

Synthesis and isotopic characterization of high-pure ^{12}C nano-calcite

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In the present study, we report a simple and innovative synthesis route for high-pure ^{12}C nanosized calcite particles. Herein, $\text{Ca}(\text{OH})_2$ nanoparticles portlandite were directly carbonated with high-pure $^{12}\text{CO}_2$ (99.99% ICP-MS certified) gas using a static bed reactor under anisobaric conditions (initial $^{12}\text{CO}_2$ gas pressure = 20 bars and $T = 303\text{ K}$).

Calcite nature and particle size (including its morphology) were controlled by X-ray diffraction (XRD) and field emission gun scanning electron microscopy (FESEM), respectively. Its isotopic characterization by isotopic CO_2 Cavity Ring-Down Spectroscopy (CRDS from Picarro) analyzer has confirmed the very low negative delta of the ^{13}C (**Figure 1**), i.e. higher content in ^{12}C with respect to standard (measured against Vienna Pee Dee Belemnite *VPDB*).

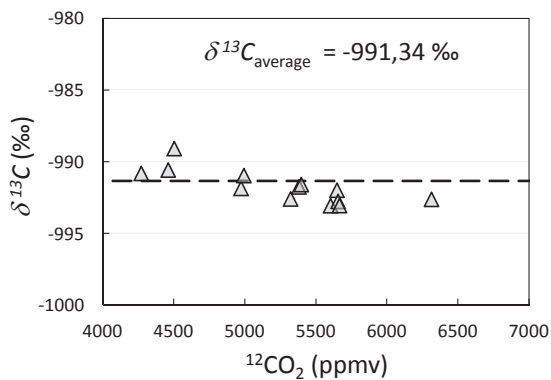


Figure 1: $\delta^{13}\text{C}$ value of $\text{Ca}^{12}\text{CO}_3$ as a function of $^{12}\text{CO}_2$ (in ppmv). The dashed line shows an average value of $\delta^{13}\text{C} = -991,34\text{ ‰}$.

To the best of our knowledge, this is the first time ever that such $\delta^{13}\text{C}$ measurement is reported for a synthetic material. Remarking that $\delta^{13}\text{C}$ are expressed in permil and are typically in the range from -100 to +100. This new high-pure ^{12}C nano-calcite opens new possibilities to investigate on the carbon ^{12}C - ^{13}C dynamic exchange at the calcite-fluid interfaces with relevance in natural and artificial systems.

Si isotope fractionation during silica precipitation in flow-through experiments

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Silicon isotopes are a promising proxy for (near-) surface processes and conditions. However, an unequivocal interpretation of isotope signatures in natural silica deposits is often hampered by the lack of quantitative constraints on isotopic fractionation for the environment of interest. To help alleviate these limitations, we performed precipitation experiments using flow-through reactors wherein silica precipitated from a saturated solution in the 10-60°C temperature range. Principal objective was to determine the sign and magnitude of silicon isotope fractionation during controlled precipitation of amorphous silica induced by a temperature drop.

A starting solution, brought to saturation in amorphous silica at 90°C, was forced to pass flow-through reactors containing seeds of amorphous silica powder. The reactors were placed in a water bath with a pre-set cooler temperature. Time-series results, obtained through monitoring the Si concentration in output solutions, were used to optimize the experimental conditions under which steady-state deposition could be achieved. This comprehensive set of test runs exposed strong effects from flow-rate, surface area of the seeding material and degree of supersaturation in the reactors.

Silicon isotope ratios ($^{30}\text{Si}/^{28}\text{Si}$ and $^{29}\text{Si}/^{28}\text{Si}$), measured in input and output solutions using a Thermo Neptune MC-ICPMS, showed a systematic time-dependent behaviour as well. Isotope shifts in initial run products, expressed as $\Delta^{30}\text{Si}_{\text{out-in}}$ ($\delta^{30}\text{Si}_{\text{output}} - \delta^{30}\text{Si}_{\text{input}}$), ranged between -2.0 and +0.1‰, mainly depending on temperature and surface area of the silica seeds. Long-term runs (up to 2 month) were required to approach a steady isotopic signal in the output solution, which is taken to reflect equilibrium. In these cases, the output results are consistent with preferential incorporation of the light isotope in the precipitating silica, in qualitative agreement with expected fractionation behaviour. Our experimental results obtained so far yielded a maximum $\Delta^{30}\text{Si}_{\text{out-in}}$ value of +1.4‰, which was found when the precipitation temperature was lowest. The magnitude of fractionation tended to increase with decreasing temperature.

Our experimental set-up mimics a submarine hydrothermal vent system where silica deposition is associated with a steep temperature gradient. The results corroborate the potential of $\delta^{30}\text{Si}$ signatures of (precursors of) cherts as a paleo-proxy for ambient conditions, but question their robustness as indicator of paleo-temperatures alone.