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1 **Control of brine composition over reactive transport processes in calcium carbonate**
2 **rock dissolution: time-lapse imaging of evolving dissolution patterns**

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9 **Highlights**

- 10 • Ketton rock was dissolved using solutions with different salinities
11 • Amount of Ca²⁺ and NaCl salt in solution impacts the dissolution patterns
12 • Salinity exhibits an opposing influence on dissolution rate and calcite solubility.
13 • Time-lapse imaging reveals the distinct structural evolution of the dissolution patterns

14
15 **Keywords:** Carbonate dissolution; Micro-CT; Reactive transport; Acid well stimulation;
16 Wormhole formation; Porosity-Permeability relation

17 **Abstract**

18 This study investigates the impact of brine composition—specifically calcium ions and NaCl-
19 based salinity—on the development of dissolution features in Ketton, a porous calcium
20 carbonate rock. Utilizing a laboratory XMT (X-ray microtomography) scanner, we captured
21 time-lapse in situ images of Ketton samples throughout various dissolution experiments,
22 conducting four distinct flow-through experiments with differing brine solutions at a flow
23 rate of 0.26 ml min⁻¹. The scans yielded a voxel size of 6 μm, enabling the assessment of the
24 temporal evolution of porosity and pore structure through image analysis and permeability

25 evaluations via single-phase fluid flow simulations employing direct numerical solutions and
26 network modeling, as opposed to direct measurement.

27 Time-lapse imaging technique has delineated the extent to which the concentrations of CaCl_2
28 and NaCl in the injecting solution control the structural evolution of dissolution patterns,
29 subsequently triggering the development of characteristic dissolution pattern. The inflow
30 solution with no Ca^{2+} ions and with the minimal salt content manifested maximum
31 dissolution near the sample inlet, coupled with the formation of numerous dissolution
32 channels, i.e., wormholes. Conversely, solutions with a trace amount of Ca^{2+} ions induced
33 focused dissolution, resulting in the formation of sparsely located channels. Inflow solutions
34 with high concentrations of both Ca^{2+} ions and salt facilitated uniformly dispersed
35 dissolution, primarily within microporous domains, initiating particle detachment and
36 displacement and leading to localized pore-clogging. The relative increase in permeability, in
37 each experiment, was correlated with the developed dissolution pattern. It was discerned that
38 varying ratios of salt and calcium concentrations in the injected solution systematically
39 influenced image-based permeability simulations and porosity, allowing for the depiction of
40 an empirical porosity-permeability relationship.

41 **1. INTRODUCTION**

42 Carbonate formations constitute ~20% of sedimentary basins and ~60% of the world's
43 hydrocarbon reservoirs (Morse and Mackenzie, 1990; Akbar et.al., 2000;
44 Schlumberger 2019) and calcite is the dominant mineral in these reservoirs. Applications
45 such as CO_2 sequestration or acid stimulation for enhanced oil and gas production from
46 carbonate reservoirs involve the interaction of an acidic fluid with the calcite. This leads to
47 the dissolution of calcite and the creation of secondary porosity and permeability.

48 Numerous studies have shown that parameters such as injection rate, the acidity of the
49 injected solution, and initial heterogeneity of the porous medium can impact the dissolution
50 processes and control the subsequent evolution of rock properties (e.g., Esteves et al., 2020;
51 Golfier et al., 2002; Hoefner and Fogler, 1988; Luquot and Gouze, 2009; Meile and Tuncay,
52 2006; Menke et al., 2017; Soullaine et al., 2017; Yoo et.al., 2021). In particular, dissolution
53 kinetics along with the acid injection rate is known to form characteristic dissolution pattern
54 (e.g., Daccord et al., 1993; Elkhoury et al., 2013; Golfier et al., 2002; Hoefner et al., 1987;
55 Hoefner and Fogler, 1988; Luquot et al., 2014; Luquot and Gouze, 2009; Maheshwari et al.,
56 2013; Panga et al., 2005). At the pore scale, the interaction of an acid with calcite mineral is a
57 combination of two processes: (i) the transport rate of the aqueous ions to and from the
58 mineral surface and (ii) the dissolution reaction taking place at the mineral surface.
59 Manipulation of the rate of any of these processes affects the effective dissolution rate and
60 consequently the dissolution patterns. In general, five types of dissolution patterns have been
61 reported, corresponding to different dissolution kinetics for a given acid injection rate (e.g.,
62 Fredd and Fogler 1998; Hoefner and Fogler, 1988; Maheshwari et.al., 2013; Soullaine et al.,
63 2017): 1) face dissolution, 2) conical wormholes, 3) dominant wormholes, 4) ramified
64 wormholes, and (5) uniform dissolution. For example, when the injected solution is highly
65 reactive such that the transport time scale of the acid is longer compared to the reaction time
66 scale of the acid, the acid is mostly consumed to dissolve the rock close to its inlet face. This
67 leads to the development of the face dissolution pattern. Acid solutions with low reactivity,
68 on the other hand, can penetrate further into the rock, causing uniform dissolution since time
69 scale of transport becomes smaller than the time scale of chemical reaction. In summary, with
70 decrease in the dissolution rate, the dissolution regime changes from the face dissolution
71 regime to the uniform dissolution regime, while passing through the intermediate regimes
72 corresponding to the different wormhole dissolution patterns. These patterns have a major

73 control on the required amount of acid volume that needs to flow through the sample to
74 achieve specific permeability increase for the same amount of porosity increment (e.g., Fredd
75 and Fogler 1998; Hoefner and Fogler, 1988; Maheshwari et.al., 2013; Soulaine et. al., 2017;
76 Yoo et.al., 2021). For example, among the five dissolution patterns, the dominant wormholes
77 are the most conducting channels and require the least volume of acid injection to enhance
78 the permeability by a certain amount.

79 One way of controlling which dissolution regime is achieved in reactive-transport dissolution
80 is by addition of dissolution-inhibiting or -enhancing compounds. Examples are the addition
81 of microemulsion (Hoefner et al., 1987), varying the CO₂ concentration (Luquot et al., 2014)
82 or using SO₄²⁻ ions in the injected acid (Garcia-Rios et al., 2015). Luquot et al., 2014 showed
83 that high pCO₂ developed preferential flow paths while lower pCO₂ resulted in uniform
84 dissolution. Garcia-Rios et al., 2015 observed the inhibitory effect of SO₄²⁻ ions on calcite
85 dissolution rates while observing no significant effect on the created dissolution patterns.

86 The impact of salinity and dissolution-inhibiting or -enhancing ions and compounds present
87 in formation water on pore geometry evolution during dissolution of porous carbonate rocks
88 is less well-known. Hanor (1994) reported that the salinities of pore waters in subsurface
89 basins may span over five orders of magnitude i.e., from few mg l⁻¹ in shallow meteoric
90 systems to over 400000 mg l⁻¹ in evaporite-rich sedimentary basin such as Michigan Basin, in
91 USA. Moreover, in the formation brines, Ca²⁺ is the second most abundant cation after Na⁺.
92 The concentration of Ca²⁺ can even exceed the Na⁺ concentration in formation waters with
93 salinities higher than 300000 mg l⁻¹ (Gledhill and Morse, 2006). Therefore, understanding the
94 geochemistry of high salinity and Ca²⁺ rich formation waters is important in the assessment of
95 (the permeability evolution in) carbonate minerals enriched sedimentary basins for
96 applications such as CO₂ sequestration or acid stimulation for enhanced oil production.

97 Several batch dissolution experiments have examined the influence of the salinity of the
98 solution and Ca^{2+} concentration on the calcite dissolution rates (Anabaraonye et al., 2019;
99 Buhmann and Dreybrodt, 1987; Finneran and Morse, 2009; Gledhill and Morse, 2006;
100 Gutjahr et al., 1996; Pokrovsky et al., 2005; Sjöberg and Rickard, 1985). For transport-
101 controlled dissolution regime, no impact of the NaCl-based ionic strength on calcite
102 dissolution rates is observed when $I < 1\text{M}$ (Pokrovsky et.al., 2005), while strong inhibition of
103 calcite dissolution rates is observed with NaCl-salinity $> 1\text{M}$ (Gledhill and Morse, 2006). The
104 impact of Ca^{2+} ions in solution on the dissolution rate is contested in literature. Some authors
105 found that calcium inhibits calcite dissolution in neutral to basic conditions only (Sjöberg and
106 Rickard, 1985), while others found that calcium ions enhance calcite dissolution rates
107 (Gutjahr et al. 1996; Gledhill and Morse 2006).

108 While there is a clear, albeit incoherent, impact of calcium and salinity on calcium carbonate
109 dissolution rates, the implication of this influence on the development of secondary porosity
110 and permeability in carbonate rocks is unknown. We are not aware of any reactive flow
111 experimental studies that have explored the control of NaCl and Ca^{2+} concentration on the
112 dissolution patterns.

113 Through time-lapse imaging, we have examined the influence of the amount of NaCl and
114 Ca^{2+} ions in the injected solution over the structural evolution of dissolution patterns and
115 subsequent development of characteristic dissolution pattern in Ketton samples. We present
116 the results of four flow experiments using different acidic solutions with constant flow rate
117 into four samples of oolitic limestone. The composition of these solutions, i.e., amount of salt
118 and Ca^{2+} ions, was chosen to cover a wide range of dissolution kinetics. X-ray
119 microtomography (XMT) image analysis and effluent analysis were used to calculate the
120 removed mass of calcite and consequent changes in the porosity of the samples. The link
121 between dissolution and permeability enhancement of the samples was investigated using

122 numerical simulation of single-phase flow using two approaches: pore network modelling
123 (PNM) approach utilizing the pore network extracted from the XMT images and direct
124 numerical simulation (DNS) method, also utilizing the XMT images. Finally, for each
125 experiment, development in permeability was related to the modified porosity of the sample.

126 **2. MATERIAL AND METHODS**

127 For this study, we have utilized a relatively homogeneous carbonate rock type: Ketton
128 limestone. This oolitic limestone is a part of the Lincolnshire Formation, which was
129 deposited around 165 million years ago. Four cylindrical shape samples named K1, K2, K3,
130 and K4, of 6 mm in diameter and ~12mm in length were drilled side by side out of a
131 limestone block. Calcite-equilibrated solutions were prepared using deionized water at an
132 atmospheric pressure and room temperature conditions. The composition of these solutions
133 calculated using PHREEQC (Parkhurst and Appelo, 2013) and Pitzer database is provided in
134 Table S1. The samples were pre-saturated using a protocol based on that of Boone et al.
135 (2014) outside of the flow cell under vacuum condition with a calcite-equilibrated solution
136 for about 48hrs. After mounting the pre-saturated sample in the flow cell, any air still present
137 in the sample was flushed by flowing the calcite-equilibrated solution through the sample for
138 ~2000 pore volumes at three flow rates, 10 ml min⁻¹, 5 ml min⁻¹ and 1 ml min⁻¹. Then an
139 image was taken to visually verify that no air was present within the sample and the full
140 saturation of the pore space was achieved. To impose a uniform radial fluid at the injection
141 face of the sample, an inert porous sintered glass plug (Robu glass por 0 filter) was placed in
142 front of the inlet side of the carbonate plug. Both plugs were inserted into a Viton sleeve,
143 placed in a custom-built Hassler-type flow cell made from X-ray transparent PEEK. A
144 confining pressure of ~20 bar was applied on the sleeve to avoid fluid bypassing the sample.
145 The fit of the sleeve to the sample was assessed visually on the raw data and was observed to

146 fit very tightly (Figure S1). Additionally, the confinement pressure meter indicated a
147 consistent pressure of ~20 bar during the experiment, indicating a leak-free flow.

148 Note that flow was established from bottom to top of the sample while all presented images
149 in the subsequent sections are upside down. All experiments were performed under room
150 temperature and a confining pressure of ~20 bars.

