Contributions of visible and invisible pores to reactive transport in dolomite


Supplementary Information

The Supplementary Information includes:

- Graphical Abstract Caption
- Supplementary Methods
- Figures S-1 and S-2
- Tables S-1 to S-3
- Supplementary Information References

Graphical Abstract Caption

Visualisation of porosity increases during CO₂-driven dissolution experiments at injection rates of 0.1 (left) and 0.01 (right) mL/min. Pores plotted in yellow existed within the pre-experiment sample, while the blue volume represents porosity created as a result of experimental alteration.
Supplementary Methods

Core Characterisation

X-ray Computed Tomography

XRCT imagery was originally presented by Luhmann et al. (2014), but was re-processed and re-analysed here to permit quantitative analysis and visualisation of porosity creation during CO₂-driven dissolution of dolomite. All rock cores were scanned at similar energy and current conditions and reconstructed at a voxel resolution of 8 μm, which is a result of the relatively large size of the rock cores. Still, the full resolution of the reconstructed volume of each core has a file size ~10 GB, making it difficult to perform volume subtraction between pre- and post-experiment 3D images of cores. For this reason, we rescaled the resolution to 15 μm prior to analysing them using Avizo Fire 9.0 and/or PerGeos. Pre- and post-experiment 3D volumes were first registered using a rigid transformation which is restricted to translation and rotation in three directions. Once aligned, the 3D volumes were segmented to select the macro-scale pore space using interactive thresholding which produced a binary volume; we then subtracted the pre-experimental volume from the post-experiment volume. The resulting binary volume contains the new pore space that developed during the experiments (see Graphical Abstract).

To permit fitting and analysis of a single, combined XRCT and (U)SANS data set representing porosity over pore sizes ranging from ~1 nm to ~1 mm, we converted the real space XRCT data into Fourier space. This conversion was performed using radial autocorrelation functions calculated from the processed (binarised) XRCT data sets using the PerGeos software package. Since, for a two-phase system (e.g., rocks and pores in the present study), the neutron scattering intensity (i.e., that which is measured through (U)SANS analyses) is proportional to the Fourier transform of the geometric correlation function (Debye et al., 1957), this two-point autocorrelation function calculated from the XRCT imagery can be directly translated to absolute neutron scattering intensities. Equations and procedures for performing these calculations were previously outlined by Radlinski et al. (2004b), Anovitz et al. (2013), and Gu et al. (2020). Matlab™ scripts previously developed by Gu et al. (2020), and generously shared with us, were used in the present study. A unique aspect of our work in relation to the previously published combined imaging-(U)SANS studies is that we used 3D XRCT imagery, instead of the two-dimensional scanning electron microscopy imaging typically used in other analyses in the literature. Our approach has two distinct advantages over those previously published data sets: 1) our calculated correlation functions are generally significantly smoother because of the significantly larger sample size; and 2) our significantly larger sample volume permits more statistically robust analysis of the analysed rock samples. A comparison of the calculated data for all cores with available data is presented in Figure S-1.

The uncertainty on XRCT data acquisition and processing is difficult to determine. In one particularly well-constrained attempt to quantify this uncertainty, Porter and Wildenschild (2010) calculated absolute errors of <1.5% on porosity, relative to “spherical cap” analytical estimates of porosity generated through several XRCT processing schemes performed on well-constrained data sets. The observation that the volumes of core-scale porosity changes, as measured by XRCT, agree well with the volumetric removal of dolomite calculated from effluent Ca and Mg concentrations (Luhmann et al., 2014) reinforces the relatively small uncertainty on these XRCT analyses.

