

## The contribution of nanoscale pores to anomalous trace element release during dolomite dissolution

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Carbonate rocks are prime targets for geologic CO<sub>2</sub> storage as the global energy economy transitions away from fossil fuels. To elucidate the processes occurring during CO<sub>2</sub> injection into dolomite reservoirs, we previously presented a series of flow-through experiments examining the dissolution of dolomite cores by CO<sub>2</sub>-rich brines<sup>[1]</sup>. In all experiments, the release of Ba, Mn, and Sr, present in trace concentrations within the dolomite, far exceeded that expected from stoichiometric dolomite dissolution. However, porosity changes, as measured by X-ray tomography (XRCT, 8 μm resolution) agreed with the volumetric removal of dolomite calculated from effluent Ca and Mg concentrations.

Based on the anomalous rates of trace element release, we hypothesized that nm- to μm-scale pores allowed the reactant brines to penetrate into the dolomite and selectively remove the minor, less compatible elements without dissolving significant amounts of the dolomite itself. To test this hypothesis, we performed a series of Small and Ultra-Small Angle Neutron Scattering ((U)SANS) measurements on pre- and post-experimental cores. These measurements demonstrate that approximately half of the total pore volume (i.e., ~1/2 of the total ~15-17% porosity) in the dolomite cores occurs at pore sizes <10 μm, and is thus invisible at the scale of XRCT measurements.

To examine the impact of these nanoscale pores on dolomite reactivity, we ran a series of 3D, micro-continuum reactive transport simulations by directly discretizing the 3D XRCT volumes in PFLOTRAN. The simulated domains contained ~17.7 million elements, with the nanoscale porosity being assigned to the solid volume fraction. These simulations demonstrate that the anomalous rates of trace element release are only possible if their solubility is limited by their end-member mineral (e.g., strontianite for Sr), rather than by bulk dolomite solubility. Together, these measurements and simulations demonstrate the need for new conceptual models that include the contribution of nanoscale porosity to reactive transport of elements in carbonate rocks.

<sup>[1]</sup>Luhmann et al. (2014) *Chem. Geol.* 380: 145-160