151 **2.1 Chemical composition of injecting solutions**

152 Four solutions with the same HCl concentration of $0.001 \text{ mol dm}^{-3}$ but different salinity and
153 Ca^{2+} concentration was prepared. All solutions were prepared by adding the appropriate
154 amount of the reagents with, CaCl_2 , NaCl , and HCl to deionized water under atmospheric
155 conditions. pH values of these solutions are provided in Table 1. The first solution had an
156 ionic strength of 0.2 mol dm^{-3} , without calcium ions (referred to as no calcium low salinity
157 solution, or NCLS). A second solution had a similar ionic strength but contained $1 \times 10^{-3} \text{ mol}$
158 dm^{-3} of Ca^{2+} ions (low calcium low salinity solution, or LCLS). The third type of solution had
159 an ionic strength of 1.2 mol dm^{-3} , without calcium ions (no calcium high salinity solution, or
160 NCHS). Finally, the fourth solution had a similar ionic strength as the third but contained
161 $0.335 \text{ mol dm}^{-3}$ of Ca^{2+} ions (high calcium high salinity solution, or HCHS). For all four
162 experiments, acidic solutions were injected with a same and constant flow rate of 4.16×10^{-9}
163 m^3s^{-1} (i.e., $Q = 0.26 \text{ ml min}^{-1}$).

164 The concentration of Ca^{2+} ions in inflow and outflow solutions was measured with the ICP-
165 OES method. This method can measure Ca^{2+} concentration within a range of
166 $0.5\text{-}5 \times 10^{-3} \text{ mol dm}^{-3}$. Therefore, most of the solutions were diluted using 0.7M HNO_3 acid,
167 to a dilution ratio of 1:100, while some of the solutions related to experiment HCHS were
168 diluted by a ratio of 1:1000. The pH of the original inflow and outflow solutions (i.e., without

169 dilution) was measured with a pH 3110 portable pH meter and pH electrode SenTix™ or (for
170 the HCHS experiment) WTW - Sensolyt 900-P.

171 The solution composition of all inflow solutions was calculated using PHREEQC (Parkhurst
172 and Appelo, 2013) with the Pitzer database. These calculations showed that the activity
173 coefficient of H⁺ is close to unity for all solutions (Table S1). For inflow solutions NCLS and
174 LCLS, the measured value of pH matched with the calculated value of pH. It should be noted
175 that the measured pH values for the NCHS and the HCHS was affected by the non-
176 compatibility of the utilized electrode with the high concentration of ions in the solutions. As
177 a consequence, the measured value of pH of these solutions using above mentioned electrode
178 differed from the calculated value of pH. In order to clarify the uncertainties over pH values,
179 we have re-measured pH with a different pH electrode WTW - Sensolyt 900-P and
180 multimeter WTW portable pH meter Multiline Multi 3630 IDS. These measurements were
181 performed on a separate solution prepared with the same recipe as that of the inflow solution
182 for experiment HCHS. A measured pH value of 3.03 for this solution using pH electrode
183 WTW - Sensolyt 900-P further affirms the non-compatibility of the pH electrode SenTix™
184 for measurements in high salt (calcium and chloride) solutions. Table 1 summarizes
185 experimental details related to flow and solution chemistry. Note that the Pitzer model is not
186 tailored to the exact conditions at the start of, and during our experiments. Therefore, the SI's
187 calculated for calcite (Table 1) should be treated with caution.

188 **2.2 Data acquisition and processing**

189 *In situ* imaging of the sample was performed using a laboratory-based environmental micro-
190 CT scanner built at Ghent University (Bultreys et al., 2016). The starting step of each
191 experiment was the saturation of the sample with calcite-equilibrated water, followed by
192 scanning of the sample. The scanning was performed with an X-ray beam energy of 110kV
193 and an exposure time of 80ms. The reconstructed voxel size of the images was 6 μm per

194 voxel and three stacks were required to cover the full length of the sample. Such full sample
195 length scanning was performed at the beginning and the end of the experiment. During acid
196 injection, the scanner was fixed near the inlet of the sample; therefore, time-lapse scans
197 correspond to the top ~6 mm section of the sample. Hereafter, these time-lapse scans are
198 referred as half-length sample volumes. For both full-length scans and half-length scans, a
199 total of 2200 projections, covering a 360° rotation of the scanner, were obtained in 15
200 minutes. Details on the processing steps of both types of scans is provided in SI Section 1.

201 **2.3 Skeleton analysis**

202 In this study, we used the skeletonization methods to characterize the wormholes created
203 during limestone dissolution. The skeletonization workflow converts the three-dimensional
204 pore space into a one-dimensional object while preserving topological and geometrical
205 features. This process of dimension reduction includes iterative removal of individual voxels
206 from a volume until a single line of voxels (i.e., the medial axis of the volume) remains along
207 the pore space. This yields a simplified skeleton representation of the pore space, in which
208 each voxel stores properties of the original complex 3D pore space through attributes like
209 thickness, orientation and length. Detailed steps on the skeletonization of wormholes and
210 subsequent quantification of the wormhole are provided in SI Sections S2 and S3,
211 respectively.

212 **2.4 Pore network extraction and flow modelling**

213 We have calculated the velocity field and permeability of the sample at a different stage of
214 the dissolution process. For this purpose, we have utilized a pore network model because it
215 requires less computational time than direct numerical simulation. Single phase flow was
216 simulated on the extracted pore network. For simulating flow, the inlet face of the network
217 was maintained at a constant value of Darcy velocity (i.e., constant average pore inlet

218 velocity) and the outlet face at an atmospheric pressure condition, after which the pressure
219 and velocity in each pore were found by imposing mass conservation. The Darcy velocity
220 was calculated as:

$$u_D = \frac{Q}{A} \quad (1)$$

221 where, Q is the volumetric flow rate ($\text{m}^3 \text{s}^{-1}$) and A is the cross-section area of the sample
222 (m^2).

223 From the Darcy velocity (u_D) and pressure difference between the inlet and outlet faces
224 (ΔP_{PNM}), the permeability of the network is obtained from:

$$k_{PNM} = \frac{\mu u_D L}{\Delta P_{PNM}} \quad (2)$$

225 where, μ is the viscosity of water, $0.001 \text{ Pa}\cdot\text{s}$, and L is the pore network length along the flow
226 direction.

227 The remaining boundaries of the network parallel to the flow direction were implemented as
228 no-flow boundaries. Further details on the modeled equations can be found in Raouf et al.
229 (2012).

230 **2.5 Direct flow simulation of pore-scale images**

231 In order to evaluate the permeability changes during dissolution, XMT images which were
232 acquired at the start and end of the experiment were used as 3D pore space domains for the
233 microscale fluid flow simulation.

234 The XMT-based pore spaces were first simplified and scaled using open-source image
235 processing software, MeshLab (MeshLab, version 2021.05; <https://www.meshlab.net>). The
236 resulting pore space was used for fluid flow simulations under same flow direction as that of

237 experiments. Flow equation were solved with a pressure difference imposed on either side of
238 the sample and a no-slip boundary condition at the lateral faces of the domain.

239 OpenFOAM, an open-source CFD toolbox, was used to perform single phase flow simulation
240 (Aslannejad et al., 2018; Bedram and Moosavi, 2011). For meshing purposes, a native
241 meshing tool of OpenFOAM (in this case, snappyHexMesh) was used. The flow simulation
242 required a significant number of discretization cells (i.e., base refinement level: $100 \times 100 \times$
243 250); therefore, the parallel computation was done using 8-cores. Classic Semi-Implicit
244 Method for Pressure Linked Equations (SIMPLE) algorithm was used to solve flow equation.

245 Absolute permeability, k_{DNS} (m^2) was calculated using the Darcy equation:

$$k_{DNS} = \frac{\mu Q L_x}{\Delta P_{DNS} L_y L_z} \quad (3)$$

246 where, Q ($m^3.s^{-1}$) is flow rate, L_x , L_y and L_z are the domain dimensions in each direction and
247 ΔP_{DNS} is the imposed pressure difference. A mesh sensitivity study was performed by
248 varying the number of discretization cells in the x, y, and z directions. Along with the base
249 refinement level, two more refinement levels i.e., refinement level 1: $100 \times 100 \times 150$ and
250 refinement level 2: $200 \times 200 \times 250$, were simulated. Cropped sample length-based dataset of
251 Sample K1 belonging to the start and end of the experiment was utilized. We observed that a
252 4x increment in discretization cell numbers (base refinement level and refinement level 2)
253 results in $\sim 8\%$ permeability variation for the unreacted rock volume and $\sim 18\%$ permeability
254 variation for the dissolved rock volume, while the relative change in permeability due to
255 dissolution is comparable among different mesh configurations (Figure S2).

256 **2.6 Sample characterization prior to experiments**

257 Characterization of the Ketton samples is based on the XMT images, FIB-SEM images, EDS
258 analysis, XRD analysis, and properties of the extracted pore networks.

259 XMT images showed that Ketton is composed of spherical grains and can be considered a
260 relatively homogeneous carbonate rock at the macroscopic scale (Figure S1 and S4). Electron
261 microscopy imaging of the surface and cross-sectional view of a randomly chosen spherical
262 grain were done using FIB-SEM imaging technique. Results showed the extent of the intra-
263 grain porosity (Figure S7). SEM images of the part of the sample showed textural
264 heterogeneity at a microscopic scale (Figure S8). We observed that some part of the grain
265 was made of rhombohedral particles, which is a typical morphology of calcite. Other parts of
266 the grain were made of needle-shaped particles, which is a typical morphology of aragonite
267 (e.g. Nan et al., 2008). EDS analysis suggested that these particles were majorly composed of
268 Ca, C and O (Figure S9).

269 In order to identify the particle polymorph, we conducted XRD analysis of three new samples
270 that were extracted from the same Ketton limestone block. Figure S10 shows the comparison
271 of the XRD spectra of a representative sample with the RRUFF reference of calcite,
272 suggesting that Ketton is predominately composed of the calcite and that the needle-shaped
273 particles are probably the pseudomorphs i.e., aragonite converted into calcite (Figure S8).

274 Next, the petrophysical properties of the four samples i.e., K1, K2, K3 and K4 were
275 investigated through analysis of the initial XMT images and of the extracted pore networks
276 for the initial conditions in the samples. The initial porosity of each sample was calculated by
277 dividing the volume of pore space by the total volume of the sample. The initial permeability
278 of each sample was calculated from the single-phase flow simulation on extracted pore
279 networks. A comparison of the porosity of all samples shows that K1, K2 and K3 have
280 similar initial porosity while K4 has a different initial porosity (Table 1).

281 Figure S11 shows the statistical distribution of some of the characteristic properties of the
282 initial pore space of the samples. K1, K2 and K3 have similar throat radii and K2 and K3

283 have similar pore sizes. K4 has a slightly wider range of pore sizes and throat widths than
 284 K1-K3, while all four samples have a similar distribution of coordination numbers. Figure
 285 S11e shows the frequency distribution of the normalized velocity which was obtained by
 286 normalizing the velocity value of each throat (i.e., obtained from PNM) by the Darcy
 287 velocity. The Darcy velocity was obtained by dividing the flow rate with the cross-sectional
 288 area of the sample. The frequency distribution of normalized velocity indicated the
 289 probability of faster and slower velocity channels in comparison with the Darcy velocity. K2
 290 and K4 have a somewhat greater number of fast channels as compared to K1 and K3. The
 291 observed velocity field in this study is similar to the previously reported velocity field for
 292 Ketton samples (Al-Khulaifi et al., 2017). Overall, the narrowness of the velocity channel
 293 suggested that all four samples have relatively similar initial pore structure (Figure S11e).

294 **2.7 Quantification of the changed volume of calcite**

295 $\Delta V_{Calcite,effluent}^n$, the cumulative value of changed amount of calcite volume (m^3), was
 296 obtained as:

$$\Delta V_{Calcite,effluent}^n = \frac{Q M_{calcite}}{\rho_{calcite}} \sum_{i=1}^n \Delta cCa^i (t^i - t^{i-1}) \quad (4)$$

297 where, n is the sampling steps, Q is the flow rate ($m^3 s^{-1}$), $\rho_{calcite}$ is the density of calcite
 298 ($2710 \text{ Kg } m^{-3}$), $M_{calcite}$ is the molecular mass of calcite ($0.1 \text{ Kg } mol^{-1}$) and ΔcCa is the
 299 difference between outflow and inflow Ca^{2+} concentration ($mol m^{-3}$).

