The role of hydrous components in properties and behavior of amorphous calcium carbonate

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Hydrous components, including structural H_2O and OH, are present in biogenic and synthetic amorphous calcium carbonate (ACC) in variable amounts depending on the organism and conditions of formation. Hydrous components have become a focus of particular interest inasmuch as transformation of hydrated ACC to crystalline calcium carbonate may be linked to loss of H_2O. Thermal analysis combined with NMR spectroscopy shows that multiple hydrous components are present in many ACC samples and their type and proportion influence stability and transformation of ACC to crystalline calcium carbonate. These hydrous components can be differentiated on the basis of NMR data, and include translationally rigid structural H_2O, restrictedly mobile H_2O, fluid-like H_2O, and OH. Comparison of biogenic and synthetic ACC reveals that some hydrous components present in hydrated synthetic samples are absent in hydrated biogenic samples. ACC samples that differ in their hydrous components also exhibit differences in stability and transformation behavior, as well as differences in crystallization temperature with heating.

Observed differences in hydrous component populations among ACC samples are linked to synthesis method or environment of formation, demonstrating that pathway of formation influences ACC properties and transformation behavior.

Different populations of hydrous components in ACC do not result in significant structural differences as revealed by total X-ray scattering and pair distribution function (PDF) analysis. When compared to hydrated synthetic samples, only small differences are observed in X-ray PDFs of ACC partially dehydrated via thermal treatment. Whereas lack of sensitivity of X-rays to H atoms is partly responsible for this, it is also likely that much of the underlying coordination of calcium and carbonate is only minimally affected by differences in the amount and type of H_2O present. The structural roles of different types of hydrous components, along with the presence of additives, appear to be the main factors that control properties and behavior of ACC.