1}$) from the McArthur River deposit

Sample	Location	Y	La	Ce	Pr	Nd	Sm	Eu	Tb
H293-98.3									
1	Core	1837 $\pm$ 174	2 $\pm$ 0	6 $\pm$ 1	2 $\pm$ 0	13 $\pm$ 1	21 $\pm$ 2	28 $\pm$ 2	n.d.
2	Core	2011 $\pm$ 159	2 $\pm$ 0	8 $\pm$ 2	3 $\pm$ 0	15 $\pm$ 2	22 $\pm$ 2	30 $\pm$ 2	n.d.
3	Core	1875 $\pm$ 162	1 $\pm$ 0	4 $\pm$ 1	2 $\pm$ 0	10 $\pm$ 1	23 $\pm$ 2	30 $\pm$ 2	n.d.
4	Core	1813 $\pm$ 145	1 $\pm$ 0	3 $\pm$ 1	2 $\pm$ 0	9 $\pm$ 1	21 $\pm$ 2	26 $\pm$ 2	n.d.
5	Core	1821 $\pm$ 171	2 $\pm$ 0	4 $\pm$ 1	2 $\pm$ 0	11 $\pm$ 1	23 $\pm$ 2	29 $\pm$ 2	n.d.
1'	Core	1797 $\pm$ 182	1 $\pm$ 0	3 $\pm$ 1	2 $\pm$ 0	9 $\pm$ 1	23 $\pm$ 4	26 $\pm$ 4	47.3 $\pm$ 6.0
6	Border	5207 $\pm$ 437	8 $\pm$ 1	43 $\pm$ 10	23 $\pm$ 3	131 $\pm$ 15	118 $\pm$ 11	113 $\pm$ 9	n.d.
7	Border	5059 $\pm$ 402	8 $\pm$ 1	50 $\pm$ 12	27 $\pm$ 3	148 $\pm$ 15	122 $\pm$ 10	120 $\pm$ 9	n.d.
8	Border	5323 $\pm$ 431	6 $\pm$ 1	49 $\pm$ 11	28 $\pm$ 3	154 $\pm$ 16	140 $\pm$ 11	132 $\pm$ 10	n.d.
9	Border	5180 $\pm$ 360	9 $\pm$ 1	56 $\pm$ 13	32 $\pm$ 3	174 $\pm$ 17	147 $\pm$ 11	145 $\pm$ 11	n.d.
10	Border	5063 $\pm$ 368	10 $\pm$ 1	53 $\pm$ 12	33 $\pm$ 3	186 $\pm$ 19	169 $\pm$ 13	174 $\pm$ 13	n.d.
2'	Border	4867 $\pm$ 484	8 $\pm$ 1	39 $\pm$ 10	24 $\pm$ 3	137 $\pm$ 20	119 $\pm$ 18	111 $\pm$ 16	114.7 $\pm$ 14.4
11	LAZ	8524 $\pm$ 658	33 $\pm$ 3	143 $\pm$ 33	85 $\pm$ 8	469 $\pm$ 48	272 $\pm$ 22	237 $\pm$ 18	n.d.
12	LAZ	8730 $\pm$ 699	22 $\pm$ 2	150 $\pm$ 35	83 $\pm$ 8	440 $\pm$ 46	238 $\pm$ 19	215 $\pm$ 17	n.d.
13	LAZ	7374 $\pm$ 588	42 $\pm$ 4	128 $\pm$ 30	65 $\pm$ 6	349 $\pm$ 37	226 $\pm$ 19	191 $\pm$ 15	n.d.
H393-134.6									
1		3626 $\pm$ 1375	55 $\pm$ 7	88 $\pm$ 24	23 $\pm$ 3	97 $\pm$ 12	109 $\pm$ 10	113 $\pm$ 10	n.d.
2		4240 $\pm$ 355	177 $\pm$ 22	282 $\pm$ 69	53 $\pm$ 6	167 $\pm$ 22	141 $\pm$ 12	134 $\pm$ 11	n.d.