300 $\Delta V_{Calcite,XMT}$, the change in the number of solid voxels of XMT images in an experiment
 301 duration denoted by time t, is given as:

$$\Delta V_{Calcite,XMT} = V_{Calcite,XMT}^t - V_{Calcite,XMT}^{t=0} \quad (5)$$

302 Average reaction rate was calculated from the time-based evolution of the macroporosity as:

$$r_{calcite}(t) = \frac{\rho_{calcite}}{\Delta M_{calcite}} \frac{\Delta \phi_{XMT}(t)}{\Delta t} \frac{V_b}{A(t)} \quad (6)$$

303 where, $r_{calcite}(t)$ is the average reaction rate ($\text{mol m}^{-2} \text{s}^{-1}$), $\Delta \phi_{XMT}(t)$ is the change in the
 304 macroporosity of the sample between the scan time t as compared to the initial porosity, Δt
 305 (s) is the acquisition time of the image and $A(t)$ (m^2) is the surface area obtained by adding up
 306 the voxel faces forming the boundary between solid and pore phase and V_b (m^3) is the total
 307 volume of the sample. It should be noted that above reaction rates are based only on
 308 macroporosity while neglecting the changes in the microporosity. Average reaction rates at
 309 different time steps of the experiment was calculated from the XMT images of the half-length
 310 sample. The average reaction rate at the beginning and at the end of the experiment was
 311 calculated from the XMT images of the cropped length sample. Note that the average
 312 reaction rate calculated from Equation 6 inherited an error depending on the time interval of
 313 scans used in the calculation (i.e., Δt). We observed that for the scan time interval used in this
 314 study, this error was around 20% (SI Section S4, Figure S12).

315 Equation 6 calculates the average reaction rate from the average macroporosity changes.
 316 Additionally, we have calculated local reaction rate as:

$$r_{z_{calcite}}(z) = \frac{\rho_{calcite}}{M_{calcite}} \frac{\Delta \phi_{XMT}(z)}{\Delta t} \quad (7)$$

317 where, $r_{z_{calcite}}(z)$ is local reaction rate (mol m^{-3}) calculated from the change in the slice-
 318 averaged porosity of the sample (i.e., Figure 4b) occurred in the experiment duration, Δt , and
 319 at a distance of z from the sample inlet.

320 In order to understand the coupling of transport and reaction times scales, we have defined
 321 two dimensionless numbers i.e., Peclet number and Damköhler number.

322 The Peclet number (Pe) compared the time scale of advection to that of diffusion and was
 323 defined as:

$$Pe(t) = \frac{U_{av}(t) l(t)}{D} \quad (8)$$

324 where, U_{av} (m s^{-1}) is the average pore velocity obtained by dividing constant Darcy velocity
 325 with the image-based porosity at different time steps, l is the mean pore radius calculated
 326 from the extracted pore network of the sample and D is the diffusion coefficient (3.36×10^{-9}
 327 $\text{m}^2 \text{s}^{-1}$).

328 The Damköhler number (Da) compared the convection time scale with the reaction time
 329 scale:

$$Da(t) = \frac{rZ_{calcite} MV_{calcite}}{A U_{av}(t)} \quad (9)$$

330 where, $MV_{calcite}$ is the molar volume of calcite ($3.69 \times 10^{-5} \text{m}^3 \text{mol}^{-1}$), $rZ_{calcite}$ indicates the
 331 reactive strength of the injecting acid ($\text{mol m}^{-3} \text{s}^{-1}$) at the inlet of the sample calculated from
 332 Equation 7 and A is the specific surface area of the cropped sample length at the beginning of
 333 the experiment.

334 The Pe and Da number, at different time steps were calculated from the XMT data of the half
 335 sample length, while, at the beginning and at the end of the experiment were calculated from
 336 the XMT data of the cropped sample length.

Experiment	NCLS	LCLS	NCHS	HCHS	Method
Ketton sample	K1	K2	K3	K4	-
Flow rate (m^3s^{-1})	4.16×10^{-9}	4.16×10^{-9}	4.16×10^{-9}	4.16×10^{-9}	-
Darcy velocity (m s^{-1})	1.54×10^{-4}	1.54×10^{-4}	1.54×10^{-4}	1.54×10^{-4}	-
Injection duration (s)	72000	72000	43200	57000	-
Injected pore volume	6722	6977	3507	4489	-
Inflow pH(Calculated)	3.1	3.1	3.00	3.05	PHREEQC Pitzer
Inflow pH (Measured)	3.01	2.97	2.77	3.03 ^c	pH electrode SenTix™ or WTW
Inflow Ca^{2+} (mol dm^{-3})	-	1×10^{-3}	-	335×10^{-3}	ICP-OES
Inflow -salinity (mol dm^{-3})	0.2×10^{-3}	0.2×10^{-3}	1.16×10^{-3}	1.12×10^{-3}	ICP-OES
Inflow-saturation index (SI)	-	-11.45	-	-8.04	PHREEQC Pitzer
Porosity at $t = 0\text{s}$ (%)	13.42	12.1	13.88	16.3	XMT ^a
Permeability (k_{PNM}) at $t = 0\text{s}$ (m^2)	1.13×10^{-12}	6.37×10^{-13}	1.31×10^{-12}	3.18×10^{-12}	Flow simulation on cropped sample length using PNM
Permeability (k_{DNS}) at $t = 0\text{s}$ (m^2)	1.98×10^{-12}	4.75×10^{-12}	1.77×10^{-12}	3.97×10^{-12}	Flow simulation on cropped sample length using DNS
Average equivalent diameter at $t = 0\text{s}$ (m)	0.89×10^{-4}	0.53×10^{-4}	0.51×10^{-4}	0.65×10^{-4}	XMT ^a
Average volume of pores at $t = 0\text{s}$ (m^3)	0.57×10^{-11}	0.29×10^{-11}	0.31×10^{-11}	0.47×10^{-11}	XMT ^a
Number of pores in the extracted pore network	6832	6259	6948	6130	PNM ^b
Number of throats in the extracted pore network	12419	10915	12919	10919	PNM ^b
Average pore radius at $t = 0\text{s}$ (m)	5.46×10^{-5}	4.97×10^{-5}	4.93×10^{-5}	5.31×10^{-5}	PNM ^b
Average throat radius at $t = 0\text{s}$ (m)	2.59×10^{-5}	2.61×10^{-5}	2.59×10^{-5}	2.93×10^{-5}	PNM ^b
Average coordination number at $t = 0\text{s}$	3.64	3.49	3.72	3.56	PNM ^b
Average pore velocity at $t = 0\text{s}$ (m s^{-1})	2.43×10^{-5}	2.79×10^{-5}	2.47×10^{-5}	2.47×10^{-5}	PNM ^b
Size of the full sample length (Voxels)	1319×1317×2494	1316×1316×2418	1317×1319×2552	1317×1318×2342	XMT Images

Size of the cropped sample length (Voxels)	1319×1317×1950	1316×1316×1950	1317×1319×1950	1317×1318×1850	XMT Images
Size of the half sample length (Voxels)	1319×1317×818	1316×1316×850	1317×1319×850	1317×1318×782	XMT Images
Scan interval of the half sample length (min)	40,136, 154, 154, 154, 154, 154, 154	90, 90, 90, 99, 105, 120, 126	150,30,180,120,12 0,160,136,56	40,215,20,75,165,1 65,165,165,165,25	-

Table 1: Parameters for all four dissolution experiments including the skeleton (pore network) information. ^a XMT image of cropped sample length. ^b Pore Network Model of cropped sample length. ^c pH measurements were done on a separate solution made according to the same recipe and using a WTW – Sensolyt 900-P pH electrode; for this solution, the SenTix electrode was affected by the high concentration of ions in the solutions.

337 **3. RESULTS AND DISCUSSION**

338 This study is based on four reactive flow experiments (Table 1 and Table S1): NCLS (No
339 Calcium Low Salinity), LCLS (Low Calcium Low Salinity), NCHS (No Calcium High
340 Salinity) and HCHS (High Calcium High Salinity). The analysis of effluent solution for all
341 four experiments is provided in Section 3.1.1. The results are compared with the XMT
342 image-based analysis in Section 3.1.2. Next, we assess the temporal evolution of bulk
343 porosity and local porosity in Section 3.1.3 and corresponding effective reaction rate in
344 Section 3.1.4. Further, we examine the characteristics of the dissolution structures developed
345 in each experiment in Section 3.2. Finally, the impact of the dissolution structures on
346 permeability changes is provided in Section 3.3.

347 **3.1 Mass transfer analysis**

348 **3.1.1 Effluent Analysis**

349 Figure 1a presents the temporal evolution of the normalized Ca^{2+} concentration (ΔCa),
350 which represents the difference between outflow and inflow Ca^{2+} concentration during the
351 sampling interval. Positive values of ΔCa for experiments NCLS, LCLS and NCHS
352 indicates persisting dissolution throughout the experiments. From the first sampling point
353 onwards, the experiment NCLS maintained a steady-state value of outlet Ca^{2+} concentration
354 and ΔCa . Experiment LCLS, on the contrary, initially provided a lower outflow
355 concentration compared to NCLS, which later approach towards a higher steady-state value.
356 For experiment NCHS, outflow Ca^{2+} concentration showed a decreasing trend. From the
357 saturation index of the injected solutions, we estimated the maximum amount of Ca^{2+}
358 concentration which could be dissolved before these solutions would reach equilibrium with
359 respect to calcite. Comparison of these estimates with the measured ΔCa suggests that the
360 outflow solutions of experiments NCLS, LCLS and NCHS were almost in equilibrium with

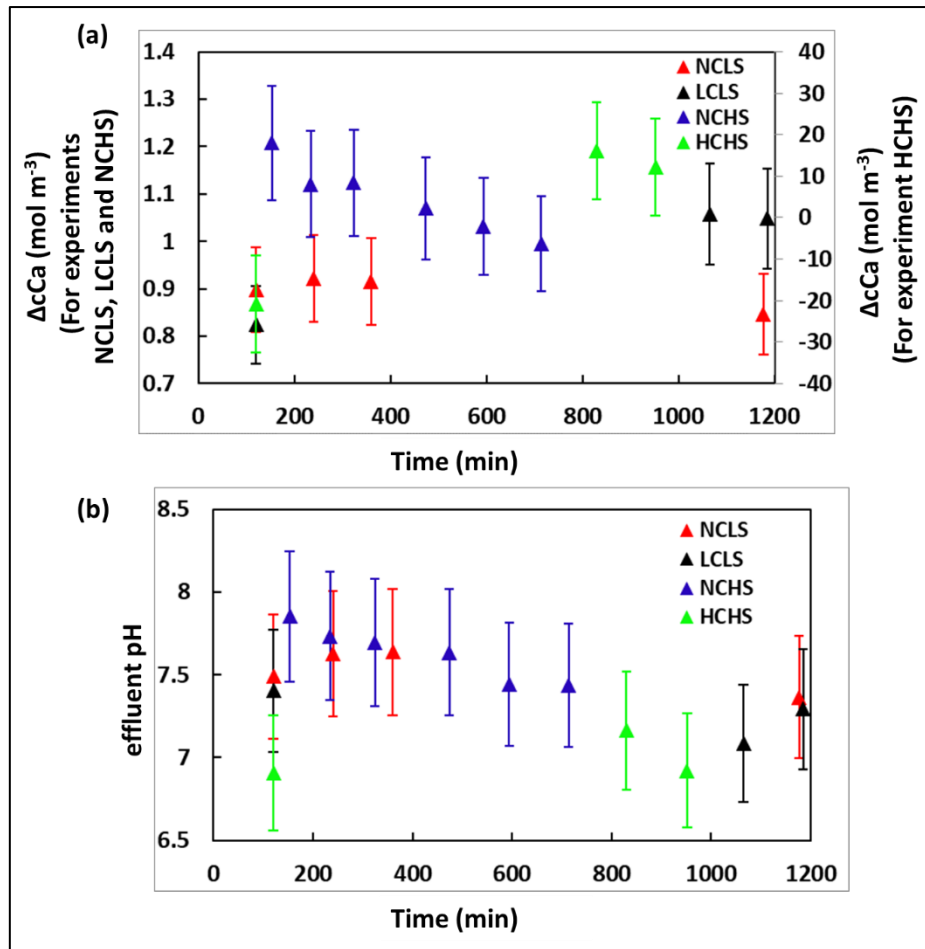
361 calcite (Figure 2a). Note that, the differences between the quantities of dissolved Ca^{2+} ions
362 observed in the experiment and those in the simulation most likely reflect the impact of
363 differences in sample's initial permeability on the overall amount of calcite dissolved during
364 the experiments. Future investigations on homogenous porous media (e.g., 3D-printed) could
365 circumvent such uncertainties.

