

## Synthesis of U and Pb-doped calcite: a novel reference material for *in situ* U–Pb dating of carbonates

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Direct age determination of carbonate minerals provides valuable insight to paleoenvironmental change, tectonics, and sub-surface fluid-flow. The U–Pb method using 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. A natural calcite cement WC-1 (254.4 ± 6.4 Ma) [1] is suitable as a reference material to correct elemental fractionation with LA-ICP-MS. However, the resulting uncertainty on a sample date is limited by the heterogeneity of U and Pb distribution in the reference material. Our objective is to synthesize calcite with homogeneous U and Pb concentrations and isotope ratios to be used as novel reference materials. To achieve this, we incorporate incompatible U and Pb into calcite through heat-induced crystallization from amorphous calcium carbonate precipitated from U, Pb-doped reagent solution. LA-ICP-MS analyses of results so far revealed that the U/Ca and Pb/Ca ratios in the synthetic calcites were generally homogeneous with relative standard deviation (2SD,  $n = 10$ ) better than 4% and 7%, respectively. The Pb/Ca homogeneity of calcites doped with < 1 µg/g Pb was up to ~25%. The <sup>207</sup>Pb/<sup>206</sup>Pb ratio of the synthetic calcites was very homogeneous with <1% variation, whereas the <sup>238</sup>U/<sup>206</sup>Pb ratio was less homogeneous (2%–7% variation). To evaluate the suitability of the synthetic calcite as a reference material, we measured the age of WC-1 using the synthetic calcite for elemental fractionation correction; we could date WC-1 with a precision and accuracy of ~3% (246.6 ± 7.3 Ma). This method is a promising alternative in addition to characterising natural carbonate materials for elemental and isotopic composition.

[1] Roberts, Rasbury, Parrish, Smith, Horstwood & Condon (2017), *Geochemistry, Geophysics, Geosystems* 18, 2807–2814.