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Origin of uranium deposits revealed by their rare earth element signature

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ABSTRACT

Uranium deposits form in a wide range of geological settings, including deep magmatic to surficial conditions, and range in age from Archaean to recent. These temporal and spatial variations have given rise to an extreme diversity of ore deposits. However, understanding their conditions of formation has remained challenging. This article reports rare earth element (REE) abundances, measured by microbeam methods in uranium oxides, for a series of worldwide uranium occurrences. The REE patterns are very specific to each deposit type and directly reflect the conditions of their

genesis. We propose an evaluation of the first-order parameters controlling the REE behaviour in each mineralised system. This study demonstrates that the REE pattern is the most efficient tool for constraining the geological models of uranium deposits and for genetically discriminating new uranium discoveries. This approach may form the starting point for a new procedure in the fight against nuclear trafficking.

Terra Nova, 00, 1–6, 2011

Introduction

Uranium ores are the indispensable raw material for nuclear fuel preparation and are currently heavily prospected. Unlike the majority of metals, the metallogeny of uranium is specifically characterised by an extreme diversity of deposits that are directly related to the various conditions under which U deposits formed in geological environments (Cuney, 2009). More than 800 uranium deposits are identified globally and at least 16 deposit types are referenced by the International Atomic Energy Agency (IAEA, 2009). The current classifications, however, do not provide meaningful indications to understand the formation of uranium deposits and, thus, to genetically discriminate them. Furthermore, to date, no link between uranium oxide geochemistry and the genetic conditions for uranium oxide formation has been clearly established.

Uranium oxides, ideally UO₂, termed uraninite or pitchblende for the high temperature and collomorph low temperature varieties, respectively, are the most common and abundant

components of uranium ores. They incorporate variable quantities of trace elements during their crystallisation, possibly demonstrating the diversity of the physical–chemical characteristics (e.g. temperature or fluid composition) of the mineralising fluids (Janeczek and Ewing, 1992). However, the composition of the uranium oxides (primary plus radiogenic elements) is frequently modified by post-depositional re-equilibration with later fluids under variable physical–chemical conditions (Alexandre and Kyser, 2005), thus limiting the accuracy of U, O or Pb isotope ratios and U–Th–Pb ages (Fayek *et al.*, 2002; Brenneka *et al.*, 2010) as a tool to discriminate uranium deposit types. An underexplored, but potentially powerful tool to understand the formation of uranium deposits is the rare earth element (REE) composition of U-oxides. Indeed, the fractionation of REEs is particularly interesting in uranium oxides, because they are less sensitive to redox changes and their ionic radii (1.16–0.977 Å) are close to that of U⁴⁺ (1 Å) in eightfold coordination (Shannon, 1976), which allows them to easily substitute for U with only minor modification by post-crystallisation events.

Previous developments and considerations

Pioneer determinations of REE contents within uranium oxides (Fryer

and Taylor, 1987; Pagel *et al.*, 1987; Maas and McCulloch, 1990; Hidaka *et al.*, 1992; Hidaka and Gauthier-Lafaye, 2001), although highly promising, were limited by: (i) the small number of uranium deposit types considered; (ii) the small number of analyses available for each deposit type; (iii) the sensitivity and accuracy of REE analyses due to technical limitations; (iv) the lack of discrimination between altered and unaltered zones in the studied samples; and (v) the lack of genetic constraints on the studied deposits.

Decisive advances in REE analysis in uranium oxides have resulted from the recent development of microbeam analysis by secondary ion mass spectrometry (SIMS; Bonhoure *et al.*, 2007). In the present article, further improvements by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) analysis are presented. The full analytical details for this technique are given elsewhere (see Supplementary Material). Compared to previously used techniques, LA-ICPMS allows fast analysis of areas down to a diameter of 5 µm, at a much faster rate, and without interferences between REEs (Figure S1). The application of these microbeam methods (SIMS and LA-ICPMS) now allows the creation of a large and robust database of REE distribution in uranium oxides from major deposit types whose genetic conditions are

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reasonably well constrained. This database can help to evaluate the first-order parameters controlling the REE abundances in each mineralised system, and will allow the use of REEs as a tool for metallogenic discrimination of uranium provinces.