366 In the case of experiment HCHS, normalized ΔCa was negative initially, followed by
367 positive values (Figure 1a). As stated earlier, the inflow solution HCHS was acidic, with the
368 measured pH value of 3.05, and undersaturated with respect to the calcite. Through the
369 examination of mixing calculations (specifically, PHREEQC + Pitzer calculations when
370 mixing varying fractions of inflow solution HCHS with a solution in equilibrium with
371 calcite), we did not identify any ratios resulting in either supersaturated mixtures or salting-
372 out conditions. Moreover, from the saturation index, we estimated that this solution can
373 dissolve up to around $0.7 \times 10^{-3} \text{ mol dm}^{-3}$ calcite, before reaching equilibrium with respect to
374 calcite (Figure 2a). Therefore, it is most likely that the initial negative ΔCa value does not
375 represent calcite precipitation but was caused by error accumulation during the strong
376 dilution necessary on in- and outflow samples in preparation of ICP-OES measurements from
377 which ΔCa values were calculated. We suspect the calculated Ca^{2+} concentrations for HCHS
378 samples included an uncertainty larger than the standard error of 10% (SI Section S5.1,
379 Figure S13).

380 We observed the impact of salinity and Ca^{2+} concentration of the inflow solutions on the
381 equilibrium concentrations (Figure 2a). As expected, inflow solutions containing Ca^{2+} ions
382 (i.e., LCLS and HCHS) required a lower amount of Ca^{2+} ions to reach to the equilibrium as
383 compared to the inflow solutions with no Ca^{2+} ions (i.e., NCLS and NCHS) (Figure 2a).
384 Similarly, increments in salinity led to enhanced solubility of calcite, with more saline inflow

385 solutions dissolving larger amounts of calcite than the inflow solutions with lower salinity
386 (i.e., NCLS) (Figure 2a).

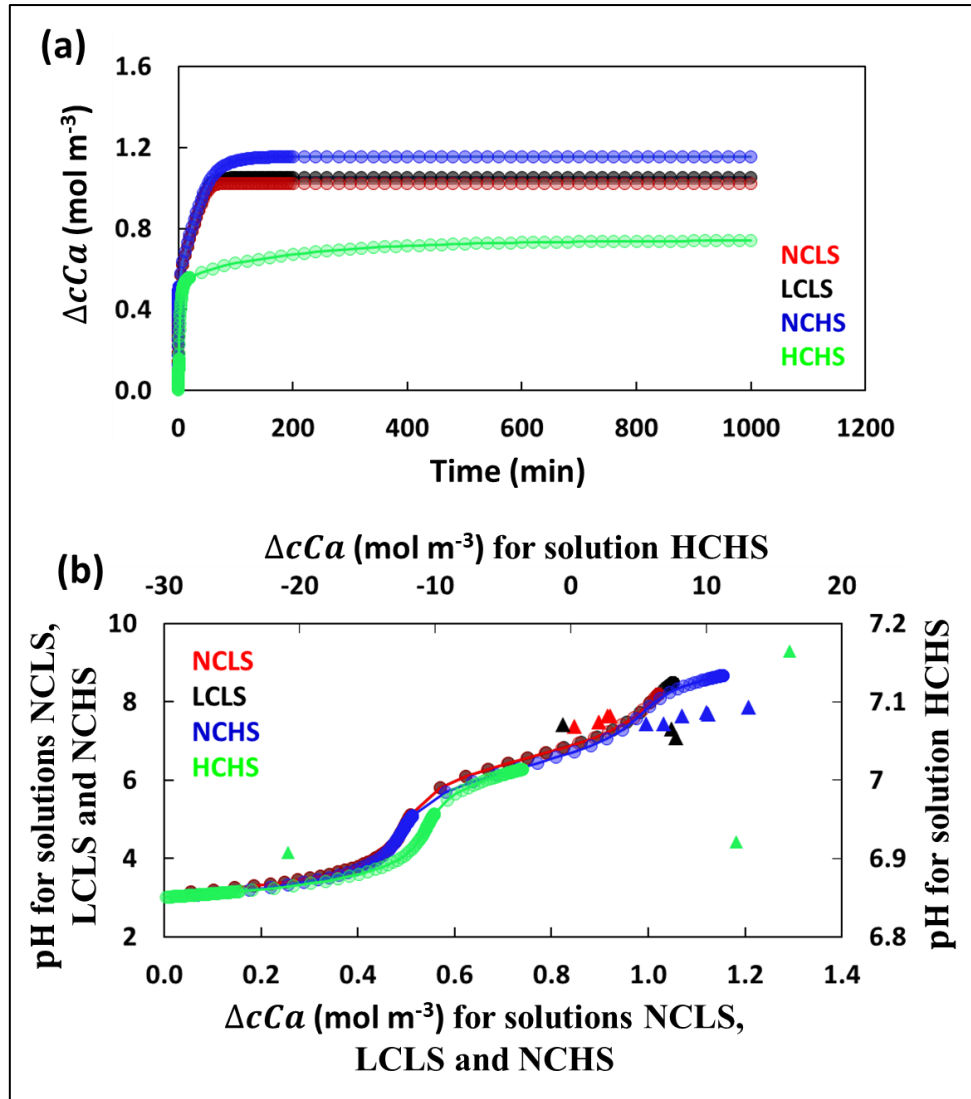
387 Figure 1b shows the measured pH of the effluent samples from all four experiments. Inflow
388 solutions all had an approximate pH value of 3.0 (Table S1). The higher pH values measured
389 in the outflow indicate dissolution-induced solution buffering. The amount of fluid buffering
390 directly relates to the amount of Ca^{2+} ions produced (Figure 1). Initially, experiment NCHS
391 showed both the highest value of pH and Ca^{2+} concentration at the outflow, followed by a
392 decreasing trend (Figure 1). For experiment NCLS, outflow pH remained constant and for
393 experiment LCLS, outflow pH showed an increasing trend. We observed a good agreement
394 between the measured outflow pH and predicted outflow pH (Figure 2b). For the experiment
395 HCHS, the pH of the outflow solution was calculated corresponding to the equilibrium
396 concentration. For this experiment, we observed a higher difference between the calculated
397 pH and the measured pH (Figure 2b). This is probably due to the higher uncertainty
398 associated with the pH measurement in highly saline Ca^{2+} -rich outflow solution.



399

400 **Figure 1: (a) Measured Ca²⁺ concentrations from effluent solution for experiments**
 401 **NCLS, LCLS, NCHS (left-hand vertical axis) and HCHS (right-hand vertical axis) (b)**
 402 **Measured pH from effluent solution for all four experiments**

403



404

405 **Figure 2: PHREEQC simulations for all four injected solutions showing (a) the**
 406 **maximum amount of ΔcCa which can be dissolved before the solution reaches to the**
 407 **equilibrium and (b) pH of the solution as a function of the added amount of ΔcCa .**

408

409 3.1.2 Effluent concentrations vs XMT Analysis

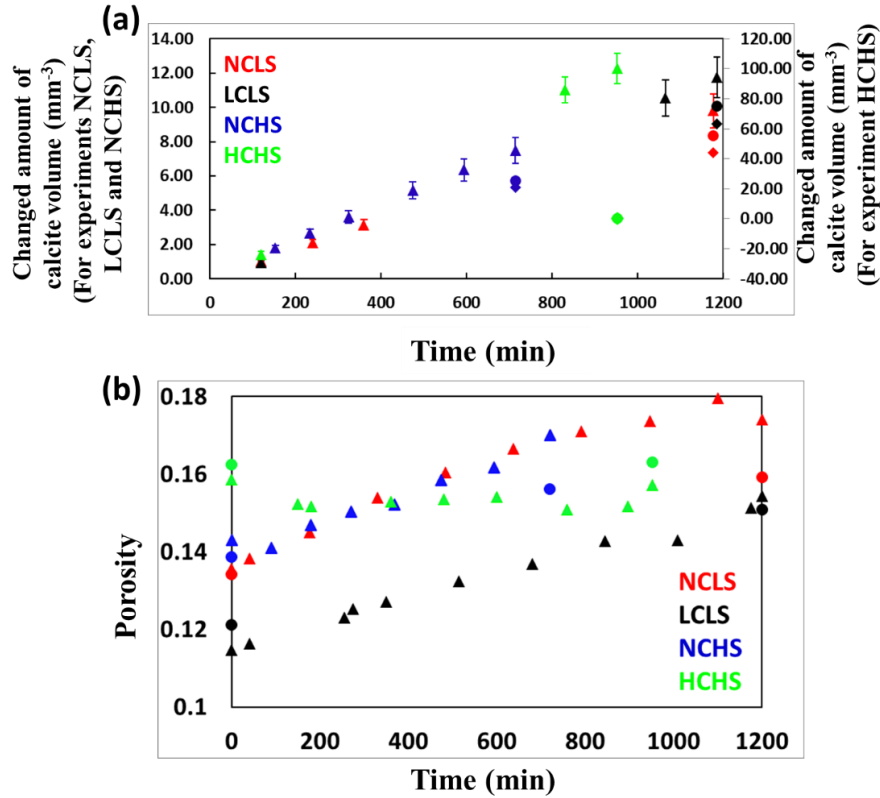
410 The comparison of the calcium concentration in the effluent with ketton volume (loss) with
 411 XMT helps to (further) quantify the amount of dissolution in the different experiments.

412 Figure 3a shows a comparison of the changed amount of calcite volume, calculated using
 413 ΔcCa with values obtained from XMT image analysis using Equations 4 and 5, respectively.

414 For experiments NCLS, LCLS and NCHS, we observed a difference of ~around 14-25%

415 between values obtained from effluent analysis and those from XMT images (Figure 3a). A
416 potential cause of this discrepancy could be resolution of imaging (voxel size 6 μm). This
417 difference would be dependent on the length of the sample along the flow direction used in
418 volume change calculations. Increased difference for cropped length sample-based analysis,
419 as shown in Figure 3a, is due to dominance of dissolution close to the sample inlet. As
420 discussed in Section 2.3, the remaining part of this study will be based on the analysis of the
421 cropped length sample. Figure S5 shows the cropping position through a vertical slice of
422 sample K1. It should be noted that while the calculated mass of dissolved calcite from the
423 effluent and XMT analyses doesn't exhibit an exact correspondence, they do, in essence,
424 agree on the relative extent of dissolution rate among the NCLS, LCLS, and NCHS
425 experiments.

426 For experiment HCHS, the difference between effluent analysis and XMT images was more
427 significant (Figure 3a). This, along with the arguments provided in Section 3.1 further
428 suggests that the ICP-OES measurement of solutions containing a high amount of Ca^{2+} ions
429 might have inherited higher uncertainty.



430

431 **Figure 3: (a) Cumulative changes in the solid calcite volume calculated from effluent**
 432 **analysis (triangle) and using XMT images (circle, full sample length and diamond,**
 433 **cropped sample length) for experiments NCLS, LCLS, NCHS (left-hand vertical axis)**
 434 **and HCHS (right-hand vertical axis). (b) temporal evolution of the macroporosity**
 435 **calculated from XMT images (circle, cropped sample length and triangle, half sample**
 436 **length) for all four experiments.**

437 3.1.3 Porosity

438 The time-lapse imaging of the sample allowed *in situ* tracking and analysis of the dissolution-
 439 induced changes in the porosity. Figure 3b shows the temporal evolution of macroporosity
 440 during the four experiments calculated from XMT images. Injection of undersaturated
 441 solutions led to an increase in the macroporosity of samples for experiments NCLS, LCLS,
 442 and NCHS. Consequently, total increments in the macroporosity are of magnitudes 0.025,

443 0.0296 and 0.0158 for experiments NCLS, LCLS, and NCHS, respectively. It should be
444 noted that the observed reduction in porosity in the NCLS experiment towards the end could
445 potentially be attributed to the clogging of certain pores by migrating calcite particles after
446 detachment due to dissolution of some of the matrix.