3		4096 $\pm$ 365	171 $\pm$ 14	255 $\pm$ 59	46 $\pm$ 5	150 $\pm$ 17	139 $\pm$ 12	147 $\pm$ 12	n.d.
4		4399 $\pm$ 404	64 $\pm$ 6	114 $\pm$ 27	26 $\pm$ 3	117 $\pm$ 13	127 $\pm$ 11	133 $\pm$ 11	n.d.
5		4105 $\pm$ 340	238 $\pm$ 22	353 $\pm$ 82	62 $\pm$ 6	183 $\pm$ 20	137 $\pm$ 12	135 $\pm$ 11	n.d.
6		3907 $\pm$ 344	94 $\pm$ 10	148 $\pm$ 35	26 $\pm$ 3	105 $\pm$ 13	93 $\pm$ 9	98 $\pm$ 9	n.d.
H347-76.3									
1		4819 $\pm$ 525	19 $\pm$ 2	77 $\pm$ 19	39 $\pm$ 5	202 $\pm$ 23	174 $\pm$ 17	130 $\pm$ 13	n.d.
2		4201 $\pm$ 470	31 $\pm$ 5	75 $\pm$ 18	29 $\pm$ 3	142 $\pm$ 16	132 $\pm$ 13	102 $\pm$ 10	n.d.
3		4747 $\pm$ 613	9 $\pm$ 1	69 $\pm$ 17	41 $\pm$ 5	219 $\pm$ 27	187 $\pm$ 20	142 $\pm$ 16	n.d.
4		4652 $\pm$ 1184	9 $\pm$ 2	69 $\pm$ 21	39 $\pm$ 11	223 $\pm$ 41	184 $\pm$ 31	137 $\pm$ 26	n.d.
1'		4791 $\pm$ 633	122 $\pm$ 22	104 $\pm$ 28	47 $\pm$ 9	235 $\pm$ 44	187 $\pm$ 38	117 $\pm$ 24	148.4 $\pm$ 27.4
Mo221-79.8									
1		1818 $\pm$ 277	22 $\pm$ 4	37 $\pm$ 11	13 $\pm$ 3	68 $\pm$ 14	83 $\pm$ 19	74 $\pm$ 17	122.4 $\pm$ 27.3
H785-74.6									
1		6757 $\pm$ 658	42 $\pm$ 7	39 $\pm$ 10	21 $\pm$ 3	135 $\pm$ 20	143 $\pm$ 21	128 $\pm$ 19	123.9 $\pm$ 15.3
2		6683 $\pm$ 639	14 $\pm$ 2	22 $\pm$ 6	16 $\pm$ 2	117 $\pm$ 17	137 $\pm$ 20	123 $\pm$ 18	128.7 $\pm$ 15.5
3		6823 $\pm$ 697	7 $\pm$ 1	17 $\pm$ 4	14 $\pm$ 2	107 $\pm$ 17	130 $\pm$ 21	119 $\pm$ 19	124.6 $\pm$ 18.5
4		6882 $\pm$ 680	8 $\pm$ 1	18 $\pm$ 5	15 $\pm$ 2	115 $\pm$ 17	141 $\pm$ 21	129 $\pm$ 19	132.0 $\pm$ 16.8
5		6988 $\pm$ 697	9 $\pm$ 1	20 $\pm$ 8	15 $\pm$ 2	116 $\pm$ 43	141 $\pm$ 22	128 $\pm$ 20	134.0 $\pm$ 17.3
6	Pitchblende	463 $\pm$ 56	86 $\pm$ 13	60 $\pm$ 16	16 $\pm$ 3	54 $\pm$ 10	52 $\pm$ 10	30 $\pm$ 6	21.7 $\pm$ 3.7