Results

Sixty-six REE analyses of uranium oxides (Table S1) have been performed by SIMS and LA-ICPMS (Table S2). The samples are from 18 uranium occurrences worldwide (Fig. 1), including world class uranium deposits and covering the six major deposit types that represent 55% of the world uranium resource (IAEA, 2009): intrusive, synmetamorphic, unconformity-related, vein-type, roll-front and volcanic-related. For each individual sample, the analysed areas were stringently selected after petrographic study, analysis by scanning electron microscopy (SEM), electron microprobe (EMP) and U/Pb dating by SIMS. This intensive preliminary work permits the precise identification of zonings, overgrowths and/or post-depositional alterations at the micrometre scale (Fig. 2). Only the most homogeneous and the best preserved earliest generation of uranium oxides characterising each occurrence was used in the determination of the primary REE signature of the mineralising system.

Each uranium deposit type is remarkably characterised by a specific

chondrite-normalised REE pattern (Fig. 3), regardless of the age and the geodynamic context of each deposit type. The distinctive REE signature in uranium oxides is directly related to the variability of the mineralising processes and geological settings between uranium deposit types (Table S1). Although the REE behaviour in each mineralising system is not yet fully constrained, the following preliminary interpretations on the origin of distinctive REE patterns can be proposed (Fig. 4).

Controls on REE fixation in uranium oxides

At temperatures > 350 °C, the dilatational nature of the uraninite structure allows the incorporation of large amounts of REEs without fractionation ($\Sigma\text{LREE}/\Sigma\text{HREE} \approx 1$, intrusive and synmetamorphic deposits), resulting in a ‘flat’ REE pattern, and a strong negative Eu anomaly reflecting early fractionation of plagioclase in the silicate melt for intrusive deposits (Cuney, 2010). Below 350 °C, the total REE content decreases and a fractionation occurs between REEs due to the crystallographic control of the mineral structure, with preferential incorporation of REEs having a ionic radii close to that of U^{4+} (Tb–Er), leading to a ‘bell shape’ REE pattern centred on Tb to Er. A possible Eu anomaly is visible for some deposit types (synmetamorphic and vein-type for example) and was caused by the reducing

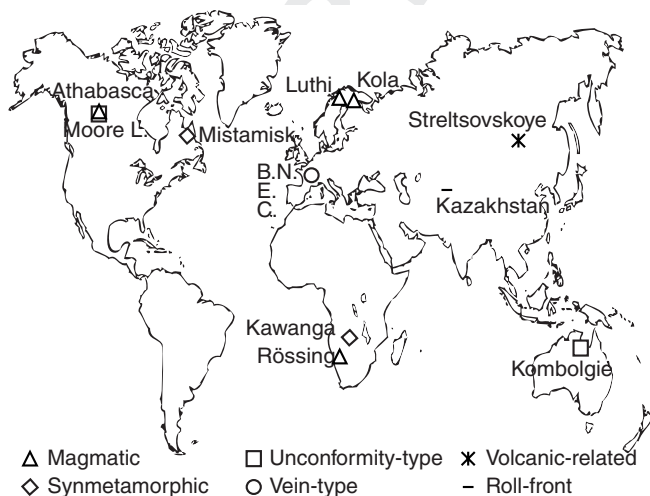


Fig. 1 xxxxxxxxxxxx.

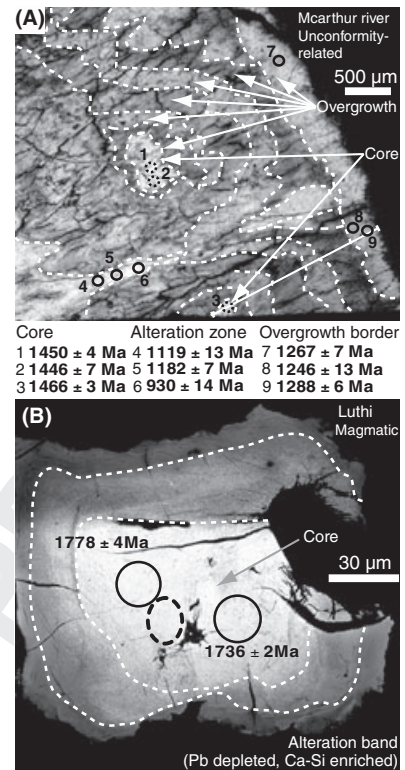


Fig. 2 xxxxxxxxxxxx.

