

# Chemomechanical Influences During Replacement of Limestones by Siderite

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A fundamental and predictive understanding of mineral-fluid interactions is important for a wide range of energy topics including carbon sequestration, nuclear waste management and legacy contamination clean up. The properties of aqueous solution are altered by confinement, which can be present within natural geomaterials, e.g., in grain boundaries and nanopores. Mineral replacement reactions have been reported to proceed via grain boundaries possibly due to higher diffusion rates than in solids. In addition to confinement effects, chemomechanical effects such as crystallization pressure induced fracturing can also alter mineral-fluid interactions.

To test the effects of porosity and grain boundaries on replacement in single component and impurity-containing systems we experimentally investigated the model system of limestone replacement by siderite by batch reactor experiments at 200°C from 2 to 120 days with FeCl<sub>2</sub>. Variation in initial microstructure and solid impurities were used to identify reaction controls. Changes in porosity were spatially resolved analyzed using inverse scattering techniques ((ultra) small angle neutron/X-ray scattering), and these were combined with imaging by scanning (SEM) and transmission electron microscopy (TEM). In high-porosity limestones replacement is rapid (complete replacement within 2 days), and transport controlled, whereas in low-porosity limestones elevated porosity throughout the whole rock volume was observed that was independent of the reaction rim. Image analysis showed widening of selected grain boundaries with increasing reaction time. This led to increased grain boundary width distributions that were observed as higher porosity by scattering methods. SEM imaging showed that nucleation of siderite crystals either at dolomite impurities within the limestone or other defects lead to exertion of crystallization pressure, widening grain boundaries, which led to formation of preferential transport pathways that limited replacement of solid impurity-containing limestone rocks. This highlights how chemomechanical effects can alter reaction pathways.