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On the development of solvent mediated transformations in the CaCO3-H2O system: The role of tetrahedral anions

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Under Earth's surface conditions CaCO3 occurs as different crystalline phases, both anhydrous (vaterite, aragonite, and calcite) and hydrated (monohydrocalcite and ikaite), and a number of amorphous phases with different water contents. These phases can form by both biotic and abiotic means and many of them play fundamental roles in biomineralization processes. Although calcite is the lowest energy polymorph, the metastable formation of other CaCO3 polymorphs is common in a wide range of environments. Metastable phases can be temporarily stabilized but, in the long term, transform into calcite through an energetically downhill sequence of transformations, along which some polymorphs can be passed by [1].

It is well known that the presence of certain ions in the crystallization medium promotes the formation of CaCO3 metastable phases and inhibit their transformation into calcite. These effects have usually been attributed to kinetic factors. However, foreign ions can incorporate into the structure of the different polymorphs, thereby changing their energetic properties. Because the free energy of CaCO3 polymorphs is relatively close, any modification of their energetic properties could determine stability crossovers [2] that would affect the polymorph selection at nucleation and the development of transformations between polymorphs. Therefore, when foreign ions are present in the crystallization medium, both kinetics and thermodynamic factors have to be considered to understand the formation of CaCO3.

Recent studies have shown that tetrahedral anions like phosphate, sulphate or chromate are among the most influential in the crystallization of CaCO3, contributing to the stabilization of amorphous calcium carbonate in biogenic systems [3] or vaterite [4] in inorganic systems. We present here experimental results that illustrate the influence of some tetrahedral anions on the crystallization of CaCO3 from aqueous solutions. These results include examples of both unexpected polymorph formation and transformation pathways that carry the pass by of polymorphs or even inverted trends. These observations are interpreted considering the effect that the isomorphic substitution of a small amount of carbonate ions by tetrahedral ions might have on the relative energies of different CaCO3 phases.

References:

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