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In situ and time resolved quantification of the kinetics and mechanisms of CaCO3 nucleation and growth

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The crystal chemistry, occurrence and relevance of amorphous $CaCO_3$ and its crystalline polymorphs in inorganic and organic environments have been studied for decades and are nowadays relatively well known [1]. However, due to the fast kinetics of the reactions that take place in solution [2], there is virtually no quantitative data available about the kinetics and mechanisms of the nucleation, growth and transformation of these phases in aqueous solutions.

In this study we demonstrate that in situ and time resolved synchrotron-based Energy Dispersive X-Ray Diffraction combined with the corresponding solution chemistry and imaging can be successfully applied to evaluate quantitatively kinetic rates and mechanisms of the crystallization and transformation of $CaCO_3$ phases in solution. The precipitation of amorphous calcium carbonate (ACC) and its crystallization to vaterite and calcite was followed in closed thermostated reactors at temperatures between 7.5 and 40°C with the time-resolved data collected every 15 secs. The growth/decay of vaterite and calcite diffraction peaks was fitted using a Johnson-Mehl-Avrami-Kolmogorov model [3] to evaluate the kinetics and mechanisms of crystallization [4]. The results show that vaterite grows fast via a 3D growth process following a first order reaction and the subsequent transformation to calcite takes place slower, being controlled by the dissolution of the vaterite precursor. From the temperature dependent data apparent activation energies of nucleation and crystallization for both crystalline $CaCO_3$ polymorphs have been calculated. In addition, wet chemical data and imaging also confirm these findings. Finally, this approach was applied also to other carbonate systems (i.e., dolomite , Ca/Mg carbonates).

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