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Role of mineralogical, structural and hydrodynamic rock properties in conduits formation in three distinct carbonate rock types

M. Leger, L. Luquot and D. Roubinet

Abstract

Adopting sustainable strategies to manage water resources of karst reservoirs requires to understand the carbonate rock reactivity that is responsible for the formation of these reservoirs, as well as the role of the rock mineralogy in the conduit formation. To this end, three carbonate rocks (chalk, crinoidal limestone and dolomite) with different mineralogy and internal structure are submitted to laboratory dissolution experiments by injecting an acid solution under atmospheric conditions and various hydrodynamic conditions with a homemade experimental device. The core samples are characterized by petrophysical investigations with laboratory and imagery techniques before and after the experiments, and the changes in chemical and hydraulic properties are recorded during the experiment. The resulting carbonate dissolution leads to the formation of preferential conduits and the increase in porosity and permeability of the samples. For the three rock types, the dissolution rate mainly depends on the mineral composition, the flow conditions and the initial structural properties. In addition, we observe that (i) for each rock type, the lower Péclet conditions applied to the samples, the lower global dissolu-

tion rate, (ii) for each hydrodynamic condition, chalk and crinoidal limestone have the highest and smallest dissolution rates, respectively, (iii) for a similar amount of injected acid, the dissolution is lower in dolomite than in calcite, and (iv) high rock heterogeneities in the chalk samples are responsible for high renewal rates that induce high dissolution rates.

Keywords

Carbonate rock, Reactive transport, Dissolution rate, Micro-tomography, Karst, Wormholes

1. Introduction

The reactivity of carbonate rocks in natural or anthropogenic environment is a well-known fact in the scientific community. Nevertheless, there are still a lot of questions about this reaction process whereas its understanding is particularly essential as carbonate rocks reservoirs play an important role in human development. They are often used for water, oil or gas extraction, as well as for geothermal energy production or CO₂ sequestration (Rege and Fogler, 1989; Chilingarian et al., 1992; Noiriél et al., 2005; Moore and Wade, 2013; Akono et al., 2019).

Carbonate rocks display very heterogeneous media due to their high mineralogy variety and the high complexity of their structural properties over scales (Choquette and Pray, 1970; Lucia, 1983; Lønøy, 2006). A thermodynamic disequilibrium between a fluid and this medium is responsible for dissolution and karst formation for instance (Ford and Williams, 2007). In order to better understand dissolution processes inside carbonate rocks, laboratory experiments and numerical simulations are conducted under variable

17 conditions on different carbonate rock types. The two adimensional numbers
 18 Péclet (Pe) and Damköhler (Da) are generally used to link the initial con-
 19 ditions of experiments and the resulting dissolution patterns inside the rock
 20 (Golfier et al., 2002). The Péclet number defines the dominant mechanism,
 21 between advection and diffusion, for transport processes occurring inside the
 22 rock, whereas the Damköhler number characterizes the importance of this
 23 transport compared to reaction (Lasaga, 1984; de Marsily, 1986; Daccord
 24 et al., 1993). They are both dependent on the velocity at which the re-
 25 active fluid passes through the system, and on the characteristic length of
 26 it. Different experimental conditions are then related to different dissolu-
 27 tion patterns, going from uniform dissolution to compact wormholes. The
 28 properties of the fluid injected inside the rock are shown as the most decisive
 29 factors in the development of dissolution regimes in a lot of experimental and
 30 numerical studies (Fredd and Fogler, 1998; Golfier et al., 2002; Noiriél et al.,
 31 2004; Luquot and Gouze, 2009; Smith et al., 2013; Vialle et al., 2014; Menke
 32 et al., 2015; Rohmer et al., 2016; Lebedev et al., 2017; Akono et al., 2019). In
 33 order to better understand the impact of the dissolution process on the rock,
 34 laboratory dissolution experiments are usually conducted on samples where
 35 the rock properties were initially characterized by laboratory measurements
 36 and/or from 3D-images calculations. Acidic fluid is then injected at various
 37 concentrations and flow rates in the samples. The evolution of rock proper-
 38 ties, such as porosity, permeability, structural and mechanical properties, is
 39 monitored during the experiments. The effects of dissolution on limestone at
 40 room and reservoir conditions were studied (Fredd and Fogler, 1998; Noiriél
 41 et al., 2004; Luquot and Gouze, 2009; Noiriél et al., 2009; Vialle and Vanorio,

2011; Gharbi et al., 2013; Mangane et al., 2013; Vialle et al., 2014; Steefel et al., 2015; Lebedev et al., 2017; Akono et al., 2019), as well as the ones on dolomite, preferentially at reservoir conditions (Smith et al., 2013; Luhmann et al., 2014; Tutolo et al., 2014; Wang et al., 2021). Few studies analyze the role of the rock mineralogy or the initial internal rock structure, or concentrate on more complex rocks with pluri-minerals rock composition. Some studies showed that a heterogeneous pore size or pore shape distribution will affect the dissolution mechanisms and lead to different dissolution patterns inside the rock (Hoefner and Fogler, 1988; Noiriél et al., 2005; Vialle et al., 2013; Luquot et al., 2014; Wang et al., 2021). Others defined new dissolution patterns associated with internal rock structure (Menke et al., 2017). Recently, we demonstrated that local heterogeneities have a stronger control on dissolution localization than Pe and Da conditions (Leger et al., 2022). At large scale, large structural heterogeneities such as fractures impact the dissolution rate and shape since the dissolution preferentially takes place along these large heterogeneities, leading to dissolution mechanisms controlled by transport (Elkhoury et al., 2013; Garcia-Rios et al., 2017).

By studying dissolution patterns on different carbonate types in similar conditions, some studies partially tried to establish the role of local structural properties and mineral composition compared to flow and chemical boundary conditions. Sandstone and limestone show specific responses to dissolution (Rohmer et al., 2016). Silicates inside sandstone favoring dissolution due to non-reactive grains inside silicates, which leads to a larger reaction surface and then a higher dissolution rate and a more homogeneous dissolution (Garcia-Rios et al., 2017). Additionally, structural properties inside these

67 two rock types are responsible for different dissolution patterns at local scale
68 inside the studied samples (Vialle et al., 2013). It has been demonstrated
69 that textural differences inside various fractured limestone rock types influ-
70 ence dissolution patterns but do not have a significant impact on dissolution
71 rates (Levenson et al., 2015). These studies do not allow seeing the impact
72 of mineralogy differences in the dissolution of carbonate rock types.

73 In order to acquire further insights on this matter, the present study pre-
74 dominantly focuses on the differences in dissolution patterns depending on
75 the mineralogy and on the structure of different carbonate rock types, as
76 well as on the experimental hydrodynamic conditions. To this end, three
77 distinct carbonate rock types are selected for their differences in structure
78 and mineralogy: chalk, crinoidal limestone and dolomite. Acid injections
79 are conducted on samples cored from these three rock types at atmospheric
80 conditions. With the same acidic fluid, four Péclet conditions, associated to
81 different flow rates depending on the rock type, were applied to the samples
82 with a homemade experimental device. Samples are characterized with labo-
83 ratory and images methods before and after these experiments, during which
84 chemical and hydraulic properties are recorded. The rock properties evolu-
85 tion, associated with the initial structural and mineral differences between
86 the three rock types and the experimental conditions, is analyzed in order
87 to determine the influence of each of these parameters on the dissolution
88 patterns induced by the acid injection into the rocks. The discussion of this
89 study will focus on the role of initial properties until the conduits formation.

2. Materials and Methods

The studied rock samples and the full experimental protocol used here are presented in details in Leger and Luquot (2021) and Leger et al. (2022), and the key parts of the experimental protocol are reminded in Supplementary Material. In this section, basic information are provided in order to understand the methodology and the obtained results.

2.1. Rock properties and characterization

The eleven cores samples studied are part of three different carbonate types. They were cored in three rock blocks in the same orientation in cores of 20-30 mm length and 18 mm diameter, surrounded with epoxy resin and PVC pipe for a total diameter of 25 mm, i.e., one inch. Four samples come from a chalk cave near Le Havre, Normandie, north-western France, and are characterized by flint chalk from the lower Senonian. This group of samples is named *Normandie* and the samples labels are N03, N05, N08 and N09. A set of five samples was cored into a limestone block from Euville quarry near Nancy, north-eastern France, and is defined as crinoidal limestone from the Oxfordian. It is called *Euville* and the cores are named E01, E02, E04, E05 and E08. The two last samples were cored in the Lexos quarry near Toulouse, south-western France, described as a reddish recrystallized limestone from the Bajocian lately dolomitized. The set of samples is named *Lexos* with samples L01 and L04.

X-ray Diffraction (XRD) on a Bruker D8 Discover, X-ray Fluorescence (XRF) measurements and Scanning Electron Microscopy (SEM) on a FEI Quanta 200 FEG observations show that Normandie and Euville rocks are fully composed of calcite (CaCO_3), whereas Lexos is made up of dolomite

115 $(\text{CaMg}(\text{CO}_3)_2)$. The dolomite formula is determined using the Ca and Mg
 116 outlet concentrations during the percolation experiments assuming that the
 117 dissolution is stoichiometric and no precipitation reaction occurs from the
 118 dissolution. For the two experiments on dolomite, constant $\frac{Ca}{Mg}$ ratio is ob-
 119 served at the outlet and the dolomite formula is established to be $\text{Ca}_{1.06}\text{Mg}_{0.94}(\text{CO}_3)_2$.
 120 Scanning Electron Microscopy (SEM) and 3D X-ray micro-tomography (XRMT)
 121 display images where structural differences between the three rocks are shown,
 122 especially in pores size and shape. As it can be seen in Figure 1, Euville dis-
 123 plays the largest pores followed by Lexos and then Normandie.