conditions during the precipitation of the uranium oxides. However, processes other than pure crystallographic control also influence REE fixation in hydrothermal deposits. For unconformity-related deposits, LREE integration into the U-oxide structure is attenuated by the crystallisation of cogenetic LREE-rich Al-Phosphate-Sulphate (APS) minerals (Gaboreau et al., 2007), which preferentially partition the LREE (Fig. 5), leading to LREE-depleted asymmetric bell shape patterns. For vein-type and roll-front deposits, REE abundances in the uranium oxides are highly fractionated and their REE patterns, irrespective of the temperature, mimic those of the host rocks (Fig. 5). This indicates the dominance of a control by the REE source despite the different geological conditions for both deposit types. In addition, no major fractionation occurs during source leaching, REE transport and uranium oxide crystallisation. This REE behaviour is also exhibited by Variscan fluorite deposits that are contemporaneous with the vein-type deposits described herein (Schwinn and Markl, 2005) and in

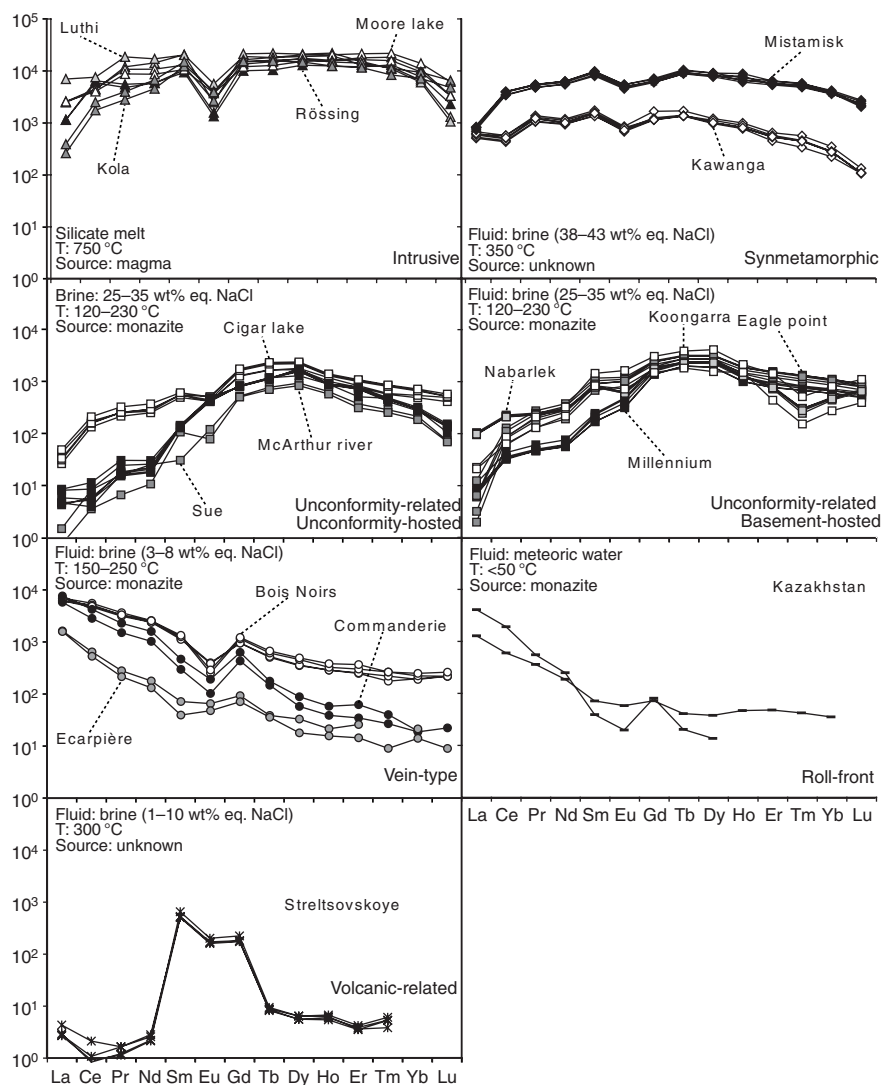


Fig. 3 xxxxxxxxxxxx.

