

## Adopting a combined U-Th-Pb strategy to date speleothems >200 ka

CHRISTOPHER J.M. SMITH<sup>1\*</sup>, DAVID A. RICHARDS<sup>1</sup>, DANIEL J. CONDON<sup>2</sup>, MATTHEW S.A. HORSTWOOD<sup>2</sup>, RANDALL R. PARRISH<sup>2</sup>, JON WOODHEAD<sup>3</sup> AND DEREK C. FORD<sup>4</sup>

<sup>1</sup>School of Geographical Sciences, University of Bristol, UK  
(\*correspondence: chris.smith@bristol.ac.uk)

<sup>2</sup>NERC Isotope Geosciences Laboratory, British Geological Survey, UK

<sup>3</sup>School of Earth Sciences, University of Melbourne, Australia

<sup>4</sup>School of Geography and Earth Sciences, McMaster University, Canada

Speleothems are widely recognised as valuable records of palaeoenvironmental and landscape change with robust and precise chronologies to ~500 ka, principally based on the U-Th decay scheme. However, the practical upper limit for speleothem dating can be extended by the adoption of U-Th-Pb methodologies that account for disequilibrium in the decay chain, see review by Woodhead & Pickering (2012) [1]. While the range of applications is expanding, widespread adoption of these methods is hampered by the need to accurately predict, with high precision, the initial state of U-series disequilibrium (i.e.  $(^{234}\text{U}/^{238}\text{U})_{\text{initial}}$ ), and also analyse material with a sufficient range of U/Pb to provide high precision isochron age determinations.

For a suite of speleothems spanning the late Pliocene to late Pleistocene exhibiting variable U (1-100  $\mu\text{g g}^{-1}$ ) and low non-radiogenic Pb (<50  $\text{ng g}^{-1}$ ), we have adopted a combined U-Th-Pb dating strategy to take full advantage of the sensitivity and spatial resolution of available techniques. For individual growth layers, we have used: (1) rapid in-situ U-Pb LA-MC-ICPMS (193 nm ArF excimer laser) techniques, which enables fast throughput, high spatial resolution and a wide range in U/Pb for individual spots; (2) conventional U-Pb ID TIMS, for high-precision three-dimensional isochrons at lower spatial lower resolution; (3) U-Th MC-ICPMS static Faraday methods, to obtain high-precision estimates of initial  $^{234}\text{U}/^{238}\text{U}$  for material  $\geq 500$  ka.

We discuss the relative merits of each of the above methods and their combined use, focusing in particular on the compromises that have to be made between spatial resolution and age precision for speleothems with different growth rates and ages.

[1] Woodhead & Pickering, (2012) *Chem Geol* **322-323**, 290-299.

## Diamond inclusions reveal fugitive mantle nitrogen

E.M. SMITH<sup>1\*</sup>, M.G. KOPYLOVA<sup>1</sup>, M.L. FREZZOTTI<sup>2</sup> AND V.P. AFANASIEV<sup>3</sup>

<sup>1</sup>Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia, 2207 Main Mall, Vancouver, BC V6T 1Z4, Canada (\*correspondence: esmith@eos.ubc.ca)

<sup>2</sup>Department of Geological Sciences and Geotechnologies, University of Milano-Bicocca, Piazza della Scienza 4, 20126 Milano, Italy

<sup>3</sup>Sobolev Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, pr. Akademika Koptuyuga 3, Novosibirsk, 630090, Russia

Mantle volatiles in mid-ocean ridge basalts and fluid inclusions in mantle xenoliths are dominated by CO<sub>2</sub>. Nitrogen generally appears as a trace component. However, we report diamonds from three different localities, the Kaapvaal, Congo, and Siberian cratons, that have N-rich fluid inclusions and melt inclusions.

Nitrogen in the inclusions was analyzed with micro-Raman spectroscopy. Fluid inclusions in the Siberian diamond are CO<sub>2</sub>-N<sub>2</sub> mixtures with 40±4 mol% N<sub>2</sub>. Melt inclusions in the diamonds from the Kaapvaal and Congo cratons contain exsolved bubbles of volatiles that are nearly pure N<sub>2</sub>, with <9 mol% CO<sub>2</sub>. At the time of trapping, the silicate melt would have contained ~1 wt% dissolved N<sub>2</sub>.

These melt and fluid inclusions are well-preserved samples of mobile, undegassed mantle phases. Such N-rich fluids/melts reveal an unrecognized type of concentrated N flux escaping the convecting mantle. This critical observation casts uncertainty on current flux models, which otherwise suggest considerable net influx to the mantle via subduction that does not return to surface (at mid-ocean ridges, volcanic arcs, back-arc basins, and hotspots).

We propose that the N<sub>2</sub> in our samples was liberated by oxidation from NH<sub>4</sub><sup>+</sup>-bearing silicates. The coexistence of N<sub>2</sub> and oxidized carbon species in fluid/melt inclusions supports the idea that oxidizing conditions help to mobilize N and C. This implies redox conditions control mantle nitrogen behaviour, both in terms of storage and geodynamic cycling.

Additionally, the oxidation of NH<sub>4</sub><sup>+</sup> to N<sub>2</sub> could be accompanied by isotopic fractionation. This would allow isotopically light N<sub>2</sub> (low <sup>15</sup>N/<sup>14</sup>N) to be derived from isotopically heavy subducted or stored NH<sub>4</sub><sup>+</sup> (higher <sup>15</sup>N/<sup>14</sup>N). This isotopic fractionation may explain the gross mismatch between isotopically heavy N influxed by subduction and the isotopically light N effluxed from the mantle, in diamonds and mid-ocean ridge basalts, for example.