

## Improved Kinetics for Mineral Dissolution Reactions in Pore-Scale Reactive Transport Modeling

Schabernack, J.; Fischer, C.;

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1       **Improved Kinetics for Mineral Dissolution Reactions**  
2       **in Pore-Scale Reactive Transport Modeling**

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4                   Jonas Schabernack<sup>a\*</sup>, Cornelius Fischer<sup>a</sup>

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6       <sup>a</sup>Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Department of  
7       Reactive Transport, D-04318 Leipzig, Permoserstr. 15, Germany

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9                   \*Corresponding author: Jonas Schabernack  
10                  E-Mail address: \*j.schabernack@hzdr.de, c.fischer@hzdr.de  
11

## 12 **Abstract**

13 Recent numerical investigations revealed that the heterogeneity of the dissolution rate observed  
14 in numerous experiments cannot be explained by fluid transport effects. This heterogeneity is  
15 attributed to intrinsic surface reactivity. Therefore, reactive transport models (RTM) require  
16 parameterization of the surface reactivity for accurate predictions. For this purpose, a  
17 nanotopographic parametrization based on surface slope has been recently suggested. In this  
18 study, we utilize and improve this parametrization for RTMs of pore-scale systems, from the crystal  
19 surface to the single crystal geometry, going beyond the previous reactivity parametrization. 2D  
20 and 3D RTMs were developed using COMSOL Multiphysics for calcite systems based on  
21 experimental measurements. We compared the results between classically parameterized RTMs,  
22 RTMs with new slope parameterization, and experimental data. The effect of flow on dissolution  
23 under conditions far-from-equilibrium is found to be negligible, highlighting the importance of  
24 surface reactivity in the dissolution reaction. For the first time, the new slope factor was able to  
25 accurately reproduce the experimental results on a crystal surface with large field-of-view, large  
26 height variability of the topography, and over a long-term reaction period. The new  
27 parameterization had greatly improved sensitivity for intermediate reactivity ranges compared to  
28 the previous parameterization. A 3D model is used to present the general applicability of the  
29 parameterization for use in realistic geometric data sets. Thus, we also show that neglecting  
30 surface reactivity in an RTM leads to incorrect predictions regarding the porosity, pore geometry,  
31 and surface topography of the system. Our new slope factor can successfully serve as a first-order  
32 proxy for the distribution of surface reactivity in 3D pore-scale rock systems. The description of  
33 surface reactivity is crucial for accurate long-term modeling of natural rock systems.

34

## 35 **Keywords**

36 Pore-Scale Reactive Transport Modeling; Mineral Dissolution; Crystal Surface Reactivity;  
37 Kinetics

## 38 **1. Introduction**

39 Mineral dissolution plays a key role in various natural processes such as weathering or reservoir  
40 rock formation, as well as in technical applications such as corrosion, mining, and waste  
41 management. Predicting mineral dissolution over long timescales (>100,000 years) is crucial to  
42 describe the stability of geomaterials in important applications, e.g., nuclear waste repositories for  
43 underground storage (Ewing et al., 2016). Such predictions require a detailed understanding of  
44 the mechanistic processes involved in the dissolution reactions. An adequate model  
45 parametrization based on mechanistic insight is required to simulate the long-term behavior of any  
46 given system.

47  
48 Mineral dissolution is typically quantified via a dissolution rate. In the past, bulk-powder  
49 experiments have been applied to study the dissolution of various minerals (e.g., Chou et al.,  
50 1989; Plummer et al., 1978). In these experiments, a single, mineral-specific value for dissolution  
51 rate is determined. However, the reported individual dissolution rates for the same mineral, similar  
52 fluid compositions, and experimental conditions can vary by several orders of magnitude (Arvidson  
53 et al., 2003; Bollermann and Fischer, 2020). Surface-sensitive microscopy techniques such as  
54 atomic force microscopy (AFM) (Lange et al., 2021; Pollet-Villard et al., 2016) or vertical scanning  
55 interferometry (VSI) (Bouissonnié et al., 2018; Fischer et al., 2012) can directly observe mineral  
56 surfaces during dissolution and reveal the evolution of surface topography over time. Tomographic  
57 measurements of dissolving materials can be obtained using techniques such as X-ray  
58 microtomography ( $\mu$ -CT) (Noiriel and Soulaine, 2021; Noiriel et al., 2020). The use of these  
59 surface-sensitive methods revealed a large intrinsic variability in surface dissolution rates under  
60 identical conditions, besides the well-known extrinsic variability (e.g., Noiriel and Daval, 2017;  
61 Saldi et al., 2017).

62  
63 Mineral surface reactivity is not a material constant but arises due to nano- and microstructural  
64 heterogeneities caused by 2D and 3D defects in the crystal lattice. The heterogeneous distribution  
65 of surface reactivity has been extensively investigated for calcite (Arvidson et al., 2003; Liang and  
66 Baer, 1997), and a recent compilation can be found in Bollermann and Fischer (2020). New  
67 aspects include inherited reactivity of nanostructured surfaces (Fischer et al., 2018) as well as  
68 temporal fluctuations at far-from-equilibrium conditions (Fischer and Lüttge, 2018). Similar studies  
69 exist for a variety of minerals such as feldspars (Lange et al., 2021; Pollet-Villard et al., 2016;  
70 Zhang and Lüttge, 2009), quartz (Kurganskaya and Lüttge, 2013), and sheet silicates  
71 (Kurganskaya et al., 2012). The lattice defects result in the formation of steps and etch pits on the

72 crystal surface during reactions. Due to the resulting nanotopography, atomic surface sites with  
73 varying coordination and consequently different intrinsic reactivity such as terrace, step, or kink  
74 atoms are present on the crystal surface. The local surface reactivity is determined by the  
75 concentration of highly reactive kink sites on the crystal surface, according to findings from  
76 experimental and numerical investigations (Arvidson et al., 2003; Chen et al., 2014; Fischer et al.,  
77 2014). A high concentration of kink sites is typically found at etch pits, surface steps, and crystal  
78 corners. Thus, a single dissolution rate cannot adequately describe the complex dissolution  
79 kinetics at the crystal surface. Even on larger length scales, the variability in surface reactivity  
80 does not average out. This has been shown for both large crystals with edges, corners, faces  
81 (Noiriel et al., 2020; Noiriel et al., 2019) as well as polycrystalline materials (Bollermann and  
82 Fischer, 2020; Kahl et al., 2020). Powder samples consisting of small crystals typically do not  
83 show 2D or 3D lattice defects and exhibit a homogeneous crystal surface consisting almost  
84 entirely of kink and step sites with high reactivity (Bollermann and Fischer, 2020). Therefore,  
85 predictive approaches for mineral dissolution must consider and implement the distribution and  
86 density of reactive surface sites.

87  
88 In addition to experimental studies on mineral dissolution rates, numerical approaches have been  
89 applied to fundamentally understand the mechanisms of dissolution reactions at surfaces. At the  
90 nanometer to micrometer scale, kinetic Monte Carlo (KMC) simulations can be applied to study  
91 the evolution of surface topography, dissolution rates, and the distribution of surface reactivity as  
92 dissolution progresses. KMC can be used to predict dissolution nanotopographies and provides  
93 important mechanistic inferences about the dissolution reaction (Kurganskaya and Luttge, 2013).  
94 Using this method, it is possible to predict the kink site density and thus the surface reactivity  
95 (Kurganskaya and Luttge, 2016). For small crystal sizes, the KMC method can simulate the  
96 dissolution of whole crystal grains considering multiple surfaces (Luttge et al., 2013; Martin et al.,  
97 2020). Larger system sizes can be achieved by using KMC-parameterized Voronoi simulations,  
98 which reduce computational costs while providing similar results (Rohlfes et al., 2018). KMC results  
99 can be validated with and compared to experimental data obtained with AFM or VSI  
100 measurements, and therefore provide a powerful tool for predicting reaction rates.

101  
102 At larger scales, reactive transport models (RTM) are commonly applied to simulate fluid flow,  
103 species transport and various processes in natural and engineered systems on various scales  
104 (Druhan and Tournassat, 2020; Molins et al., 2014; Prasianakis et al., 2017; Shao et al., 2009;  
105 Tournassat and Steefel, 2019; Yuan et al., 2016). RTMs can predict the evolution of various  
106 chemical and physical system parameters over a wide range of time scales. At the pore scale ( $\mu\text{m}$

107 scale), the models typically describe the system with two distinct phases: solid and liquid. The  
108 model systems consist of pore space available for both fluid flow and transport, and solid mineral  
109 grains that interface with the fluid (Molins et al., 2021). Comprehensive reviews of flow and  
110 transport modeling are available for porous media (Blunt et al., 2013) and fractures (Berkowitz,  
111 2002).

112  
113 At the fluid-mineral interface, various interactions such as sorption, dissolution, or precipitation  
114 reactions have to be considered depending on the physicochemical conditions in the system.  
115 Chemical reactions in RTM are governed by the chemical driving force to reach equilibrium. In the  
116 fluid, aqueous complexation occurs as an equilibrium reaction depending on the species in the  
117 system (Molins et al., 2014; Steefel et al., 2015). Mineral interfaces dissolve when the fluid is  
118 undersaturated in the species of the respective mineral component. In the case of calcite, the main  
119 driving force for dissolution is the pH of the liquid, while  $p\text{CO}_2$  has only a weak influence  
120 (Pokrovsky et al., 2005). The calculation of mineral dissolution in pore-scale RTMs is based on  
121 rate laws derived from transition state theory, using rate constants derived from bulk powder  
122 experiments (Molins et al., 2014). Thus, the rate calculations are based solely on extrinsic  
123 constraints linked via fluid composition.

124  
125 In contrast, the rate equation does not account for the previously mentioned experimental findings  
126 on heterogeneous dissolution rates and intrinsic surface reactivity. This illustrates the limited use  
127 of such rate constants for predicting reacting crystalline systems (Karimzadeh and Fischer, 2021).  
128 In transport-controlled regimes, the reactant concentrations in the fluid very efficiently control the  
129 rate constants describing the reactivity of the processes involved. In surface-controlled conditions,  
130 the influence of surface reactivity is by definition more important than transport effects in the  
131 system. Therefore, neglecting intrinsic reactivity significantly affects the simulation results and the  
132 predictive power of the model. Superimposing the variability of surface reactivity on transport-  
133 controlled systems may induce small changes in simulation results since the main influence on  
134 dissolution rates originates from concentration gradients in the fluid. In addition to surface  
135 reactivity, natural mineral surfaces show distinct nano- to microtopographies arising from  
136 heterogeneous dissolution. Therefore, simulations must account for this small-scale interfacial  
137 roughness. Recent studies have addressed the influence of roughness in pore-scale RTMs and  
138 its effects on transport and mineral dissolution (Deng et al., 2018; Rasoulzadeh et al., 2020; Zou  
139 et al., 2017). However, these studies focus on either larger fractures (Zou et al., 2017) or artificially  
140 created surface roughness (Deng et al., 2018; Rasoulzadeh et al., 2020). In comparison to  
141 measured topographies in dissolution experiments, the height/depth of artificial topography

142 features is greatly exaggerated, e.g., comparing the roughness used by Deng et al. (2018) with  
143 pit depths  $\leq 100 \mu\text{m}$  to the VSI measurements of Bibi et al. (2018) with depths up to  $\leq 2 \mu\text{m}$ .

144  
145 Further studies investigated mineral dissolution in 3D  $\mu$ -CT rock samples and the influence of the  
146 flow field on the reaction rate (Menke et al., 2017; Menke et al., 2016). High porosity in the rock  
147 formations leads to uniform dissolution, while lower porosities lead to channeling of the flow. The  
148 average rock dissolution rate can be orders of magnitude lower than for measurements on flat  
149 surface samples. This rate reduction is caused by transport limitations in regions far from fast flow  
150 channels and is greatest for channeled flow samples. Numerical simulations based on the  $\mu$ -CT  
151 datasets confirmed the rate reduction for systems with high porosity heterogeneities (Pereira  
152 Nunes et al., 2016a; Pereira Nunes et al., 2016b).

153  
154 A recent study by Agrawal et al. (2021) investigated the effect of hydrodynamics on dissolution  
155 rate variability by simulating calcite dissolution based on experimental dissolution rate map data  
156 Bollermann and Fischer (2020). Their investigations focused on the heterogeneity of flow owing  
157 to increasing surface roughness during dissolution. They showed that local variability of  
158 hydrodynamic effects could not explain the experimental dissolution rate distribution. Thus,  
159 micrometer-scale heterogeneity of fluid flow field and composition was negligible. The surface  
160 roughness in the studied system had no significant hydrodynamic effects on the resulting reaction  
161 rates. Overall, the numerical approach failed to reproduce the experimental results, highlighting  
162 the need for parameterization of surface reactivity in RTM dissolution rate calculations, especially  
163 for surface-controlled conditions. To address this shortcoming, Karimzadeh and Fischer (2021)  
164 suggested a surface slope-based parameter, called the surface slope factor (SSF), to serve as a  
165 surrogate value for the reactivity distribution. The concept is based on the idea that highly reactive  
166 kink sites occur in high concentrations at atomic steps. A high concentration of atomic steps is  
167 found at sites with strong height changes in the  $\mu\text{m}$  range on the mineral surface, which can be  
168 identified with high slope values. Parameterized simulation of a dissolving calcite surface showed  
169 good agreement with experimentally obtained dissolution rates.