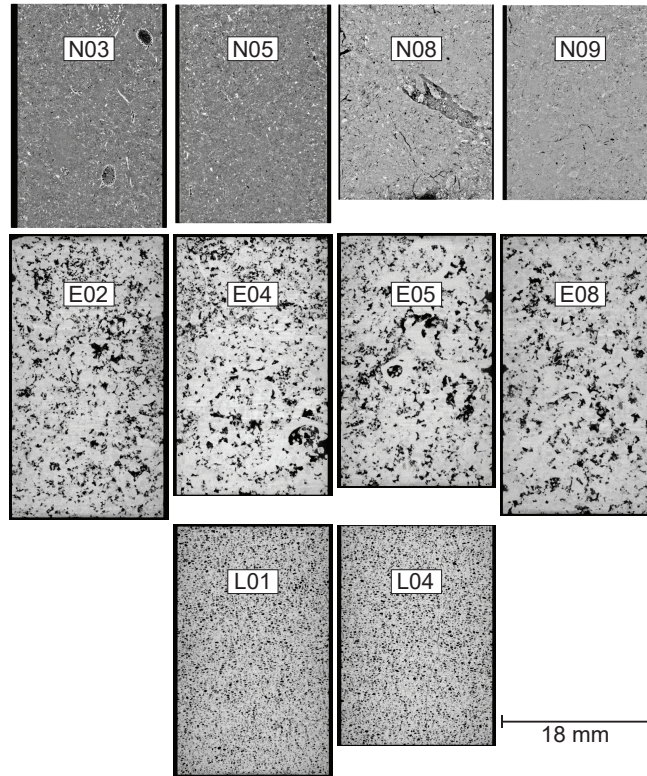


Figure 1: 2D vertical slices from 3D X-ray micro-tomography (XRMT) images of the initial structure of all the samples from the three rock types.

124 To characterize the cores samples, petrophysical measurements were done
 125 by non-destructive laboratory methods. Porosity, permeability and velocities
 126 of P and S waves are carried out on dry and/or saturated samples. Current
 127 injection inside the saturated samples gives the rock conductivity and allows
 128 to calculate structural properties from Archie’s law (Archie, 1942), such as
 129 the formation factor F , cementation index m and electrical tortuosity τ_e .
 130 Characterization of pore size distribution between 0.5 and 140 μm is carried
 131 out by centrifugation. XRMT images are collected with a pixel size of 12 μm
 132 and are analyzed with a homemade software to obtain complementary infor-
 133 mation about the samples. The properties calculated from the 3D images
 134 are porosity, permeability, hydraulic tortuosity τ_h and relative pores size $\frac{S}{V}$.
 135 A pore size distribution is also obtained from a probabilistic method display-
 136 ing chord lengths. Details on rock types, calculation methods and protocols,
 137 complete results and discussion on the samples properties are provided in
 138 Leger and Luquot (2021).

139 *2.2. Experimental protocol*

140 The experimental protocol described here is the same as the one used
 141 in Leger et al. (2022). Under atmospheric pressure and temperature condi-
 142 tions, acidic solution is injected through the samples. The injected solution
 143 is composed of water previously balanced with the different rock types, acetic
 144 acid CH_3COOH and sodium acetate CH_3COONa . The acid concentration
 145 is about 10^{-2} mol/L with a pH of 4. Figure 2 displays the homemade ex-
 146 perimental device used for the percolation experiments. The acid solution is
 147 stored in a beaker where conductivity and pH are monitored continuously,
 148 and is injected through the core sample by a peristaltic pump. Sensors of

149 absolute and differential pressure continuously record the pressure difference
 150 between the sample inlet and outlet. At the device outlet, samplings of 5 mL
 151 are continuously carried out during day time and punctually during night
 152 time. pH, conductivity and cation concentrations are measured for each
 153 sampled fluid.

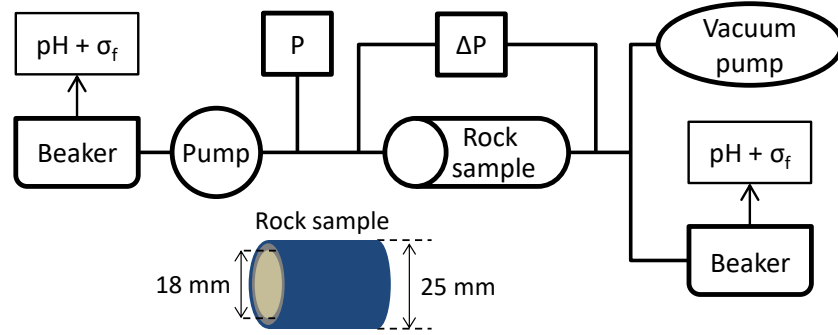


Figure 2: Top: Homemade experimental device used for the percolation experiments, with P the absolute pressure sensor and ΔP the differential pressure sensor. Bottom: Scheme of the cylindrical core rock sample fixed inside a PVC tube.

154 The aim of this study being to compare the behavior of three different
 155 rock types during percolation experiments, similar experimental conditions
 156 are applied to the samples from the different rock types. In order to evaluate
 157 the impact of the hydraulic conditions, four Péclet numbers (Pe_1 , Pe_2 , Pe_3
 158 and Pe_4) are chosen and the corresponding flow rates are applied to the
 159 samples. Pe is defined as $Pe = \frac{ul}{d}$ with u the flow velocity injected in
 160 each sample [m/s], l the characteristic length of the pores [m] and d the
 161 molecular diffusion coefficient for fresh water at 25°C set to 5×10^{-9} m²/s.
 162 The characteristic length l is based on the pore size distribution calculated
 163 in Leger and Luquot (2021) and is displayed in ranges that depend on the
 164 considered rock type. Therefore, average Pe values for each rock type are

165 resulting from these l ranges, and the average values between the three rock
 166 types are considered to simplify the description. Péclet numbers stand as
 167 $Pe_1 = 0.09$, $Pe_2 = 0.65$, $Pe_3 = 1.97$ and $Pe_4 = 5.26$.

168 The experimental conditions and the associated samples are summarized
 169 in Table 1. Note that the experiments conducted on the Normandie samples
 170 come from Leger et al. (2022). Reproduction experiments are conducted for
 171 Normandie and Euville with similar conditions for N03 and N08 on one side,
 172 and E01 and E02 on the other side. To simplify the results interpretation,
 173 the experiments conducted with the hydraulic conditions Pe_3 and Pe_4 will
 174 be discussed together in Sections 3 and 4.

Pe	Normandie		Euville		Lexos	
	Sample	Q	Sample	Q	Sample	Q
Pe_1	N09	8.0e-10	E08	9.3e-11		
Pe_2	N03 & N08	7.0e-9	E01 & E02	5.0e-10	L01	3.2e-9
Pe_3	N05	1.8e-8	E05	2.5e-9	L04	7.6e-9
Pe_4			E04	6.0e-9		

Table 1: Experimental transport conditions, Péclet numbers Pe [-] and flow rates Q [m^3/s], of the percolation experiments.

175 2.3. Experimental output

176 The measurement of pressure difference allows to calculate the evolution
 177 of the samples permeability k during the experiment using the Darcy law:

$$k = \frac{QL\mu}{A\Delta P}, \quad (1)$$

178 where Q is the flow rate [m^3/s], L the sample length [m], μ the dynamic
 179 viscosity of water [Pa.s] set to 0.001 Pa.s, A the surface of fluid injection [m^2]

180 and ΔP the differential pressure between the inlet and outlet of the sample
 181 [Pa].

182 Concentration of Ca ions for the three rock types and that of Mg for Lexos
 183 rock are measured by ICP-AES (Inductively Coupled Plasma Atomic Emis-
 184 sion Spectroscopy, Cirad, Montpellier) in the outlet samplings collected at
 185 time t_i ($i = 1, \dots, N$) with N the number of samples. The porosity is deduced
 186 from these concentrations based on the equivalence between the quantity
 187 of Ca or Ca Mg collected in the outlet fluid samples and the quantity of
 188 dissolved calcite or dolomite from the rocks, respectively. The calcium car-
 189 bonate mass dissolved between times t_{i-1} and t_i , $m_{\text{CaCO}_3 t_i}$, is then expressed
 190 as

$$m_{\text{CaCO}_3 t_i} = \frac{([\text{Ca}]_{t_i} - [\text{Ca}]_{t_0})(t_i - t_{i-1})Q}{M_{\text{Ca}}} M_{\text{CaCO}_3} \quad (2)$$

191 with $[\text{Ca}]_{t_i}$ the calcium concentration at the sampling time t_i [g/m³], $[\text{Ca}]_{t_0}$
 192 the initial calcium concentration [g/m³], $t_i - t_{i-1}$ the time spent since the
 193 last sampling [s], Q the flow rate [m³/s], and M_{Ca} and M_{CaCO_3} the molecular
 194 masses of calcium and calcium carbonate, respectively [g/mol]. Concerning
 195 the dolomite rock type, the proportion of the mass of Ca and Mg from
 196 the dolomite formula $\text{Ca}_{1.06}\text{Mg}_{0.94}(\text{CO}_3)_2$ allows to calculate $m_{\text{CaMg}(\text{CO}_3)_2 t_i}$.
 197 The equivalent volume of dissolved calcite and dolomite in the rock sample
 198 between each sampling step, V_{t_i} , is calculated by dividing m_{t_i} by the density
 199 of calcite and dolomite. Finally, the porosity ϕ_{t_i} is obtained from

$$\phi_{t_i} = \phi_{t_{i-1}} + \frac{V_{t_i}}{V_{ech}} \quad (3)$$

200 with V_{ech} the sample volume [m³]. The initialization of the previous equation

for $t = 0$ is made by using the initial laboratory porosity ϕ_L while the final value at the end of the experiment is labeled ϕ_{ch} .