current geothermal systems (Van Middlesworth and Wood, 1998; Lewis *et al.*, 1998; Fig. 5). The conditions that define a transition between crystallographic-controlled (unconformity-related and synmetamorphic types) and source-controlled (vein and roll-front types) REE patterns in hydrothermal uranium deposits are unclear. Indeed, unconformity-related, vein type and roll-front deposits share relatively low to moderate formation temperature and a common REE source (i.e. monazite). These common characteristics should prefigure similar REE patterns for the three types, which is not the case. However, unconformity-related and synmetamorphic deposits are both formed

from highly saline brines (25–43 wt% eq. NaCl) while vein-type and roll-front deposits form from relatively low salinity fluids (0–8wt% eq. NaCl). Therefore, the fluid salinity appears to have a strong but still poorly constrained impact on REE fractionation from source leaching, and during REE transport and U-oxide deposition. One of the main questions is the role played by the ligands, especially chlorine in highly saline fluids. None of the above-mentioned parameters can be reasonably proposed to explain the REE patterns of volcanic-related deposits which are characterised by a relative anomalous enrichment of the second REE tetrad (Masuda *et al.*, 1987; McLennan, 1994).

Although a thorough understanding of REE fractionation in U-oxides would require the analysis of REEs in the ore fluid coupled with extensive experimental and thermodynamic data, as for other metals (Lottermoser, 1992), the REEs through their highly specific modes of fixation provide a key for the metallogenic discrimination of uranium deposits. Indeed, unlike zircons (Hoskin and Ireland, 2000), the variability of the genetic conditions related to the formation of each deposit type yields characteristic signatures for uranium oxides. Two deposits having the same REE pattern are thus characterised by having similar genetic conditions. This result provides a crucial contribution to the controversial

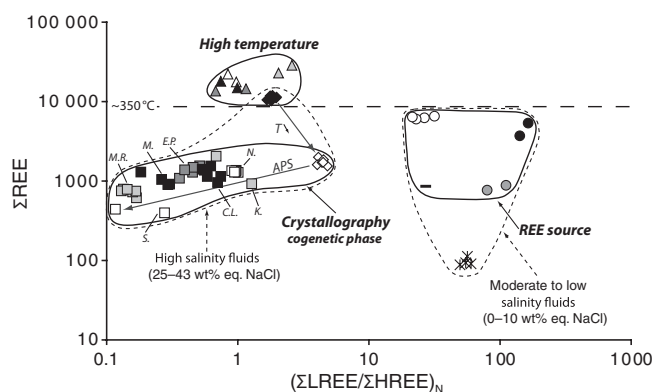


Fig. 4 xxxxxxxxxxxx.

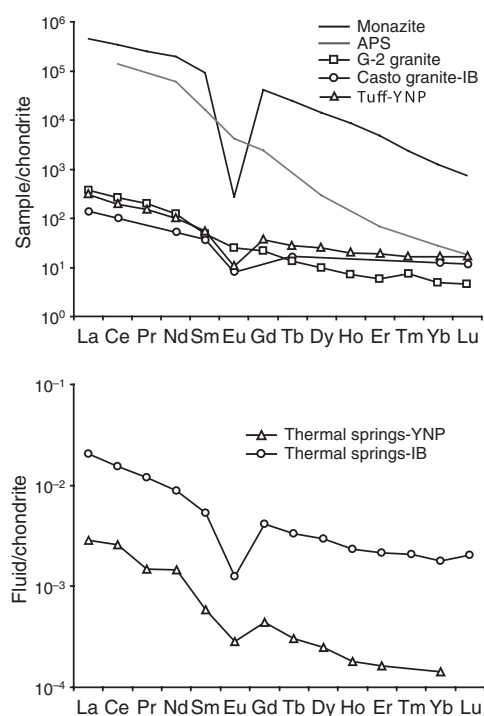


Fig. 5 xxxxxxxxxxxx.

