

Kinetics of carbon isotopic exchange with high purity ^{12}C nano-calcite

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We report a simple and innovative route for the synthesis of high-purity ^{12}C -enriched nanosized calcite particles (called: ^{12}C nano-calcite). The method involves the direct carbonation of $\text{Ca}(\text{OH})_2$ with high-purity ^{12}C CO_2 gas using a static bed reactor under anisobaric conditions (initial CO_2 pressure = 20 bar and $T = 30^\circ\text{C}$). X-ray diffraction (XRD) line broadening and Field Emission Gun Scanning Electron Microscopy (FESEM) indicate a particle size of 100-200 nm. Isotopic characterization by Cavity Ring Down Spectroscopy (CRDS) confirms a highly ^{12}C -enriched product ($\delta^{13}\text{C} = -992\text{‰}$ relative to VPDB). To the best of our knowledge this is the most ^{12}C enriched synthetic calcite ever reported and opens up new possibilities to investigate the early diagenesis of calcite, as well as $^{12}\text{C} \leftrightarrow ^{13}\text{C}$ exchange dynamics at the calcite-fluid interface.

Carbon exchange of the ^{12}C nano-calcite with atmospheric CO_2 ($\delta^{13}\text{C} = -8\text{‰}$) has been studied at 20°C and 50°C to determine the time for isotopic equilibration; based on current kinetic trajectories equilibration is predicted to occur in 9 years and 3 years, respectively. The rate determining process for calcite isotopic equilibration is thought to be the re-precipitation step, consistent with previous studies [1], but much slower due to an extremely low initial nucleation area [2]. The driving force for equilibration is likely the higher Gibbs free energy of the nano-calcite due to surface energy effects, providing an energy of $\sim 2 \text{ kJ mol}^{-1}$, and leading to supersaturated conditions relative to bulk calcite.

The assumption in paleobiological studies that calcite reflects aqueous isotopic compositions arising from biological activity may not be justified if the calcite initially precipitated re-equilibrates with atmospheric CO_2 . Such a scenario is more likely in the case of nano-sized calcite (high surface area) in contact with atmospheric equilibrated water, and while slow in a laboratory setting, would be extremely fast compared to geologic timescales.

[1] Mozeto *et al* (1984) *Geochimica et Cosmochimica Acta* **48**, 495-504 [2] Reddy & Nancollas (1971) *Journal of Colloid and Interface Science* **36**, 166-172