After dissolution, in order to estimate the impact of the experiments on the rock properties, the same laboratory and imaging characterization as before the experiments is conducted on the samples (Section 2.1). To this purpose, centrifugation is conducted in the direction of the pressure difference and in the opposite one, which allows to characterize a possible anisotropy in pore size distribution.

3. Results

3.1. Hydro-chemical results from percolation experiments

Chemical data obtained over time for all the percolation experiments are displayed in Figure 3. In a general way, we observe that the outlet pH values (pH_{out}), fluid conductivities (σ_f) and Ca and Mg concentrations ($[\text{Ca}]$ and $[\text{Mg}]$) are higher than the inlet values. The increase in these values indicates that calcite and dolomite dissolution is occurring during the experiments. The curve shapes are globally the same for each parameter, with a first point corresponding to the mixing between water at equilibrium with rock and acidic fluid, a plateau reached when the dissolution begins and then a decrease more or less pronounced at different times depending on the samples. We observe that the decrease in the parameters occurs much sooner for the samples from Normandie than for the samples from Euville and Lexos, whatever the Péclet condition applied.

Even if the curves shape are similar, several observations can be done. The values reached on the plateau for pH, conductivity and Ca and Mg concentrations depend on the rock types and on the Péclet number applied.

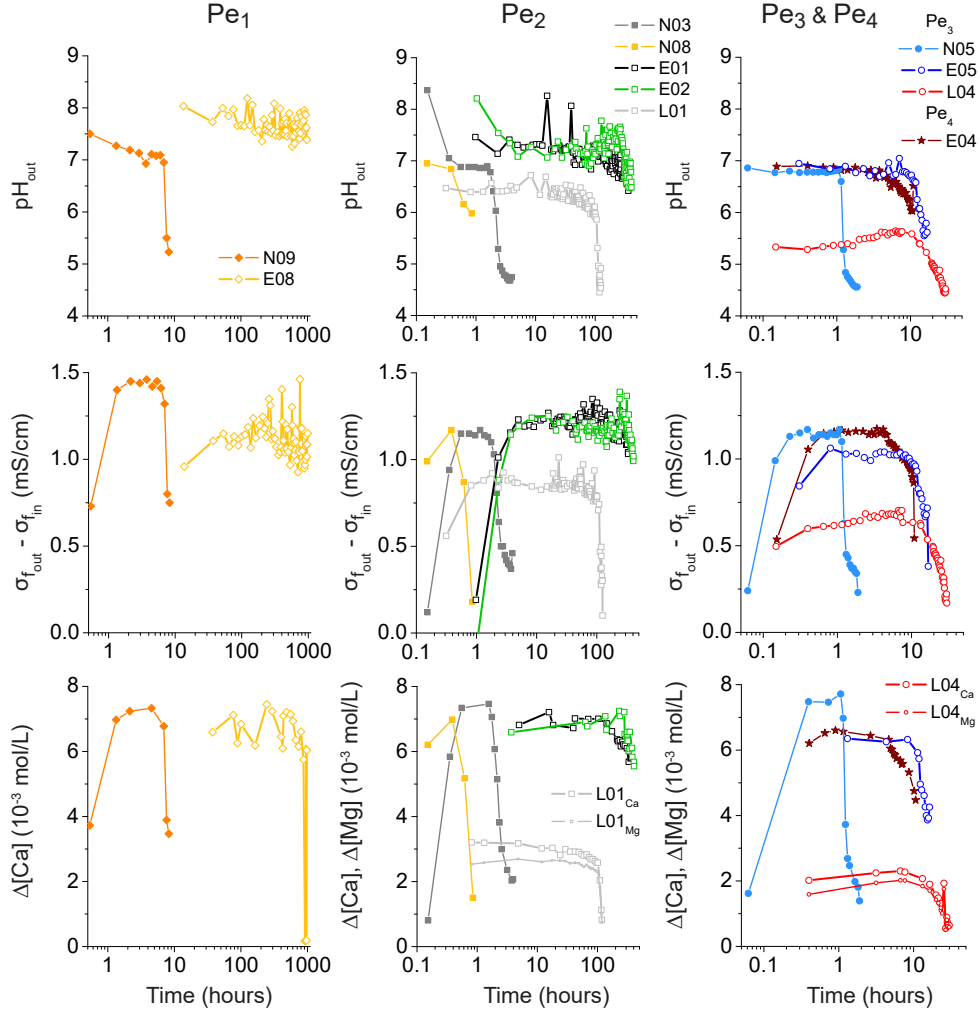


Figure 3: Evolution of the pH at the outlet of the experiments (pH_{out} , first row), the differences in fluid conductivity (σ_f , second row) and calcium and magnesium concentrations between the outlet and inlet of the percolating experiments ($\Delta[Ca]$ and $\Delta[Mg]$, third row), with Péclet numbers $Pe_1 = 0.09$ (first column, diamonds), $Pe_2 = 0.65$ (second column, squares), $Pe_3 = 1.97$ (third column, circles) and $Pe_4 = 5.26$ (third column, stars). Samples labels with N stand for Normandie chalk, E for Euville crinoidal limestone and L for Lexos dolomite.

226 Firstly, for each rock type, the plateau values reached for pH and conduc-
 227 tivity are independent from the Péclet condition applied. They are similar

228 for each sample from Normandie and Euville, as they are all considered to
 229 be REV. However, we observe a change in the plateau value for Lexos be-
 230 cause of the high heterogeneity initially located in L04 $_{Pe_3}$. Concerning outlet
 231 ions concentrations, samples from Normandie display similar values on the
 232 plateau regardless of the Péclet number applied to them, while the plateau
 233 values for Euville and Lexos samples decrease with the increase in Pe. Sec-
 234 ondly, whatever the Pe is, fluid conductivity and ions concentration obtained
 235 for dolomite samples (Lexos) are always lower than the ones of full calcite
 236 samples (Normandie and Euville). Concerning Pe_3 , the outlet pH of L04 $_{Pe_3}$
 237 is lower of 1.5 than the one of N05 $_{Pe_3}$ and E05 $_{Pe_3}$, whereas the conductivity
 238 difference is twice lower. The difference is less pronounced for Pe_2 , where
 239 L01 $_{Pe_2}$ displays a plateau of pH $_{out}$ lower of 0.5 than Normandie and lower of
 240 1 than Euville, and a plateau of conductivity lower of 1 than Normandie and
 241 Euville ones. The lower values of pH $_{out}$ in Lexos experiments are due to the
 242 smaller quantity of dolomite molecules dissolved compared to calcite ones.
 243 Even if the dissolution of one mole of dolomite consumes two times more H $^+$
 244 than one mole of calcite, limestone samples (Normandie and Euville) display
 245 more than twice Ca concentration than dolomite samples. Additionally, we
 246 observe that the ratio between Ca and Mg is almost constant during the
 247 two experiments for Lexos samples and established to be representative of a
 248 stoichiometric dissolution. The corresponding formula is then used for mass
 249 balance calculation as explained in Section 2.3.

250 As explained in Section 2.3, permeability evolution over time during the
 251 percolation experiments is calculated from the differential pressure monitor-
 252 ing, and is displayed in Figure 4. We observe an increase in permeability

253 when we previously observed a decrease in ion concentrations in the effluent.
 254 As previously mentioned and explained in Leger et al. (2022), some decreases
 255 in permeability can be noticed during the experiments, and are probably due
 256 to pores clogging and particles dragging inside the samples (Noiriel et al.,
 257 2005; Luquot et al., 2014; Garing et al., 2015).