170  
171 This study aims to investigate the general applicability of surface slope as a way to parameterize  
172 reactivity for improved RTM approaches. The goal is to identify a general pathway to parameterize  
173 surface reactivity in pore-scale 3D RTMs, e.g., with  $\mu$ -CT-derived pore space and mineral grain  
174 geometries. For this, we start with the classical pore-scale dissolution RTM approach at far-from-  
175 equilibrium conditions using VSI maps of a calcite single crystal (Bibi et al., 2018). This dataset  
176 provides a larger field-of-view (FOV) than previous studies on single crystals (Karimzadeh and

177 Fischer, 2021) or polycrystalline (Agrawal et al., 2021) surfaces. The surface exhibits large height  
178 variations on a single crystal surface (up to 2  $\mu\text{m}$ ), compared to the surfaces from Karimzadeh  
179 and Fischer (2021) with up to 0.1  $\mu\text{m}$  variations. The polycrystalline surfaces of Agrawal et al.  
180 (2021) also show up to 2  $\mu\text{m}$  height variation, but the height differences are mainly limited to grain  
181 boundaries and do not provide insight into the evolution of large height differences on single crystal  
182 surfaces. Additionally, the data set of Bibi et al. (2018) provides surface measurements for a  
183 dissolution reaction time of 6 h, which can be used directly for model validation. With these  
184 temporal and spatial scale differences, we can test the performance of the SSF parameterization  
185 on larger systems and explore a feasible way to upscale the approach to larger 3D systems  
186 consisting of multiple crystal grains. To achieve the goal of 3D applicability, we improve the SSF  
187 calculation to be independent of the spatial orientation of the surface. In a final step, we apply the  
188 slope parameterization approach to a simple 3D artificial rock model and test the influence of  
189 surface reactivity on the prediction of mineral dissolution in this system. Overall, this study tests  
190 the validity of the SSF parameterization approach for reactivity on a uniquely large data set and  
191 aims to provide an upscaling pathway for larger 3D rock pore network geometries.



## 192 **2. Methods**

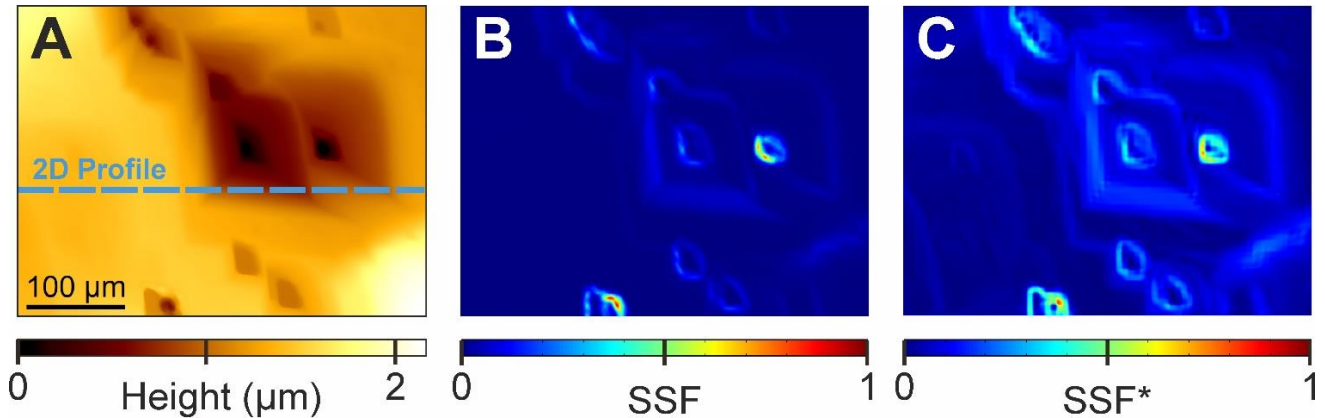
193 A classical pore-scale RTM approach was applied to test its predictive capabilities towards mineral  
194 dissolution rates. Three different cases were simulated: (1) flow through a 2D channel with a rough  
195 surface, (2) flow over rough single crystal surfaces, and (3) flow through an artificial rock (3D)  
196 model. All simulations were performed with COMSOL Multiphysics, using a finite element method  
197 (FEM).

198

### 199 **2.1 Material**

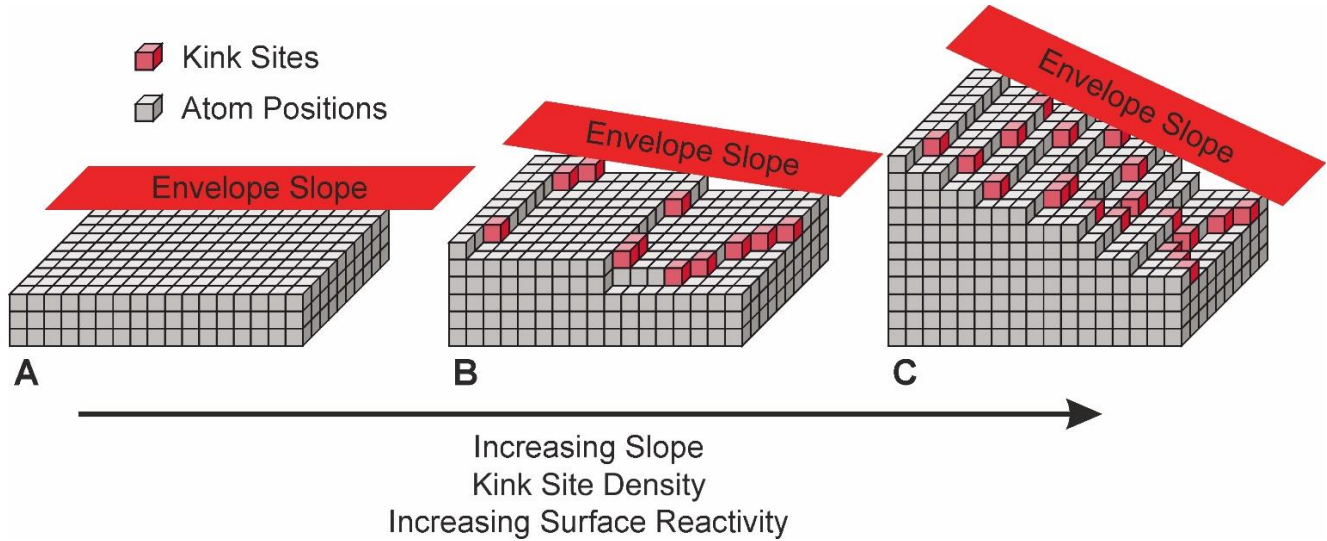
#### 200 **2.1.1 Surface topography analysis**

201 In both 2D and 3D simulations, the fluid-mineral interface was defined using the rough surface  
202 topography of a calcite single crystal measured by interferometry microscopy, published in Bibi et  
203 al. (2018). There, the surface topography of a pre-reacted (10-14) calcite face with etch pits was  
204 measured over a dissolution period of 6 h. This resulted in the collection of 80 surface topography  
205 datasets by quasi-in situ measurements, allowing for the calculation of dissolution rates via  
206 difference maps. The topography selected for implementation in our RTM was measured towards  
207 the end of the dissolution experiment after 6 h (**Fig. 1 A**). This data set was selected because it  
208 exhibited the greatest variation in surface height, which is expected to have the strongest influence  
209 on hydrodynamics. The corresponding dissolution rate map was calculated using the height  
210 changes between 6 and 6.5 h. This rate map was then compared to rate maps simulated using  
211 different dissolution rate equations. The measured surface area was  $414\ \mu\text{m} \times 313\ \mu\text{m}$  with a  
212 maximum height variation of  $\sim 2.2\ \mu\text{m}$  in the selected data set. A flow rate of 6 mL per minute was  
213 applied during dissolution, resulting in a residence time of  $< 8\ \text{s}$ , ensuring conditions of surface-  
214 controlled reaction. Using the provided fluid volume of 0.5 mL and assuming a cubic shape, we  
215 can convert the flow rate to a flow velocity of  $\sim 1500\ \mu\text{m/s}$ . In the 2D case, a single topography  
216 profile line was extracted parallel to the x-direction, resulting in a domain length of  $414\ \mu\text{m}$  (**Fig. 1**  
217 **A**, blue line).



**Figure 1:** (A) Topography of the calcite single crystal surface selected for simulation. The topography is the same as the initial topography used for dissolution rate calculation in Fig. 4 h in Bibi et al. (2018). This surface map shows the largest height variation of all the initial topography measurements. The blue dashed line indicates the surface profile line used in the 2D simulations (cf. **Figs. 4** and **5**). (B) SSF distribution calculated using **Eq. (1)**, based on the approach of Karimzadeh and Fischer (2021). (C) SSF\* distribution with the improved slope equation (**Eq. (2)**). The improved equation shows much higher sensitivity, especially in the regions of low to intermediate slope (e.g. shallow etch pits) where the features could not be resolved previously.

218  
 219 **2.1.2 Surface slope analysis and data treatment**  
 220 Karimzadeh and Fischer (2021) suggested the use of surface slope as a way to parameterize the  
 221 distribution of reactivity on mineral surfaces, which is not included in the classical rate equation  
 222 approach. The concept is based on the heterogeneous distribution of reactive atomic sites on the  
 223 surface as a function of local step density. This step density is higher in regions with strong height  
 224 variations over small length scales compared to atomically flat planes (**Fig. 2**). At the  $\mu\text{m}$  scale,  
 225 these height variations can be observed via the surface slope, with high slope values indicating a  
 226 strong accumulation of atomic steps on the surface. Atomic steps consist of atomic surface sites  
 227 with the highest reactivity for dissolution reactions: Step sites and in particular kink sites  
 228 (Bollermann and Fischer, 2020). A high atomic step density may thus indicate a high concentration  
 229 of reactive sites, leading to an overall increase in local reactivity. Areas of high surface tilt are  
 230 mainly located at surface features such as etch pits and larger steps.



**Figure 2:** Schematic drawing of the surface slope on an atomic scale using the example of a Kossel-Stranski crystal surface. The envelope slope is represented by a red surface. (A) An atomically flat surface with no inclination and no crystal steps on the surface. (B) Crystal surface with a few steps leading to an intermediate slope. There are highly reactive kinks in the steps (red cubes). (C) Crystal surface with increased slope, resulting in higher step density and thus higher concentration of kink sites on the same surface. Based on this concept, the slope factor is used as a proxy parameter to describe the density distribution of steps and kinks and therefore the reactivity distribution on mineral surfaces.

231  
 232 Karimzadeh and Fischer (2021) calculated the SSF by using the surface gradient in the z-direction  
 233 as a component of the surface normal vector perpendicular to the surface geometry:

$$SSF(x, y) = n_z = \nabla f(z) \quad (1)$$

234 This value can be calculated for any surface point, allowing the parameterization of each element  
 235 at the interface. The resulting SSF distribution is shown in **Fig. 1 B**. The disadvantage of this  
 236 calculation is that the general orientation of the surface must be perpendicular to the z-direction  
 237 in order to capture a deviation using **Eq. (1)**. In real 3D systems with grains consisting of multiple  
 238 surfaces, this approach is not applicable. To overcome this problem, we have improved the SSF  
 239 equation to use the arctangent of the surface gradients of the normal vector in all spatial directions  
 240 and relate it to the average orientation of the surface:

$$SSF^*(x, y) = \tan^{-1}(|nx - \bar{n}\bar{x}| + |ny - \bar{n}\bar{y}| + |nz - \bar{n}\bar{z}|) \quad (2)$$

241 This allows SSF calculation independent of the spatial orientation of the surface. Additionally, this  
 242 equation is more sensitive to low slope values. In comparison to **Fig. 1 B**, calculated **with Eq. (1)**,  
 243 the new SSF\* calculation increases the areas with low to medium SSF values and shows features  
 244 such as shallow etch pits, which were not resolved by the previous calculation (**Fig. 1 C**).

245

246 **2.1.3 Slope Factor Normalization**

247 The relationship between dissolution rate and SSF must be adjusted by normalizing between the

248 two values. Karimzadeh and Fischer (2021) and the present study use a simple linear SSF

249 normalization. Here, the maximum rate corresponds to an SSF value of one, a rate of zero

250 corresponds to an SSF of zero, and a linear distribution of rates mediates between the two extreme

251 values. For our application to calcite single-crystal surfaces, this normalization produces results

252 in good agreement with the experimental data, as presented in the following sections of this study.

