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Ablation behaviour of titanite and constraints for U–Th–Pb geochronology using a quadrupole ICP-MS coupled to a 193 nm excimer laser

Afifé El Korh
University of Bern, Institute of Geological Sciences, Bern, Switzerland (afife.elkorh@geo.unibe.ch)

U–Pb geochronology using LA-ICP-MS has become a widespread and powerful tool for in-situ U–Pb dating of zircon. The LA-ICP-MS technique has recently been developed for in-situ U–Th–Pb titanite geochronology as well [e.g. 1,2]. Age accuracy depends strongly on protocol adopted for the analyses. In particular it is essential to evaluate the possibility of using non matrix-matched standards and samples (e.g. zircon and titanite) to obtain precise and accurate ages.
In order to understand the behaviour of U, Th and Pb with respect to Ti, Ca and Si in titanite, ablation experiments were carried out using a spot ablation mode on the Khan titanite (522.2 $\pm$ 2.2 Ma; [3]) using a 193 nm ArF excimer laser ablation system coupled to a quadrupole ICP-MS. The temporal changes of the intensity ratios indicate a similar behaviour for Ca, Ti, U and Th, while Pb and Si share a similar behaviour to each other. The time-dependent element fractionation increases with increasing energy density and repetition rate conditions and with decreasing the spot size.
The 206Pb/238U, 207Pb/235U and 208Pb/232Th ratios were measured in Khan titanite as well as in Plešovice zircon (337.13 $\pm$ 0.37 Ma; [4]). With increasing ablation repetition rate and/or energy density and decreasing the spot size, the fractionation of the 206Pb/238U, 207Pb/235U and 208Pb/232Th ratios increases for both zircon and titanite. The shape of the laser-induced fractionation is different for titanite and zircon at the same operating conditions.
The mass bias coefficients (known ratio/measured ratio) calculated for the 206Pb/238U, 207Pb/235U, and 208Pb/232Th ratios in Khan titanite and Plešovice zircon generally decrease with decreasing the spot size, and with increasing the repetition rate and/or the energy density. The mass bias coefficients are higher for Khan titanite than for Plešovice zircon, at similar laser operating conditions. Ages obtained for Khan titanite using Plešovice zircon as external standard are shifted from the reference value.
Matrix effects related to a difference of mass bias coefficients, angle and shape of the time-dependent fractionation, and matrix composition, are sources of systematic errors between zircon and titanite. The Khan titanite can hardly be substituted by a zircon as external reference standard if precise U–Th–Pb ages are required for titanite.

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