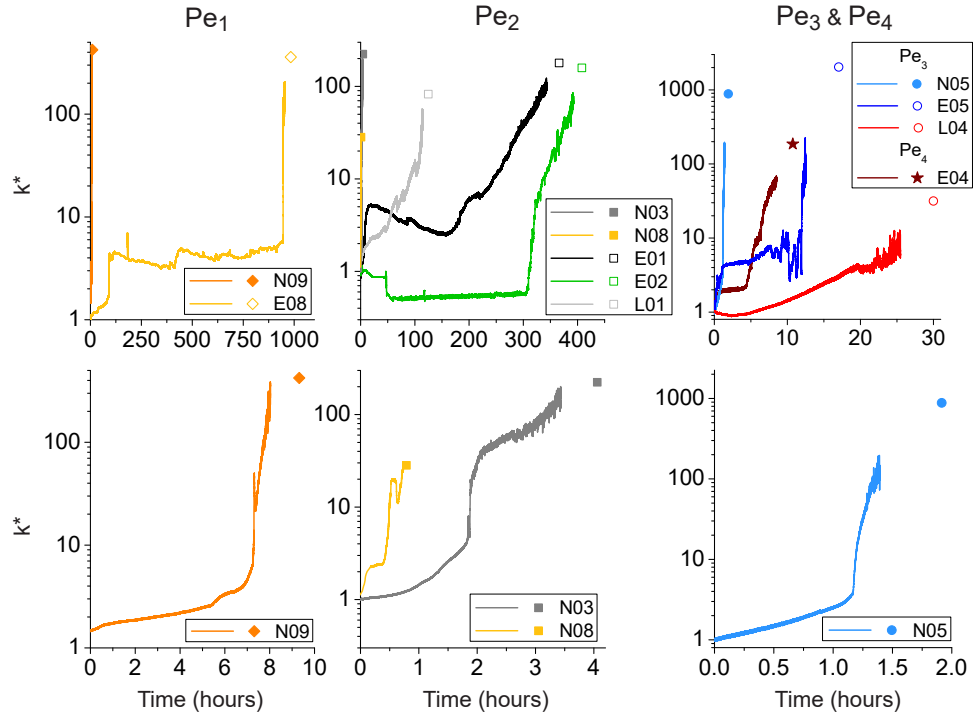


Figure 4: Evolution of the normalized rock permeability k^* [-] during the percolating experiments, where k^* is defined as the permeability of the sample along the experiment normalized by its initial permeability. The dot represents the final value of permeability. Graphics are displayed according to Péclet numbers, in columns (Pe_1 , Pe_2 and $Pe_3 \& Pe_4$). Due to the large differences in experiments duration, a zoom of Normandie values is displayed on the second row.

258 Depending on the Pe applied to the samples, the normalized permeability
 259 (k^*) evolves in different ways. An important and sudden increase in perme-
 260 ability occurs at different times depending on the samples, and is due to

the percolation inside the core, already defined in previous studies (Daccord, 1987; Fredd and Fogler, 1998; Golfier et al., 2002; Brosse et al., 2005; Luquot and Gouze, 2009; Szymczak and Ladd, 2009; Guarracino et al., 2014; Vialle et al., 2014; Menke et al., 2016; Akono et al., 2019). For Normandie and Euville samples, this sharp increase is followed by a more moderate one, less visible for samples submitted to Pe_1 . However, permeability of Lexos samples increases gradually during the experiments. Concerning the importance of the increase in permeability, it is not linear with the Péclet numbers applied to the samples. Indeed, N08 $_{Pe_2}$ and L04 $_{Pe_3}$ display both the lowest k^* increase, with an increase of only 28 of their permeability. N05 $_{Pe_3}$ and E05 $_{Pe_3}$ present the highest final relative permeability, with 879 and 2035, respectively. Concerning the other samples, those with Pe_2 display all similar final k^* between 100 and 200 ; whereas N09 $_{Pe_1}$ and E08 $_{Pe_1}$ both increase their permeability of about 400. Finally, E04 $_{Pe_4}$ displays an increase of 186.

3.2. *Effective petrophysical and hydraulic parameters*

In this section, a focus is made on the petrophysical and hydraulic properties obtained from laboratory measurements and 3D X-ray tomographic images before and after the percolation experiments. These results are displayed in Table 2 and Table 4. The sample E01 $_{Pe_2}$ from Euville rock type was not imaged before, so it is not discussed in this part.

Results presented in Table 2 firstly show that the initial properties differ between each rock type. Indeed, Normandie samples are the most porous ones and Euville are the least. Euville samples have the highest formation factors F_L & F_{XR} and tortuosities τ_e & τ_h , while Normandie samples have the lowest, and Lexos samples have parameter values situated between them.

286 However, permeabilities and cementation indexes are relatively similar for the
287 three rock types. More results on initial rock properties and discussion are
288 available in Leger and Luquot (2021) and in Supplementary Material.

289 The final porosities of each sample are obtained from laboratory measure-
290 ments (ϕ_L), microtomographic images ϕ_{XR} and are also calculated from Ca
291 and Mg concentrations with Equation (3) (ϕ_{ch}). The dissolution experiments
292 of the three rock types are not responsible for a significant change in poros-
293 ity, especially in ϕ_L where some porosity variations are so tiny that they are
294 included in the error measurement, while permeability k_L and k_{XR} increase.
295 Other structural parameters (i.e., formation factor F_L & F_{XR} and tortuosity
296 τ_e & τ_h), calculated from electrical measurements and X-ray images, decrease.

Samples	Péclet	ϕ_L	ϕ_{XR}	k_L	k_{XR}	F_L	F_{XR}	τ_e	τ_h	
N09	Pe ₁	27.2	9.1	0.71	65.2	24.2	31.3	2.57	1.68	
N03	Pe ₂	38.0	8.3	11.19	12.6	8.3	36.2	1.78	1.74	
N08	Pe ₂	28.8	9.7	8.14	505	26.6	28.8	2.77	1.67	
N05	Pe ₃	37.8	7.9	9.07	25.5	7.8	34.1	1.72	1.64	
E08	Pe ₁	12.6	5.6	0.06	5.4	178.6	140.6	4.75	2.80	
E01	Pe ₂	13.2	-	0.28	-	116.2	-	3.91	-	
E02	Pe ₂	14.8	8.0	0.44	10.9	101.0	71.6	3.87	2.40	
E05	Pe ₃	12.8	5.9	1.47	24.8	222.2	95.6	5.34	2.38	
E04	Pe ₄	14.6	7.2	3.77	112.2	103.1	65.1	3.87	2.17	
L01	Pe ₂	18.2	7.4	1.82	1.1	49.0	102.1	2.99	2.74	
L04	Pe ₃	18.8	4.7	11.61	10.8	68.5	47.1	3.59	1.48	
Samples	Pe	ϕ_L	ϕ_{XR}	ϕ_{ch}	k_L	k_{XR}	F_L	F_{XR}	τ_e	τ_h
N09	Pe ₁	27.2	10.0	27.4	300	1291	15.0	27.3	2.08	1.65
N03	Pe ₂	35.7	8.9	38.3	2500	8059	5.2	24.7	1.36	1.48
N08	Pe ₂	29.7	10.4	28.8	230	1497	11.7	25.5	2.03	1.63
N05	Pe ₃	36.5	8.8	38.2	8000	11304	5.2	26.6	1.38	1.53
E08	Pe ₁	12.9	6.6	13.5	20	28	105.3	87.8	3.68	2.41
E01	Pe ₂	14.7	8.2	15.0	50	18231	29.0	56.1	2.06	2.14
E02	Pe ₂	16.3	9.8	16.9	70	2092	26.1	39.8	2.06	1.98
E05	Pe ₃	12.8	7.1	13.2	3000	7481	50.3	57.0	2.53	2.01
E04	Pe ₄	14.8	7.8	15.1	700	5502	41.5	52.6	2.48	2.03
L01	Pe ₂	20.6	8.9	21.0	150	229550	13.7	23.1	1.68	1.44
L04	Pe ₃	19.3	5.6	20.0	320	5556	25.3	35.5	2.21	1.41

Initial

Final

Table 2: Petrophysical properties of samples at initial and final states, i.e., before and after the percolation experiments, from laboratory measurements (porosity ϕ_L [%], permeability k_L [mD], formation factor F_L [-], electrical tortuosity τ_e [-]) and 3D X-ray imaging calculations (porosity ϕ_{XR} [%], permeability k_{XR} [mD], formation factor F_{XR} [-], electrical tortuosity τ_h [-]). The index L stands for Laboratory measurements, XR for X Ray tomographic images and ϕ_{ch} is the porosity from chemistry calculations. The sample E01 was not imaged before experiments. For each rock type, the samples are ordered according to increasing Péclet values.

Each rock type does not react in the same way to percolation experiments. Firstly, concerning Normandie, two groups of samples can be defined. N03_{Pe2} and N05_{Pe3} samples both increase the most their permeability and decrease the most their structural properties, contrary to N08_{Pe2} and N09_{Pe1} samples. Therefore, N03_{Pe2} and N05_{Pe3} samples begin with the lowest permeability to finally reach the highest. Their high decrease in formation factor and tortuosity leads to similar final values between all the samples. N08_{Pe2} is the sample with the lowest increase in permeability, while it displays the highest decrease in formation factor and tortuosity. A full description of this rock type can be found in Leger et al. (2022).

Secondly, for Euville rock, the samples E01_{Pe2} and E02_{Pe2} display the highest increase in porosity, whereas the increase in permeability is the lowest. They also display the highest decrease in formation factors and tortuosities. E05_{Pe3} is the sample which increases the most its permeability. However, E08_{Pe1} stays the one with the lowest permeability, before and after the experiment. With the highest step in permeability, the sample E05_{Pe3} also presents the highest decrease in structural properties, starting with higher values than the other samples and finishing with similar values than all, except E08_{Pe1}. Formation factors and tortuosity values do not decrease much for this latter, which displays the highest final values of structural properties.

Finally, the Lexos set is only composed by two samples. Before the percolation experiments, L04_{Pe3} has higher initial permeability, formation factor F_L and tortuosity τ_e . The experiments lead to a higher increase in porosity and permeability for the sample L01_{Pe2}, along with a higher decrease in structural factors (F_L & F_{XR} and τ_e & τ_h).