253 However, for different mineral systems, a more complex and case-adapted SSF normalization

254 might be required. In general, there are two main options for adjusting the SSF normalization. The

255 first is the slope of the normalization curve, which can be adjusted by changing the SSF value at

256 which the maximum dissolution rate is reached. The gradient is used to describe the average

257 kinetics of the complete crystal surface. As a second option, the shape of the normalization curve

258 can be modified if a linear shape does not correctly represent the surface reactivity. Here,

259 intermediate support points can be included in the SSF normalization to vary the gradient in

260 specific regions where reactivity is increased or decreased in comparison to the average surface

261 kinetics. Additionally, weighting factors can be included for local rate change in certain slope

262 regions.

263 By using these control options, SSF can be applied to any crystal surface. Tuning of the SSF

264 normalization needs to be performed by fitting simulation results to experimental rate spectra.

265 Once a normalization with a good fit is achieved, it can be used for all further simulations with

266 surfaces of the same mineral.

267

268 **2.2 Fluid flow and transport**

269 The simulation exemplifies the reaction kinetics in a single pore with a calcite crystal surface as

270 pore wall in the micrometer range in a geological system (**Fig. 3**). Only slow fluid velocities were

271 considered for fluid flow in the system (Reynolds number  $\ll 1$ ). All simulations were performed at

272 an average velocity of 1000  $\mu\text{m/s}$  unless otherwise stated, similar to the estimated experimental

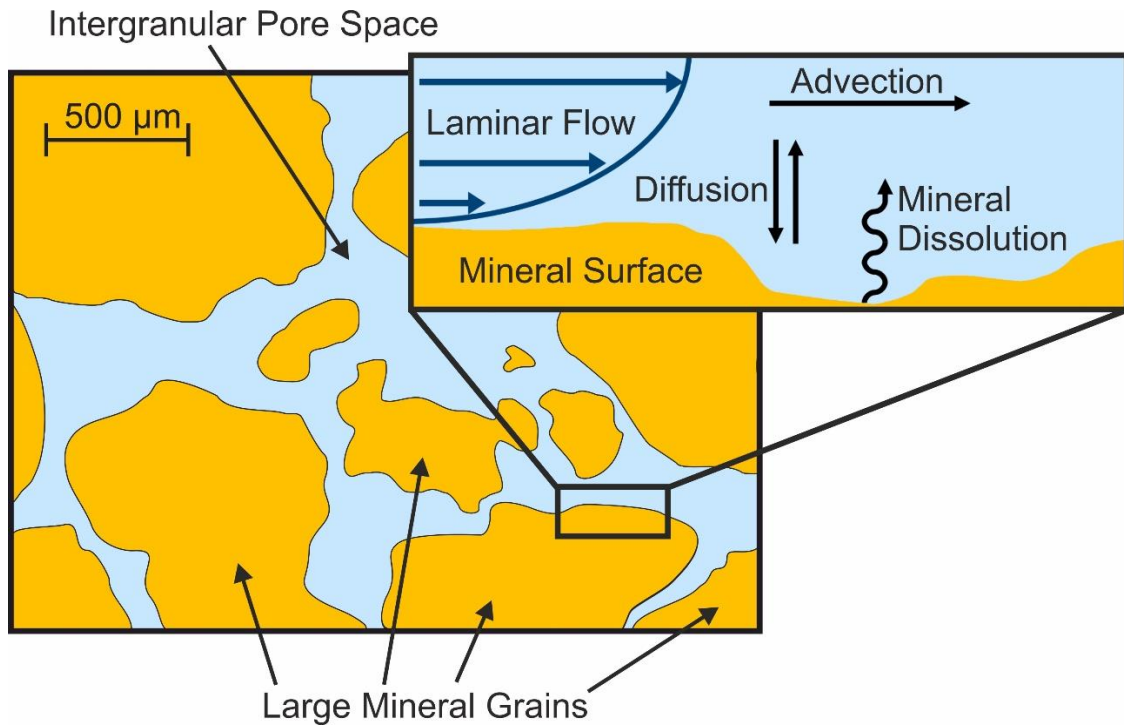
273 velocity of 1500  $\mu\text{m/s}$ . The fluid flow in our system was simulated assuming laminar flow

274 conditions. The Navier-Stokes equation for the flow of an incompressible viscous fluid was applied:

$$\rho \left( \frac{\partial u}{\partial t} + u \cdot \nabla u \right) = -\nabla p + \mu \nabla^2 u \quad (3)$$

$$\nabla \cdot u = 0 \quad (4)$$

275 where  $\rho$  is the fluid density ( $\text{kg}\cdot\text{m}^{-3}$ ),  $u$  is the fluid velocity ( $\text{m}\cdot\text{s}^{-1}$ ),  $t$  is the time (s),  $p$  is the fluid  
 276 pressure (Pa) and  $\mu$  is the dynamic viscosity ( $\text{Pa}\cdot\text{s}$ ). The flow was simulated above the calcite  
 277 surface for a height of  $75\ \mu\text{m}$  in 2D,  $30\ \mu\text{m}$  in 3D, and  $10\ \mu\text{m}$  in 3D with moving boundaries. The  
 278 geometry of the artificial rock is a cube with an edge length of  $1500\ \mu\text{m}$ . A fully developed flow or  
 279 normal inflow velocity when using moving boundaries was applied at the inlet and a constant  
 280 pressure condition was applied at the outlet. For the boundary interface with the calcite or other  
 281 grain surfaces, the “no-slip” condition ( $u = 0$ ) was applied. For the surface simulations, a leaking  
 282 wall boundary condition with a fluid velocity in the x-direction was applied to the upper boundary,  
 283 selected in proportion to the average flow velocity in the system ( $u_{\text{upper}} = 1.5 \cdot u_{\text{avg}}$ ). For the two  
 284 vertical boundaries parallel to the flow direction, the open boundary condition without viscous  
 285 stress and without slip condition for moving boundaries was applied. For the artificial rock  
 286 geometry, the calcite grain had the dimensions of  $313 \times 414 \times 300\ \mu\text{m}^3$  and the additional inert  
 287 grains had a radius of  $400\ \mu\text{m}$  for the large grain and  $250\ \mu\text{m}$  for the four small grains.  
 288



**Figure 3:** Schematic representation of a sedimentary rock consisting of larger grain components and intergranular pore space. The pore space can be filled with fine-grained minerals and cement or be empty and available for fluid flow. The inset shows an enlarged view of the mineral surface with all processes considered in the simulations.

289  
 290 For the simulation of species transport in the system, we applied the advection-diffusion-reaction  
 291 equation for general transport:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D_i \nabla c_i) - u \cdot \nabla c_i + R_i \quad (5)$$

292 where  $D_i$  is the diffusion coefficient ( $\text{m}^2 \cdot \text{s}^{-1}$ ),  $c_i$  is the concentration ( $\text{mol} \cdot \text{m}^{-3}$ ) and  $R_i$  is the reaction  
 293 input ( $\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$ ) of species  $i$ . Unless otherwise stated, a diffusion coefficient of  $1 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$  was  
 294 used for all species in all simulations.

295 To quantify the importance of advection, diffusion, and reaction rates under different flow and  
 296 transport conditions, two dimensionless parameters were used: The Péclet number (Pe) and  
 297 Damköhler number (Da). The test of different flow conditions was performed in the 2D simulation  
 298 case. The Péclet number is the ratio of the advection rate to the diffusion rate and is calculated  
 299 as:

$$\text{Pe} = \frac{u_{\text{avg}} \cdot L}{D} \quad (6)$$

300 where  $L$  is the characteristic length (m). Here we selected the diameter of the flow channel for  $L$ .  
 301  $\text{Pe} > 1$  shows an advection-dominated transport regime, whereas a  $\text{Pe} < 1$  indicates a diffusion-  
 302 dominated transport regime.

303 The Damköhler number relates the reaction time scale at the surface to the advection time scale  
 304 and is calculated as:

$$\text{Da} = \frac{T_A}{T_R} \quad (7)$$

$$T_A = \frac{L}{u_{\text{avg}}} \quad (8)$$

$$T_R = \frac{C_{\text{Calcite}}}{S_R} \quad (9)$$

305 where  $T_A$  is the advection and  $T_R$  the surface reaction time scale.  $C_{\text{Calcite}}$  is the density of surface  
 306 sites of calcite ( $\text{mol} \cdot \text{m}^{-2}$ ) and was obtained from Wolthers et al. (2008).  $S_R$  is the surface reaction  
 307 rate ( $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) and the reaction rate calculated at  $x = 100 \mu\text{m}$  was selected for the calculation  
 308 of Da.  $\text{Da} > 1$  indicates that the dissolution rate is limited by transport, while  $\text{Da} < 1$  indicates  
 309 dissolution rates limited by the surface reaction rate.

310

### 311 **2.3 Geochemistry**

312 As in the experiment, the solid phase in the model consisted of pure calcite. Initially, the species  
 313 concentrations in the pore solution were adjusted to be in equilibrium with the calcite crystal  
 314 surface, so that the dissolution was zero. At the beginning of the simulation, the concentrations in

315 the incoming fluid were slowly changed to obtain a solution with a pH of 8.82, as used in the  
 316 experiment of Bibi et al. (2018). All species concentrations of the initial equilibrium solution and  
 317 the influent solution are listed in **Table 1**. A zero gradient boundary condition was applied at the  
 318 outlet. All other boundaries except the fluid-mineral interface were modeled with a no-flux  
 319 boundary condition.  
 320

**Table 1:** Species concentration of the initial equilibrium fluid (Agrawal et al., 2020) and the influent fluid corresponding to the pH condition used in Bibi et al. (2018). CO<sub>2</sub> (gas) is removed from the system for the final 3D slope simulations to reduce the computational cost, while still adequately describing the system.

Species	Equilibrium Solution (mol/m <sup>3</sup> ) (Agrawal et al., 2020)	Inflowing Solution (mol/m <sup>3</sup> )
CO <sub>2</sub> (gas)	6.67·10 <sup>-4</sup>	31.622
CO <sub>2</sub> (aq)	2.27·10 <sup>-5</sup>	1.077·10 <sup>-2</sup>
CO <sub>3</sub> <sup>2-</sup>	3.38·10 <sup>-2</sup>	1.189·10 <sup>-1</sup>
HCO <sub>3</sub> <sup>-</sup>	8.35·10 <sup>-2</sup>	3.320·10 <sup>0</sup>
H <sup>+</sup>	1.27·10 <sup>-7</sup>	1.589·10 <sup>-6</sup>
OH <sup>-</sup>	8.35·10 <sup>-2</sup>	6.942·10 <sup>-3</sup>
Ca <sup>2+</sup>	0.117	0
pH	9.91	8.82

321  
 322 At the interface, the surface of the calcite crystals can dissolve and release Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> into  
 323 the solution. This was implemented by using a flux boundary condition. In RTMs, the dissolution  
 324 of the crystalline matter is usually simulated by applying a rate law according to transition state  
 325 theory (Lasaga and Lüttge, 2003; Steefel et al., 2015). For calcite, the standard rate law is:

$$Rate_{\text{Calcite}} \left[ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right] = (k_1 \cdot a_{\text{H}^+} + k_2 \cdot a_{\text{CO}_2(\text{aq})} + k_3 \cdot a_{\text{H}_2\text{O}}) \cdot \left( 1 - 10^{\frac{2}{3} \text{SI}} \right) \quad (10)$$

$$\text{SI} = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}}{K_{\text{sp}}} \quad (11)$$

326 where  $k_1$ ,  $k_2$  and  $k_3$  are the reaction rate constants and  $a$  is the activity of all species involved in  
 327 the process. SI is the saturation index and is computed from the ratio of the ion activity product  
 328 and the solubility constant  $K_{\text{sp}}$ . There are multiple sources from literature for the reaction rate  
 329 constants and the solubility constant (Busenberg et al., 1986; Plummer et al., 1978). In our model,

330 we use the values reported by Chou et al. (1989):  $k_1 = 8.9 \cdot 10^{-5}$ ,  $k_2 = 5.0 \cdot 10^{-8}$ ,  $k_3 = 6.5 \cdot 10^{-11}$  and  
331  $K_{sp} = 10^{-8.46}$  at 25°C.

332 To describe surface reactivity in the rate equation, we include the previously introduced SSF as a  
333 simple factor dependent on the local slope values:

$$Rate_{SSF}(x, y) = SSF(x, y) \cdot Rate_{Calcite}(x, y) \quad (12)$$

## 334 **2.4 Simulation of Topography Evolution**

335 In order to simulate the changing topography of the crystal surface with proceeding dissolution,  
336 we introduced a moving boundary condition for the calcite surface and the calcite grain. We used  
337 the “deformed geometry” function available in COMSOL for this calculation. Based on the local  
338 dissolution rate, we calculated a local surface retreat velocity  $v$  ( $m \cdot s^{-1}$ ) using the molar volume of  
339 calcite  $V_m$  ( $m^3 \cdot mol^{-1}$ ):

$$v_{Retreat}(x, y) = Rate_{\alpha}(x, y) \cdot V_m \quad (13)$$

340 This retreat velocity was then applied to the dissolving calcite surface, which in turn can change  
341 the slope and therefore the reactivity distribution as the simulation time progresses. Over larger  
342 simulation times, height changes of up to several micrometers can be simulated.



