

# REE Concentrations in Zircon and the Origin of Uranium in the Unconformity-related U Deposits in the Athabasca Basin, Canada

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## Summary

Rare Earth elements (REE) in zircons from the Athabasca Basin sandstone and its crystalline basement and in uraninites from basement- and sandstone-hosted unconformity-type uranium deposits were analyzed using laser ablation inductively-coupled plasma mass spectrometer. Considering that REE and uranium have similar geochemical properties, the purpose of this study was to distinguish the initial uranium source for the deposits in the basement. The REE patterns of sandstone- and of basement-hosted zircons are similar, showing strong enrichment in heavy REE, whereas the uraninite patterns are more variable and typically are “hump”-shaped, which reflects the greater incompatibility of the heavy REE into the uraninite structure. The REE concentrations in basement-hosted zircons are significantly higher than those in sandstone-hosted zircons, typically by one order of magnitude. The concentrations of REE in uraninites are similar to those in sandstone-hosted zircons, which appear to be the most likely source of uranium.

## Introduction

The Paleoproterozoic Athabasca Basin in northern Saskatchewan, Canada, hosts approximately one third of the world uranium deposits (OECD, 2006). The origin of uranium in these unconformity-related deposits has been debated, with two possible sources, U-rich granitoids and pegmatites within the Achaean basement (e.g., Hecht and Cuney, 2000) and the sandstones of the Athabasca Formation (e.g., Hoeve and Sibbald, 1978; Alexandre et al., 2009). In both cases, oxidizing fluids would have mobilized uranium from U-rich mineral phases such as zircon and monazite, and deposited it at a suitable chemical and physical trap at or near the basement-basin unconformity. Several indirect arguments exist in support of each hypothesis, but few direct indications have been tested until now. The rare Earth elements (REE) could represent a direct indication, considering that the REE have the same mobility and general geochemical properties as uranium. When U-rich accessory phases were altered, the released REE and U would have similar migration and deposition histories, and therefore the REE patterns and concentrations in uraninite would reflect that of the mineral phase from which uranium itself originated.

## Sampling and analytical method

Samples from the basement and from sandstone were collected from the McArthur River and the Rabbit Lake deposits in eastern Athabasca Basin, from the Maurice Bay deposit and the Spring Point barren alteration system on the northwestern margin of the basin, from the Centennial deposit and a background drill hole (VR01) in the southwest part of the basin. Uraninite samples were collected from both sandstone-hosted (Centennial and Maurice Bay) and basement-hosted (McArthur River, Dawn Lake, and Rabbit Lake) deposits. In total, 39 sandstone-hosted zircons, 41 basement-hosted zircons, and 56 uraninite grains were analyzed.

Thin sections were prepared from all samples and were examined petrographically, using optical and electron microscopy. LA-ICPMS analysis of zircon and uraninite was made using the ThermoFisher X-Series II at the Queen's Facility for Isotope Research (Queen's University, Kingston, Ontario). This instrument is equipped with a New Wave UP-213 Nd:YAG laser-ablation system using a small volume (ca. 2.5 cm<sup>3</sup>) and laminar-flow SuperCell™ ablation cell. Ablation was performed in an atmosphere of pure He (0.6 l/min), with the ablated aerosol mixed with Ar (0.8 l/min) immediately after the ablation cell prior to direct introduction into the torch. Pre-defined areas of the polished thin sections were ablated and spot sizes of the analyses were 30 μm in diameter. The following m/z were measured: <sup>29</sup>Si, <sup>89</sup>Y, <sup>90</sup>Zr, <sup>133</sup>Cs, <sup>137</sup>Ba, <sup>139</sup>La, <sup>140</sup>Ce, <sup>141</sup>Pr, <sup>146</sup>Nd, <sup>147</sup>Sm, <sup>153</sup>Eu, <sup>157</sup>Gd, <sup>159</sup>Tb, <sup>163</sup>Dy, <sup>165</sup>Ho, <sup>166</sup>Er, <sup>169</sup>Tm, <sup>172</sup>Yb, <sup>175</sup>Lu, <sup>176</sup>Hf, <sup>177</sup>Hf, <sup>178</sup>Hf, <sup>179</sup>Hf, <sup>180</sup>Hf, <sup>206</sup>Pb, <sup>207</sup>Pb, <sup>208</sup>Pb, <sup>232</sup>Th and <sup>238</sup>U. The analysis time for each sample was 100 s, comprising a 30 s measurement of background (laser off, gases on) and a 70 s analysis with laser on. Data reduction was undertaken according to standard methods (Longerich et al., 1996) using Zr as the internal standard. Instrument drift was performed using NIST 612 and calibration was performed using zircon standard 91500 (Wiedenbeck et al., 1995).

