

## Conditions for uranium transport in unconformity-related U deposits

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Our knowledge of massive metal transfer within the Earth's crust is limited by the lack of direct analysis of deep fluids and experimental work. During the Mesoproterozoic Era (1.6-1.0 Gyr ago), giant uranium deposits were formed from large-scale circulation of uranium-bearing brines at the interface between sedimentary basins and their crystalline basements (unconformity-related uranium deposits) [1, 2].

However, the key processes leading the exceptionally high ore grades and tonnages of these deposits, especially the transport of uranium in the brines, remained poorly understood.

Here, we show that the uranium was transported under unexpectedly low pH conditions and at the highest concentrations recorded for crustal fluids so far.

By using laser ablation inductively coupled plasma mass spectrometry analysis of natural fluid inclusions we found that the uranium concentration varies over four orders of magnitudes in the ore-forming brines (from  $10^{-6}$  up to  $2.8 \times 10^{-3}$  mol.l<sup>-1</sup> U).

We combined these results with the first experimental determination of the solubility of U (VI) in H<sub>2</sub>O-NaCl mixtures analogous to the ore-forming brines (up to 6 mol.l<sup>-1</sup> NaCl) and we found that the pH (between 3 and 4 at 155°C) is the major control on U (VI) solubility in these conditions.

More generally, models for the formation of 'world-class' hydrothermal ore deposits imply either protracted fluid flow with relatively low metal concentration, or more discrete events characterised by exceptionally metal-rich fluids. Our results strongly suggest that the second hypothesis can be applied to the world's richest uranium deposits.

[1] Richard *et al.* (2010) *Terra Nova* **22**, 303–308. [2] Boiron *et al.* (2010) *Geofluids* **10**, 270–292.

## Taking advantage of both U-Th and U-Pb disequilibrium methods for speleothem geochronology

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The success of speleothems as accurate chronological markers of landscape evolution and climate change is well acknowledged, but accuracy and precision become particularly limiting beyond 350 ka for a number of reasons beyond the theoretical, including interlaboratory comparison and common standard/half-life usage. We illustrate here plans to take advantage of high-precision U-Th methods in concert with U-Pb techniques [1-3], which have the added advantage of community-supported accuracy (via EARTHTIME), to date important material in the range 0.35 to 1 Ma.

We are currently optimising a combination of U-Th-Pb techniques that utilise solution and *in situ* methods with MC-ICP-MS at the BIG and NIGL to analyse a variety of secondary calcite deposits previously demonstrated to be beyond the age range of traditional methods. We focus on an unusually U-rich flowstone sample ( $>60 \mu\text{g g}^{-1} \text{ }^{238}\text{U}$ ) from the Grotte Valerie system in the Mackenzie Mountains, NWT, Canada [4]. Ten high-resolution sub-samples were cut as wafers from the growth layers identified in original publication. Several sub-samples have an extremely high  $^{230}\text{Th}/^{232}\text{Th}$  atomic ratio ( $> 3$ ), which demonstrates that the Th isotope signal is dominated by the radiogenic component. We obtained an age and  $2\sigma$  uncertainty of  $120 \pm 1.2$  ka from the youngest phase of growth. U-Th ages for older sub-samples, between 8.5 and 30 mm above base are not finite, and are therefore  $> 500$  ka. We present preliminary U-Pb ages and *in situ* LA U-Th-Pb and gamma mapping for this older material. The latter are also used to screen future sub-samples useful for a host of applications.

[1] Cliff *et al.* (2010) *Quat. Geochron* **5**, 452–258. [2] Polyak *et al.* (2008) *Science*, **319**, 1377–1380. [3] Woodhead *et al.* (2006) *Quat. Geochron*, **1**, 208–221. [4] Harmon *et al.* (1977) *Canadian J. Earth Sci* **14**, 2543–2552.