Table 5 (continued).
SIMS determinations of REE in uranium oxides ($\mu\text{g g}^{-1}$) from the McArthur River deposit

Sample	Location	Dy	Ho	Er	Tm	Yb	Lu	REE	LREE	HREE
H293-98.3										
1	Core	416 $\pm$ 37	n.d.	126 $\pm$ 10	n.d.	78 $\pm$ 7	4 $\pm$ 0	1590	72	620
2	Core	428 $\pm$ 36	n.d.	125 $\pm$ 9	n.d.	78 $\pm$ 6	4 $\pm$ 0	1503	79	630
3	Core	468 $\pm$ 39	n.d.	137 $\pm$ 10	n.d.	87 $\pm$ 7	4 $\pm$ 0	1663	70	692
4	Core	445 $\pm$ 37	n.d.	129 $\pm$ 9	n.d.	78 $\pm$ 6	4 $\pm$ 0	1475	62	652
5	Core	465 $\pm$ 40	n.d.	135 $\pm$ 11	n.d.	90 $\pm$ 7	4 $\pm$ 0	1715	70	690
1'	Core	346 $\pm$ 49	55 $\pm$ 8	89 $\pm$ 13	13 $\pm$ 2	65 $\pm$ 12	3 $\pm$ 0	672	63	500
6	Border	1157 $\pm$ 97	n.d.	335 $\pm$ 25	n.d.	189 $\pm$ 15	9 $\pm$ 1	5300	436	1681
7	Border	1053 $\pm$ 86	n.d.	313 $\pm$ 22	n.d.	169 $\pm$ 13	8 $\pm$ 1	4823	475	1535
8	Border	1163 $\pm$ 96	n.d.	353 $\pm$ 25	n.d.	227 $\pm$ 18	11 $\pm$ 1	5591	509	1743
9	Border	1176 $\pm$ 91	n.d.	365 $\pm$ 24	n.d.	227 $\pm$ 16	13 $\pm$ 1	4458	563	1768
10	Border	1119 $\pm$ 88	n.d.	345 $\pm$ 23	n.d.	245 $\pm$ 18	13 $\pm$ 1	5067	624	1709
2'	Border	780 $\pm$ 108	133 $\pm$ 18	231 $\pm$ 32	32 $\pm$ 5	112 $\pm$ 21	7 $\pm$ 1	1995	437	1123
11	LAZ	1403 $\pm$ 115	n.d.	514 $\pm$ 36	n.d.	322 $\pm$ 25	14 $\pm$ 1	7805	1240	2239
12	LAZ	1299 $\pm$ 109	n.d.	494 $\pm$ 36	n.d.	300 $\pm$ 24	12 $\pm$ 1	7854	1148	2093
13	LAZ	1234 $\pm$ 104	n.d.	453 $\pm$ 33	n.d.	285 $\pm$ 23	12 $\pm$ 1	7900	1001	1972
H393-134.6										
1		1062 $\pm$ 98	n.d.	293 $\pm$ 25	n.d.	196 $\pm$ 20	23 $\pm$ 2	2940	484	1551
2		1161 $\pm$ 100	n.d.	327 $\pm$ 25	n.d.	198 $\pm$ 17	20 $\pm$ 2	3894	955	1686
3		1138 $\pm$ 102	n.d.	328 $\pm$ 27	n.d.	205 $\pm$ 19	23 $\pm$ 2	3742	907	1671
4		1204 $\pm$ 103	n.d.	342 $\pm$ 26	n.d.	192 $\pm$ 17	19 $\pm$ 2	3530	582	1738
5		1129 $\pm$ 95	n.d.	319 $\pm$ 25	n.d.	192 $\pm$ 16	18 $\pm$ 2	4155	1108	1640
6		965 $\pm$ 85	n.d.	273 $\pm$ 23	n.d.	175 $\pm$ 16	18 $\pm$ 2	2883	564	1412
H347-76.3										
1		1393 $\pm$ 147	n.d.	417 $\pm$ 42	n.d.	234 $\pm$ 29	31 $\pm$ 4	3709	640	2044
2		1169 $\pm$ 124	n.d.	347 $\pm$ 35	n.d.	192 $\pm$ 24	25 $\pm$ 3	3041	510	1708
3		1413 $\pm$ 170	n.d.	413 $\pm$ 50	n.d.	235 $\pm$ 36	36 $\pm$ 6	3665	666	2061
4		1500 $\pm$ 230	n.d.	442 $\pm$ 65	n.d.	266 $\pm$ 40	40 $\pm$ 7	3911	661	2209
1'		852 $\pm$ 161	141 $\pm$ 27	223 $\pm$ 44	29 $\pm$ 6	124 $\pm$ 35	8 $\pm$ 2	2844	811	1199
Mo221-79.8										
1		763 $\pm$ 168	120 $\pm$ 27	182 $\pm$ 43	26 $\pm$ 7	129 $\pm$ 24	10 $\pm$ 3	1950	297	1074
H785-74.6										
1		793 $\pm$ 110	133 $\pm$ 18	201 $\pm$ 28	24 $\pm$ 3	88 $\pm$ 16	7 $\pm$ 1	2083	508	1081
2		814 $\pm$ 111	139 $\pm$ 18	225 $\pm$ 31	27 $\pm$ 4	95 $\pm$ 17	7 $\pm$ 1	2067	429	1134
3		785 $\pm$ 119	135 $\pm$ 21	214 $\pm$ 33	25 $\pm$ 4	105 $\pm$ 21	7 $\pm$ 1	1995	394	1104
4		833 $\pm$ 118	142 $\pm$ 20	231 $\pm$ 33	28 $\pm$ 4	96 $\pm$ 18	7 $\pm$ 1	2112	426	1159
5		839 $\pm$ 120	145 $\pm$ 20	233 $\pm$ 34	28 $\pm$ 4	102 $\pm$ 19	7 $\pm$ 1	2143	428	1174
6	Pitchblende	123 $\pm$ 22	18 $\pm$ 3	30 $\pm$ 5	4 $\pm$ 1	15 $\pm$ 4	1 $\pm$ 0	618	298	167