447 For the experiment HCHS, macroporosity of the top half of the sample first slightly
448 decreased and then this decreased macroporosity was nearly maintained until the end of the
449 experiment, where a slight increment was observed (Figure 3b). Luquot et al., 2014 has also
450 observed similar decrement in the macroporosity for the acids with lower corrosiveness (i.e.,
451 less strong undersaturation). They noted that the acids with lower reactive strength attack the
452 microporosity of the grain and resultant small particles clog the macropores. The change in
453 macroporosity obtained from XMT images does not resolve such changes in microporosity.
454 Therefore, changes in the microporosity of the sample were investigated through changes in
455 grey volume in the full samples between beginning and end of the experiment (SI Section
456 S5.2). For the same sections of the sample (i.e., cropped sample length) of this experiment,
457 we observed that the total change in the grey volume (i.e., microporosity + macroporosity)
458 was $3.3 \times 10^{-9} \text{ m}^3$ as compared to the segmented volume (i.e., macroporosity) of a value of
459 $0.16 \times 10^{-9} \text{ m}^3$ (Figure S14: semi quantitative). This suggests that the inflow solution HCHS
460 had dissolved more sub-resolution calcite matrix and the detached fine grains accumulated in
461 the macropores (cf. Luquot et al., 2014).

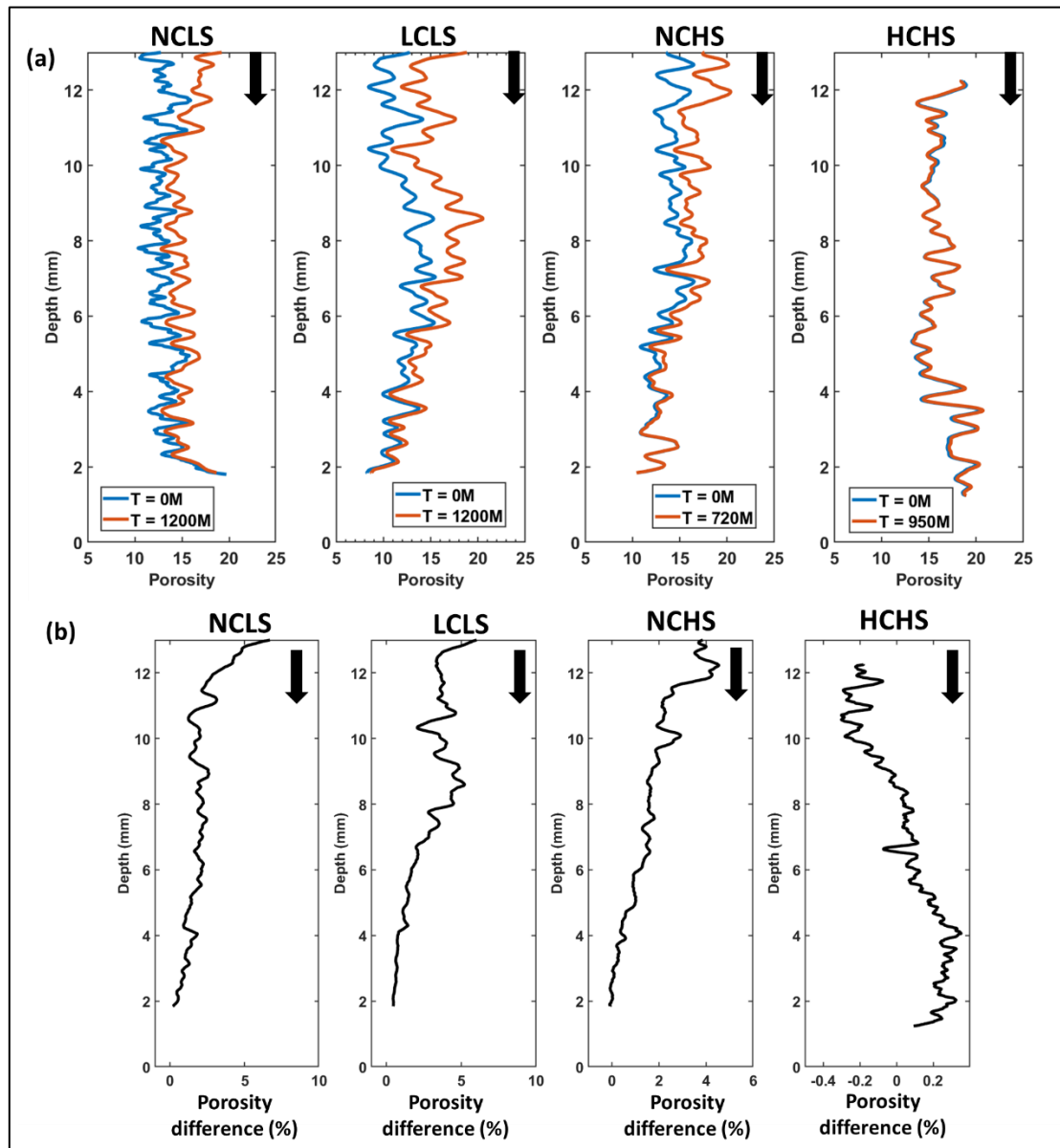
462 Figure 4 provides a vertical profile of porosity along the direction of the flow. Each data
463 point was obtained by averaging using a moving windows including 30 consecutive 2D slices
464 (i.e., corresponding to 0.18mm). Comparison of the vertical porosity profile of the samples
465 from the initial and final time steps of the dissolution experiment unveiled the following
466 information:

467 Firstly, for experiment NCLS, we observed a strong deviation of evolved porosity
468 distribution along the flow path compared to initial porosity distribution whereas, for
469 experiment LCLS and NCHS, evolved porosity distribution was similar to initial porosity
470 distribution (Figure 4a). This is caused by the difference in reactive strength of the injecting
471 fluid, as also discussed Section 3.2.1.

472 Next, we observed that solution NCLS created maximum porosity changes in the first 2 mm
473 part of the sample whereas for solution LCLS, the effective depth of reaction front (i.e.,
474 corresponds to a porosity difference (new porosity (%) - old porosity (%)) of more than 3%)
475 was around 5mm (Figure 4b). In the case of solution NCHS, the top 3mm part of the sample
476 experienced an average of 3% porosity change. The depth of penetration of the reaction front
477 is related to the amount of fluid buffering. Fluid buffering is a result of a complex interplay of
478 initial reactive strength of the injecting fluid and transport time scale (e.g., Agrawal et al.,
479 2020; Gray et al., 2018; Molins et al., 2014). Section 3.1.4 explores this relationship between
480 reaction and transport time scale for an individual experiment. For experiments NCLS,
481 LCLS, and NCHS, the whole sample showed positive porosity changes, whereas, for
482 experiment HCHS, the top part of the sample showed negative porosity changes (Figure 4b).
483 It is worth noting that for experiment HCHS, % macroporosity difference is less than 0.5%
484 and that dissolution in micropores played an important role. Alternatively, the SI values
485 obtained with our generalized Pitzer model may be inaccurate (Harvie and Weare, 1984;
486 Felmy and Weare, 1986), and locally calcite supersaturation may have occurred, leading to
487 the observed pore clogging/porosity decrease.

488 Note that, due to the constraints with the data acquisition as mentioned in Section 2.2, bulk
489 porosity for the first- and last-time steps of the experiment was calculated from the data of the
490 full sample (Figure 3b). However, porosity for the intermediate time steps was calculated
491 from the data of half-length sample i.e., part of the sample near the injection point. The

492 difference between porosity data of these two samples size at time $t=0$ denotes the initial
 493 heterogeneity of the samples (Figure 4a) whereas, the difference at the end of the experiment
 494 is a result of dissolution heterogeneity along the direction of flow (Figure 4b).



495

496 **Figure 4: Porosity changes in all four experiments showing (a) the slice-averaged**
 497 **porosity values (%) along the sample, and (b) difference between porosity values (%).**
 498 **The vertical profiles corresponded to the XMT images of the cropped sample length at**
 499 **the beginning and the end of experiment. In order to increase the visibility, only a part**
 500 **of the vertical profile (i.e., from 1.8 till 12.5 mm) is shown. Figure S15 shows the full**

501 vertical profile (i.e., from 1.8 mm till 13.5 mm). Black arrow indicates the flow
502 direction. Note the different x-axis ranges utilized for panel (b). Note that flow was
503 established from bottom to top of the sample and all presented images are upside down.

504 3.1.4 Reaction rate and dimensionless numbers

505 Time-lapse XMT scans of the sample enabled monitoring of the macroporosity of the sample
506 as the experiment progressed. This porosity was utilized to obtain the changed amount of
507 calcite mass to calculate the evolution of the average reaction rate over the course of the
508 experiments. Figure 5a shows the evolution of the average reaction rate for all four
509 experiments. Figure 6 shows the vertical profile of the local reaction rate calculated from the
510 XMT images of the full sample obtained at the beginning and the end of the experiment.

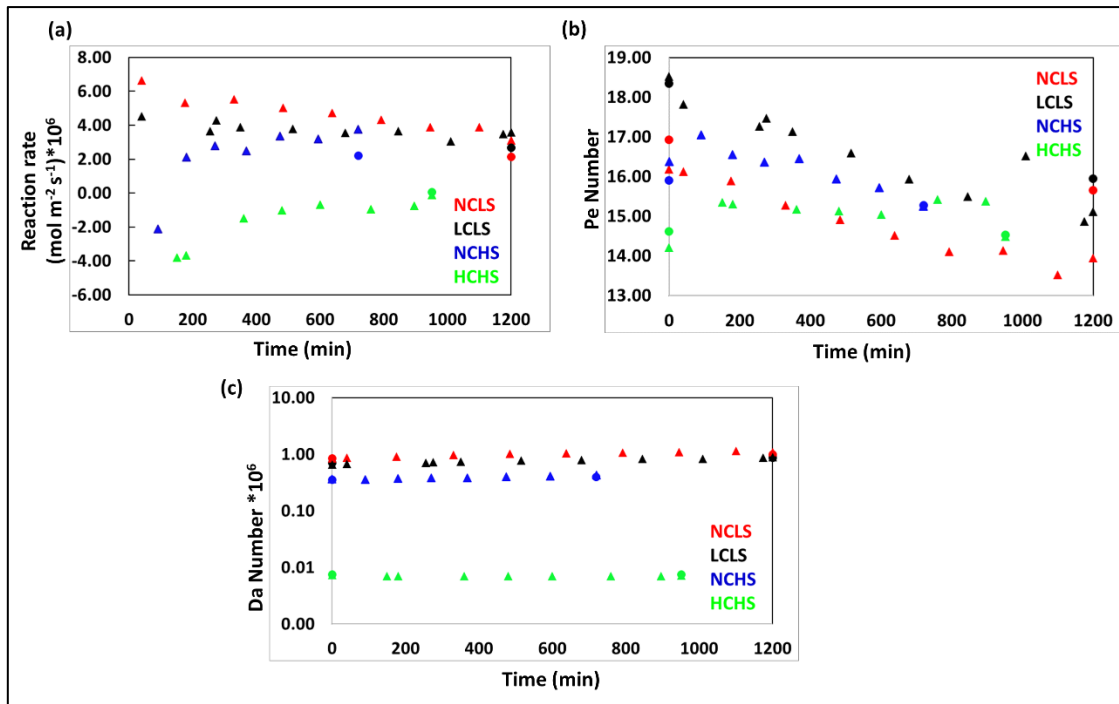
511 We observed that the addition of the Ca^{2+} ions in the inflow solution decreased the calcite
512 dissolution rate (NCLS vs LCLS and NCHS vs HCHS in Figures 5a and 6). For example, at
513 40 minutes, the average dissolution rate corresponding to the NCLS solution was 47.3%
514 higher than the solution LCLS. Similarly, the solution NCHS (i.e., no Ca^{2+} ions and high
515 salinity) also showed a higher average dissolution rate as compared to the solution HCHS
516 (i.e., $337 \times 10^{-3} \text{ mol dm}^{-3} \text{ Ca}^{2+}$ ions and high salinity). In the past, several studies have shown
517 such inhibitory impact of the Ca^{2+} ions over the calcite dissolution kinetics (Buhmann and
518 Dreybrodt, 1987; Sjöberg and Rickard, 1985).