### 343 **3. Results and Discussion**

344 The results of this study are presented in five sections, each consisting of results section followed  
345 by a discussion section. In the first section (3.1), we use a 2D cross-sectional simulation over the  
346 rough calcite surface to evaluate the influence of hydrodynamics on the surface dissolution rate.  
347 In a second step (3.2), we compare the classically simulated dissolution rates with experimental  
348 data and focus on specific crystal surface sections to investigate whether the classical approach  
349 can adequately describe the mineral dissolution. In subchapter 3.3, simulation results using the  
350 new SSF parameterization are compared to both, the classical simulation approach and  
351 experimental results. Subsection 3.4 examines the temporal evolution of the surface topography  
352 and the prediction of the dissolution rate using the new SSF parametrization and including the  
353 spatial modification of surface reactivity. In the final step (3.5), the reactivity parameterization is  
354 applied to an artificial 3D rock geometry, in contrast to the simpler situation of a single crystal  
355 surface. Here we compare results to calculations without reactivity parameterization and highlight  
356 the differences. We show a pathway to apply the surface-dependent SSF for use with realistic  
357 rock geometry data.

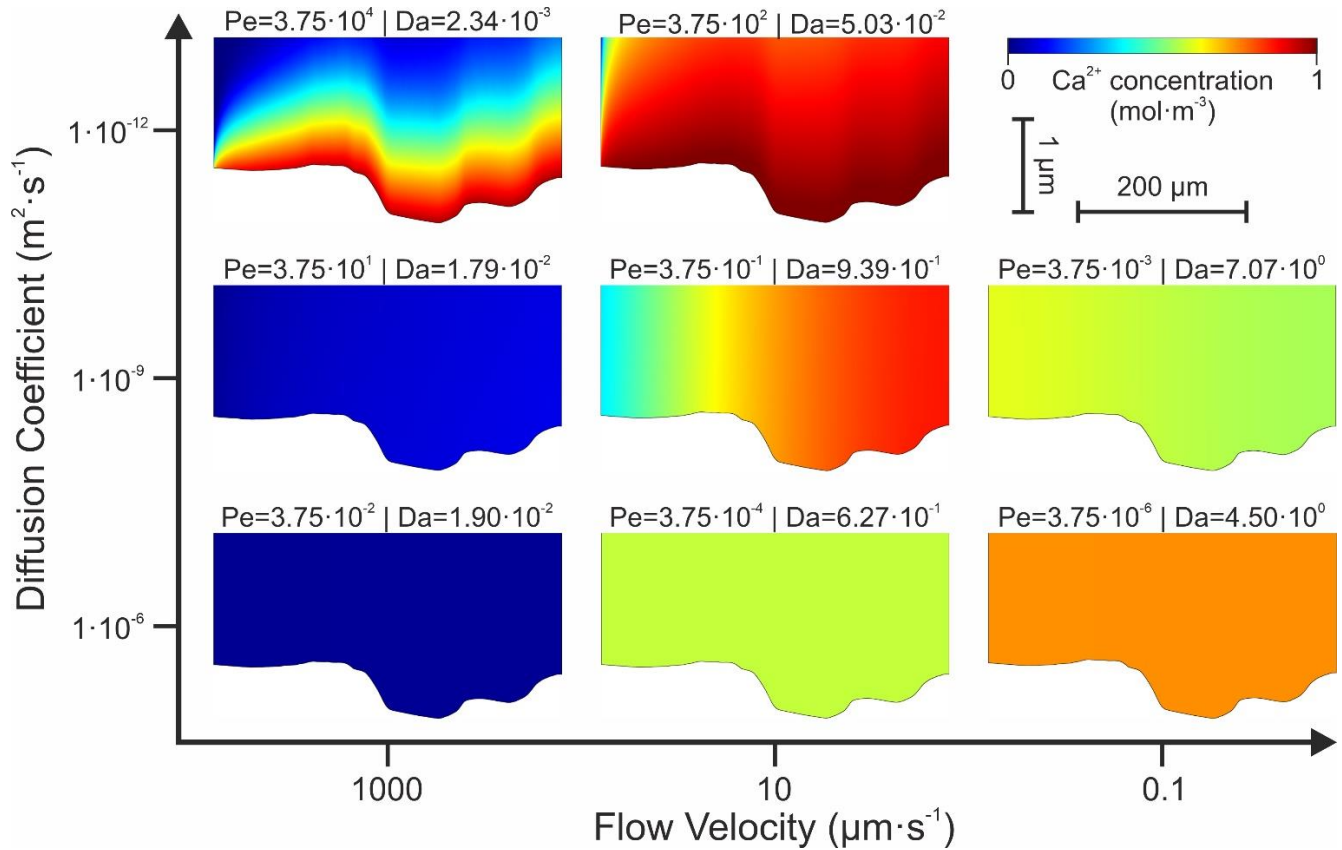
358

#### 359 **3.1 Influence of heterogeneity of surface topography on transport and reaction** 360 **rates (2D simulation)**

##### 361 **3.1.1 Results**

362 In this RTM, we simulated dissolution rates along the calcite-fluid interface with rough topography  
363 available from VSI data. We varied the reaction and transport conditions at the surface by  
364 changing flow velocities and diffusion coefficients. The flow velocities were used to control surface  
365 dissolution rate limitations ( $Da$ ), with low flow velocities leading to transport-controlled conditions  
366 and high flow velocities leading to surface reaction rate-controlled conditions. The main transport  
367 mode, advection or diffusion, was controlled by varying the diffusion coefficients. All selected flow  
368 velocities and diffusion coefficients, as well as the resulting  $Pe$  and  $Da$  numbers for the eight  
369 simulated cases, are presented in **Fig. 4**. The resulting calcium concentration profiles up to  $2\ \mu\text{m}$   
370 above the calcite surface are shown in **Fig. 4**. Calcium is released only by the dissolution reaction  
371 at the surface, as the inflowing fluid has a calcium concentration of zero.

372



**Figure 4:** Simulated  $\text{Ca}^{2+}$  concentration profiles up to  $2\ \mu\text{m}$  above the rough calcite surface under different transport and reaction conditions. The respective Péclet and Damköhler numbers are given for each case. Advection-controlled ( $\text{Pe} > 1$ ) conditions lead to boundary layer formation with high concentration of solute species. Diffusion-controlled conditions ( $\text{Pe} < 1$ ) result in a homogeneous distribution of solute species. Higher flow velocities result in overall lower  $\text{Ca}^{2+}$  concentrations in the domain. Experimental conditions ( $u \approx 1500\ \mu\text{m}/\text{s}$ ,  $D \approx 1\cdot 10^{-9}\ \text{m}^2\cdot\text{s}^{-1}$ ) in Bibi et al. (2018) are expected to lead to a solute concentration distribution similar to the case with high flow velocities and intermediate diffusion coefficient ( $\text{Pe} = 3.75\cdot 10^1$ ,  $\text{Da} = 1.79\cdot 10^{-2}$ ).

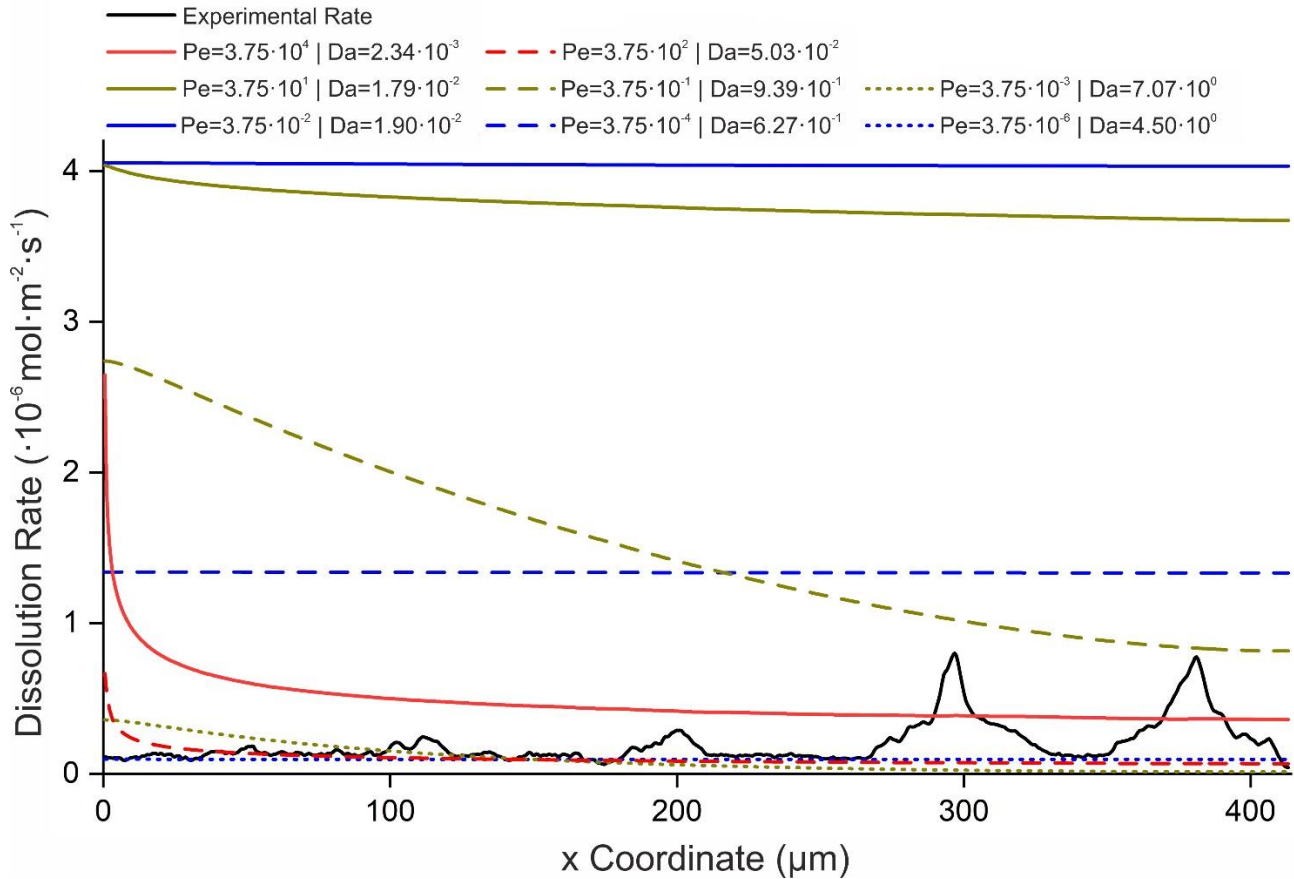
373

374 When diffusive transport dominates in the system (cf. cases in the bottom row), the calcium  
 375 released from the surface is homogeneously distributed in the liquid without any gradient being  
 376 observed. An increasing in fluid velocities under diffusion-dominated conditions causes an overall  
 377 lower calcium concentration in the fluid (cf. case at bottom right vs. case at bottom left). Under  
 378 transport conditions where the influence of advective transport increases, a concentration gradient  
 379 is developed from the inlet to the outlet (cf. case in the central section). This effect is better  
 380 observed in the simulations with low diffusion strength (cf. case in the upper left). Predominant  
 381 advective transport leads to the formation of a boundary layer with high calcium concentration and  
 382 to the formation of a concentration gradient between the surface and the center of the flow channel  
 383 (cf. case in the upper left). The thickness of the boundary layer decreases with increasing velocity.  
 384 We expect that the experiment in Bibi et al. (2018), based on the estimated experimental

385 conditions of  $u \approx 1500 \mu\text{m/s}$  and  $D \approx 1 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ , leads to a concentration distribution similar to  
386 the case with high flow velocity and intermediate diffusion ( $Pe = 3.75 \cdot 10^1$ ,  $Da = 1.79 \cdot 10^{-2}$ ).

387 For all simulation cases, the dissolution rates based on the classical rate equation along the  
388 interface from inlet ( $x = 0 \mu\text{m}$ ) to outlet ( $x = 414 \mu\text{m}$ ) are shown in **Fig. 5**. When diffusion is the  
389 dominant transport mode, the dissolution rates are constant over the entire length. A decrease in  
390 fluid flow rate under these conditions is expected to change the limitation of the reaction rate from  
391 surface- to transport-controlled conditions. The only visible effect in the simulation results is the  
392 decrease in the overall dissolution rate while it remains constant along the interface. With  
393 increasing advective transport, a gradient in dissolution rate is observed from the inlet to the outlet.  
394 At the highest advective influence, a high gradient near the inlet is followed by a low dissolution  
395 rate, which is largely constant. As expected, dissolution rates increase with flow velocity and  
396 surface reactivity control until a near-zero calcium concentration is reached in the fluid, where the  
397 rate maximum is observed. This result is similar to the dissolution plateau reported by Liang and  
398 Baer (1997), which occurs when dissolution is controlled solely by the surface reaction rate.

