The effect of rare earth elements in the crystallisation of calcium carbonate from solution at ambient temperature

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The rare earth elements (REE) are a group of 17 elements that are of great importance in today's world due to their wide usage in the hi-tech industry and in clean energy applications [1,2]. Despite their importance, their separation from their ore is challenging and costly and their demand is rapidly and constantly increasing. The current techniques for separating rare earth elements are inefficient due to the large amounts of toxic and radioactive waste they produce. Therefore there is great interest to develop advanced clean and efficient separation methods. Common carbonate minerals like calcite or aragonite may be helpful for this purpose. Experimental work has demonstrated that REE adsorb on the surface of Ca-Mg-Sr carbonates and are strongly partitioned into these minerals, substituting for Ca^{2+} [3-5], while poorly ordered precursors (amorphous Ca-Mg carbonate) and metastable phases (ikaite, monohydrocalcite and vaterite) are known to uptake foreign ions from solution [6,7]. However, there is little information regarding the nucleation and growth of $CaCO_3$ polymorphs in the presence of REEs.

This study aims to understand the effects of REE during the crystallisation of $CaCO_3$ polymorphs. For this purpose, several experiments at low starting saturation conditions (directly from solution) were carried out at ambient temperature, consisting of mixing 4 mM solutions of Na_2CO_3 and $CaCl_2$ doped with small concentrations (0.05 – 0.3 mM) of different REE (La, Nd, Dy), alone or in combination. Reactions were followed with UV-Vis spectrophotometry at time intervals of 1 sec. The nature of crystallising solids and their quantification was determined with powder X-ray diffraction (XRD) and the growth morphology of the solids was characterised with scanning electron microscopy with energy dispersive microscopy (SEM-EDS). Our results show that the interaction of REE during the crystallisation of $CaCO_3$ was translated into a slowdown of the crystallisation kinetics compared to the pure $CaCO_3$ system. The delay in the induction time and rate of crystallisation were proportional to the number of REEs present in solution, their atomic number and concentration. The growth of vaterite and calcite polymorphs in the presence of REE ions resulted into an increase of crystal imperfections and change of growth mechanism with increasing concentration and atomic number of REE.

References

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