519 We observed that the dissolution rate of macroporosity at the sample inlet for solution NCHS
520 was approximately 54% less than solution NCLS (refer to Figure 6). Additionally, the mean
521 dissolution rate of macroporosity, calculated over half the sample length, was found to be
522 lower in experiment NCHS compared to NCLS (see Figure 5a). Prior effluent analysis
523 revealed higher outflow Ca^{2+} concentrations in experiment NCHS than in NCLS (Figure 1a).
524 A plausible justification is the conflicting impacts of salinity on the dissolution rate and the

525 solubility of calcite. In saline solutions, the dissolution rate might be hindered, but the
526 solubility of calcite might be enhanced. Consequently, saline solutions, despite exhibiting
527 diminished macroporosity-based dissolution rates near the sample inlet, were able to dissolve
528 more calcite across the entire sample length before reaching equilibrium with calcite. Another
529 possible explanation is that a higher dissolution rate in microporosity regions in the NCHS
530 experiment compared to NCLS experiment is currently not reflected in the calculated
531 dissolution rates.

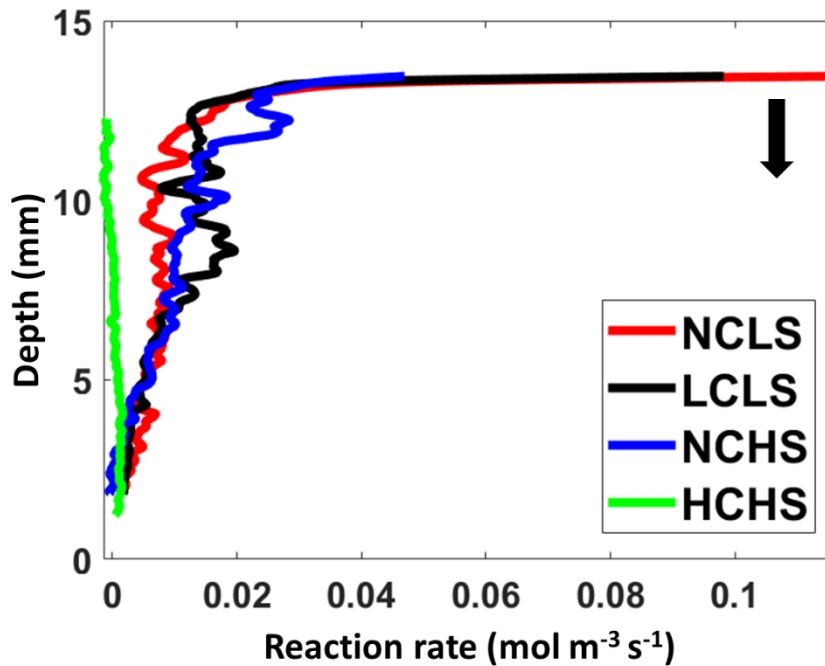
532 The Pe number for all four experiments was greater than one, indicating advection-controlled
533 transport regimes such that the rate of renewal of the fluid inside pore space of the sample
534 was dominated by advection (Figure 5b). For all experiments, the Da number was less than
535 1.0. This suggests that the dissolution conditions in the sample were reaction-limited
536 (Figure 5c) as the time scale of advection is shorter than that of dissolution reaction. As the
537 experiment progressed, we observed a decrease in the Pe number. This is because wormholes
538 are dominantly responsible for porosity changes and average pore size did not increase by the
539 same proportion as porosity increased.

540 For the studied reaction-controlled dissolution regime, this decrease of the Pe number also
541 contributes to a decrement in the average dissolution rate (Figure 5a). This impact of the
542 temporal evolution of the Pe number over the average dissolution rate was much clearer in
543 experiment NCLS compared to LCLS and NCHS experiments.



544

545 **Figure 5: Temporal evolution of (a) the average reaction rate based on Equation 6, (b)**
 546 ***Pe* Number, and (c) *Da* number, calculated from XMT images (circle, cropped sample**
 547 **length and triangle, half sample length).**



548

549 **Figure 6: The full vertical profiles of the slice-averaged dissolution rate for all four**
 550 **experiments calculated using Equation 7. The black arrow indicates the flow direction.**

551 **3.2 Evolution of the dissolution structure**

552 All four experiments were performed with the same injection rate and on samples from the
 553 same rock type with very comparable pore structure (Figure S11). Therefore, as expected, the
 554 reactive strength of the injecting solutions was directly reflected by the *Da* number. The *Da*
 555 number is highest for experiment NCLS, then LCLS, NCHS, and HCHS. Previously, the
 556 control of the *Da* number on the dissolution patterns has been investigated through both
 557 experimental and numerical studies (Fredd and Fogler, 1998; Golfier et al., 2002; Hoefner
 558 and Fogler, 1988; Luquot et al., 2014; Maheshwari et al., 2013). Table 2 provides overview
 559 of the dissolution patterns observed in the previous studies. In the next sections, we discuss
 560 the qualitative and quantitative aspects of the dissolution patterns developed in each
 561 experiment.

Sample rock	Pe	Convective Da	Type of Dissolution	Reference
NaCl Salt grains packed porous media	8.32×10^{-4}	120	Face dissolution	Golfier et.al., 2002
	4.14×10^{-3}	24	Conical wormhole	
	1.66	6.01×10^{-2}	Dominant wormhole	
	83.2	1.2×10^{-3}	Ramified wormhole	
	832	1.2×10^{-14}	Uniform dissolution	
Oolitic grainstone from the Lusitanian Basin	0.2	$0.1-1 \times 10^{-4}$	Dominant wormhole and uniform dissolution	Luquot et.al., 2014
Ketton carbonate rock	9	0.5	Dominant wormhole	Gray et.al., 2018
Ketton carbonate rock	2100	2.8×10^{-5}	Uniform dissolution	Menke et.al., 2015
Ketton carbonate rock	14-19	7.28×10^{-9} - 8.53×10^{-7}	Dominant wormhole – Uniform dissolution	This study

562 **Table 2: Overview of the dissolution pattern observed in the previous studies.**

563 **3.2.1 Dissolution structures in experiments NCLS, LCLS and NCHS**

564 Experiment NCLS was performed with a solution that has low salinity, devoid of Ca^{2+} ions.
565 This injected solution initiated the dissolution with an effective reaction rate of a magnitude
566 of $7 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$ (Figure 5a). Addition of a small amount Ca^{2+} ions (experiment LCLS),
567 lowered initial effective reaction rate to $4 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$ (Figure 5a). In the experiment
568 NCHS, injection of a saline solution that did not contain Ca^{2+} ions, caused a lower dissolution
569 rate than in experiments NCLS and LCLS (Figure 5a and 6).

570 The time-lapse scanning of the pore space allowed a qualitative analysis of the temporal
571 evolution of the dissolution structures in these experiments. In experiment NCLS, it was
572 noted that dissolution was remarkably uniform in the radial direction during the initial 40
573 minutes (Figure 7a), indicating that the initial phase of dissolution was primarily influenced
574 by fluid acidity rather than the sample's initial pore structure (Figure 7a). Such difference
575 between the modified porosity and the initial porosity was also clear in the vertical porosity
576 profiles provided in Figure 4a. The radially homogeneous dissolution occurred in the first
577 $\sim 2\text{mm}$ of the flow path, after which selective dissolution paths continued further along the
578 flow direction (Figure 7a). This development of dissolving channels was most likely guided
579 by the initial heterogeneity and structure of the sample. Conversely, for experiments with
580 lower Da numbers (i.e., LCLS and NCHS the formation of the dissolution structure was more
581 significantly influenced by the heterogeneous pore structure of the sample, as contrasted with
582 experiment NCLS (Figure 7b-c, and 4a). For example, in the experiment LCLS, after 40
583 minutes of acid injection, dissolution created sparsely localized flow channels (Figure 7b).
584 From the scans of the half sample length, we observed that the sample's pore space evolved
585 into several conducting channels. The trajectories and length of these channels were
586 established within a certain experiment duration (i.e., 484 minutes in experiment NCLS, 255
587 minutes in experiment LCLS and 369 minutes in experiment NCHS) while the diameter of
588 channel continued to grow (Figure 7 and S16). From the scan of the full sample, which was

589 acquired at the end of the experiment (i.e., 1200 minutes for the experiments NCLS and
590 LCLS; 720 minutes for the experiment NCHS), we observed that most of these channels did
591 not develop much beyond the half sample length that was scanned during the experiment
592 (Figure 8). In the experiment NCLS, two of the channels extended over the full length of the
593 sample, while in the experiments LCLS and NCHS, only one such dominant channel was
594 formed (Figure 8).

595 Next, through skeleton analysis, we characterized and quantified final form of the dissolution
596 structures in these three experiments (Figure S17; Table S2). The quantification was based on
597 attributes derived from the individual segments of the channels and side branches: the length
598 (sum of the segment length), radius (radius of the segments) and mean radius (average of the
599 segment radius).

600 The evolution of the dissolution structures also indicates that the less reactive injecting
601 solutions (i.e., higher Ca^{2+} and/or salt concentration) resulted in localization of the channels.
602 This was evident from the decreasing number of inlet nodes (where the number of inlet nodes
603 shows unique/main flow channels) with the decreasing Da number (Table S2). All the
604 channels originating from the inlet nodes were divided into three categories based on their
605 lengths (Figures S18-S20; Table S2). Figure S21 shows the histogram of the channel lengths
606 for experiments NCLS, LCLS and NCHS. We observed that in the experiment NCLS, two
607 dominant channels of a length ~ 14 mm were formed. In contrast, in the experiments LCLS
608 and NCHS, only one dominant channel of the length of 12.30 and 10.28 mm, respectively,
609 was formed.

610 The impact of the reactivity of the injected solution on the starting diameter of the channel
611 was also observed (i.e., in the vicinity of the sample inlet). For example, in the experiment
612 NCLS, the starting diameter of two of the category 1 channels was larger than 0.6 mm while,
613 in the experiments LCLS, the starting diameter of both of the category 1 channels was

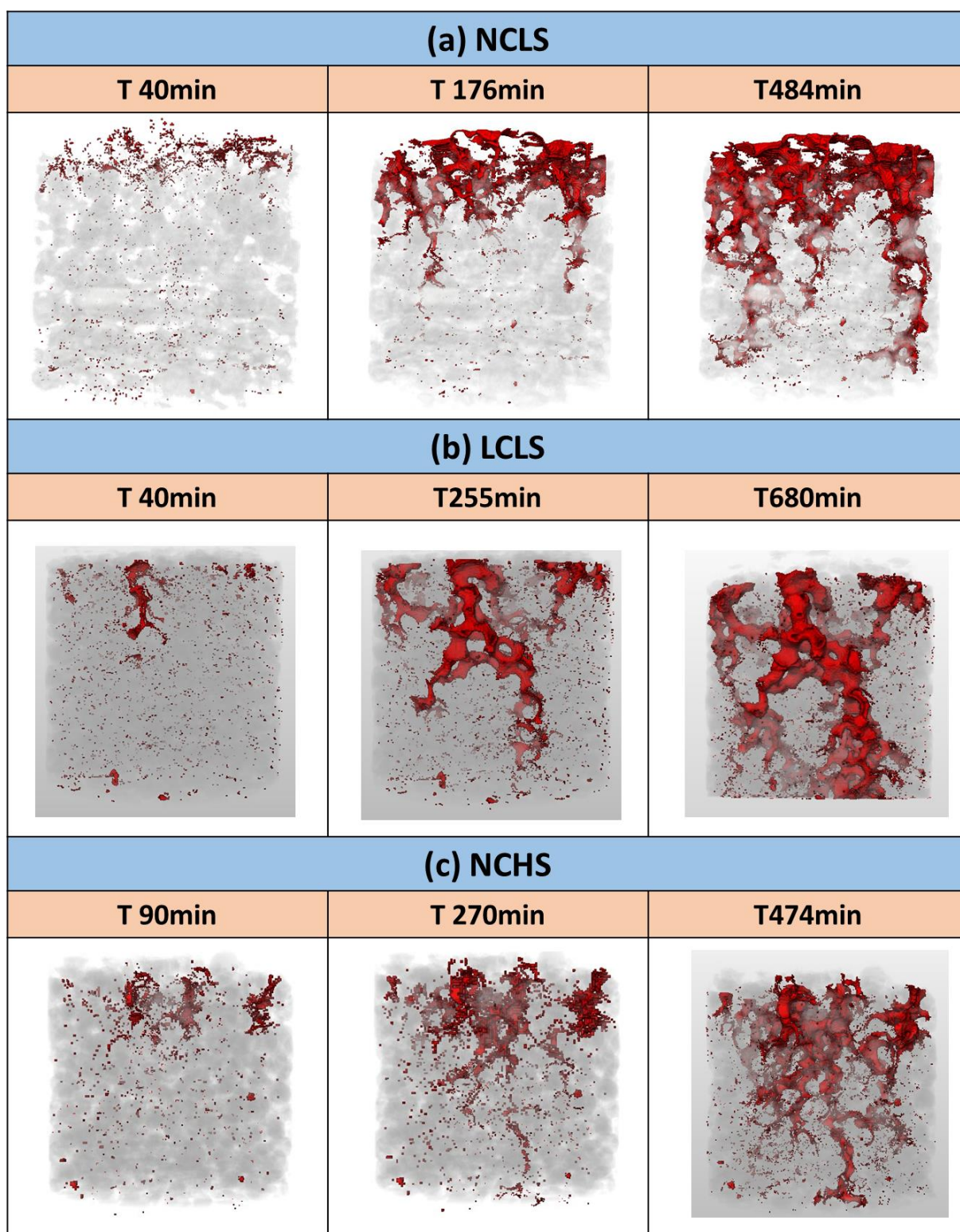
614 smaller than 0.4 mm (Figure S22a and b). Moreover, the Da number also represents the
615 buffering of fluid as it moves along the sample (Agrawal et al., 2020). This is reflected in the
616 vertical radius profile (i.e., in the direction of flow) of the channels. In the experiments LCLS
617 and NCHS, the vertical radius profiles of the category 1 channels were more homogeneous
618 than the experiment NCLS (Figure S22).