399  
400 The comparison between RTM and experimental reveals a large difference in the behavior of the  
401 dissolution rate. The experimental rate shows a constant baseline dissolution with distinct peaks  
402 at certain locations on the surface. These locations are the steps forming the two etch pits included  
403 in the selected profile line. In none of the simulated cases are there peaks in the dissolution rate  
404 that could be associated with features of the surface topography such as steps. Comparison of  
405 the experimental results with the simulation case with similar conditions ( $Pe = 3.75 \cdot 10^1$ ,  $Da =$   
406  $1.79 \cdot 10^{-2}$ ) reveals two major differences. First, the overall rate is overestimated in the model with  
407 an average rate of about  $4 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ , whereas in the experiment a maximum rate of about  
408  $1 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$  is reached when it peaks. Second, no rate peaks are observed in the RTM, and  
409 a gradient is predicted that is not seen in the experimental data. Even with a wide range of  
410 conditions, the RTM is not able to reproduce the experimental result.



**Figure 5:** Calcite dissolution rate at the topographic boundary under different flow and transport conditions: Blue for high  $D$ , yellow for intermediate  $D$ , and red for low  $D$  values. Solid lines represent high  $u$ , dashed lines intermediate  $u$ , and dotted lines low  $u$  values. The arrangement of the color scale legend corresponds to the image setup in **Fig. 4**. Strong diffusive transport leads to a constant dissolution rate. With decreasing influence of diffusive transport, the rate follows a decreasing gradient from inlet to outlet. Higher flow velocities increase the overall dissolution rate. No rate variability is visible under any condition, in contrast to the rate variability in the experimental profile. Experimental conditions were set to satisfy  $Pe > 1$ ,  $Da < 1$  (Bibi et al., 2018; Liang and Baer, 1997).

411

### 412 3.1.2 Discussion

413 Hydrodynamic conditions can play a key role in the distribution of dissolution rates on mineral  
 414 surfaces. Under transport-controlled conditions, the flow velocity and diffusion of solute species  
 415 are the key parameters describing the dissolution reactions and thus determine their distribution.  
 416 When shifting to a surface reactivity-driven dissolution regime with high transport efficiency due to  
 417 high flow velocities or diffusion, the mineral surfaces exhibit a heterogeneous distribution of rates,  
 418 as shown by measurements using surface-sensitive techniques (Bibi et al., 2018; Fischer et al.,  
 419 2014). Do hydrodynamic effects cause and/or modify this heterogeneous rate pattern or is it  
 420 dictated solely by intrinsic crystal properties (Agrawal et al., 2021; Fischer et al., 2014)?

421 To answer this question, we investigate the species concentrations at different transport conditions  
 422 during the dissolution reaction. The simulations with conditions matching the experimental

423 specifications failed to reproduce the heterogeneous distribution of the dissolution rate. The  
424 topography of the mineral surface can affect the fluid flow and create concentration gradients  
425 leading to varying dissolution rates. A similar effect has been reported by Deng et al. (2018), who  
426 used RTM to study pore-scale dissolution of calcite at rough pore walls. They reported that an  
427 increase in surface roughness due to a larger surface area resulted in an overall increase in the  
428 dissolution rate. This increase is not linear, as increasing roughness creates immobile or  
429 recirculating fluid zones in surface pits. Here, the concentrations of dissolved ions increase,  
430 limiting the dissolution rate via a high local saturation (**Eqs. 11 and 12**). However, the surface  
431 roughness applied by Deng et al. (2018) produces pits with a wide range of depth-to-width ratios  
432 ( $d/w$  ratio), ranging from 1 : 5 to 1 : 20. In contrast, the  $d/w$  ratios observed on the reacted crystal  
433 surface show values 1 : >85. No formation of recirculation zones was observed in our simulations.  
434 The only rate-decreasing effect under the experimental conditions is some hydrodynamic shadow  
435 regions, which are responsible for only a very small rate reduction. Calculations show that such  
436 rate decrease is about two to three orders of magnitude below the overall dissolution rate for  $d/w$   
437 ratios of 1 : >85. This rate decrease is less than the line width of the VSI rate curve in **Fig. 5**. In  
438 comparison, for an artificial cuboidal pit on a flat surface, the concentration accumulation in a pit  
439 with a depth-to-width ratio of 1 : 100 results in a 0.1% rate decrease, while a pit with a ratio of 1 :  
440 10 results in a 1% decrease. Rasoulzadeh et al. (2020) report similar results where they  
441 investigated the influence of sinusoidal pits ( $\sim 1 : 2$   $d/w$  ratio) on calcite dissolution rates. The  
442 difference in dissolution rates between sine maximum and minimum is  $\ll 1\%$ , and at higher  
443 Reynolds numbers the rate maximum shifts towards the wall facing the fluid flow. Other numerical  
444 studies have shown similar results in the past. Harb and Alkire (1989) investigated the growth of  
445 corrosion pits using a finite element model. Their simulations of a shallow, rounded pit ( $d/w$  ratio  
446  $\sim 1 : 3.5$ ) on the pore wall show that flow can enter the pit without forming recirculation zones  
447 whose flow velocity decreases only slightly. The simulated concentration of dissolved ions showed  
448 an increased concentration in the center of the pit. In the simulations of fluid flow over circular pits  
449 by Higdon (1985), the importance of pit width relative to depth for the formation of recirculation  
450 zones can be observed. In the case of the shallowest simulated pit ( $d/w$  ratio  $\sim 1 : 4.5$ ), the flow  
451 field can enter completely into the center of the pit. As the pit depth increases (up to a  $d/w$  ratio  $\sim$   
452 1 : 2), a recirculation zone forms at the bottom of the pit, similar to the results of Deng et al. (2018).  
453

454 The reported rate reduction effect is strongest in the surface pits. In contrast, the experimental  
455 data show that the highest reaction rates are found at the positions of the two largest etch pits on  
456 the profile (**Fig. 5**). Thus, we conclude that there appears to be a competing effect between the  
457 rate reduction due to local hydrodynamics and the rate increase due to the high local surface

458 reactivity at the etch pit walls. Therefore, neglecting surface reactivity in RTMs leads to an  
459 incomplete description of the dissolution. Agrawal et al. (2021) investigated calcite surface  
460 sections of smaller dimensions (21  $\mu\text{m}$ ) that exhibited pits with higher d/w ratios (1 : 2.5) in an  
461 RTM due to the polycrystalline nature of the sample. Their results confirmed the absence of  
462 transport-controlled rate variability in the experimental approach. Overall, these studies confirmed  
463 the general conclusion about intrinsic dissolution rate variability. Nevertheless, the elevated and  
464 constant rates of the simulation results (**Figs. 5 and 6**) require a new numerical treatment  
465 (Karimzadeh and Fischer, 2021).

## 466 **3.2 Mineral dissolution under surface controlled conditions (3D simulation)**

### 467 **3.2.1 Results**

468 The dataset investigated by Bibi et al. (2018) covers a relatively large field of view (FOV) compared  
469 to the FOV investigated in previous studies, e.g., Agrawal et al. (2021) with surfaces of  $21 \times 21 \mu\text{m}^2$   
470 and Karimzadeh and Fischer (2021) with  $95 \times 95 \mu\text{m}^2$ . Additionally, a long reaction period of 6 h  
471 is covered by around 80 individual surface measurements in the present dataset. Thus, this  
472 dataset provides several important clues for the validation of an RTM parametrization focusing on  
473 the reactivity of the crystal surface.

474  
475 To cover specific parts of the surface reactivity, the 3D calcite surface is divided into three separate  
476 cases for simulation, shown in **Fig. 6**. Case (A) consists of the complete measured surface from  
477 Bibi et al. (2018) (**Fig. 1 A**) with a FOV of  $414 \times 313 \mu\text{m}^2$ . Two subsections are selected to cover  
478 the extreme features of the surface topography: the deepest etch pit on the surface (B) with a FOV  
479 of  $116 \times 105 \mu\text{m}^2$  and the highest step structure (C) with a FOV of  $101 \times 100 \mu\text{m}^2$ . All simulations  
480 here use the same flow velocity ( $1000 \mu\text{m}\cdot\text{s}^{-1}$ ) and diffusion coefficient ( $1 \cdot 10^{-9} \text{m}^2\cdot\text{s}^{-1}$ ), identical to  
481 the 2D simulation with  $\text{Pe} = 3.75 \cdot 10^1$  and  $\text{Da} = 1.79 \cdot 10^{-2}$ , which we expect based on the  
482 experimental constraints (**Figs. 4 and 5**). **Figure 6** shows the surface topography (I) and the  
483 experimental dissolution rate (II) and compares them with the model result (III and IV). Row V  
484 shows the difference in dissolution rates between a model with the VSI surface topography and a  
485 model with a flat surface of the same size to quantify the influence of surface topography. The  
486 maps of experimental dissolution rates show the heterogeneous distribution of dissolution rates  
487 discussed previously, which can be associated with the surface topography structures such as  
488 etch pits and steps. In contrast, the simulation yields a very similar rate distribution for all three  
489 cases. Two effects are observed when comparing the models with the VSI surface to a model with  
490 a flat surface (**Fig. 6 V**). The first effect consists of numerical errors visible for the smaller model  
491 sizes of cases (B) and (C), caused by random local minima or maxima in the hydrogen  
492 concentration along the lateral boundaries. This could be due to chosen boundary conditions. The  
493 second effect shows a decrease in the dissolution rate at the locations of the etch pits, similar to  
494 the effect discussed in Section 3.1.2. In our simulation, this decrease in dissolution rate caused  
495 by transport is two to three orders of magnitude smaller than the calculated rate and therefore  
496 does not significantly affect the overall rate distribution. For the large surface step, no visible effect  
497 of topography on the dissolution rate can be detected.

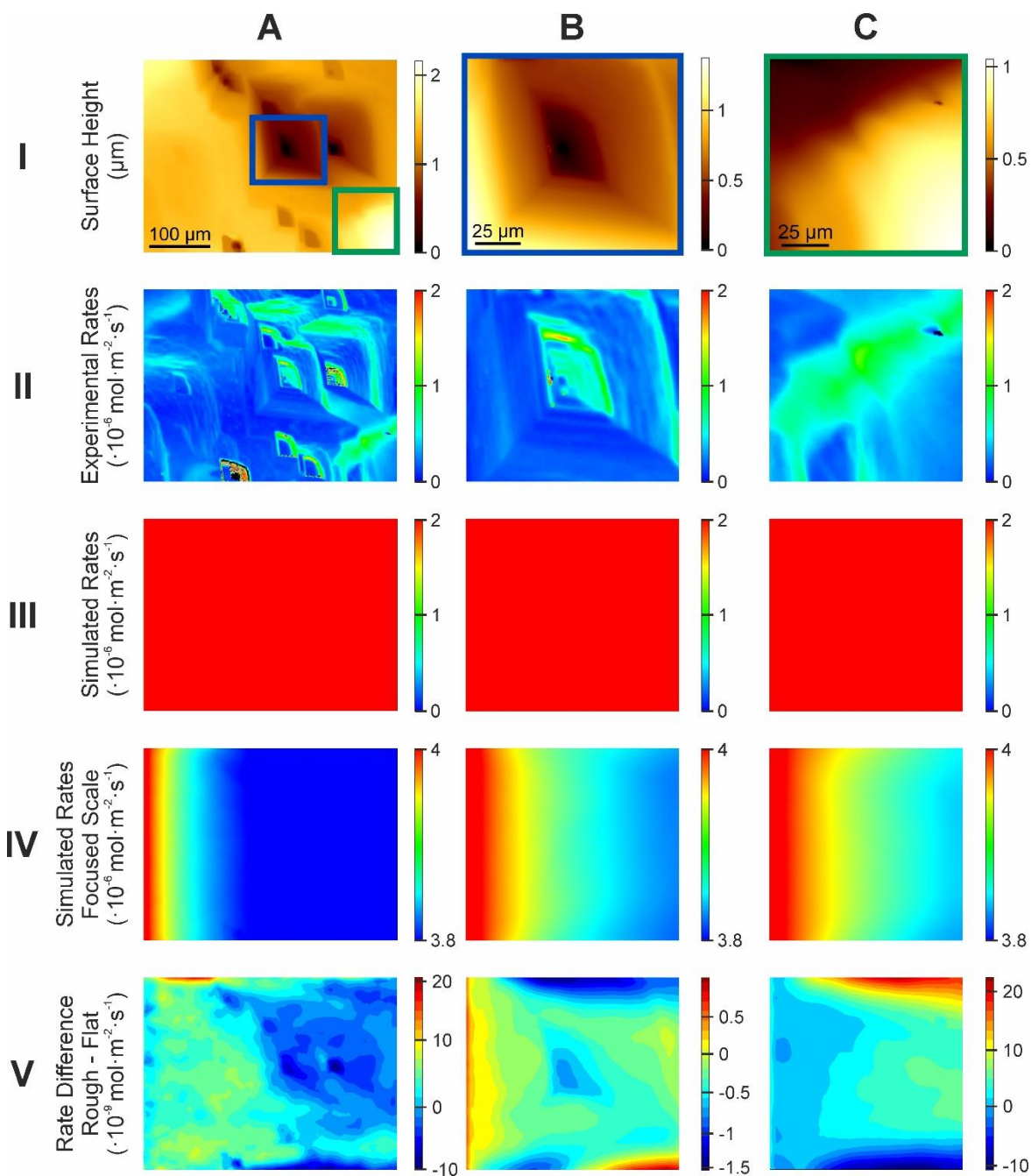
498  
499 Further details on the dissolution rate distribution can be derived from the rate spectra of the  
500 respective cases for RTM and experiment (**Fig. 7**). The rate spectrum for the entire surface shows