3.3. Pore size and dissolution shape

3.3.1. Pore diameter distribution

For each rock type, pore diameter distributions are obtained before and after the experiments by centrifugation method, and the results are displayed in Figure 5. A distribution is obtained in both drainage directions with slightly different diameter classes depending on the rock type. For Normandie samples, a strong anisotropy is observed after the dissolution experiments, discussed in Leger et al. (2022), and we concluded that the drainage in the opposite direction of dissolution flow is the most representative of the pore size distribution. Euville and Lexos samples do not present as much anisotropy as Normandie samples, and therefore, only distributions obtained from the opposite drainage direction are shown in Figure 5.

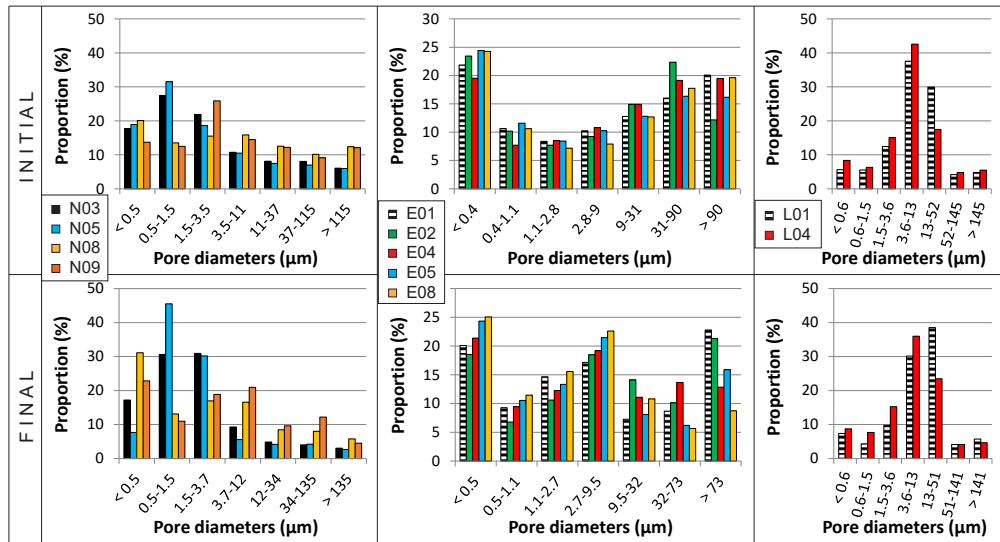


Figure 5: Pore diameters distribution for each sample in each rock type from centrifugation measurements. The Péclet conditions applied to the samples are: Pe_1 (N09, E08), Pe_2 (N03, N08, E01, E02, L01), Pe_3 (N05, E05, L04) and Pe_4 (E04).

In a general way, we observe that the changes in the pore diameters dis-

335 tributions before and after the percolation experiments are dependent on the
 336 rock type. Indeed, samples from Normandie and Euville show a large increase
 337 in their proportion of micropores (pores smaller than the XR pixel size equal
 338 to $12\ \mu\text{m}$) with a decrease in large pores proportion. On the opposite, the
 339 two samples from Lexos display only few changes between before and after
 340 dissolution with a relatively small decrease in micropores proportion, leading
 341 to a small increase in macropores proportion. More specifically, concerning
 342 Normandie, the evolution depends on the samples. N03_{Pe_2} and N05_{Pe_3} sam-
 343 ples display an increase in pores with sizes between 0.5 and $3.7\ \mu\text{m}$, while
 344 a decrease in all the other classes is observed. However, N08_{Pe_2} and N09_{Pe_1}
 345 samples show a global increase in all the small pore diameters classes. All
 346 the samples from Euville rock display similar trends in the evolution of small
 347 pores. The proportion of very small pores (smaller than $0.5\ \mu\text{m}$) globally
 348 remains the same, and the proportion of pores with sizes between 0.5 and
 349 $9.5\ \mu\text{m}$ increases. Then, the proportion of large pores decreases for the ma-
 350 jority of the samples with more pores larger than $73\ \mu\text{m}$ in E01_{Pe_2} and E02_{Pe_2}
 351 than in the other samples.

352 *3.3.2. Pore size distribution and orientation*

353 The homemade software allows to extract the chord length probability
 354 distribution of each sample from the 3D images. The equivalent pore size
 355 distributions from these calculations are displayed in Figure 6. On one hand,
 356 we observe that the pore size globally increases with the experiments, the
 357 quantity of small pores (below $24\ \mu\text{m}$) decreasing and the quantity of large
 358 pores (over $100\ \mu\text{m}$) increasing. On the other hand, the three rock types
 359 show different behaviors, before and after experiments, and samples of each

360 rock type also display differences.

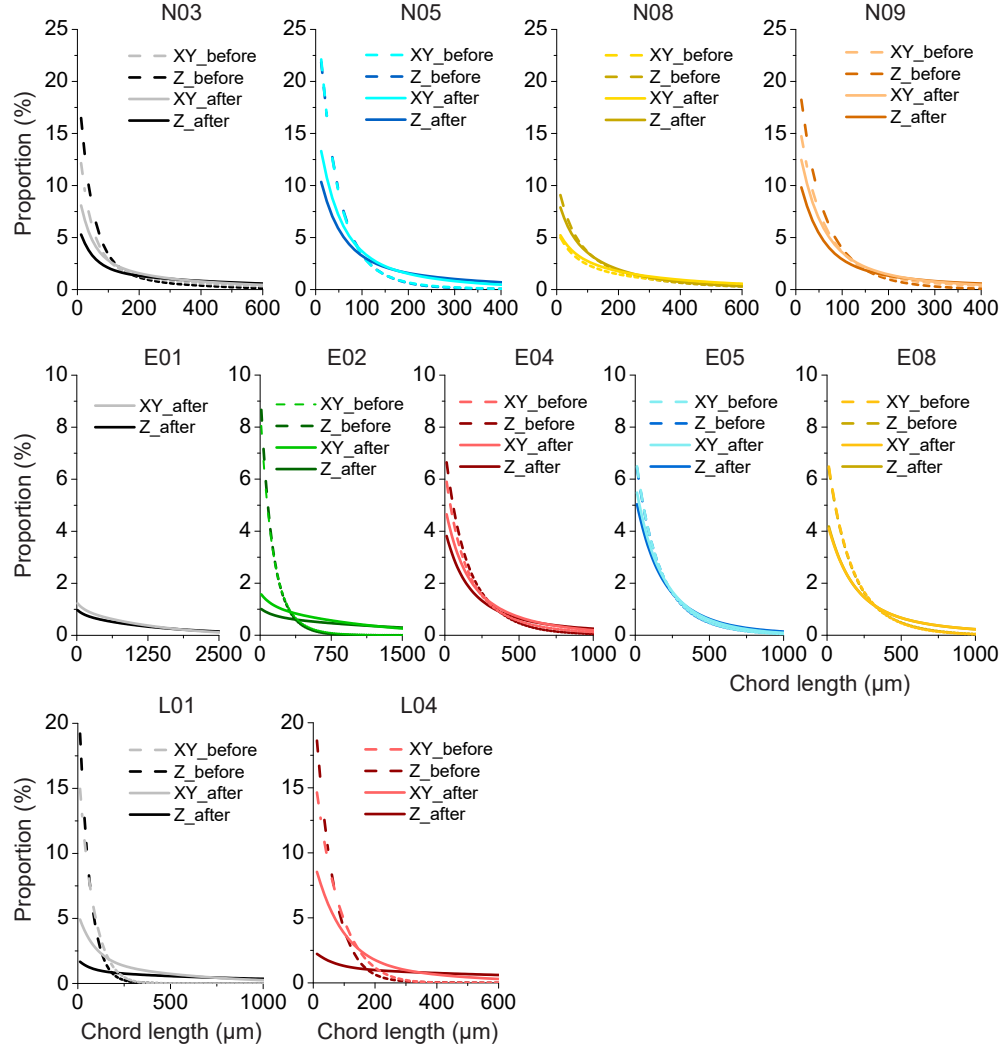


Figure 6: Chord lengths distribution for each sample before (dotted lines) and after (solid lines) percolation. Lines with light colors are for average lengths along X and Y axes, while lines with dark colors are for chord lengths along Z axis. Normandie, Euville and Lexos samples are located on the first, second and third rows, respectively. The Péclet conditions applied to the samples are: Pe_1 (N09, E08), Pe_2 (N03, N08, E01, E02, L01), Pe_3 (N05, E05, L04) and Pe_4 (E04).

361 Focusing on the global evolution of pore diameters, Normandie samples

are divided into two groups. $N03_{Pe_2}$ and $N05_{Pe_3}$ change the most with the experiment, dividing by two their quantity of small pores and doubling their quantity of large pores, while $N08_{Pe_2}$ and $N09_{Pe_1}$ barely change. This is the same for Euville samples, where $E02_{Pe_2}$ sample decreases a lot its quantity of small pores compared to the other samples. Conversely, the two samples from Lexos change similarly even if the sample $L04_{Pe_3}$ keeps more small pores after experiment than $L01_{Pe_2}$.