619 Furthermore, in the experiment LCLS, for each category 1 channel, the number of side
620 branches and the length of the side branches were significantly higher than the experiment
621 NCLS (Table S2, Figure S23a-b and S24a-b). The increased ramification of dissolution
622 channels with decreasing Da number has also been observed by Luquot et al. (2014). On the
623 contrary, the dissolution pattern in the experiment NCHS developed with the least amount of
624 ramification as evident from the least number of end nodes (Table S2, Figure S23c).

625

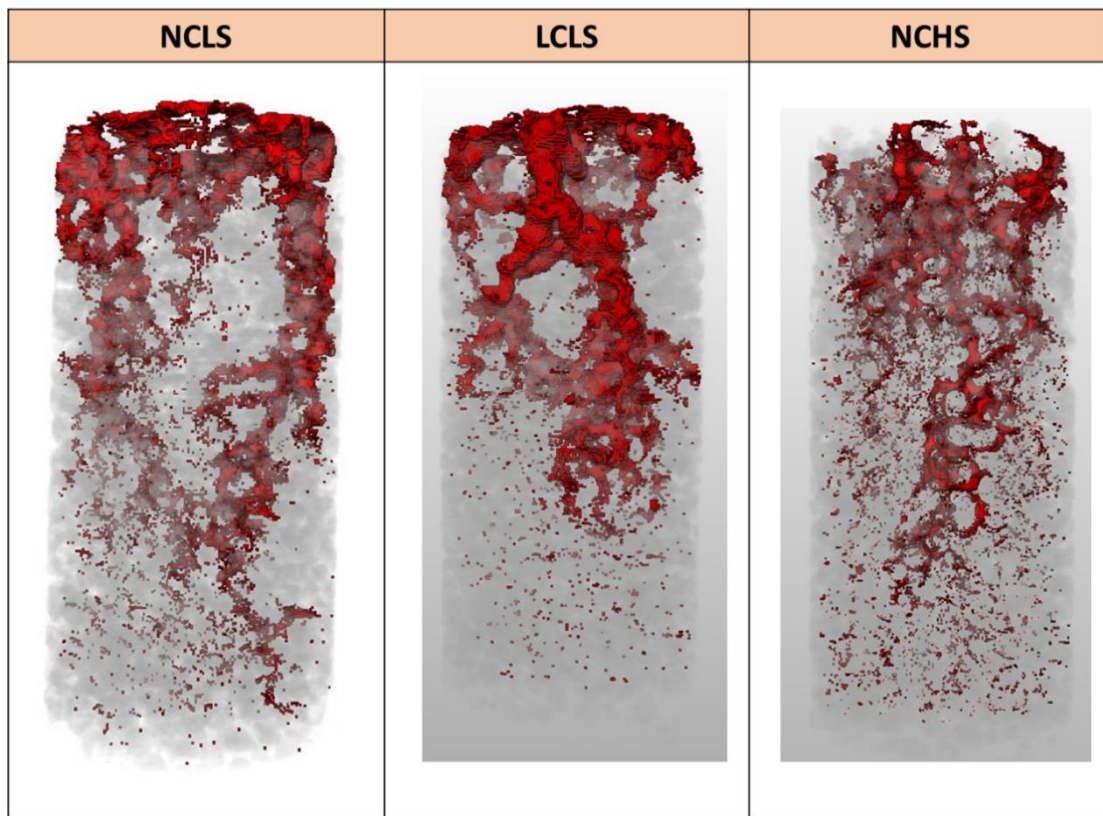
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627



628

629 **Figure 7: Temporal evolution of the dissolution patterns in experiment (a) NCLS, (b)**
 630 **LCLS and (c) NCHS. XMT images of these samples at the remaining time steps are**
 631 **shown in Figure S16.**



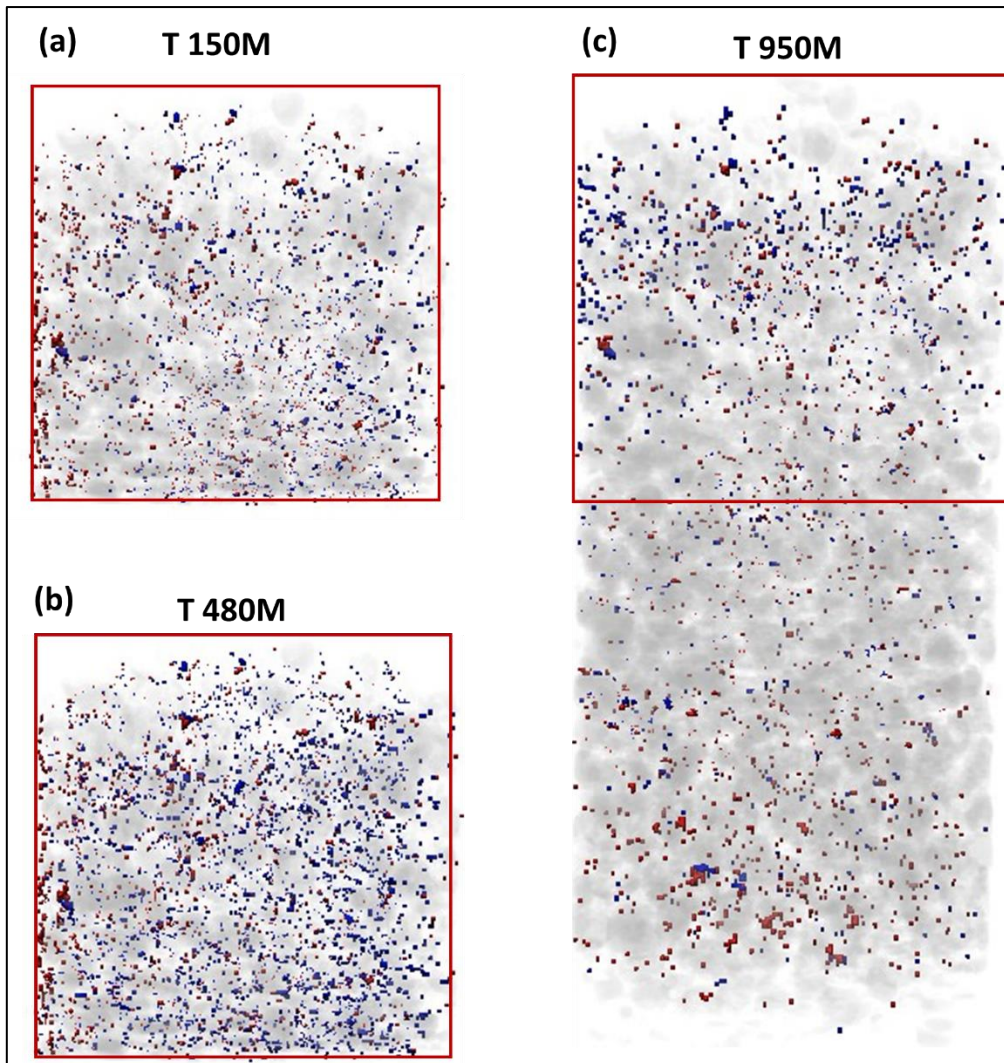
632

633 **Figure 8: Final form of the dissolution patterns in experiments NCLS, LCLS and**
 634 **NCHS. Note that the duration of experiments NCLS, LCLS and NCHS was 1200, 1200**
 635 **and 720 minutes.**

636 3.2.2 Experiment HCHS

637 We observed that the presence of a high amount of Ca^{2+} ions lowered the effective
 638 dissolution rate by two orders of magnitude compared to experiment NCHS (Figure 5a). As
 639 mentioned earlier, the macroporosity of the top part of the sample decreased throughout this
 640 experiment (Figure 3b and 4). Figure 9 presents the temporal evolution of the pore space
 641 where the locations of removed solid mass and of added solid mass are highlighted. As
 642 explained earlier, the injected HCHS was acidic and undersaturated with respect to the calcite
 643 and mixing calculations (performed in PHREEQC with default Pitzer database) showed that
 644 it is unlikely that mixing variable amounts of the HCHS solution with the equilibrated initial
 645 solution present in the sample can result in a composition that is supersaturated with respect

646 to calcite. A possible explanation of the accumulated solid mass in the pore space is related to
647 the dissolution of the microporous matrix, causing solid particles to detach from the matrix
648 and migrate through the pore space. This is described by the so-called sugar lump model
649 (Luquot et. al., 2014). From the XMT image after 150 minutes of acid injection, we observed
650 that small amounts of such displaced particles were uniformly distributed in the pore space
651 (blue in Figure 9). Dissolution of the microporous matrix was confirmed by grey value
652 analysis of the images (Figure S14; semi quantitative), which showed an increase in the sum
653 of microporosity and macroporosity. From the scan of the full sample at the end of the
654 experiment (Figure 9c), we observed that the amount of clogging by displaced solid particles
655 was higher closer to the inlet. This is consistent with most of the dissolution occurring closer
656 to the inlet, also in the microporous domain, leading to more detachment and local
657 displacement of particles. Alternatively, use of the default Pitzer model in PHREEQC for the
658 calculation of the solution chemistry might have led to an overestimation of the
659 undersaturation state of the inflow solution (Harvie and Weare, 1984; Felmy and Weare,
660 1986) and locally calcite supersaturation may have occurred, leading to the observed pore
661 clogging.