Neutron Scattering

(UC)SANS measurements were performed at the National Institute of Standards and Technology Center for Neutron Research (NCNR) reactor facility in Gaithersburg, MD, USA and the ISIS neutron and muon source in the United Kingdom. The (U)SANS measurements were performed on both pristine and post-experiment samples, which were prepared as doubly polished, 150 μm thick sections superglued to unfrosted quartz glass slides by Burnham Petrographics, LLC in Rathdrum, ID, USA. We chose two end-member experimental rock cores representative of flow rates of 0.01 and 0.1 mL/min (Expts. 3 and 8, respectively, from Luhmann et al. (2014)) for the post-experiment analysis. The initial round of measurements on the post-experiment samples, which were performed at NCNR, were focused on the upstream end of the post-experiment core samples where XRCT measurements demonstrated the majority of porosity formation occurred. Subsequently, SANS measurements were performed at ISIS on the downstream ends of the core samples. These subsequent ISIS SANS measurements demonstrate that, at least over the pore size interval interrogated with SANS measurements, the upstream and downstream sections of the post-experiment cores show no significant variations in scattering over the (U)SANS range.
NCNR (U)SANS measurements

Cadmium apertures were used to define the diameter of the incident beam for all NCNR (U)SANS measurements at 3/8 inch and 1/2 inch for the experimental and pristine samples, respectively. NCNR SANS measurements were performed using the NG3 (now known as NGB30) instrument (Glinka et al., 1998). Scattering intensities were measured at sample-to-detector distances of 1.33, 4, and 13.17 m using a neutron wavelength ($\lambda$) = 6 Å. Measurements were repeated at 13.17 m using $\lambda$ = 8.4 Å and MgF$_2$ lenses in order to extend the SANS measurements as far up into the USANS region as possible. USANS measurements were performed on the BT5 instrument (Barker et al., 2005) in slit-height geometry with $\lambda$ = 2.38 Å.

All measurements were corrected for scattering from the quartz glass slide upon which they were mounted. Two-dimensional SANS measurements at each sample-to-detector distance were corrected for sample transmission and radially averaged over binned ranges to obtain values of scattering intensity at discrete values of momentum transfer, $Q$. USANS measurements were corrected for empty-beam and background scattering, normalized to absolute intensities, and desmeared using the NCNR Igor Pro© macros (Kline, 2006).

Overall, the NCNR SANS and USANS measurements covered momentum transfer ranges from ~5 $\times$ 10$^{-5}$ to ~0.001 and ~0.001 to ~0.01 Å$^{-1}$, respectively, which allows for combined analysis of the full data set. Once combined data sets were obtained, incoherent background scattering, caused mostly by hydrogen within the sample, was removed from the combined curves using the PRINSAS software package (Hinde, 2004).

ISIS SANS measurements

The downstream segments of cores from the experimental samples prepared for (U)SANS analysis were analysed at ISIS neutron and muon source to gain insight into the evolution of pores in these portions of the core, which underwent significantly less reaction than their upstream counterparts (Luhmann et al., 2014). The ISIS SANS2d instrument functions in time of flight (TOF) mode, meaning that a white beam of neutrons (between 1.75 and 12.5 Å in our particular configuration) reach the sample every ISIS pulse (10 Hz). During SANS2d data acquisition, scattering is measured over a much wider momentum transfer ($Q$ in Figs. S-1 and S-2) simultaneously, since the neutron source is not monochromatic but rather a wavelength range, permitting the use of only one sample to detector distance, 12 m in our case. Samples were masked with a 8 mm circular aperture, which translates to a measured volume of 30.2 mm$^3$. Sample transmission was measured as a function of wavelength in order to correct the measured intensities. A pristine sample was measured at both NCNR and ISIS and yielded nearly identical results, thus confirming the inter-comparison of data acquired at both neutron sources.

