

The Role of Grain Boundaries During the Experimental Dolomitization of Limestones

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Previous studies indicated confining effects on water include changes in density and hence diffusivities in comparison to bulk water [1,2]. Different areas within rocks can be considered confined, e.g. nanopores and grain boundaries. Previous studies indicated the importance of grain boundaries for mineral replacement reactions [3]. It remained unclear, how the changed properties of confined water in grain boundaries affect mineral dissolution and (re-) precipitation rates.

To investigate this question, we studied the model system of limestone replacement by dolomite. Microstructure of the starting limestone was systematically varied from high-porosity to low-porosity. In batch reactor experiments, limestones were contacted with MgCl₂ solution at 200 C for 32 to 317 days. By combining chemical imaging (scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), electron probe microanalyses (EPMA) and transmission electron microscopy (TEM)) with (ultra) small angle scattering techniques (X-rays and neutrons), we assessed both chemical and microstructural changes over time during the replacement reaction.

Due to the higher reactive surface area in high porosity limestone, higher starting porosity increased the reaction speed. In low porosity limestone, we identified grain boundaries as advantageous pathways for replacement reactions. Based on microstructural analyses via small angle scattering in combination with grain boundary width analyses via TEM, we were able to constrain grain boundary diffusion rates to be between bulk water and bulk solid diffusion rates.

References:

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[2] Rother G., Stack A. G., Gautam S., Liu T., Cole D. R. and Busch A. (2020) Water Uptake by Silica Nanopores: Impacts of Surface Hydrophilicity and Pore Size. *J. Phys. Chem. C* **124**, 15188–15194.

[3] Etschmann B., Brugger J., Pearce M. A., Ta C., Brautigan D., Jung M. and Pring A. (2014) Grain boundaries as microreactors during reactive fluid flow: experimental