HAZ correspond to zones of high average atomic number, appearing in light grey on BSE images. LAZ correspond to zones of low average atomic number, appearing in dark grey on BSE images.

All uncertainties are 95% confidence limits. Tb, Ho and Tm were only determined during a later analytical session (April 2004). Gd could not be analytically determined.

HREE Dy + Tb + Yb. LREE La + Ce + Pr + Nd + Sm + Eu.

deposits, such as Nabarlek, Australia (Maas and McCulloch 1990), Collins Bay, Canada (Fryer and Taylor 1987), Cluff D, Canada (Pagel *et al.* 1987), and McArthur River (Fayek and Kyser 1997).

However, a more detailed analysis of the REE patterns obtained during the present work, by analysing very carefully selected areas and using a matrix-matched reference material, revealed some significant differences:

(i) REE absolute abundance and fractionation patterns were reproducible within a single generation of non- to weakly-altered uranium oxide (Figure 5),

(ii) REE absolute abundance and intermediate and heavy REE fractionation patterns were similar for the less altered zones from different samples. Such zones gave the same U-Pb ages as the Shea Creek samples dated at ca. 1275 Ma (SHE 100-1-7-59.2, SHE 94-1-742.4, SHE 99-2-704.7) and the three McArthur samples dated at ca. 1330 Ma (H393-143.6, H347-76.3, MO221.79.8),

(iii) REE absolute abundance could vary by more than one order of magnitude from the earliest dated uranium oxide generation to a later one in the same deposit, as observed in the McArthur River deposit (sample H293-93-3, Figure 5);

(iv) LREE contents could be elevated greatly in altered uranium oxides, as exemplified by the analyses performed on the less- and more-altered zones of the same generation of uranium oxide in the Shea Creek deposit (sample SHE 99-2, 704.7), but more moderately in others (SHE 94-1-742.4), and with preservation of the heavy REE distribution and abundance. The HREE fractionation patterns are also well preserved between the less- and more-altered zones of recrystallised uraninite generations giving young U-Pb isotopic ages of 400 Ma down to 130 Ma in sample SHE 100-1-717.8.

(v) LREEs tended to be less fractionated in the Shea Creek deposit than in the McArthur River deposit. However, considering that LREE are more mobile than HREE in uraninite, variations in LREE are not characteristic of the origin, but mainly indicate the degree of alteration of the uranium oxides.

(vi) Pitchblende deposited much later (at about 130 Ma) in sample SHE 100-1-717.8, still presented a bell-shaped pattern, but with much lower REE contents,

possibly related to the lower temperature of deposition of this uranium oxide generation. Pitchblende showed also an abnormal enrichment in LREE, similar to the altered uraninite of older depositional age.

