Development of (U-Th)/He geochronology of columbite ores

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Goal

Columbite-tantalite (called also as 'coltan') belongs to the most important source minerals of high-tech elements [1]. Its genesis is mainly connected to granitic pegmatites ranging from the Archean to the Cenozoic. The major- and trace element pattern, and the formation age (typically determined by different techniques of U-Pb geochronology) [2] are used for understanding the development of the deposits, and also as diagnostic tools in provenance studies of ores. We aim to develop a double-dating procedure combining columbite U/Pb geochronology with (U-Th)/He thermochronology.

First He measurements - indications of high closure temperature

In order to avoid effects from zoning of the samples we used air-abraded multi-grain aliquots for dating. Our experiments support that the crystal lattice of columbite is tight, i.e. He is not leaking. The degassing tests were performed in an IR-laser-heated full-metal helium extraction line at the GÖochronology Laboratory. The duration and temperature needed for the complete gas release indicate that the closure temperature of columbite is higher than 250 °C. This temperature is considerably higher than the He closure temperatures of commonly used minerals like apatite (~ 60-70 °C; e.g. [3]), however, considerably lower than the closure temperature of the U-Pb geochronometer in zircon or in other oxides. Consequently, He-thermochronology of columbite can provide constraints to the post-emplacement thermal evolution and erosion history of the deposits. In consequence, the double-dating of columbite is thought to provide useful fingerprints for the provenance studies of ores.

Digestion technique

After degassing it is necessary to perform a complete dissolution of the crystals to measure precisely the U, Th and Sm by ICP-MS. In case of Ta, Nb, Fe and Mn rich solutions the precipitation and the adsorptive loss of U is a common problem. By a series of experiments on synthetic and natural columbite solutions we developed a chloride-based digestion technique that keeps the uranium and thorium quantitatively in low acid concentration solutions.

The first columbite (U-Th)/He ages

A well studied columbite specimen from Madagascar yielded a He age of 450 ± 27 Ma, which is slightly younger than its U-Pb TIMS age of 505.4 ± 1.0 Ma. In other pilot samples from African districts, the lag-times between the U-Pb formation and He cooling ages are considerably longer.

[1] Melcher (2008) *SGA News* **23**, 1-14. [2] Smith (2004) *Contrib Mineral Petrol* **147**, 549–564. [3] Farley (2002) *Rev Mineral Geochem* **47**, 819-844.

Enhanced calibration of a new natural gamma radiation technique for quantifying U, Th, and K concentrations in marine sediments

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Determining accurate concentrations of U, Th, and K in marine sediments and rocks is critical for a variety of oceanographic fields such as subseafloor microbiology, paleoceanography, sedimentology and mineralogy, and marine biogeochemistry. Rapid elemental characterization of marine cores will also enhance correlation with downhole geochemical logging. A newly developed natural gamma radiation (NGR) system aboard the Integrated Ocean Drilling Program's (IODP's) *JOIDES Resolution* research vessel provides improved measurement efficiency and lowered background signals to significantly increase the statistical reliability and quality of NGR data [1]. We are developing a combined analytical and modelling technique that converts these high-resolution energy spectra to concentrations with the use of core standards and U/K and Th/K ratios estimated from comparisons to Monte Carlo simulated and experimental spectra.

To further refine the Monte Carlo inversion technique it is critical to calibrate it by comparison to quantitatively measured concentrations of U, Th, and K in the core material. We present results based on the analysis of 38 marine sediment samples from four sites in the South Pacific Gyre recovered during IODP Expedition 329. We analyzed these sediments by ICP-ES and ICP-MS to provide a highly precise and accurate comparative data set. The ICP-ES (for K) and ICP-MS (for U, Th) data were themselves calibrated against international Standard Reference Materials and are both precise and accurate.

Our preliminary results indicate that the NGR technique captured the variability of K concentrations with depth, but systematically underestimated the absolute K concentrations by approximately a factor of two. U and Th NGR concentrations are also seen to deviate from the ICP concentrations, but much of the disparity may be driven by the offset in K concentrations. Since the NGR method calculates U and Th concentrations from U/K and Th/K ratios that are determined from Monte Carlo simulations and experimental data, an improper calibration of K can impact the accuracy of U and Th estimates. Continued improvements of the NGR K concentration calculation are likely to result in more accurate estimates of U and Th concentrations.

Additionally, inconsistencies between the data sets for sediments younger than ~1.5 Myr may arise because the NGR analysis infers U and Th concentrations from the radiation of their daughter products, which can have contrasting chemical behaviour (e.g. adsorptive character) between the different isotopes. We will present our strategies to address these effects, and discuss our efforts to continue development of this evolving new technique.

[1] Vasiliev et al., (2011) *J. of Applied Geophysics* **75**, 455-463.