An evolution in the pore shapes is also visible. For the Normandie set, $N05_{Pe_3}$ is the only sample displaying spherical pores before the experiments, the others mostly presenting large pores transverse to the flow direction (XY). The dissolution barely changes $N08_{Pe_2}$ pore shape, while large pores in the other samples get longer along the flow direction (Z). Concerning Euville samples, they all present spherical pores before the experiments. The sample $E08_{Pe_1}$, performed with Pe_1 conditions, keeps this shape. However, for the other samples, the large pores enlarge along the flow direction (Z) in different proportion, $E02_{Pe_2}$ displaying the highest difference between the two directions. Lexos samples also have spherical pores before the experiments and display large pores that are larger in the flow direction than in the transverse one after dissolution.

3.3.3. Resulting main flow paths

Micro-tomography images acquisition allows seeing the resulting main flow paths formed during the dissolution experiments (Figure 7). Preferential flow paths created by the acid injections are clearly visible for all the rock types. Initially, these conduits were not present in the cores but some heterogeneities were, as it is shown in Figure 1. A pre-existing filled channel exists

387 in the central part of N08_{Pe2}, while N09_{Pe1} displays some micro-cracks. Re-
 388 sults for Normandie samples are fully discussed in Leger et al. (2022). E04_{Pe4}
 389 and E05_{Pe3} both present some zones of initial higher porosity. The first one
 390 is composed of two areas, one at the inlet and the other one at the outlet,
 391 the acid injection creating a conduit between them, where the rock was more
 392 cemented. Inside E05_{Pe3}, the initial higher porosity zone is located on one
 393 side (the left one in Figure 7), inducing a preferential dissolution there. The
 394 samples E08_{Pe1} and L04_{Pe3} both have pre-existing conduits which were not
 395 connected to the core sides but help the dissolution process. Additionally,
 396 the conduit shapes are different according to the rock type. Dissolution in
 397 Normandie chalk samples allows less ramifications than dissolution in Euville
 398 crinoidal limestone samples. Indeed, conduits are more linear and precise in
 399 the first case. Inside Lexos dolomite samples, dissolution seems to create
 400 very linear conduits with few ramifications.

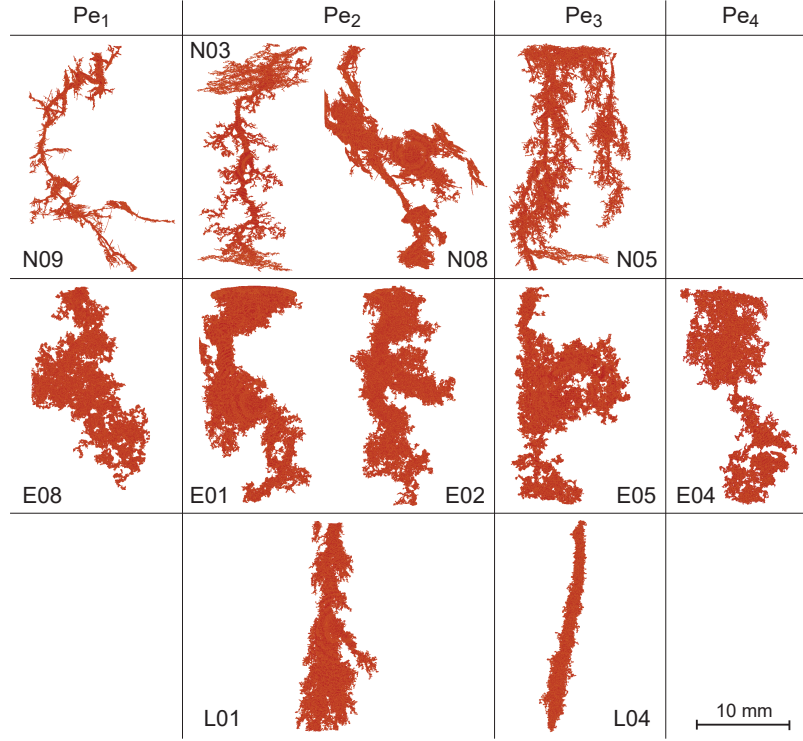


Figure 7: Main path conduits of each sample depending on the four Péclet numbers (in columns) and the rock type (in rows). The samples are all displayed with the acid injection above them. The scale in the bottom right applies to all the samples.

4. Discussion

4.1. Changes in porosity and percolation time

The results presented in Section 3 show that the percolation experiments induce an increase in porosity (ϕ_{ch} from ϕ_L , see Equation (3)) for the three rock types. The evolution of porosity is calculated from outlet cations concentrations (only Ca or both Ca and Mg depending on the rock type) and is displayed in Figure 8. Porosity does not change in the same way depending on the rock type and the Péclet condition of each sample. In a general way, Normandie samples present the lowest increase in porosity, between 0.08 and

0.35%, whereas porosity in Euville samples increases between 0.39 and 2.06%
and porosity in Lexos between 1.28 and 2.84% (Figure 8).

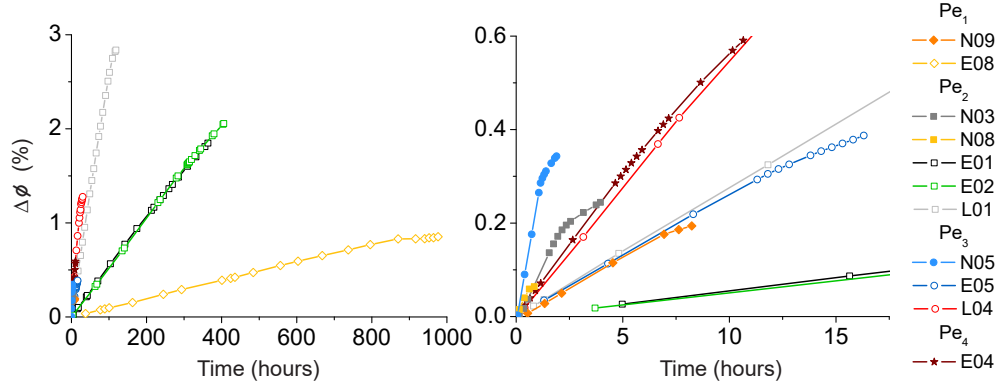


Figure 8: Evolution of rock porosity change, $\Delta\phi$, defined as the porosity measured at time t minus the initial porosity measured in laboratory $\Delta\phi(t) = \phi(t) - \phi_L$ evaluated from Ca and Mg ions concentrations analyzed in the outlet fluid during percolating experiments and using Equation (3). The graph on the right is a zoom of the graph on the left.

As observed in Section 3.1, a break in the porosity curves occurs at different times for each sample (Figure 8). It is more or less pronounced depending on the samples and it defines the percolation time t_p . The corresponding values for each sample are noted in Table 3. For each rock type, we observe in Figure 8 that the higher the Péclet condition applied to the samples, the faster the break in the curves happens and percolation occurs, inducing a lower t_p . The sample $N08_{Pe_2}$ is an exception here due to an important initial heterogeneity, and explanations about this are discussed in Leger et al. (2022). Additionally, concerning rock types only composed of calcite, chalk (Normandie) having a higher initial porosity than crinoidal limestone (Euville), its initial poral volume is higher. To create a conduit, the quantity of rock needed to be dissolved is then less important, inducing a lower increase

424 in its absolute porosity.

Samples	Pe	t_p	R	R'
N09	Pe_1	7.3	5.86e-9	7.33
N03	Pe_2	1.9	5.17e-8	7.39
N08	Pe_2	0.45	4.49e-8	6.41
N05	Pe_3	1.2	1.31e-7	7.49
E08	Pe_1	893	6.26e-10	6.73
E01	Pe_2	160	3.41e-9	6.82
E02	Pe_2	309	3.45e-9	6.90
E05	Pe_3	11.9	1.58e-8	6.32
E04	Pe_4	4.4	3.86e-8	6.49
L01	Pe_2	105	8.75e-9	2.76
L04	Pe_3	7.7	1.65e-8	2.17

Table 3: Table of experimental properties of each sample. Pe is the Péclet condition applied, R the dissolution rate per acid injection time [mol/s], R' the dissolution rate per acid injection volume [mol/m³] and t_p is the percolation time [h].

425 Inside each rock type, the absolute increase in porosity shown in Figure 8
426 does not seem correlated with the experimental conditions. For Normandie
427 samples, except N08 $_{Pe_2}$, porosity increases more when a higher Péclet is ap-
428 plied. In N08 $_{Pe_2}$, we observe a minimal increase of 0.08% while it is dissolved
429 with Pe_2 . For Euville, samples dissolved with Pe_2 (E01 $_{Pe_2}$ and E02 $_{Pe_2}$) dis-
430 play a larger increase in porosity than E08 $_{Pe_1}$ that is dissolved with Pe_1 .
431 However, these three samples increase their porosity more than samples for
432 which Pe_3 and Pe_4 conditions are applied. For Lexos, L01 $_{Pe_2}$ increases more
433 its porosity than L04 $_{Pe_3}$. However, when considering each Péclet condition
434 applied, the absolute increase in porosity $\Delta\phi$ is always higher in Lexos sam-
435 ples than Euville samples, which have higher increases than Normandie ones.
436 This result seems inconsistent as dolomite dissolution rate is lower than that
437 of calcite (up to one order of magnitude) in similar conditions (Chou et al.,

1989; Gautelier et al., 1999; Morse and Arvidson, 2002; Liu et al., 2005; Pokrovsky et al., 2005). Indeed, in Figure 3, we observe that the outlet Ca concentration for Lexos samples is between one half and one third of Euville samples. This apparent higher porosity increase for Lexos samples than for limestone samples in similar conditions is linked to two different properties. The first one is the mineral molar volume that is higher for the dolomite than for calcite with $64.3 \text{ cm}^3/\text{mol}$ and $37 \text{ cm}^3/\text{mol}$, respectively. The dissolved volume corresponding to one molecule of dolomite is then higher than calcite. The porosity increase in dolomite sample is thus higher than in limestone sample for a same quantity of dissolved mineral. The second important property is the flow rate. In fact, for a similar Pe number, the imposed constant flow rate is different from one rock type to another due to the differences in pore size distribution. Consequently, flow rates applied to dolomite (Lexos) samples are higher than flow rates applied to calcite (Euville) samples (Table 1).