Figure S-1 Comparison of pre- and post-experiment XRCT data (transformed into neutron intensity space) for 8 of the 9 experiments presented by Luhmann et al. (2014) (one of the cores at the 0.01 mL/min experiments does not have a pre-experimental scan). Each individual plot is labeled with the overall porosity change ($\Delta\phi$) and the flow rate for the given experiment.
**Data combination**

Processed (U)SANS data sets were combined with XRCT data using Matlab™ and are presented in Figure S-2. In all cases, significant overlap was achieved between individual XRCT, USANS, and SANS data sets. The highest and lowest Q data points, which tended to deviate slightly from the power-law behaviour of the overall data set (typically because of less robust data quality at the limits of each instrument’s resolution), were trimmed to enable better visualisation and fitting. Since the sample preparation requirements for (U)SANS analysis (i.e., polished thick section) is necessarily incompatible with the subsequent usage of the identical sample for hydrothermal flow-through experiments, our analysis of the evolution of pore size distributions as a result of CO$_2$-driven dissolution was performed by comparing the post-experiment analyses with a combined “pre-experiment” dataset consisting of the pre-experiment XRCT imaged volume (converted to $I(Q)$ vs $Q$ as discussed above) and (U)SANS analyses of unaltered rocks from the same hand sample. The (U)SANS measurements performed on the two pristine samples are nearly identical, suggesting that they are representative of the entire hand sample from which the individual experimental cores were drilled.

**Data Analysis with PRINSAS**

The combined XRCT-USANS-SANS data sets for the two post-experiment samples and the two pristine samples were processed using the PRINSAS software package (Hinde, 2004). Incoherent scattering was removed using the PRINSAS fitting and removal function, and the combined data set was analysed by modelling the rock samples as a polydisperse distribution of pores and solid (Clarkson et al., 2012; Jin et al., 2011; Radlinski et al., 2004a; Tutolo et al., 2016). The scattering length density for dolomite was calculated using the NCNR SLD calculator (https://www.ncnr.nist.gov/resources/activation/) to be $5.388 \times 10^{-6}$ Å$^{-2}$. The uncertainty on pore size distribution calculations is of course dependent upon the uncertainties of the SANS, USANS, and XRCT data sets as well as the PRINSAS fitting process. Radlinski et al. (2004b) suggest that the relative error for the absolute value of pore number densities (i.e., the fraction of pores of a certain size) is independent of pore size, and is generally better than ±50 %.

**Micro-continuum simulations with PFLOTRAN**

The concept of using micro-continuum simulations to investigate pore-scale geochemical processes was discussed in detail by Steefel et al. (2015) using a series of simulations performed on two-dimensional modelled domain directly discretized from imaging data sets. In the present study, due to the availability of 3D imaging data and the computational efficiency of the PFLOTRAN software package, we were able to expand this approach to a three-dimensional (3D) modelled domain. Nonetheless, because of the significant computational burden associated with the 3D micro-continuum simulations, we decided to focus our modelling efforts on only one of the two post-experiment cores analysed by (U)SANS. We chose the one representative of 0.01 mL/min flow rate to minimize the advective transport, thereby permitting the most complete observations of the relative contribution of large and small pores through...
diffusion during our experiments. We chose to perform the simulations using a post-experiment rather than pre-experiment geometry because the post-experiment core is representative of the final stages of the experiment where a steady-state flux of both major and trace elements had been obtained and the rate of porosity change was lower than in previous stages of the experiment.

### Table S-1 Porosity changes during dolomite dissolution experiments.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Initial porosity (%)</th>
<th>Final porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>XRCT</td>
<td>Saturation</td>
</tr>
<tr>
<td>1</td>
<td>7.6</td>
<td>13.30</td>
</tr>
<tr>
<td>2</td>
<td>7.9</td>
<td>15.13</td>
</tr>
<tr>
<td>3</td>
<td>6.3</td>
<td>13.94</td>
</tr>
<tr>
<td>4</td>
<td>6.7</td>
<td>14.05</td>
</tr>
<tr>
<td>5</td>
<td>7.7</td>
<td>13.75</td>
</tr>
<tr>
<td>6</td>
<td>6.8</td>
<td>13.55</td>
</tr>
<tr>
<td>7</td>
<td>6.2</td>
<td>14.45</td>
</tr>
<tr>
<td>8</td>
<td>6.2</td>
<td>12.78</td>
</tr>
<tr>
<td>9</td>
<td>6.9</td>
<td>12.72</td>
</tr>
</tbody>
</table>

Note:

- †Lahmann et al. (2014)
- Calculated from the pre- (for XRCT measurement) or post- (for saturation measurement) experiment porosity using measured concentrations and dissolution of ideal dolomite (2.9 g/cm³)
- †Calculated from a correlation between porosity and dry mass/volume measured on all other cores.