## Analytical results

### *Petrographic observations*

The amount of zircons in the Athabasca Group sandstones is significantly lower than in the crystalline basement, with the exception of the barren alteration system of Spring Point (Fig. 1). The zircons in the sandstones are larger and more altered than those in the basement. These observations are explained by the larger amount of fluid circulation in the sandstones, where diagenetic processes have contributed to the destruction of the smaller zircon grains and the stronger alteration of the remaining larger ones leading to the mobilization of REE and uranium. Inversely, the lower fluid circulation in the basement rocks has contributed to the preservation of smaller zircon grains and the decreased alteration of zircon.

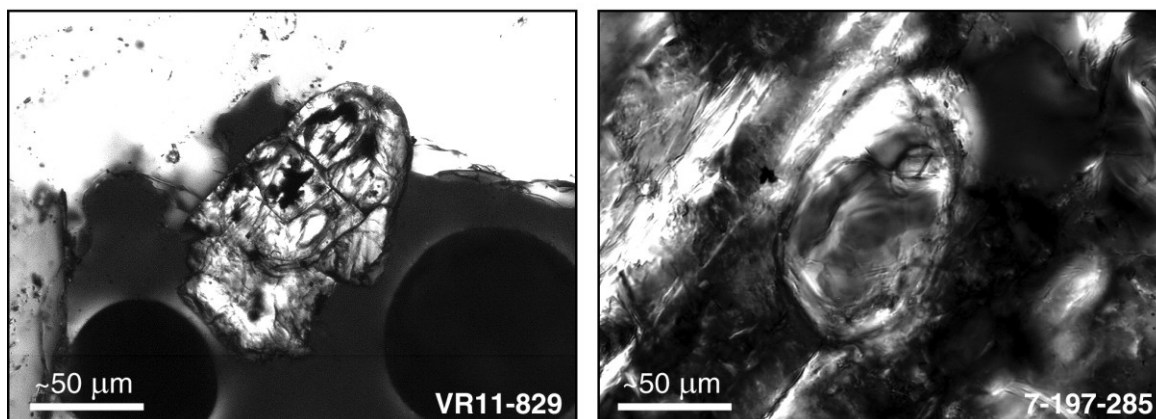


Figure 1. Example of sandstone-hosted zircons (Centennial, left) and basement-hosted ones (Rabbit Lake, right). Note that the lower part of the sandstone-hosted zircon is corroded, whereas its upper part is mostly intact, due to protection by the surrounding quartz. The basement-hosted zircon (left) is relatively fresh, even though it is surrounded by clay alteration.

### *REE patterns*

The chondrite-normalized (McDonough and Sun, 1995) REE patterns of zircons from the sandstone are similar to those in the basement (Fig. 2), with the light REE (LREE) moderately enriched relative to chondrite (ca. 100 times) and the heavy REE (HREE) strongly enriched relative to chondrite (up to 10,000 times). The REE patterns of uraninite are different and form a

broad ‘hump’ with the LREE and the HREE moderately enriched relative to chondrite (ca. 100 times) and the intermediate REE strongly enriched relative to chondrite (1,000 to 10,000 times), as has been previously reported (Collins Bay uraninite, Athabasca Basin; Jackson et al., 1992). It would appear that the REE patterns of uraninite are not dependent of the REE source, but likely reflect the greater incompatibility of the HREE into the uraninite structure, and thus direct comparisons of the zircon and uraninite REE pattern shape cannot be used as a source diagnostic tool.