501 a single peak at around  $0.2 \cdot 10^{-6} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  and a large range of dissolution rates  $>2 \cdot 10^{-6} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ . The two subsections show different contributions. At the large etch pits, the overall reactivity  
502 is increased compared to the entire surface, but the general distribution of the spectrum remains  
503 similar. No clear peak is visible at the surface step, but a wide range of surface portions with higher  
504 rate contributions is seen. In contrast, the RTM rate spectra show a completely different rate  
505 distribution. All rates are  $>3.6 \cdot 10^{-6} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  and the maximum range of rates is  $<0.4 \cdot 10^{-6} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  for the entire surface, resulting in an almost singular rate value. The smaller surface  
506 sections show the same rate distribution, but with a shift of the minimum value to higher rates.  
507 This shift is due to the small rate gradient from inlet to outlet mentioned earlier, which decreases  
508 as the surface sections become smaller. Here, the rate is even more confined to a small range.  
509 The rate spectra confirm the large discrepancies between model and experiment observed in the  
510 rate maps.  
511  
512

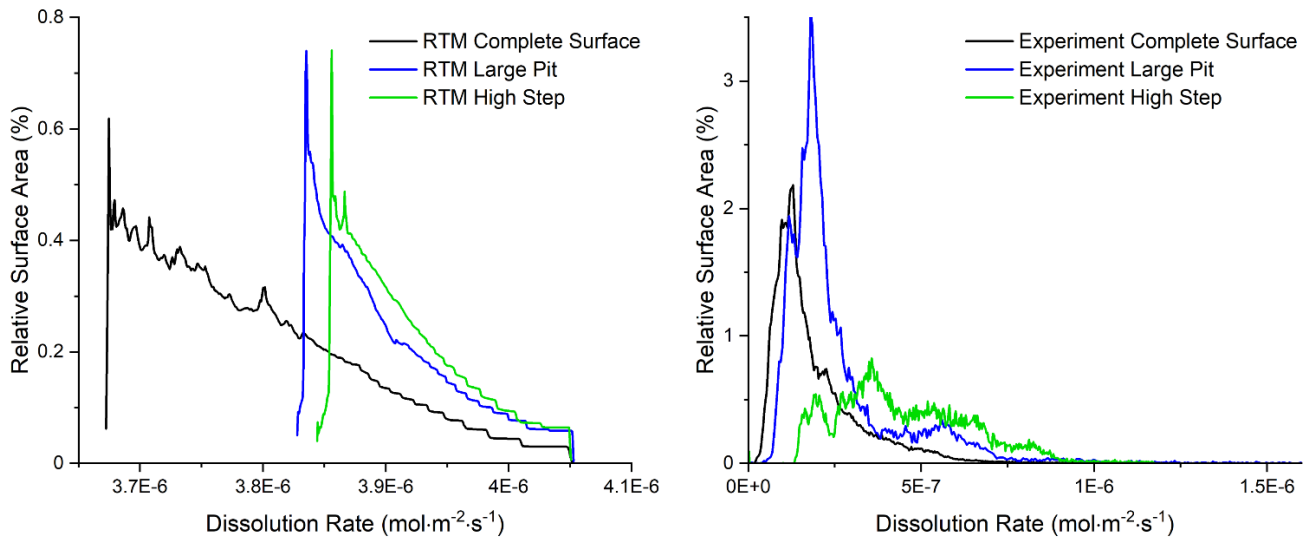
513

514 In general, the RTM dissolution rate distribution closely resembles the previous 2D result and does  
515 not reproduce the experimental findings with the same sample topography. Only a minor influence  
516 of topography was observed, which does not contribute significantly to the overall rate distribution.





**Figure 6:** (A) Full data set of calcite single crystal surface with the two areas of interest for detailed investigation marked on the height map: (B) large etch pit and (C) large surface step. For all areas, (I) the height, (II) the experimental dissolution rate, (III) the simulated rate, and (IV) the difference in dissolution rate between the rough and flat mineral surface are shown. From the comparison of the maps of experimental (II) and simulated (III) dissolution rate, a clear difference is observed. The effect of topography on the simulated rates is two to three orders of magnitude less than the rate itself (IV). Pit locations show a decreased dissolution rate in the RTM (A-IV, B-IV), while the large step shows no effect on the dissolution rate (C IV). Numerical boundary errors are observed along the lateral boundaries in the difference maps (IV). These errors have only a minor influence on the total simulated dissolution rate (III).



**Figure 7:** Rate spectra corresponding to the rate maps shown in **Fig. 6** for the simulated (left) and experimental (right) results. The spectra highlight the strong differences in dissolution rates between RTM and experiment. The RTM predicts rates that are four times higher than the observed rates. The range of simulated rates is much narrower and is close to a single value for the entire surface.

518

519

### 520 3.2.2 Discussion

521 In agreement with the results from 2D RTM, the 3D simulations are not able to reproduce the  
 522 experimental dissolution rate maps measured by Bibi et al. (2018). The reason for this discrepancy  
 523 is the lack of a description of surface reactivity in the widely used calcite rate equation (**Eq. 10**). In  
 524 both our simulations and the experimental setup used to measure surface dissolution rates,  
 525 hydrodynamic conditions lead to a surface-controlled dissolution rate regime. Above a threshold,  
 526 a further increase in flow rate does not lead to any additional increase in dissolution rates (Liang  
 527 and Baer, 1997). Here, the influence of transport on rates is negligible. Mineral intrinsic effects are  
 528 thus the cause of the observed variabilities in dissolution rates under such conditions.

529

530 Various experimental studies have confirmed a heterogeneous distribution of dissolution rates  
 531 under the same transport conditions (Arvidson et al., 2003; Bollermann and Fischer, 2020). A  
 532 large difference was found between the dissolution rates of powders and mineral surfaces, which  
 533 was explained by the different concentration of reactive sites (Arvidson et al., 2003). This  
 534 highlights the limited applicability of single rate constants derived from powder measurements  
 535 such as Busenberg et al. (1986) for the calculation of dissolution rates under surface-controlled  
 536 reaction conditions. On mineral surfaces, larger structures such as etch pits or macrosteps show  
 537 greater intrinsic reactivity than flat surface sections (Pollet-Villard et al., 2016). These structures  
 538 evolve over time through step motion, leading to the widening of etch pits, the formation of larger

539 steps, and the generation of new stepwaves (Bibi et al., 2018; Fischer and Luttge, 2018). It has  
540 been shown that the use of the stepwave model in an RTM improves the description of calcite  
541 dissolution (Bouissonnié et al., 2018). Bollermann and Fischer (2020) have highlighted the  
542 importance of multiple rate components that rely on surface building blocks to cause the formation  
543 of various topographic features. A comprehensive review of surface reactivity can be found in  
544 Fischer et al. (2014). The lack of an implementation of surface reactivity in the RTM rate equation  
545 leads to the results presented (**Fig. 6** and **7**), which incorrectly predict the rate distribution and  
546 magnitude in our system.

547  
548 Atomic-scale modeling provided additional mechanistic insight into the influence of reactive atomic  
549 sites and their distribution on mineral surfaces on dissolution rates and was able to confirm  
550 previous experimental findings (Kurganskaya et al., 2012; Lasaga and Lüttge, 2003). Numerical  
551 approaches that do not include the mineral surface reactivity in their rate description are not able  
552 to achieve the same results (Agrawal et al., 2021). The effect of natural calcite surface topography  
553 on fluid flow and hence transport is small ( $< 2 \cdot 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) compared to the total simulated  
554 ( $\sim 4 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) or experimental ( $> 2 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ ) dissolution rates.

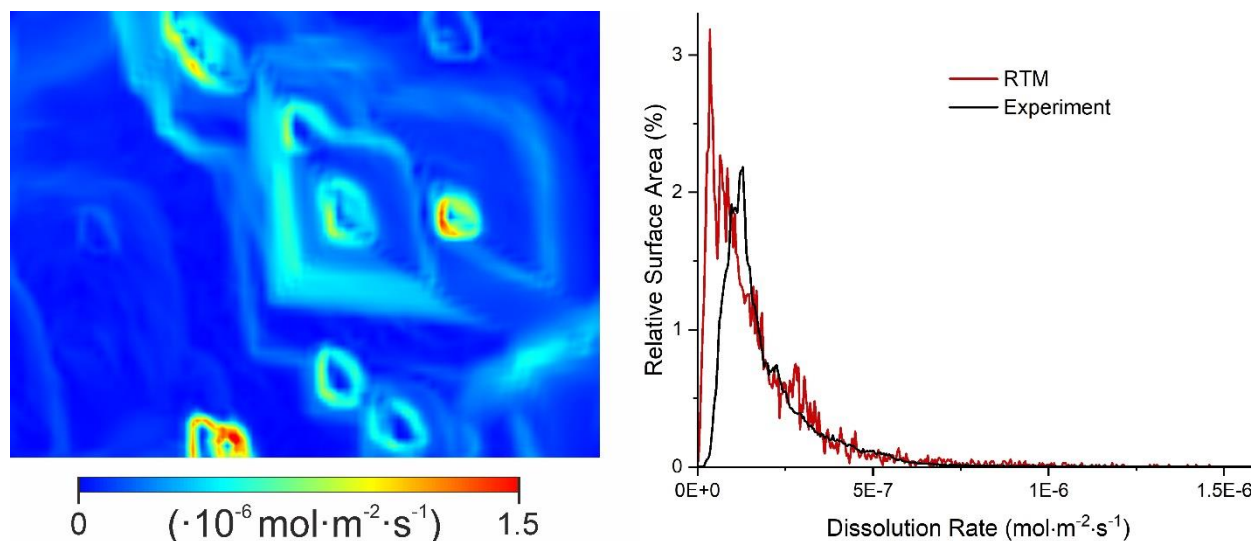
555 The recent publications by Agrawal et al. (2021) and Karimzadeh and Fischer (2021) confirm this  
556 small effect of natural mineral surfaces on the transport efficiency in the system and thus on the  
557 dissolution rate. In conclusion, the results of classical 3D RTM highlight the need for  
558 parameterization of reactivity in dissolution rate calculations, recently reported by Agrawal et al.  
559 (2021) and Karimzadeh and Fischer (2021).

### 560 **3.3 Newly-parameterized 3D RTM towards surface rate variability**

#### 561 **3.3.1 Results**

562 Based on the slope parameterization (SSF) approach recently developed by Karimzadeh and  
563 Fischer (2021), an improved SSF\* calculation was developed (**Eq. 2**). This new parameter  
564 improves the sensitivity to shallower surface structures and can be applied independently of the  
565 surface orientation in the model. In the parameterized RTM, the SSF\* is calculated for all elements  
566 of the mesh on the calcite surface (**Fig. 1**) and used as a factor in the classical rate equation (**Eq.**  
567 **12**). The distribution of the linear SSF\* normalization for the calcite surface is shown in **Fig. 1 C**.  
568 The simulation uses the same flow and transport conditions as the previous 3D simulations  
569 ( $u = 1000 \mu\text{m}\cdot\text{s}^{-1}$ ,  $D = 1\cdot 10^{-9} \text{m}^2\cdot\text{s}^{-1}$ ).