genetic model of the giant Canadian and Australian unconformity-related uranium deposits, the world's largest high grade uranium deposits (Kyser and Cuney, 2008). Similar REE patterns have been obtained in the present study for basement- and sandstone-hosted deposits from the two districts, clearly indicating similar conditions and, therefore, a unique genetic model. This conclusion contrasts with the currently accepted genetic model which proposes a difference in the uranium oxide formation conditions

for both sub-types. Until now, two fluid flow models have been proposed for the genesis of U deposits in the Athabasca Basin (described in Fayek and Kyser, 1997 and Kyser and Cuney, 2008). In the first model proposed for basement-hosted deposits, oxidising basin-derived brines interact with basement lithologies, resulting in alteration haloes and the reduction of U(VI). In the second model, invoked for unconformity-hosted deposits, the basal brines behave similarly to the first model, but the reduction of U(VI) is

due to mixing between the brines and a reducing basement-derived fluid. This genetic contrast for both sub-types was mainly based on bulk REE contents in uranium oxide chips (Fayek and Kyser, 1997). This REE content difference resulted from the analysis of recent products of remobilisation of the primary mineralisation by cold oxidising meteoric water within basement-hosted deposits (Mercadier et al., 2011). The approach described in the present study is also particularly suited to resolve ambiguities for other controversial metallogenic provinces, such as the world-class Au-U deposits of the Witwatersrand Supergroup (South Africa), for which a detrital or hydrothermal origin of metals is vigorously debated (Meier et al., 2009). If the uraninites within these sedimentary basins are mostly detrital and originated from the erosion of the surrounding Achaean magmatic rocks, the uranium oxides should have a 'flat' REE pattern as described herein for magmatic uranium oxides.

The examples above demonstrate that the proposed microbeam methodologies, which permit very fast and simple analysis on micro-sized zones, are especially suitable for application during exploratory phases, being of primary help in determining the deposit type and thus optimising exploration strategies to newly discovered uranium occurrence.

Development perspectives for forensic purpose

To limit the proliferation of uranium trafficking, the identification of the origin of nuclear material is a major concern for the forensic community (Pajo et al., 2001; Brennecka et al., 2010; Fahey et al., 2010). One of the keys in the fight against illegal nuclear trafficking is to provide markers that unambiguously identify the source of the uranium samples. As demonstrated in our study, the REE composition is one of the most powerful tools to distinguish the uranium deposit type from which a uranium oxide comes from. This approach, combined with isotope studies previously used or proposed (Pajo et al., 2001; Brennecka et al., 2010; Fahey et al., 2010), may become the starting point for a new procedure in nuclear forensics analysis. Future work in this

field would be to test the REE signature of the uranium concentrates after uranium mining and milling operations, and to compare it with the original deposit signature.

Conclusions

This study clearly demonstrates that the uranium oxides have REE abundances directly dependant of the geological conditions linked to uranium oxide formation. The uranium oxide REE patterns are a key for a definition of meaningful genetic models. The application of this method to all known uranium deposit types, coupled with conventional isotopic techniques, will therefore greatly improve the understanding of the geology of this complex metal and will help in the discovery of new uranium deposits.

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Supporting Information

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

Table S1. Description of the uranium occurrences studied for REE chemistry determination.

1 **Table S2.** SIMS and LA-ICPMS
2 results for the REE chemistry deter-
3 mination of the studied uranium
4 oxides (results in p.p.m.).

5 **Figure S1.** Comparison of the chon-
6 drite-normalised rare earth element
7 patterns for uranium oxides from
8 unconformity-related deposits ob-

tained by the previous methods (Fryer
and Taylor, 1987; Pagel *et al.*, 1987;
Maas and McCulloch, 1990) and the
punctual secondary ion mass spec-
trometry (SIMS) and laser ablation
inductively coupled plasma mass spec-
trometry (LA-ICPMS) methods devel-
oped for this study.

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