

PHASE TRANSFORMATION IN CaCO₃ POLYMORPHS: A SPECTROSCOPIC, MICROSCOPIC AND DIFFRACTION STUDY

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Demonstrating the geochemical aspects of the long term safety of a nuclear waste repository can significantly be improved by a molecular level understanding of the actinides behavior in the geosphere. In particular the interaction of radionuclides with minerals (adsorption, structural incorporation) strongly affects their mobility and retardation. This study presents recent results on the phase transformation from vaterite to calcite. To achieve a most complete picture of this important geochemical process a multi-method approach was chosen: the transformation was observed externally by powder X-ray diffraction and scanning electron microscopy. These observations are combined with site-selective time-resolved laser fluorescence spectroscopy (TRLFS), with Eu³⁺ and Cm³⁺ as atomic probes, giving an internal view of the structure. The transition from vaterite to the thermodynamically stable CaCO₃ polymorph calcite lasts several days. It could be shown that the transformation is taking place in three steps: initial precipitation of low crystalline vaterite followed by transformation into the crystalline phase. Upon suspending the vaterite in CaCO₃ solution the phase transformation starts and is completed within 72h. No transition is observed in vaterite kept in the vacuum, demonstrating that the transition follows a dissolution/precipitation mechanism. Comparison with Eu³⁺-doped calcite directly synthesized under near-equilibrium conditions shows that identical solid solutions form, independent of the reaction path. Moreover the trivalent guest cations are fully transferred to the newly formed phase. This is strong evidence for a thermodynamical driving force for the solid solution formation in these systems.