### Table S-2 Parameters used in PFLOTRAN Simulations

**Physical properties**

- "Solid" Porosity: 0.121
- Total core porosity: 0.153
- Permeability: $1.32 \times 10^{-15}$ m²
- Outlet Pressure: 15006835.2 Pascals
- Inlet Pressure: 15000000 Pascals
- Temperature: 100 °C

**Geochemical Properties**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Volume fraction</th>
<th>Surface area (m²/m³ element)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>0.999</td>
<td>3.77</td>
</tr>
<tr>
<td>Rhodochrosite</td>
<td>$1.8 \times 10^{-4}$</td>
<td>$6.79 \times 10^{-4}$</td>
</tr>
<tr>
<td>Siderite</td>
<td>$8.4 \times 10^{-4}$</td>
<td>$3.17 \times 10^{-3}$</td>
</tr>
<tr>
<td>Strontianite</td>
<td>$3.0 \times 10^{-5}$</td>
<td>$1.13 \times 10^{-4}$</td>
</tr>
<tr>
<td>Witherite</td>
<td>$1.0 \times 10^{-5}$</td>
<td>$3.77 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Physical Parameterisation

The micro-continuum simulation was performed on the post-experiment core from Experiment 8 in Luhmann et al. (2014). Physical properties used in the simulation are presented in Table S-2. This core had a final post-experiment permeability of 1.32×10⁻¹⁵ m², and a final porosity of 0.1528 (Table S-1). Due to the hard limit on the number of degrees of freedom permitted in PFLOTTRAN simulations (2⁵₂), we needed to sub-sample the 8 μm resolution XRCT data set to 60 μm resolution, yielding a 210 × 208 × 405 element simulated volume. Element porosity was set as 1 in XRCT-observable pores, which accounted for 0.032 of the total porosity, and 0.121 in “solid” elements. Summed over the entire simulated core, this yielded the measured post-experiment porosity (0.153, Table S-2). It is important to note that the 60 μm × 60 μm × 60 μm element size requires that all elements other than those which are entirely void space contain a combination of both “visible” and “invisible” pores. Thus, the concentrations and reaction rates plotted in Figure 3 represent a continuum-scale average of the pore-scale concentrations. Elements outside of the cylindrical core but still within this rectangular prism were set as inactive. The downstream face of the simulated core was set to a constant pressure boundary condition of 15 MPa, and the upstream face was set to a constant pressure of 15006835.2 Pascals that permitted an exact replication of the experimental interaction. Therefore during the experimental interaction. Thus, the concentrations and reaction rates plotted in Figure 3 represent a continuum-scale average of the pore-scale concentrations. Elements outside of the cylindrical core but still within this rectangular prism were set as inactive. The downstream face of the simulated core was set to a constant pressure boundary condition of 15 MPa, and the upstream face was set to a constant pressure of 15006835.2 Pascals that permitted an exact replication of the flow rate (0.01 mL/min), given the PFLOTTRAN-calculated properties of water and the designated permeability. Temperature of the simulated domain was held constant at 100 °C, consistent with the experimental design. Because our goal was to examine steady-state geochemical behaviour during the simulations, porosity and permeability were held constant throughout the simulation.

