

## Synthesis of calcite reference materials for *in situ* U–Pb dating through crystallization from amorphous calcium carbonates

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Calcium carbonates are ubiquitously present throughout the Earth history as animal shells, speleothems, fault-related vein fillings, and hydrothermal or cold-seep precipitates. Direct dating of carbonates provides valuable information on paleoenvironmental change, tectonics, and fluid and material cycling. Uranium–lead (U–Pb) dating using high spatial-resolution laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a key technique to date natural carbonates such as fault-hosted calcite that cannot be dated by biostratigraphy or Sr isotope stratigraphy (Roberts and Walker, 2016; Beaudoin et al., 2018). *In situ* U–Pb dating by LA-ICP-MS needs matrix-matched reference materials to correct matrix-dependent elemental fractionation in LA-ICP-MS. Roberts et al. (2017) demonstrated that a natural calcite cement WC-1 ( $254.4 \pm 6.4$  Ma) is suitable as a calcite reference material. However, the WC-1 calcite has an inhomogeneous distribution of U and Pb and lacks concordance in the U–Pb system (Roberts et al., 2017). In this study, we synthesized novel calcite reference materials with homogeneous U and Pb concentrations and isotope ratios. Incompatible elements such as Sr can be incorporated into calcite through pressure- or heat-induced crystallization from amorphous calcium carbonate (ACC) precipitated from element-doped reagent solution (Matsunuma et al., 2014; Saito et al., 2017). We incorporated U and Pb into calcite through heat-induced crystallization from U, Pb-doped ACC. The homogeneity of the U/Ca and Pb/Ca ratios in the synthetic calcite examined with LA-quadrupole (Q)-ICP-MS was generally better than 8% and 13%, respectively, in relative standard deviation (2SD,  $n = 10$ ). The  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio of the synthetic calcite measured with LA-multiple-collector (MC)-ICP-MS was homogeneous within  $\sim 1\%$  errors, whereas the  $^{238}\text{U}/^{206}\text{Pb}$  ratio was less homogeneous (3%–11% errors). The inhomogeneity in the U/Pb isotope ratio would be propagated into the analytical precision for unknown samples. In order to test the usability of the synthetic calcite, we dated WC-1 using the synthetic calcite for correction of elemental fractionation. We calculated the nominal  $^{238}\text{U}/^{206}\text{Pb}$  ratio in the synthetic calcite from its U and Pb concentrations measured by LA-Q-ICP-MS using Ca as an internal standard. We then obtained the fractionation factor to correct bias between the isotope ratios measured by LA-MC-ICP-MS and the nominal value. Using the fractionation factor, we could accurately date WC-1 with an  $\sim 3\%$  precision ( $246.6 \pm 7.3$  Ma). If the isotopic compositions of the synthetic calcite are certified by isotope-dilution technique, we could date natural carbonates with  $<10\%$  precisions using the synthetic reference calcite.

Keywords: Amorphous calcium carbonate, LA-ICP-MS, Reference material, U–Pb geochronology