REE signatures of uranium oxides from the Pen Ar Ran deposit (Vendée, France)

Geological setting: The Pen Ar Ran uranium deposit is hosted by an east-west fault that transects metamorphic formations at the northern margin of the Guérande Variscan two mica peraluminous leucogranites, which were emplaced at 310 ± 20 Ma (Autran and Cogné 1980). Enclosing metamorphic formations consist of felsic gneisses, named “porphyroids” that are presumed to be of arkosic or acidic volcanic (ignimbritic) origin. Uranium deposition was controlled by the brittle fracturing of the porphyroids in the vicinity of the contact with graphitic schist (Cathelineau 1982). Uranium mineralisation occurs as veins essentially composed of massive pitchblende. The uranium oxides are very homogenous and give nearly concordant U-Pb isotopic age at 320 ± 9 Ma (Holliger 1992) determined from *in situ* analyses by SIMS.

REE analytical results: REE patterns from the Pen Ar Ran uranium oxide are reproducible as would be predicted based on the homogeneity of the sample in both optical microscopy and BSEM images. Only small variations in their REE abundances were seen, retaining the same overall shape as chondrite-normalised plots (Figure 5). The REE patterns are strongly fractionated from the LREE to the HREE, but the REE of the second tetrad (Sm, Eu and Gd) define a strong positive anomaly (Table 6). Compared to all patterns available from the literature and from unpublished data from our laboratory, the REE distribution obtained for the Pen Ar Ran deposit is similar to the pitchblende pattern from one of the deposits of the largest uranium districts in the world related to volcanics - the Streltsovskoye caldera (Transbaikalia, Russia; Aleshin 2007) (Figure 5). Such a pattern differs strongly from the REE patterns of uranium oxides from intragranitic vein-type deposits such as from the Kruth and Beaverlodge veins (Pagel *et al.* 1987), which are characterised by a regular fractionation from the LREE to HREE without any particular anomaly, except sometimes the classical europium anomaly.

Discussion and conclusions

A methodology was set up for *in situ* determinations of REE concentrations in uranium oxides using

Table 6.
SIMS determinations ($\mu\text{g g}^{-1}$) of REE from the Pen Ar Ran uranium oxide

Sample		Y	La	Ce	Pr	Nd	Sm	Eu		Tb
PAR	1.1	121.7 ± 0.1	57.3 ± 0.1	23.7 ± 0.1	4.8 ± 0.1	14.8 ± 0.1	52.5 ± 0.1	13.9 ± 0.1	0.8 ± 0.2	
	1	147.7 ± 0.1	66.8 ± 0.1	27.2 ± 0.1	5.5 ± 0.1	17.3 ± 0.1	61.1 ± 0.1	15.5 ± 0.1	1.4 ± 0.1	
	3	134.7 ± 0.1	64.4 ± 0.1	27.6 ± 0.2	5.7 ± 0.1	18.8 ± 0.1	59.9 ± 0.2	19.8 ± 0.1	1.3 ± 0.1	
	4	143 ± 0.1	68.9 ± 0.1	27.8 ± 0.1	5.5 ± 0.1	16.7 ± 0.1	60.3 ± 0.1	15 ± 0.1	1.3 ± 0.1	
	5	175.7 ± 0.1	89.2 ± 0.1	30.2 ± 0.2	7 ± 0.1	23 ± 0.1	92.9 ± 0.1	23 ± 0.1	1.4 ± 0.1	
	6	136.2 ± 0.1	66.6 ± 0.1	27.9 ± 0.1	5.7 ± 0.1	17.9 ± 0.1	92 ± 0.1	21.5 ± 0.1	1.2 ± 0.1	
	7	159.5 ± 0.1	79.1 ± 0.1	32.9 ± 0.1	6.4 ± 0.1	18.4 ± 0.1	78.8 ± 0.1	18.9 ± 0.1	1.4 ± 0.1	
	8	176.4 ± 0.1	89.2 ± 0.1	37.1 ± 0.1	7.3 ± 0.1	23.6 ± 0.1	85 ± 0.1	20.2 ± 0.1	1.5 ± 0.2	
Sample		Dy	Ho	Er	Tm	Yb	Lu	REE	LREE	HREE
PAR	1.1	5.3 ± 0.1	1.4 ± 0.1	3 ± 0.1	0.4 ± 0.1	11.5 ± 0.3	0.1 ± 0.1	189.4	167	17.6
	1	6.3 ± 0.1	1.5 ± 0.1	3.6 ± 0.1	0.6 ± 0.1	17 ± 0.3	0.1 ± 0.1	223.8	193.4	24.7
	3	6.9 ± 0.1	1.7 ± 0.1	4 ± 0.1	0.6 ± 0.1	6 ± 0.2	0.1 ± 0.1	216.9	196.3	14.2
	4	6.3 ± 0.1	1.5 ± 0.1	3.6 ± 0.1	0.6 ± 0.1	6.7 ± 0.3	0.1 ± 0.1	214.2	194.2	14.3
	5	8.1 ± 0.1	2 ± 0.1	4.8 ± 0.1	0.6 ± 0.1	8.2 ± 0.2	0.1 ± 0.1	290.5	265.2	17.7
	6	6.7 ± 0.1	1.6 ± 0.1	3.7 ± 0.1	0.5 ± 0.1	13 ± 0.3	0.1 ± 0.1	258.5	231.7	20.9
	7	7.5 ± 0.1	1.8 ± 0.1	4.3 ± 0.1	0.6 ± 0.1	13.8 ± 0.3	0.1 ± 0.1	264	234.4	22.7
	8	8.4 ± 0.1	2 ± 0.1	4.9 ± 0.1	0.7 ± 0.1	11.5 ± 0.4	0.1 ± 0.1	291.5	262.4	21.4

