

In situ U-Pb dating of zircon by means of single-collector sector-field LA-ICP-MS

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Laser ablation - inductively coupled plasma - mass spectrometry has been demonstrated to be a suitable technique for U-Pb geochronology of zircons. The majority of published data on U-Pb dating of zircon have been obtained with LA-ICP-MS instruments based on quadrupole mass spectrometers, which for instrumental impediments (e.g., low sensitivity and low abundance sensitivity) do not collect the signal of ²³⁵U. The ²⁰⁷Pb/²³⁵U ratio is thus not independently determined and it must be derived from ²³⁸U to establish the zircon concordance.

Single-collector double-focusing sector-field mass spectrometers are usually considered too slow for LA-ICP-MS application. However, new generation of double-focusing sector-field mass spectrometers are capable of rapidly scanning the mass spectrum both magnetically and electrostatically, and they can approach the performance of quadrupoles especially in a short mass range as that usually required in isotope analyses. Advantages of this kind of mass spectrometers relative to quadrupoles are a higher sensitivity, a better abundance sensitivity and the flat top peak shape, that allows the independent determination of all ratios necessary to completely apply the U-Pb geochronological systematic to zircon.

In this work we report the analytical results obtained with a LA-ICP-MS system coupling an "Element" (Finnigan MAT) sector field mass spectrometer with a Nd:YAG laser probe that can be operated both at 266 nm and 213 nm. Acquired masses are ²⁰¹Hg, ²⁰⁴(Pb+Hg), ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th, ²³⁵U and ²³⁸U. Laser induced elemental fractionation revealed significantly lower and with a higher intra-run reproducibility at 213 nm than at 266nm laser wavelength. The day to day laser instability however requires the adoption of a matrix matched external standard for the correction of laser induced elemental fractionation. This allows also the correction for the mass bias and the sequential acquisition of transient signals.

Precision and accuracy on age determination were evaluated on a series of zircons of known age with radiogenic Pb ranging from 14 ppm to less than 1 ppm. Precision on the concordant age is always to better than 2%. Accuracy is within 2% for Pb-rich zircons and within 4% for the more depleted ones. The 213 nm laser radiation allows a significant improvement on ²⁰⁷Pb/²⁰⁶Pb, ²⁰⁸Pb/²³²Th ratios and relative ages relative to that at 266 nm.

Structural constraints to Nb and Ta incorporation in minerals

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Nb and Ta are geochemically important trace elements whose crystal-chemical behaviour has not yet fully understood. Albeit these HFS elements have the same oxidation state and very similar ionic radii, values of the Nb/Ta ratio measured in crustal and mantle rocks are highly variable. Subchondritic Nb/Ta values are found in continental crust and asthenospheric MORB-type mantle, and the presence and location in the silicate Earth of reservoirs with superchondritic Nb/Ta values is under debate. It is therefore important to know which mineral phases may control the Nb and Ta budget, and which are the mechanisms for their incorporation in the various minerals. New partitioning data and present crystal-chemical knowledge are combined to discuss the mechanisms ruling Nb and Ta incorporation in some silicates (amphibole, clinopyroxene, mica, titanite) and Ti-rich oxides (perovskite, Ti-spinel). A crystal-chemical prerequisite for Nb and Ta compatibility is the availability of one (or more) site suitable to host Ti and of a one (or more) exchange vector allowing local neutralisation of the extra positive charge provided by Nb and Ta with respect to Ti. However, sites in which Ti is the dominant cation do not allow $S^L D_{Nb}/S^L D_{Ta} > 1$, because Ta is smaller than Nb and therefore is more similar to the ideal site dimension. On this ground, a site hosting Ti and larger cations is needed to have $S^L D_{Nb}/S^L D_{Ta} > 1$. Both perovskite and titanite have a site in which Ti is dominant, and also a suitable charge balance mechanism. Accordingly, Nb and Ta are highly compatible in these minerals, and measured $S^L D_{Ta}/S^L D_{Nb}$ values are by far > 1 . Also, incorporation of the smaller Al³⁺ in titanite further increases measured $S^L D_{Ta}/S^L D_{Nb}$ values. In Ti-spinel, Nb and Ta are less compatible due to the difficulties to balance the extra charge, which is limited to the presence of divalent trace elements. Ta is still compatible, whereas $S^L D_{Nb}$ is generally < 1 . In calcic clinopyroxenes, both Nb and Ta are highly incompatible. This feature may be explained by the low ⁶Ti contents; the $S^L D_{Nb}/S^L D_{Ta}$ values are significantly higher than in the above Ti-rich minerals in agreement with measured $\langle M1-O \rangle$ longer than expected for $\langle Ti-O \rangle$. In amphiboles (especially in calcic amphiboles from mantle environments) the frequent need for high charged cations at the M1 site balancing for (partial) dehydrogenation allows Nb and Ta to behave as compatible elements. The $S^L D_{Nb}/S^L D_{Ta}$ value is controlled by the dimensions of the M1 site, so that decreasing Mg# values (i.e., larger $\langle M1-O \rangle$) allow this ratio to approach and even to exceed 1. The same behaviour is expected in micas, which possess similar mechanisms for Ti incorporation.