

U-Pb dating of carbonates by UV femtosecond LA-ICPMS: toward reliable ages from isotopic images and without the need for a carbonate primary standard

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In situ U-Pb dating of carbonates by LA-ICPMS is an increasingly used method in the field of geosciences, as it brings very strong constraints over the geological history of basins, faults or reservoirs. All ages currently published are based on nanosecond lasers linked to sector-field or multi-collector ICPMS. Here, a 257 nm femtosecond laser ablation system coupled to an High Resolution ICPMS (Element XR Jet interface, Thermofisher) was used for the direct measurement of U and Pb in previously dated (WC1, Duff Brown, ASH-15D, BH14) and unknown (Pyrenean lacustrine carbonates) calcite samples, both with spot ablation and high resolution image strategies.

For spot ablation, a 15 μm laser beam was rapidly moved (1 mms^{-1}) at the surface of the sample at high repetition rates (from 100 Hz to 1 kHz) to obtain square craters of $100 \times 100 \mu\text{m}$. We show that the use of ablation repetition rates below 300 Hz allows obtaining results comparable to nanosecond lasers in terms of accuracy and precision, without noting downhole fractionation effects. In addition, we show that in these conditions, the mass bias is identical between NIST612 and WC1 for the $^{238}\text{U}/^{206}\text{Pb}$ ratio. These results open the possibility to consider the dating of carbonate samples using only NIST612 as the primary standard.

For HR images, repeated 25 μm lines were performed using a back and forth movement of the laser beam combined with the movement of the sample and a high repetition rate (500 Hz). Images of the $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios are then obtained with several thousand pixels of resolution, over an area of less than 1 mm^2 and in 20 minutes only. The shallow ablation depth of about 15 μm makes it possible to work directly on thin sections. The images show significant variations in isotope ratios over short distances, allowing the use of an approach comparable to that of Drost et al. (2018) to directly extract a reliable age from the image produced. In addition, as with spot ablation, these initial results show that there is no mass bias between NIST612 and WC1 for the $^{238}\text{U}/^{206}\text{Pb}$ ratio.

Drost, K. et al., 2018. An Image Mapping Approach to U-Pb LA-ICP-MS Carbonate Dating and Applications to Direct Dating of Carbonate Sedimentation. *Geochem. Geophys. Geosyst.*, 19 (12), 1525-2027