4.2. *Impact of the hydraulic conditions and mineral composition on the dissolution rates*

Applying higher flow rates for Lexos samples than for Euville samples, in similar Péclet conditions, induces a larger acid renewal inside dolomite samples. It leads to a higher dissolution rate, which is defined as $R = [\text{Ca}] \times Q$ and expressed in mol/s, and related to a higher increase in the porosity that is previously described. Indeed, the slope of the increase in this porosity is directly related to the dissolution rate R , standing between 10^{-10} and 10^{-7} mol/s , depending on the sample (Table 3). This is consistent with existing studies, where for experiments realized in Pe_2 conditions, R is

463 about 5×10^{-8} mol/s in Noiriél et al. (2009) and 2×10^{-8} mol/s in Luquot
 464 et al. (2014); whereas experiments realized with higher Pe lead to R about
 465 8×10^{-7} mol/s (Vialle et al., 2014). Note also that the dissolution rates are
 466 similar for the reproductive experiments (E01_{Pe2}-E02_{Pe2}). The slope of the
 467 increase in porosity and the dissolution rate R are then both correlated with
 468 the Péclet conditions applied to the samples. Indeed, inside each rock type,
 469 samples dissolved with lower Pe display lower slopes in Figure 8 and lower
 470 R in Table 3. At the same time, when considering each Péclet condition,
 471 samples from Normandie always have higher porosity slopes and R than
 472 samples from Lexos, which are higher than Euville samples.

473 For identical Pe numbers, different flow rates are used depending on the
 474 rock pore diameters. Therefore, conversely, for two different Pe numbers,
 475 a similar flow rate could be applied. Indeed, relatively similar flow rates
 476 are applied to N03_{Pe2}, E04_{Pe4} and L04_{Pe3}, dissolved with Pe_2 , Pe_4 and Pe_3 ,
 477 respectively. N03_{Pe2} displays a dissolution rate 1.3 times higher than E04_{Pe4},
 478 which is 2.3 times higher than L04_{Pe3}. The rate between the quantity of
 479 dissolved calcite and the quantity of injected acid is calculated as $R' = \frac{R}{Q}$,
 480 and is displayed in Table 3. Lexos samples rates R' are three times lower
 481 than Normandie and Euville ones. Therefore, dolomite dissolution is much
 482 smaller than calcite one for similar quantity of injected acid. Concerning only
 483 samples fully composed of calcite, chalk displays similar but a bit higher R'
 484 than crinoidal limestone, which can be explained by a higher reactive surface
 485 area in Normandie samples characterized by a higher quantity of small grains.

4.3. Link between the initial rock structure and dissolution rate

Inside each rock type, we observe that the higher the Péclet number applied to the sample, the higher the dissolution rate. In these conditions, the sample N05_{Pe3} has the highest R while E08_{Pe1} has the lowest. We observe that some samples from different rock types display similar values of R while they are submitted to different Péclet conditions, such as N09_{Pe1} with E01_{Pe2} and E02_{Pe2}, or E04_{Pe4} with N03_{Pe2} and N08_{Pe2}. In order to see the impact of the initial rock structure and the experimental conditions on the dissolution rate, Figure 9 displays the dissolution rate R of each sample depending on the initial formation factor F_L and the Pe applied during the corresponding experiment.

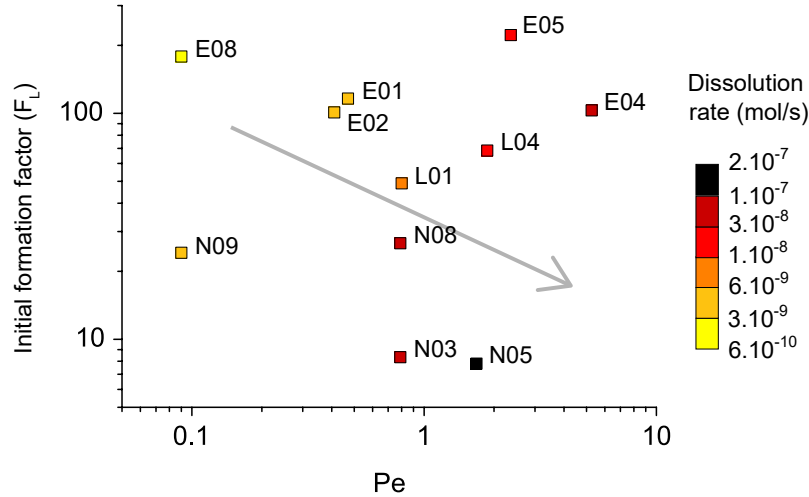


Figure 9: Dissolution rate of each sample, depending on the initial formation factor F_L and the Péclet number Pe applied during the experiments. The color scale shows darker colors for higher dissolution rates R .

Firstly, the higher the Péclet number, the darker the dots representing the samples in Figure 9, showing again that when the acid is injected with high Péclet conditions, the dissolution rate is higher inside the sample. Secondly,

500 samples from Normandie are situated on the bottom of the graph, while
 501 Euville samples are situated on the top and Lexos samples in between. This
 502 is due to the difference in formation factors, Normandie having the lowest
 503 and Euville the highest. We observe that the lower the formation factor, the
 504 darker the dots. The formation factor being defined as the ratio between the
 505 electrical conductivity of the fluid and that of the rock sample, it depends
 506 on the porosity that is accessible to the fluid and on the heterogeneities of
 507 the paths followed by the fluid. Small formation factors are for example
 508 associated to fractured rocks where the renewal rate is higher than in porous
 509 rocks (Schön, 2015; Roubinet et al., 2018). The higher renewal rate is directly
 510 linked to a higher dissolution rate. Here, Normandie samples display the
 511 lowest formation factors and highest dissolution rates. Therefore, chalk seems
 512 to be a more heterogeneous carbonate rock than crinoidal limestone and
 513 dolomite, probably due to its very high proportion of small pores associated
 514 to its higher porosity, leading to a lower cohesion compared to the two other
 515 rock types.

516 We observed in Section 3.3.2 that the experimental conditions do not
 517 seem to deeply affect the evolution of pore shape inside chalk (Normandie)
 518 and dolomite (Lexos) samples (Figure 6). However, concerning crinoidal
 519 limestone (Euville), a strong difference exists between $E01_{Pe_2}$ and $E02_{Pe_2}$
 520 and the other samples of the set. After the experiments, the quantity of
 521 small pores sharply decreases and the quantity of large pores increases. A
 522 link can be established between the quantity of acid injected into the samples
 523 during the experiments and the evolution of pore shape. Indeed, even if the
 524 percolation experiment in $E08_{Pe_1}$ lasts longer than experiments in $E01_{Pe_2}$

525 and $E02_{Pe_2}$, the difference in flow rates between the experiments leads to
526 a higher total quantity of acid injected inside $E01_{Pe_2}$ and $E02_{Pe_2}$ than in
527 $E08_{Pe_1}$. Therefore, the total quantity of acid injected into a sample has
528 more impact than the time during which the acid is injected. A very high
529 quantity of acid is then responsible of strong changes in pore shape inside
530 crinoidal limestone. Consequently, it seems that neither the flow condition
531 nor the petrophysical properties changes are the main parameters controlling
532 the reaction but that it is the amount of injected acid and the initial rock
533 properties.

534 Finally, the conduits shapes displayed in Figure 7 show that dolomite
535 samples are dissolved by creating very linear conduits with few ramifications.
536 This conduit formation explains the linear increase in permeability during the
537 experiments done on Lexos samples. These two observations can be related
538 to the low dissolution kinetic of dolomite compared to calcite. Indeed, the
539 very low rate R' calculated in these samples means a very low quantity of
540 rock dissolved per quantity of injected acid and induces a more localized
541 dissolution than in limestone samples, showing again the strong impact of
542 the initial rock properties on the dissolution process.

543 5. Conclusions

544 This study investigates the impact of mineralogy differences on the dis-
545 solution of carbonate rock through percolation experiments in similar condi-
546 tions conducted on samples from three different carbonate rock type: chalk,
547 crinoidal limestone and dolomite. At first, we demonstrated that inside each
548 rock type, the lower the Péclet condition applied to the samples, the lower
549 the dissolution rate. Looking at each Péclet condition, chalk samples display

550 the highest dissolution rates whereas crinoidal limestone samples display the
551 lowest, and dolomite ones stand in between. Secondly, we highlight that
552 the dolomite dissolution rate is much smaller than the calcite one for similar
553 quantities of acid injected into the samples. This is correlated with a lower
554 dissolution kinetic, inducing localized linear conduits associated with a linear
555 increase in permeability during dissolution experiments.