Chemical Parameterisation

Although trace cations are randomly distributed throughout the dolomite crystals, the relative recoveries of the individual elements clearly indicate that the trace constituents of the dolomite do not behave conservatively during the experimental interaction. Thus, a dolomite solid-solution including these trace elements could not suffice to match the observed results, since only stoichiometric dissolution and precipitation reactions can potentially be modelled using that approach. Thus, we modelled the trace Ba, Mn, and Sr components as the individual phases witherite (BaCO₃), rhodochrosite (MnCO₃), siderite (FeCO₃), and strontianite (SrCO₃). The equilibrium constants for these minerals, as well as relevant aqueous complexes for the elements Ba, Ca, C, Cl, Fe, Mg, Na, Sr were calculated at 100 °C and steam saturation pressure using the DBCreate software package (Kong et al., 2013) and copied manually into a modified version of the PFLOTTRAN ‘hanford.dat’ database. The solubility constant for dolomite at 100 °C measured by Bénézeth et al. (2013), which was shown by Luhmann et al. (2014) to produce more accurate predictions of the solubility of dolomite for the experiments studied here, was incorporated directly into the database. Because the redox state of the reacting fluid was neither controlled nor monitored, we do not discuss the reactivity of the siderite (FeCO₃) component of the dolomite. Fe is a trace component in all experimental fluid samples and probably behaves quasi-conservatively (i.e., is predominantly precipitated as secondary Fe-oxhydroxides upon release from the dolomite structure), and this decision should therefore have a negligible impact on the calculation of the evolution of other solution components. Identical to Luhmann et al. (2014), the rate constants for dolomite and all of its trace components were set to 1×10⁻⁴ mol/m²/s, which is the rate measured by Pokrovsky et al. (2009) at 100 °C and their maximum pCO₂ (50 bar). Their results show negligible dependence of dolomite dissolution rate under these conditions at pCO₂ ≥35 bar, suggesting that this rate constant is likely applicable to our experimental conditions. Reactive surface area for dolomite was set to that calculated using equations given by Luhmann et al. (2014), i.e., a combination of the simplified Transition State Theory rate law, the Pokrovsky et al. (2009) rate constant, the measured rate of Ca and Mg release, and the saturation state calculated on the final experimental sample. This surface area (27.3 m²/m³ of dolomite) was re-evaluated in the present study to reflect our new porosity measurements and normalized to element volume (as is required by PFLOTTRAN) by multiplying by the ratio of element porosity (0.1213) to solid volume (0.8787), yielding a normalized surface area of 3.77 m²/dolomite / m³ element. Reactive surface areas of trace components were determined by calculating a “total” surface area by considering the relative volume fractions of dolomite (0.99893) compared to trace components, and then multiplying the “total” reactive surface area to derive the reactive surface area for each trace component. The net effect of the “total” surface area calculation was negligible given the near purity of the dolomite. The extended Deby-Hückel “B-dot” model (Helgeson, 1969) was used in all PFLOTTRAN calculations to approximate activity coefficients of the charged species. Because the dominant charged species in the experimental solutions were Na⁺ and Cl⁻, the “B-dot” model should provide reasonably accurate approximation of the activity coefficients in our solutions (Tutolo et al., 2015). A summary of chemical parameters used in the simulation is included in Table S-2, where the inlet fluid (Table S-3) used in the simulation is a duplicate of the measurement by Luhmann et al. (2014).
Computational Setup

Simulations were run in parallel, on 256 cores split over 64 nodes on the Advanced Research Computing lattice cluster at the University of Calgary. Each node on lattice has 8 CPU cores, but the memory demands of the presented simulation were so significant (due to the large number of elements and the large input data sets defining the properties of each element individually) that only 4 cores per node could be used to remain under the 12 GB/node threshold on lattice. Successive files output at 0.1 h intervals for the first hour and then once every hour for the remaining four hours of simulated time demonstrate that the simulation had reached steady state over this timespan, thereby permitting comparison between the simulated and experimental results.

