

Investigation on neodymium isotopic fractionation occurring during HPLC separation

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The precise Nd isotopic composition is of major interest in nuclear (determination of nuclear fuel burn-up, ...) [1] and geosciences applications (paleoceanography, ...) [2]. Direct determination of Nd isotopic ratios in sample is hampered by isobaric interferences and chemical separation before isotopic measurements is required.

In this study, the separation of lanthanides was performed by high-performance liquid chromatography using analytical column with strong cation exchange (SCX) groups bounded to the silica surface. A gradient elution mode was used with the mobile phase containing the organic acid HMB (2-hydroxy 2-methylbutyric acid).

For this study, a *JNdi-1* standard solution was used. The Nd peak was collected in various fractions for isotope ratio measurements by MC-ICP-MS (Neptune Plus, Thermo Scientific), to evaluate Nd isotopic fractionation during elution. Raw ratios were corrected for mass bias using Nd reference values obtained by the flash evaporation method in Thermal Ionisation Mass Spectrometry [3,4].

The range of variation observed along the elution peak is about 2‰/amu, which is significant considering an external reproducibility obtained by sample standard bracketing method on the *JNdi-1* isotopic standard lower than 0.03‰ for all isotopic ratios. This trend indicates a preferential elution of heavy isotopes. This phenomenon imposes to collect the total Nd elution peak in order to determine the true isotopic ratios. The potential consequences of this behaviour on the accuracy of the measurement will be presented. This result is essential for future on-line experiments with HPLC hyphenated with MC ICPMS in order to measure accurate Nd isotopic ratios.

- [1] Bourgeois *et al.*, *J. Anal. At. Spectrom.* **26** (2011) 1660.
[2] Ilina *et al.*, *Chem. Geol.* **342** (2013) 63. [3] Dubois *et al.*, *Int. J. Mass Spectrom. Ion Process.* **120** (1992) 163. [4] Wakaki and Tanaka, *Int. J. Mass Spectrom.* **45** 323-324 (2012).

A new radiation damage based model for He diffusion in zircon

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A key assumption in zircon and apatite (U-Th)/He dating has traditionally been that the diffusion kinetics of ⁴He in the mineral of interest are constant across a broad spectrum of chemical compositions. Increasingly, practitioners of the technique are discovering that a "one-size-fits-all" approach to these kinetics is inadequate and are developing more grain-specific diffusion models to both explain data complexities, and to better constrain time-temperature histories. Here we present diffusion measurements that show how a zircon's alpha dose, which we interpret to correlate with radiation damage, influences its He diffusivity. Results from step-heating experiments on pairs of crystallographically oriented slabs of zircon are as follows: from 1.2×10^{16} α/g to 1.4×10^{18} α/g, the frequency factor measured parallel to the c-axis decreases by ~4 orders of magnitude, causing He diffusivity to decrease (e.g. by ~3 orders of magnitude at between 140 and 220 °C). Above $\sim 2 \times 10^{18}$ α/g, activation energy decreases by a factor of two, and diffusivity increases by ~9 orders of magnitude by 8.2×10^{18} α/g. We attribute these trends to two separate, though related, mechanisms. Initially, progressive damage in-growth leads to greater tortuosity of diffusion pathways, decreasing He diffusivity. As in-growth continues, damage zones become interconnected, shrinking the effective diffusion domain size and increasing the crystal's bulk He diffusivity. We parameterize the damage-diffusivity relationship and couple it to a model describing damage annealing as a function of time and temperature (as in the RDAAM of Flowers *et al.* (2009)). This new model describes the coevolution of damage, He diffusivity, and (U-Th)/He date of a zircon.