Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.29084

Monohydrocalcite ($CaCO_3$ .H_2O) to aragonite ($CaCO_3$) polymorph transformation: Kinetics and activation energy from Raman spectroscopy

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The ability to control polymorph phase is one of the ultimate challenges in crystallization, where a key goal is to produce specific high-purity phases on the requirement. Biomineralization processes are excellent examples, where organisms can select for specific polymorphs with perfect fidelity. In the present study, we report new insights on the aragonite nucleation from monohydrocalcite slurry as a function of temperature (from room T to 90°C) and as a function of initial ionic concentration at the same Mg/Ca molar ratio. Herein, competing monohydrocalcite and nesquehonite nucleation and aragonite nucleation from monohydrocalcite slurry were monitored in real-time by using Raman spectroscopy as previously reported for other minerals (1-3). On the other hand, monohydrocalcite was purified from monohydrocalcite and nesquehonite mixture by simple 2-3 successive washings using tap water. Here, nesquehonite is dissolved leading high-purity monohydrocalcite synthesis (more stable in tap water for this Ca-Mg system). As expected, the transformation kinetics from monohydrocalcite into aragonite is strongly dependent on the temperature. Herein, induction times and kinetic factors were determined from the fitting of an empirical sigmoidal model. Then kinetic factors were used to calculate the related activation energy by using Arrhenius equation. This promising study report then a simple method to synthesize massively high-purity monohydrocalcite; an emergent material to remove pollutants from water and as additive in concrete materials (CO_2 sequestration and improving mechanical properties). In addition, we demonstrated that aragonite can be also produced abiotically at room temperature, systematically observed and attributed exclusively to life of several sea shell animals.

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(3) G. Montes-Hernandez, F. Renard. Nucleation of Brushite and Hydroxyapatite from Amorphous Calcium Phosphate Phases Revealed by Dynamic in situ Raman Spectroscopy. The Journal of Physical Chemistry C 124 (2020) 15302-15311.