Pore Volume and Surface Area Calculations

As noted in Figs. 1 and 2 and the accompanying discussion, concentrations of the trace elements Ba, Mn, and Sr measured in outlet fluids from the presented experiments suggest that the pore fluids extracted up to ~60% of the Ba, ~30% of the Mn, and ~5% of the Sr from the experimental cores, while removing only ~3% of the Ca (Luhmann et al., 2014). At its most basic level, this observation implies that the experimental fluids interacted with more of the rock than can be inferred from changes in dolomite volume (and hence porosity) alone. However, the volume of dolomite which must be accessed by the fluids filling a single pore in order to achieve the measured recoveries cannot be directly visualised from the recoveries alone. Thus, we performed the following calculations in order to quantify the volume of interaction required to produce experimentally measured element recoveries for pore radii ranging from 1 nm to 10 μm.

Table S-3: Inlet chemistry used in reactive transport simulation

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (molal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{++}$</td>
<td>$0.17 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ca$^{++}$</td>
<td>$0.51 \times 10^{-3}$</td>
</tr>
<tr>
<td>Sr$^{++}$</td>
<td>$1.0 \times 10^{-9}$</td>
</tr>
<tr>
<td>H$^+$</td>
<td>4 (charge balance)</td>
</tr>
<tr>
<td>CO$_2$(aq)</td>
<td>0.6</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1</td>
</tr>
<tr>
<td>Ba$^{++}$</td>
<td>$0.06 \times 10^{-6}$</td>
</tr>
<tr>
<td>Fe$^{++}$</td>
<td>$1 \times 10^{-9}$</td>
</tr>
<tr>
<td>Mn$^{++}$</td>
<td>$1 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

Assuming that the hypothetical pore volume increase that would be required to yield the measured Ba, Mn, Sr, and Ca recoveries are 60 %, 30 %, 5 %, and 3 % of $V_{solid}$ respectively, and dividing this value by $n_p$ yields $V_{inc,hyp}$, the hypothetical volume by which an individual pore of radius = $r_f$ would need to increase:

$$V_{inc,hyp} = \frac{V_{solid} \times Recovery}{n_p}$$  \hspace{1cm} (Eq. S-5)
where \textit{Recovery} is, of course, fractional and not percentage based. Then, \( r_2 \), the radius of interaction required to achieve the trace element recovery may be calculated according to:

\[
 r_2 = \left( \frac{3 V_{\text{inc}, \text{hyp}}}{4 \pi} + r_1^3 \right)^{\frac{1}{3}}. \\
\text{(Eq. S-6)}
\]

Values of \( r_2 \) calculated using Eqn. S-6 are plotted in Figure 4. These calculations show that the increase in pore size required to achieve measured Ca recoveries in pores under 600 nm would be very low, at the most ~40 nm, or approximately 25\( \times \) the c-axis length of dolomite (15.95 Å, Steinfink and Sans (1959)), but that the interaction volume could be significantly greater for Ba, Mn, and Sr: \( r_2 \) \(- \) \( r_1 \) up to ~440 nm for Ba, ~270 nm for Mn, and ~60 nm for Sr, or 280\( \times \) c-axis length for Ba, 170\( \times \) c-axis length for Mn, and 38\( \times \) c-axis length for Sr. Notably, abundant pores exist in the 100-600 nm range (Fig. 2), and these numbers are an order of magnitude lower at \( r_1 \) = 100 nm than they are at \( r_1 \) = 600 nm.

The volume-normalized specific surface area of a pore of radius \( r_1 \) (SSA) may also be calculated according to:

\[
 SSA = \frac{3}{r_1}. \\
\text{(Eq. S-7)}
\]

The values of SSA calculated using Eqn. S-7 (presented in Fig. 4) suggest that equilibration times in nanoscale pores are orders of magnitude shorter than those in micrometre-scale pores, a factor which would promote the enhanced trace element reactivity in these pores, including the potential for the dissolution of trace element-rich dolomite and reprecipitation of trace element-poor dolomite. Although this purely surface area-based comparison is highly simplified compared to the complexities of pore-scale reactive transport, most factors, such as the longer diffusional distances required to homogenise fluid concentrations across micrometre-scale pores and the likely shorter residence time in these larger pores, would compound differences in equilibration times rather than offset them.
Supplementary Information References