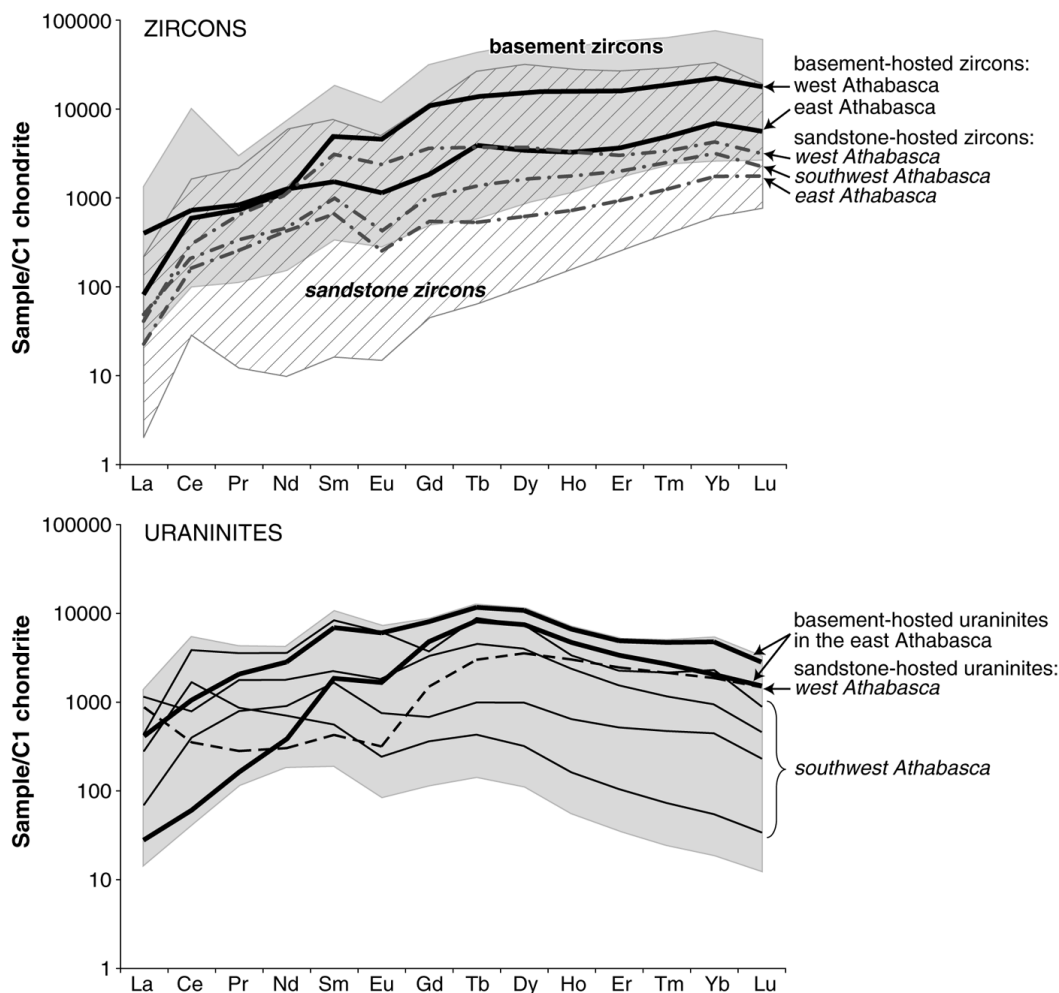


Figure 2. Rare Earth elements (REE) concentrations relative to C1 chondrite (McDonough and Sun, 1995) for zircons and uraninites from the Athabasca Basin. The gray and hatched areas represent the total variation fields for the minerals analyzed, whereas the lines represent the median values organized by location within the basin.

**REE concentrations**

On the other hand, there is a clear difference in the total concentrations of REE, as sandstone zircons contain approximately one order of magnitude less REE than the basement zircons (Fig. 2; median sandstone concentration: 2,900 ppm, median basement zircon concentration: 11,800 ppm). The median REE concentration in uraninite (ca. 4,500 ppm) is much closer to that of sandstone zircons than to that of basement zircons. Additionally, there is systematic variation within the REE concentrations in uraninites (Fig. 2), with the basement-hosted uraninites being enriched (ca. 5,100 ppm) relative to the sandstone-hosted uraninite (ca. 3,000 ppm).

## Discussion and conclusions

The petrographic observations of sandstone and basement zircon indicate a higher destruction rate in the sandstone relative to the basement, explained by the greater abundance of fluids and the higher permeability of the sandstone compared to the basement rocks. Considering that fluids present in the sandstone are more oxidizing than those in the basement, and that the sandstones are more permeable than the basement, it can be suggested that the uranium mobilization from accessory phases was significantly more efficient in the sandstone than in the basement.

Commonly the amount and degree of alteration of zircon is used as an indirect indication of mobilization of uranium from the source, however this study suggests that the REE concentration may be used to pinpoint basement versus sandstone sources. The total amount of REE in uraninite is much closer to that of sandstone-hosted zircons than of basement zircons (Fig. 2). It could be argued that the total REE concentration in uraninite is lower because of the greater incompatibility of the HREE into the uraninite structure and not because of the availability of REE in the mineralizing fluid. In order to test this hypothesis, the concentrations of LREE (La through Eu) should be considered. The average LREE concentration of uraninite is ca. 2,000 ppm, similar to that of sandstone-hosted zircons (ca. 1,800 ppm) and lower than that of basement-hosted zircons (ca. 2,800 ppm), suggesting that it is indeed the availability of REE in the mineralizing fluid that controlled their concentration in uraninite.

In conclusion, based on the total concentrations of REE or of LREE in zircons and of uraninites, it can be suggested that the sandstone-hosted zircons (and, by extension, other U-rich accessory phases), were the likely source of uranium in the unconformity-related deposits in the Athabasca Basin.

## References

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