

## **Effect of Microstructure and Chemical Reactivity of the Replacement of Limestone by Fluorite**

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Fluid flow properties in geological formations are defined by the rock microstructure and evolution of pore space. When fluids (even pore fluids) react with rocks, the mineral phases of which the rock consists can be replaced by another phase. The controls of the initial rock microstructure on such replacement reactions is not fully understood.

In our systematic study, we varied microstructure and chemical reactivity of our initial rock using the model system of calcite-fluorite replacement. In closed reactor experiments, three different limestone were reacted with NH<sub>4</sub>F solution at 120 °C for different time scales. By combining (ultra) small angle scattering techniques (X-rays and neutrons) with chemical imaging (time-of-flight secondary ion mass spectrometry, ToF-SIMS and scanning electron microscopy with energy dispersive X-ray spectroscopy, SEM-EDX), we were able to access the multi-scale porosity development with time.

What we find is that the chemical reactivity of the original phase in the replacement system controls the replacement reaction speed and mechanism stronger than the initial microstructure. The initial microstructure changes the reaction speed, extent and the regime of porosity that is affected. We found that for low porosity limestone, newly created porosity is mainly in the nanopore regime, whereas for high porosity limestone, newly created pores are macropores. When reducing the chemical reactivity of the system, replacement speed significantly drops as well as porosity generation decreases. Our findings highlight the importance of both the chemical reactivity and initial microstructure for replacement mechanisms.