662

663 **Figure 9: Temporal evolution of the pore space in the experiment HCHS. Red colour**
 664 **highlights the locations from where the solid mass was removed. Blue colour highlights**
 665 **the locations where the solid mass was added. XMT images of this sample at other time**
 666 **steps are shown in Figure S25. Note that red coloured box shown in plot (c) indicates the**
 667 **volume imaged in plots (a) and (b).**

668 **3.3 Evolution of transport properties**

669 Dissolution patterns control permeability changes in the sample, which is related to the
 670 volume of acid injection required for wormhole breakthrough (PV_{BT}). One of the earlier
 671 definitions of wormhole breakthrough is when the permeability of the sample increases by a

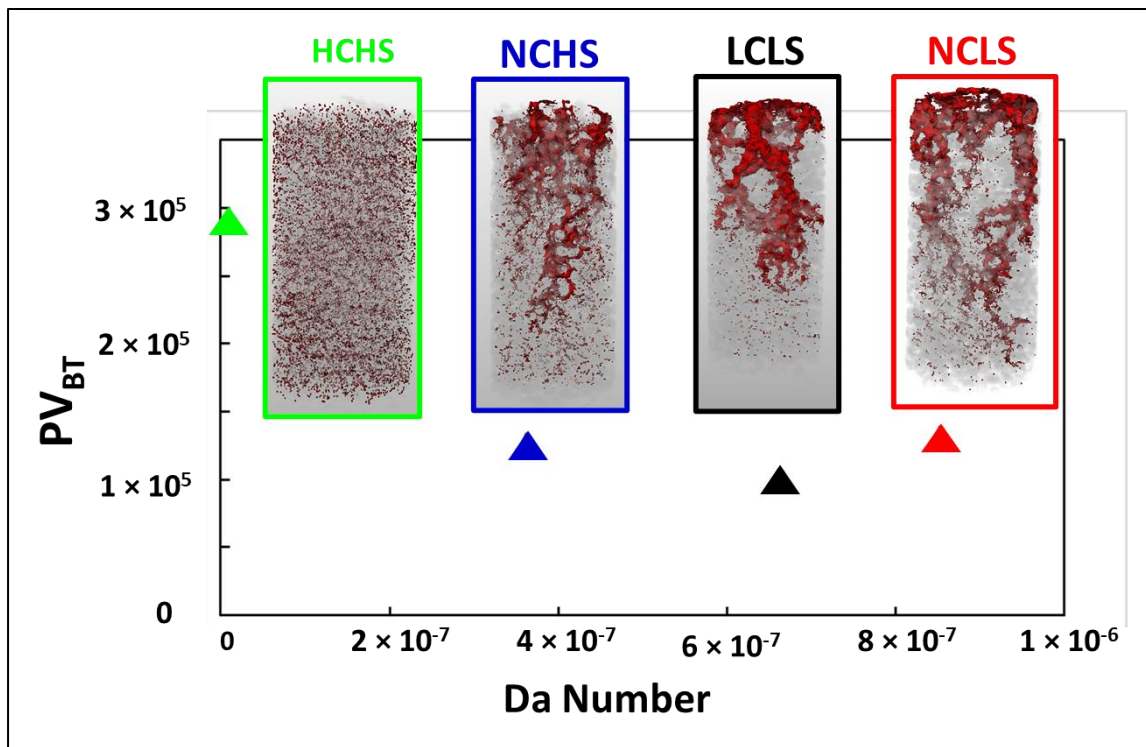
672 factor of 100 (Fredd and Fogler, 1998). The amount of acid required for a breakthrough is a
673 function of the dissolution pattern, and therefore depends on Pe and Da numbers, which
674 reflect the injection rate and the solution's corrosive nature (i.e., chemical reactivity, in the
675 current case determined by salinity and calcium concentration). For example, face dissolution
676 will require higher volumes of acid to attain a certain permeability increment than
677 wormholes.

678 Figure S26 shows the temporal evolution of permeability calculated from both the pore
679 network model and direct numerical simulation during all four experiments. For all
680 experiments, both methods yielded a similar amount of permeability change - i.e., a
681 noticeable permeability increment in the experiments NCLS, LCLS, and NCHS, and no
682 significant permeability change in experiment HCHS.

683 If we consider the definition of breakthrough from Fredd and Fogler (1998), none of the
684 experiments in this study led to a breakthrough point (Figure S27). The highest permeability
685 increment corresponding to a factor of 7.9 and 5.8 was noted for experiment LCLS based on
686 permeability values from the pore network model and direct numerical simulations,
687 respectively. We observed that the injection of the same number of pore volumes resulted in
688 the highest permeability increment for experiment LCLS and lowest for experiment HCHS
689 (Figure S27). This indicates that the dissolution pattern formed in experiment LCLS is
690 optimal, just as the Da number of this experiment is ideal among all four experiments.

691 The volume of acid required for a breakthrough was calculated through the extrapolation of
692 the direct numerical simulation-based permeability response curve as shown in Figure S27.
693 Figure 10 shows the distribution of PV_{BT} as a function of Da number. As expected for
694 experiment LCLS, the lowest amount of pore volumes was required to achieve an increase in
695 permeability by a factor of 100. This suggests that the increasing amount of salinity and Ca^{2+}

696 concentration of the injecting solution results in an increase in the number of acid pore
 697 volumes required for changing the permeability.



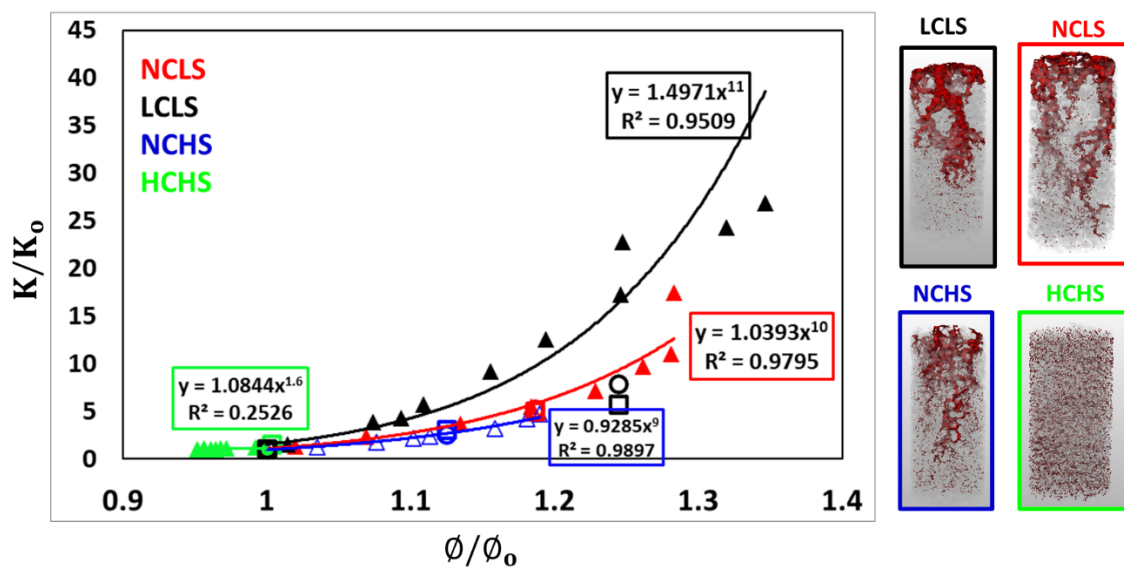
698

699 **Figure 10: The expected number of pore volumes to obtain a full breakthrough curve at**
 700 **different Da number. Note that direct numerical simulation permeability, k_{DNS} , was**
 701 **used for the calculation of PV_{BT} .**

702 Figure 11 shows the changes in permeability as a function of porosity for all four
 703 experiments. In the past, several experimental and modelling studies have used the simplified
 704 version of Kozeny -Carman relation i.e., a power-law relation as $k \sim \phi^n$, to relate the
 705 permeability changes with the evolving porosity of the sample (e.g. Bernabé et al., 2003;
 706 Luquot et al., 2014; Luquot and Gouze, 2009; Nogues et al., 2013; Pereira Nunes et al.,
 707 2016). The exponent n is a function of the initial porous medium properties and the
 708 processes which cause the changes in the pore structure. A higher value of n results in higher
 709 permeability change with small porosity changes. In the past, a number of experimental
 710 studies have reported a range of values for exponent n , corresponding to the dissolution

711 pattern developed in different types of carbonate rocks (e.g., Menke et.al., 2015; Luquot and
712 Gouze, 2009; Luquot et.al., 2014). For example, for a uniformly dissolving Ketton carbonate,
713 Menke et.al. (2015) obtained a value of 5.16 while Luquot and co-workers (2009, 2014)
714 found values of 0.29 and 0.32 corresponding to the development of homogeneous dissolution
715 pattern in Oolitic Limestone. To calculate the exponent, we used half sample length-based
716 porosity and permeability values instead of cropped sample length. This is because, for curve
717 fitting, we had multiple data points from the half sample length while only two data points
718 from the cropped sample length. We obtained the lowest value of n corresponding to the
719 uniform dissolution patterns in the experiment HCHS (Figure 10). For the variety of
720 wormholes formed in the other three experiments, we noted that the value of exponent n lies
721 between 9 and 11 (Figure 11). Luquot et.al. (2014) also obtained a high value of $n = 7.07$
722 corresponding to the formation of dominant wormholes. Since the initial porous medium
723 structures for the various experiments presented here was similar (Figure S11), this wide
724 range of n values noted in this study most likely reflects the composition of the injected
725 solution, and therefore Da number. Additionally, for all experiments except LCLS, we
726 observed an alignment in the porosity-permeability trend from half sample length and
727 cropped sample length datasets. In the case of experiment LCLS, porosity-permeability
728 changes in cropped sample length indicate a lower exponent compared to in the half sample
729 length. This is due to the initial heterogeneity of sample K2 along the flow direction as also
730 indicated by the difference in the macroporosity values at $t=0$ (Figure 3b). It cannot be ruled
731 out completely that subtle differences in the initial pore structure of different samples
732 affected the distinct pore structures that evolved during the dissolution experiment.
733 Nevertheless, our results strongly suggest that lower dissolution rates at the sample inlet
734 (experiment LCLS) favor the rapid formation of localized channels compared to solutions
735 with a higher reactivity (experiment NCLS). It can therefore be concluded that adjusting the

736 chemistry of the injecting fluid creates an interplay between reaction and transport time
 737 scales that guide a dissolving porous medium to evolve into different pore structure. This
 738 suggests that precaution should be taken in the generalization of a single porosity-
 739 permeability model for a range of reservoirs containing formation water of different
 740 salinities. Potentially, the impact of Ca^{2+} concentration and salinity can be implemented in
 741 the derivation of porosity-permeability models to improve their predictability.



742

743 **Figure 11: Permeability-porosity relationships for the four experiments. Circle and**
 744 **triangle markers show PNM results for pore network extracted from cropped sample**
 745 **length XMT images and half sample length XMT images, respectively. Square markers**
 746 **show DNS results for the cropped sample length XMT images. Note that the porosity-**
 747 **permeability relationship is obtained by fitting a power-law curve in the PNM based**
 748 **permeabilities of half sample length datasets.**

749 Conclusions

750 In this study, we employed time-lapse imaging to explore the dissolution of Ketton limestone
 751 across four samples under uniform flow conditions but varying reactive conditions, imposed
 752 by the composition of injected brine. The imaging highlighted the different stages in the

753 evolution of dissolution patterns, governed by the Da number—subsequently influenced by
754 salt concentration. XMT scans at sequential time steps showed the constant interplay between
755 changing porosity and permeability of the samples and the evolution of flow patterns and
756 average reaction rates.

757 Our observations highlighted the profound influence of brine composition on alterations in
758 porosity and permeability. The concentration of calcium ions and sodium chloride in the
759 injecting solution emerged as determinants of the calcite dissolution rate, both displaying
760 substantial inhibitory effects. Solutions with minimal salinity and no calcium ions resulted in
761 the most effective calcite dissolution rate, with predominant dissolution near the sample inlet
762 and relatively less along the flow path, creating wormholes with vertically diverse radius
763 profiles. In contrast, solutions with low calcium concentration led to the formation of
764 selective dissolution paths, yielding more uniformly structured wormholes with extensive
765 ramifications. High salt and calcium concentrations significantly decreased dissolution rates,
766 with minimal and uniformly distributed dissolution mainly within the micropore space.

767 In essence, elevated levels of salt and Ca^{2+} ions induced a reaction-limited dissolution regime,
768 maintaining the solution's corrosive properties over extensive penetration depths, resulting in
769 homogeneous dissolution. Conversely, reducing salt and Ca^{2+} concentrations shifted the
770 system towards a transport-dominated dissolution regime, leading to non-uniform dissolution,
771 as the formation of wormholes became evident due to the positive feedback between
772 increased permeability and heightened mass transfer rates (Golfier et.al., 2002).

773 The obtained range of Kozeny-Carman exponents, reflecting the relationship between rock
774 permeability and porosity evolution, was broad, attributed to the variability in the
775 corrosiveness of the injected solutions. To summarize, diverse combinations of salinity and
776 Ca^{2+} concentrations in the injected solution could alter dissolution from a disseminated and

777 microporous regime to a wormhole regime, resulting in variations in the porosity-
778 permeability relationship. It is important to acknowledge the limitations in this study, such as
779 the absence of lab measurements of porosity and permeability data, leading to uncertainties in
780 quantifying initial pore structures. Addressing these constraints through extended
781 experimental or modelling methodologies will pave the way for enhanced insights in this
782 research direction.

783 **Declaration of competing interest**

784 The authors declare that they have no known competing financial interests or personal
785 relationships that could have appeared to influence the work reported in this paper.

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799 **SUPPORTING INFORMATION AVAILABLE**

800 Additional details on experiment methods and presented results, tables 1-2 and figures 1-27.

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