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Pre-nucleation Clusters

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Pre-nucleation clusters (1) are agglomerates of ions that form prior to nucleation and precipitation of crystals. Today, the clusters have been detected for a number of minerals, and they appear to play a central role in the processes that underlie nucleation. This contribution is focussed on prenucleation clusters of calcium carbonate, which is the most abundant biomineral, but also of great geological and industrial importance.

The detection of pre-nucleation clusters of calcium carbonate by means of ion-potential measurements, pH titration as well as Analytical Ultracentrifugation is discussed. The experiments suggest that the clusters are approximately 2 nm in size, relating to ca. 70 ions in single clusters, and that nucleation proceeds via the aggregation of the clusters. The clusters contain a significant amount of water as evaluated via their density from Analytical Ultracentrifugation experiments. Evaluation of the titration data, based on a multiple-binding equilibrium of ions, evidences that the clusters are thermodynamically stable. Isothermal titration calorimetry shows that the formation of clusters is an endothermic process and driven by entropy – likely by the release of ion hydration water. The cluster stability depends on the pH value, more stable clusters form at lower pH values. At the same time, at different pH values, two different intermediates of amorphous calcium carbonate (ACC) are initially precipitated. This strongly suggests that different structures, which relate to crystalline polymorphs, are already present in pre-nucleation clusters, and are transferred to the amorphous intermediates during nucleation. Indeed, analyses of the two ACCs by means of EXAFS, Infrared and NMR Spectroscopy reveal different features in the spectra of the ACCs, which relate to the crystalline polymorphs of calcite and vaterite, respectively (2). Based on these results, the notion of proto-crystalline structures in ACC, and their impact on the polymorphism of the precipitated crystals, is discussed.

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(2) Gebauer, D.; Gunawidjaja, P. N.; Ko, J. Y. P.; Bacsik, Z.; Aziz, B.; Liu, L. J.; Hu, Y. F.; Bergström, L.; Tai, C. W.; Sham, T. K.; Edén, M.; Hedin, N. Angew. Chem. Int. Ed. 2010, 49, 8889-8891.