Using rare earth elements (REE) for tracing water masses

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Rare earth elements are a group of elements consisting of scandium, yttrium and the lanthanides. The concentrations in Dutch ground and surface water are low, at sub ppb (μg/kg) level, but measurable with an optimised ICP-MS. The lanthanides show chemically nearly identical behaviour, which results in concentrations with a constant ratio between the different elements, although the absolute concentrations can vary by more than two orders of magnitude. The measured concentrations need to be divided by the levels in a reference clay mineral, yielding a flat line for samples with a clayey signature. Water with a calciferous influence is enriched with the heavier REE compared to the lighter REE. The slope can be expressed by the quotient of the sum of the normalised ytterbium and lutetium values and the sum of the normalised lanthanum and praseodymium values. The gadolinium anomaly (an enrichment) is caused by the application of gadolinium as a contrast agent during medical MRI-scans. This last anomaly is a clear indication of anthropogenically influenced (ground) water.

Due to absence of topography and constant water substraction in the polderareas of the Netherlands, the hydrological system can be extremely complex locally. With REE-profiles and by combining all the characteristics of these REE-profiles, it is possible to make a water balance in these complex hydrological systems.

A simple method for *in situ* zircon U-Th-He dating

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In situ U-Th-He dating of zircon by laser ablation offers significant advantages over the current practice of whole grain degassing and dissolution:

1. It dramatically increases sample throughput. Grains of zircon are notoriously hard to dissolve. Measuring their U and Th content requires dissolution in hydrofluoric acid at high temperature and pressure using a Parr bomb for up to 72 hours. In contrast, measuring the U and Th content by LA-ICP-MS can be done in a matter of minutes.
2. The process of in-situ measurements of U and Th content of grains yields U-Th-Pb ages as a by-product. Thus, in-situ dated zircon crystals are double-dated by default, offering exciting new research opportunities for detrital geochronology.

We here propose a simple four step procedure to measure *in situ* U-Th-He ages without the need to know any absolute concentrations or ablation pit volumes:

1. Polish and mount two sets of grains in indium: a standard of known U-Th-He age, and the sample of interest, whose age is unknown.
2. Ablate the grains with a UV laser and measure the raw helium signal (e.g., in units of mV or Hz) of the unknown sample along with helium measurements of the age standard.
3. Measure the U and Th signals of the standard and the unknown by EMPA, SIMS, or LA-ICP-MS in the same order as the helium measurements.
4. Given the known age of the standard and its raw U and Th signals, calculate the expected He signal of the standard. Dividing the measured by the expected He signal yields a ‘gain factor’ K. The U-Th-He age of the unknown is then obtained by applying this same gain factor to its raw He signal.

This new method eliminates the need for interferometric microscopy to measure ablation pit volume, largely avoids the challenges of measuring absolute U and Th concentrations by ICP-MS, and has relatively few sources of analytical uncertainty, potentially resulting in improved precision and accuracy over alternative analytical procedures.