556 Then, inside full calcite rock type, the chalk has a larger reactive surface
557 area due to its higher quantity of small grains and it displays slightly higher
558 dissolution rates than crinoidal limestone for similar quantity of acid injected.
559 For a similar quantity of injected acid during the experiments, the flow rate
560 injected is higher in Normandie chalk and induces a higher renewal rate and
561 a lower formation factor.

562 Finally, for all rock types studied, the dissolution rate seems to be mainly
563 linked to the mineral composition and the acid flow rate, as well as the
564 amount of injected acid in the case of crinoidal limestone. The initial struc-
565 ture of the rock also plays an important role, as we observed that strong het-
566 erogeneities and structural parameters affect the dissolution rate and porosity
567 increase.

568 **Supplementary**

569 **Materials and methods**

570 *Laboratory measurements*

571 The liquid porosity (ϕ_L) and permeability (k_L) of the rock samples are
572 measured by double-weighing saturated and oven-dried samples and from an
573 experimental device applied to saturated samples, respectively. The electri-
574 cal impedance is defined by injecting electric current in the saturated samples
575 and used to define the rock conductivity, formation factor (F_L), cementation
576 index (m_L) and electrical tortuosity (τ_e) from the well-known equations pro-
577 vided in Waxman and Smits (1968); Archie (1942); Clennell (1997). The
578 P and S waves velocities (V_p and V_s) are obtained by injecting ultrasonic
579 frequency waves of 500 kHz with two piezoelectrical transducers. The pore
580 size distribution is obtained by centrifugation. Following the method de-
581 scribed by Reatto et al. (2008); Rötting et al. (2015), increasing velocities
582 are applied on saturated samples. After each cycle of velocity, the water loss
583 is determined by weighing the samples, providing the proportion of a given
584 range of pores size from Young-Laplace equation. Using velocities from 32
585 to 471 rad/s leads here to pores sizes ranging from approximately 100 to
586 0.5 μm .

587 *X-ray micro-tomography*

588 3D X-ray micro-tomography (XRMT) images are obtained using the X-
589 ray Computed Tomography (XRCT) scanner (EasyTom 150) of the Institute
590 of Evolution Sciences of Montpellier (ISEM, Montpellier, France) with a pixel
591 size of 12 μm . A homemade imaging software (Gouze et al., 2008) is used
592 to treat the images with filters to improve images quality by smoothing the

593 pixels histogram and correcting brightness. The two-phase segmentation is
 594 done with a region growing method resulting in the macropore and matrix
 595 phase, the former corresponding to pores larger than the pixel size and giving
 596 the macropore porosity ϕ_{XR} . The sample skeleton is defined as the paths
 597 connecting the center of each connected pore and is used to compute the
 598 permeability (k_{XR}), hydraulic tortuosity (τ_h), formation factor (F_{XR}) and
 599 cementation index (m_{XR}) (Kozeny, 1927; Clennell, 1997; Ghanbarian et al.,
 600 2013). The software also provides the pore volume and surface, giving the
 601 surface-volume ratio ($\frac{S}{V}$), the pore size distribution with the chord length
 602 method (Torquato and Lu, 1993) and the proportion of the percolating phase
 603 into the volume sample (PV) from statistics calculations.

604 **Petrophysical properties changes**

605 In this section, we present supplementary data of petrophysical properties
 606 that we do not discussed in the main manuscript. In particular, cementation
 607 index m_L and m_{XR} , P and S waves velocities, relative pore size $\frac{S}{V}$ and the
 608 proportion of the percolating volume from the full porosity PV are presented
 609 in Table 4.

610 Mechanical factors (Vp and Vs velocities) are globally larger for Euville
 611 and Lexos samples than for Normandie ones. For the Normandie set, N08 $_{Pe_2}$
 612 is the sample with the highest increase in P and S waves velocity. N03 $_{Pe_2}$
 613 and N05 $_{Pe_3}$ both present the lowest increase in Vp . A full description of this
 614 rock type can be found in Leger et al. (2022).

615 Both E05 $_{Pe_3}$ and E08 $_{Pe_1}$ show a smaller increase in Vp than the other
 616 samples. A particularity occurs with the sample E05 $_{Pe_3}$, which is the only
 617 one with a decreasing Vs over the dissolution.

618 Finally, both lexos samples present similar values of P waves velocity
619 and cementation index m_L . However, L04_{Pe3} has a smaller initial S wave
620 velocity. The sample L04_{Pe3} displays the highest increase in V_p . The two
621 samples differ in V_s evolution, which decreases for the sample L01_{Pe2} and
622 increases for the sample L04_{Pe3}.

623 For all the rock types, structural properties (m_{XR}) and surface ratio ($\frac{S}{V}$)
624 generally decrease, except for m_{XR} of N09_{Pe1} for which we observe no signif-
625 icant changes. No significant changes are also observed for the percolating
626 volume (PV) for Normandie and Euville samples, while Lexos samples show
627 an important increase.

628 $\frac{S}{V}$ is lower for Euville than Lexos and then Normandie. Percolating vol-
629 umes are higher than 93% for all Euville samples, while they stand from 84.7
630 to 95.9% for Normandie samples, and are below or equal to 68.3% for Lexos
631 samples.

632 Every sample of each rock type does not change in the same way with
633 dissolution. Concerning Normandie, two groups of samples can be defined.
634 N03_{Pe2} and N05_{Pe3} samples both decrease the most their structural properties
635 and surface ratio, contrary to N08_{Pe2} and N09_{Pe1} samples. However, final
636 $\frac{S}{V}$ values are about 100 mm⁻¹ for the samples N03_{Pe2}, N05_{Pe3} and N09_{Pe1},
637 while it equals 85 mm⁻¹ for the sample N08_{Pe2}. For Euville rock type, E02_{Pe2}
638 displays the highest decrease in m_{XR} and $\frac{S}{V}$, on the contrary to E04_{Pe4}.
639 For Lexos rock type, the properties of the sample L01_{Pe2} change the most
640 between before and after the experiments. We observe that the dissolution
641 barely affects the cementation index of L04_{Pe3}, while both samples reach
642 similar final values in m_{XR} , $\frac{S}{V}$ and PV . The experiments lead to a higher

⁶⁴³ decrease in structural factors (m_L) for the sample $L01_{Pe_2}$.

Initial	Samples	m_L	m_{XR}	Vp	Vs	$\frac{S}{V}$	PV
	N09 $_{Pe_1}$	2.45	1.43	2.97	1.64	103.0	94.9
	N03 $_{Pe_2}$	2.19	1.44	2.36	1.18	113.0	84.7
	N08 $_{Pe_2}$	2.63	1.44	2.33	1.30	87.6	95.9
	N05 $_{Pe_3}$	2.12	1.39	2.35	1.25	111.4	86.1
	E08 $_{Pe_1}$	2.51	1.71	3.86	2.10	33.7	93.0
	E01 $_{Pe_2}$	2.35	-	3.08	1.90	-	-
	E02 $_{Pe_2}$	2.42	1.69	2.32	1.30	41.9	99.1
	E05 $_{Pe_3}$	2.63	1.61	3.73	2.04	37.4	98.9
	E04 $_{Pe_4}$	2.41	1.59	2.56	1.42	40.8	95.1
	L01 $_{Pe_2}$	2.29	1.77	3.40	2.00	68.5	42.1
	L04 $_{Pe_3}$	2.53	1.26	3.10	1.86	65.8	68.3
Final	Samples	m_L	m_{XR}	Vp	Vs	$\frac{S}{V}$	PV
	N09 $_{Pe_1}$	2.08	1.44	3.89	1.83	98.9	94.8
	N03 $_{Pe_2}$	1.60	1.33	2.76	1.65	103.5	86.4
	N08 $_{Pe_2}$	2.03	1.43	3.74	2.01	85.0	95.7
	N05 $_{Pe_3}$	1.63	1.35	2.80	1.85	100.9	89.1
	E08 $_{Pe_1}$	2.27	1.65	5.33	2.18	33.1	92.5
	E01 $_{Pe_2}$	1.75	1.61	5.27	2.07	29.8	99.6
	E02 $_{Pe_2}$	1.80	1.59	5.08	2.00	34.8	99.5
	E05 $_{Pe_3}$	1.90	1.53	5.45	1.81	34.4	96.8
	E04 $_{Pe_4}$	1.95	1.56	5.32	1.91	38.2	99.1
	L01 $_{Pe_2}$	1.66	1.30	4.74	1.85	57.9	88.3
	L04 $_{Pe_3}$	1.96	1.24	4.81	1.94	57.7	88.6

Table 4: Petrophysical properties of samples at initial and final states, i.e., before and after the percolation experiments from laboratory measurements and 3D X-ray imaging calculations with cementation index m_L [-] & m_{XR} [-], and P and S wave velocities Vp and Vs [km/s], ratio of pore surface over pore volume $\frac{S}{V}$ [mm⁻¹] and proportion of percolating volume PV [%]. The index L stands for Laboratory measurements and XR for 3D microtomographic images. The sample E01 was not imaged before experiments. For each rock type, the samples are ordered according to increasing Péclet values.

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