570  
571 The application of SSF\* strongly alters the RTM simulation results in terms of dissolution rate (**Fig.**  
572 **8**). The resulting dissolution rate map shows a largely heterogeneous distribution of rates, very  
573 similar to the distribution in the experimental counterpart (**Fig. 6 A II**). High dissolution rates are  
574 concentrated in the deep etch pits and large steps of the calcite surface. Intermediate rates are  
575 found at shallower etch pits and smaller steps on mostly flat surface areas. Surface areas without  
576 any structures show dissolution rates close to zero, similar to the experimental results. Overall,  
577 we conclude that the simulation results are in good agreement with the measured data with  
578 respect to the heterogeneous rate distribution. This conclusion is supported by the comparison  
579 between the rate spectra of the parameterized RTM and the experiment. Both datasets show a  
580 single high rate peak, which is  $1.3\cdot 10^{-7} \text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  in the experiment and at  $0.6\cdot 10^{-7} \text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  in  
581 the simulation. At higher dissolution rates, the percentage of the surface decreases to values close  
582 to zero, with only small sections contributing the highest dissolution rates. The overall range of  
583 dissolution rates is in much better agreement with experimental observations compared to the  
584 previous model ( $0$  to  $2\cdot 10^{-6} \text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ). The previously observed rate gradient between inlet and  
585 outlet can no longer be observed, as it has little effect on the total dissolution rate ( $< 0.4\cdot 10^{-6}$   
586  $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ). Application of the previously developed SSF (Karimzadeh and Fischer, 2021) leads  
587 to a divergent map of the dissolution rate, similar to the SSF distribution in **Fig. 1 B**. In the rate  
588 spectrum, the SSF parameterization yields 40 % of the surface with zero dissolution rate. These  
589 differences highlight the improved sensitivity of the new SSF\* calculation towards smaller rate  
590 contributions to the dissolution rate spectrum. The implementation of the SSF\* leads to improved  
591 overall agreement between the dissolution rates in the experiment and the RTM in compared to  
592 the classical RTM and the previous SSF approach. As a first-order parametrization, the surface  
593 slope can adequately describe the surface reactivity distribution associated with the surface  
594 topography.



**Figure 8:** Left: Dissolution rate maps created with the improved slope factor parameterization using the surface topography from **Fig. 6 A I**. The implementation of the slope factor enhances the influence of surface steps and pits on the dissolution rate, as can be observed in the experimental rate map (**Fig. 6 A II**). Compared to the previous RTM results (**Fig. 6 A III**), the agreement between simulation and experiment is greatly improved. Right: Comparison of the dissolution rate spectra between the improved RTM approach with slope factor and the experimental results shows the better agreement compared to the previous RTM approach (**Fig. 7**).

596

### 597 3.3.2 Discussion

598 The inclusion of surface reactivity in the dissolution rate equation via the surface slope leads to  
 599 results that agree well with experimental measurements. This confirms the results of Karimzadeh  
 600 and Fischer (2021), who first introduced the use of surface slope as a proxy for reactivity. The  
 601 involvement of surface normal components in the improved SSF\* resulted in a remarkable  
 602 improvement regarding the sensitivity of the parameterization to small rate contributions at the  
 603 surface. With the previous SSF, nearly half of our sample surface would exhibit zero dissolution  
 604 rates, showing large differences from experimental observations. Additionally, the new equation  
 605 allows for spatially independent calculation of surface reactivity, which is required for 3D datasets  
 606 with whole crystal grains. The major advantage of reactivity parameterization via slope is that no  
 607 prior knowledge of the surface reactivity distribution is required once a good normalization is  
 608 established. Agrawal et al. (2021) included reactivity in their model by using the dissolution rate  
 609 map available from experimental measurements. This approach is not practical for crystal surfaces  
 610 without prior experimental dissolution data and cannot predict the evolution of reactivity as reaction  
 611 time progresses. The SSF\* parameterization presented can be applied to any new calcite surface  
 612 and approximate its reactivity on a first-order basis.

613

614 The theoretical basis of the SSF\* is obviously correct, since it can reproduce the reactivity  
615 distribution. A high slope value may indicate a high concentration of atomic-scale steps on the  
616 surface. These steps consist of multiple differently coordinated atomic sites (Luttge et al., 2013).  
617 Most important for the dissolution reaction is the high concentration of kink sites located at the  
618 atomic steps on the surface (Fischer et al., 2014). Kinks are comparatively easy to dissolve from  
619 the surface and can propagate on surface features such as steps. Thus, for calcite, the distribution  
620 of kink sites primarily controls the overall dissolution rate (Kurganskaya and Luttge, 2016). To  
621 predict surface reactivity, one must be able to predict the distribution of kink sites. At the pore-  
622 scale, the slope of a mineral surface can describe the distribution of kink sites as a first-order  
623 approximation.

624  
625 A potential issue in parameterizing the slope is known as step bunching. In this process, atomic  
626 steps can catch up with the preceding step and form stable steps of larger vertical heights  
627 (Amelinckx et al., 1957; Schwoebel and Shipsey, 1966). Bunched steps dissolve more slowly than  
628 single atomic layer steps as they lose kink sites during bundling of multiple single layer steps  
629 (Cheng and Coller, 1987). Bunching cannot be resolved with the slope value because one large  
630 step can give the same value as several small steps. This might lead to an incorrect prediction of  
631 surface reactivity by the SSF\* calculation.

632  
633 The key to a precise approximation of reactivity is the normalization of the SSF\*. As already  
634 described in the methods section, we use a simple linear normalization where a SSF\* value of  
635 one is equal to the maximum simulation rate. For the calcite surface, this normalization leads to a  
636 good approximation of the experimental data. However, such normalization is most likely not  
637 universally applicable to other crystal surfaces. It is also possible that differently oriented surfaces  
638 on the same crystal require separate normalizations of the slope factor, as observed in  
639 experiments (Saldi et al., 2017). In a more complex normalization, the overall slope of the  
640 normalization curve can be changed to tune the overall surface reactivity. If certain rate regions  
641 are over- or underestimated, sections of slope values in the rate can be decreased or increased  
642 to match the experimental rate spectrum across defined support points.

643  
644 In conclusion, our results confirm that slope parameterization can provide a good approximation  
645 of first-order surface reactivity. This improvement in the reactivity description for RTMs is essential  
646 for simulating the system under surface-controlled conditions, especially in natural environments  
647 at the pore scale.

## 648 **3.4 Temporal evolution of dissolution rates**

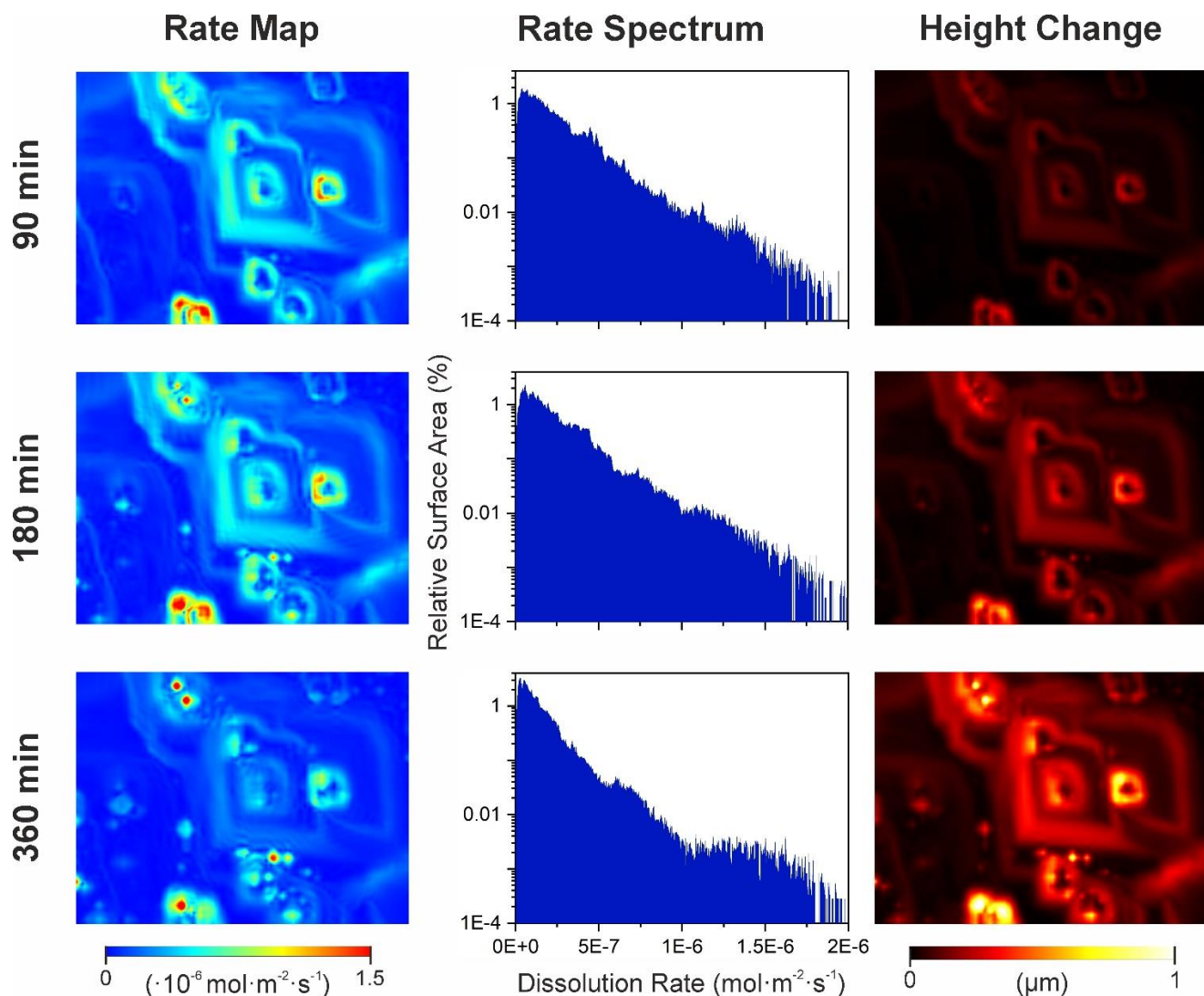
### 649 **3.4.1 Results**

650 A moving boundary based on the surface retreat velocity (**Eq. 13**) was implemented to observe  
651 surface topography evolution due to material flux over longer dissolution periods, and its influence  
652 on the simulated rate. The surface retreat is simulated for 6 h and the SSF\* is renormalized at  
653 each intermediate time step.

654  
655 Initially, strong surface retreat occurs at the etch pit walls due to the high concentration of high  
656 dissolution rates there (**Fig. 9**). As dissolution progresses, a widening of the etch pits is observed,  
657 with the etch pit walls moving outward from the central pit axis. The shift of the etch pit walls results  
658 in accompanying movement of regions of high reactivity due to the high slopes. This movement  
659 follows the crystallographically controlled shape of the calcite etch pits and is best seen in the two  
660 largest etch pits in the center of the surface image. Simultaneously, the etch pits increase in depth  
661 as the dissolution reaction progresses. The movement of the steps and etch pit walls is directly  
662 related to the movement of the surface reactivity. At high simulation times, numerical errors occur  
663 in our simulation, leading to the formation of individual pits (**Fig. 9** 360 min). These pits have  
664 extreme slope values and thus accumulate the highest dissolution rates at the surface. The use  
665 of finer meshes reduces this effect and increases the maximum simulation time.

666  
667 The rate spectrum remains similar for the first 3 h of dissolution time with the same shape as  
668 described in the previous section. This is consistent with the observations of the rate map, where  
669 the overall distribution remains similar and the highly reactive regions move only across the  
670 surface. For longer simulation times, the percentage of surface areas with rates  $>1 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$   
671 increases, while the surface areas with intermediate rates decrease. The percentage of  
672 surface area at high dissolution rates remains largely constant. This change in the rate spectrum  
673 is most likely associated with the development of pit spikes, where most of the surface tends  
674 toward lower dissolution rates. Apart from this effect, no changes in the dissolution rate spectrum  
675 were observed as dissolution progressed. The shape of the overall rate spectrum remained the  
676 same over time, with shifts between high- and low-reactive regions observed in the rate maps.





**Figure 9:** Evolution of the simulated system over 6 h of dissolution. The first column shows the rate maps after 90, 180, and 360 minutes. The second column shows all corresponding rate spectra (logarithmic y-axis). The third column shows the change in height accumulated over the reaction time. The dissolution rate distribution and spectra remain in a similar distribution during the first 180 minutes, with the reaction fronts moving outward from the pit center. After 180 minutes, individual pits develop with the highest reaction rates, while the largest sections of the surface transition to lower rates. The greatest height changes are observed at the etch pits, which widen and deepen as dissolution progresses.

677  
 678 **3.4.2 Discussion**  
 679 The temporal evolution of mineral dissolution and surface reactivity can be directly compared to  
 680 the time series measured by Bibi et al. (2018). Some differences can be observed when comparing  
 681 the rate maps. The experiment shows changes in the reactivity of the entire surface and also some  
 682 specific surface areas over time. The average dissolution rate on the surface may increase and  
 683 then decrease over time, with no pattern that can be deduced. The impact of surface structures  
 684 can also change with time. Here, the central etch pit shows variations where the pit wall shows



685 high rates, but no consistent change over time. In contrast, our simulation results remain relatively  
686 constant over time with little changes due to the movement of the steps and thus reactivity on the  
687 surface. The agreement of the simulation with the experimental results varies depending on the  
688 interval chosen. This temporal behavior cannot currently be explained (Bibi et al., 2018), and our  
689 simulation does not reproduce this behavior, leading to the conclusion that the underlying  
690 mechanism is not yet included in the current reactivity distribution.