Quoted uncertainties are the standard deviation.

secondary ion mass spectrometry (SIMS) on a CAMECA IMS-3f instrument. A uraninite reference material was calibrated for REE determinations. A series of analytical results from several types of deposits obtained using this approach are summarised here, demonstrating the utility of this technique for metallogenic studies of uranium deposits.

SIMS analyses of uranium oxides from unconformity-related uranium deposits showed that they are generally characterised by bell-shaped REE patterns centred on Tb or Dy, but total REE abundances could vary over more than one order of magnitude according to the generation of uranium oxide. The youngest generations tended to have the highest REE abundances, except for the late and lower temperature deposition of botryoidal pitchblende, which had very low REE contents. Although, alteration of the uranium oxides leads to a very strong increase in LREE contents along with silicon and calcium, they generally preserve their intermediate and heavy REE signatures. Therefore, even if the sample is altered, the primary signature of the specific uranium deposit is preserved. REE patterns with high LREE content presented as typical of sandstone-hosted, unconformity-related deposits (Fayek and Kyser 1997) correspond, in fact, to altered uranium oxides. The bell shape of the REE patterns centred on Tb or Dy - elements having the closest ionic radii to tetravalent uranium in eightfold coordination (Shannon 1976) - suggest a strong crystal-chemical control of the partitioning

of the REE into the uranium oxide structure from the uranium ore forming fluid for unconformity-related deposits, rather than an effect of the nature of REE complexing in the fluid, or of the REE signature of the source lithologies. The conditions controlling increasing REE partitioning into the uranium oxides from the earliest to the latest uraninite generations are unknown. The uranium oxide from Mistamisk, selected for the reference material belongs to a syn-metamorphic albitisation-related uranium deposit, which also has a bell-shaped pattern but characterised by a smoother fractionation and a centring of the bell on Eu.

The uranium oxide from the Pen Ar Ran deposit (Vendée, France), with its strong enrichment in REE of the second tetrad, presented a very different pattern compared to already published patterns from granite-related vein type deposits. The uranium oxides from the largest volcanic-related uranium deposit district in the world (Strel'tsovskoye, Russia) have the same pattern as the pattern of the uranium oxides from the Pen Ar Ran deposit. Such an analogy supports the model that (i) the so called "porphyroids" enclosing the Pen Ar Ran uranium deposit correspond to acidic ignimbrites metamorphosed during the Variscan orogeny, (ii) they probably represent the source of the uranium for the deposit rather than the nearby Guérande two mica peraluminous leucogranite, (iii) the REE patterns of the uranium oxides from volcanic-related deposits seem to be characterised by a strong REE enrichment of the

second tetrad. However, more systematic determinations on a series of other volcanic-related uranium deposits (work in progress) are necessary to confirm these first conclusions. It is also not presently known for this type of deposit which mechanism is controlling the fractionation of the REE between the ore forming fluid and the uranium oxides.

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