691  
692 In other publications, the temporal evolution of the dissolution rates is investigated as well.  
693 Bollermann and Fischer (2020) did not observed a steady-state behavior of the dissolution rate  
694 for polycrystalline calcite. The overall surface normal retreat remained constant over the reaction  
695 period, while the local reactivity may change over time. In our simulation result, the overall rate  
696 spectrum remains mostly constant over the dissolution period without any significant changes.  
697 Fischer and Luttge (2018) described the pulsating behavior of surface reactivity at etch pit  
698 locations over time, resulting in multiple fronts that move outward from the pit as dissolution  
699 progresses. Our model predicts a similar step movement away from the etch pit center. However,  
700 no new reaction front is generated at the center of the pit, thus no pulsating behavior could be  
701 observed.

702  
703 In general, the temporal behavior of dissolution rates and surface reactivity is poorly understood  
704 at present. Our model is not able to reproduce all currently available experimental results. It is  
705 therefore likely that the mechanisms involved have not been fully elucidated and are therefore not  
706 included in our reactivity parameterization. Further studies investigating the influence of time on  
707 dissolution reactions are needed to provide the basis for further improving the parametrization of  
708 the models.

## 709 **3.5 Implications for larger 3D datasets**

### 710 **3.5.1 Results**

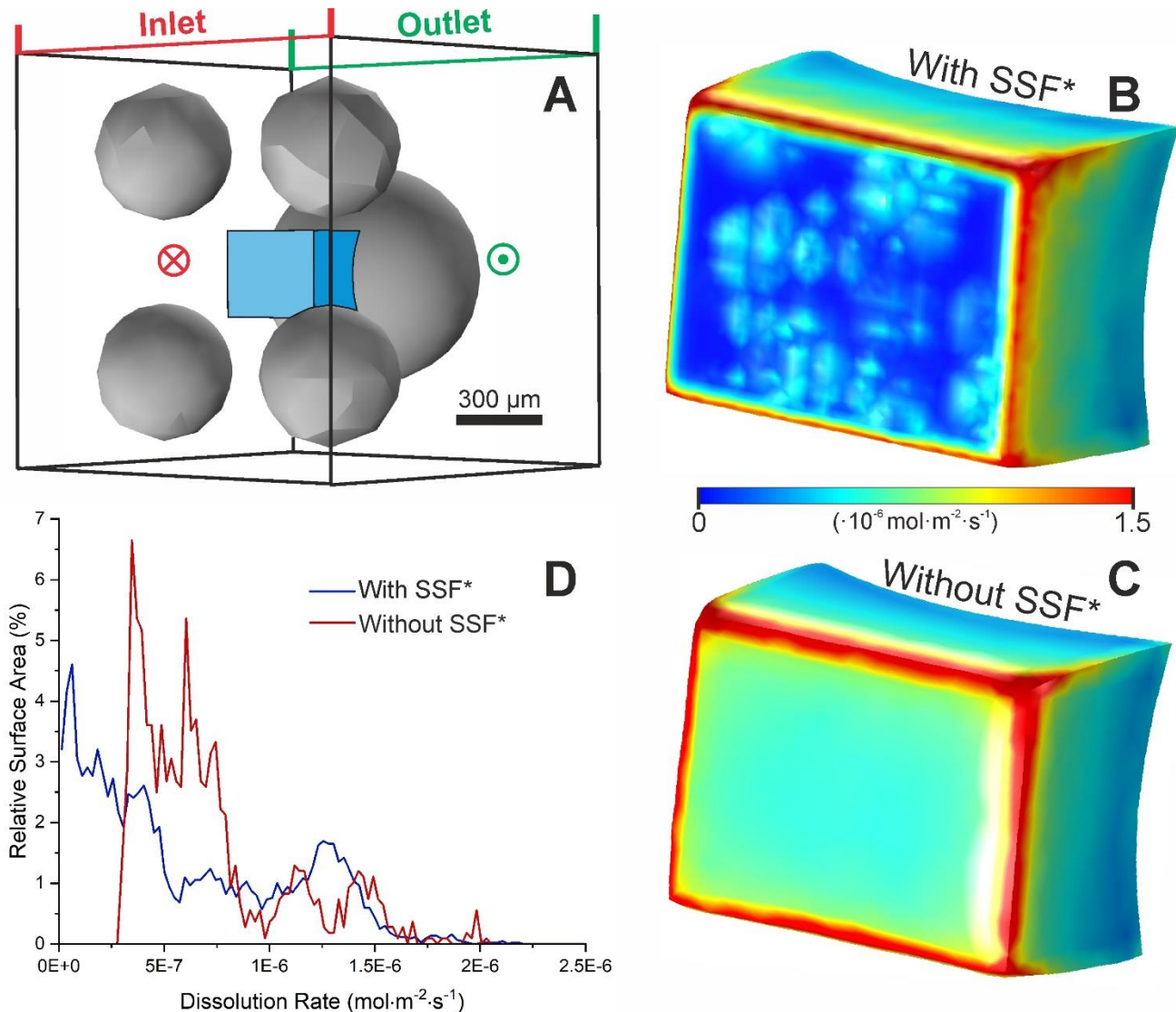
711 To test the implementation of the SSF\* in a 3D dataset consisting of multiple mineral grains, we  
712 developed a simple artificial pore geometry (**Fig. 10 A**). The geometry includes five inert quartz  
713 grains to create a heterogeneous flow field in the domain. Attached to the largest quartz crystal is  
714 a cuboidal calcite crystal that dissolves as the simulation time progresses. The front surface of the  
715 calcite crystal has the rough surface topography (**Fig. 1 A**), while the other four surfaces are  
716 entirely flat. The simulation uses the same geochemical, flow, and transport conditions as the  
717 previous 3D simulations ( $u = 1000 \mu\text{m}\cdot\text{s}^{-1}$ ,  $D = 1\cdot 10^{-9} \text{m}^2\cdot\text{s}^{-1}$ ) to induce calcite dissolution. Two  
718 simulations are performed and compared. In case (I), the classical rate equation without reactivity  
719 contribution is used, while case (II), the SSF\* is included in the rate equation to describe the  
720 dissolution of the rough front surface.

721  
722 In case (I), the highest dissolution rates are observed at the crystal edges and corners (**Fig. 10**  
723 **C**). At these locations, the fluid flow passed the crystal and generates stronger velocity gradients  
724 with comparatively high fluid velocities close to the surface. This results in high local transport  
725 efficiency and increases the dissolution in comparison to the surfaces of the crystal. All five  
726 surfaces of the calcite crystal show constant, homogenous dissolution rates. The enclosed  
727 topography does not play a role in the dissolution of the frontal surface. Case (II), which includes  
728 the SSF\* reactivity description, also shows the highest dissolution rates at the corners and edges  
729 (**Fig. 10 B**). The hydrodynamic conditions here are the same as in case (I), thus the same  
730 explanation applies. However, with proceeding dissolution, the edges become more rounded and  
731 consequently form areas with high slope values, which then continue to lead to high dissolution  
732 rates in later stages of the reaction. The lateral surfaces show the same behavior as in case (I),  
733 since they do not exhibit topography. In contrast, the frontal surface shows a strongly deviating  
734 rate distribution. The average dissolution rate is lower in comparison and the rates are not  
735 homogeneously distributed. Even after 3 days of reaction time, the topography of the surface  
736 remains and influences the reactivity. Highly reactive areas are visible on the frontal surface (**Fig.**  
737 **10 B**) and can be directly related to pit structures on the surface. The resolution of the structures  
738 in this model is relatively low compared to the previous simulations due to the overall larger system  
739 size and associated larger element size.

740  
741 **Figure 10 D** compares the dissolution rate spectra of both cases after 3 days. In case (I), the  
742 minimum rate is  $0.25 \cdot 10^{-6} \text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ , while the flat crystal faces have rates between  $0.3 \cdot 10^{-6}$   
743  $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  and  $0.8 \cdot 10^{-6} \text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ . At higher rates, two main peaks are visible. The first peak

744 at  $1.1 \cdot 10^{-6} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  represents the surface areas close to the crystal edges where the rate  
745 increases due to the higher transport efficiency. At about  $1.5 \cdot 10^{-6} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ , the dissolution rates  
746 associated with the crystal edges and corners can be observed. A small high rate peak at  $2 \cdot 10^{-6}$   
747  $\text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  indicates the rate contribution of the vertices. In contrast, case (II) has large surface  
748 fractions with near-zero dissolution rate, which is due to the application of the SSF\* on the front  
749 surface. On the front surface, increased dissolution rates due to surface reactivity contribute to  
750 the rate spectrum at about  $0.4 \cdot 10^{-6} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ . A second peak at  $1.3 \cdot 10^{-6} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  shows the  
751 high dissolution rates at the edges and corners.

752  
753 Overall, two major differences can be observed between the classical and SSF\* approaches. First,  
754 the surface topography does not play a role in the classical approach and will not change during  
755 the dissolution. In contrast, surface reactivity based on topography affects the rate distribution in  
756 the SSF\* model. The heterogeneous rate distribution leads to changes in the surface topography  
757 and consequently to changes in the reactivity distribution over time. Second, the average  
758 dissolution rate of the calcite surface decreases when reactivity is included. Therefore, the  
759 evolution of the pore space over longer time periods will differ greatly between the two models.



**Figure 10:** (A) Model sandstone with five inert quartz grains (grey spheres) and a calcite crystal (blue cuboid) located on the largest quartz grain. The calcite grain consists of four surfaces with no topography and one surface with the previously used topography dataset (opposite the quartz crystal). The inlet for flow is the left front boundary (red), and the outlet is at the opposite boundary (green). Calcite grain shape and dissolution rate distribution after 3 days of dissolution with (B) and without (C) the SSF\* parameterization. (D) Dissolution rate spectra for the entire crystal surface.

760

### 761 3.5.2 Discussion

762 Both simulations predict that the strongest influence on the dissolution rate originates from the  
 763 crystal corners and edges. This behavior has been observed previously in experiments on calcite  
 764 single crystals (Noiriel and Soullaine, 2021; Noiriel et al., 2020; Noiriel et al., 2019). Noiriel and  
 765 Soullaine (2021) discuss that some methods to compute dissolution rates from  $\mu$ -CT datasets can  
 766 lead to an overestimation at the edges of the crystal sample. In our model, the dissolution rates  
 767 are first calculated based on chemical and reactivity conditions, and then lead to a corresponding

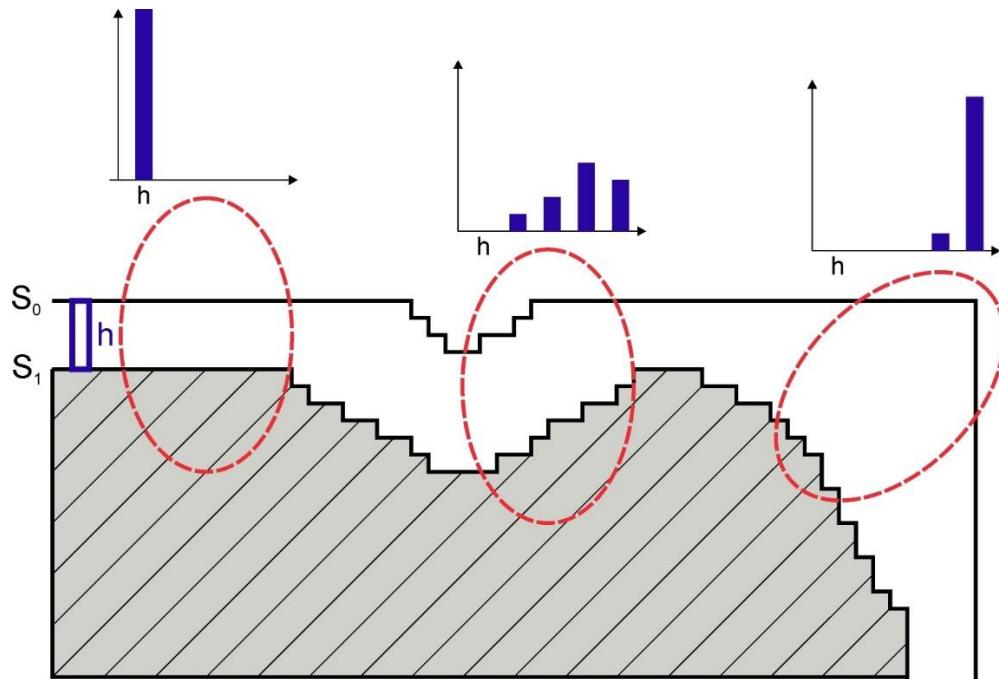
768 decrease in height. The process is thus reversed compared to the experimental path and a high  
769 dissolution rate cannot be due to this effect.

770 In case (I), the high rates at edges and corners can be caused exclusively by hydrodynamic  
771 conditions and are not related to intrinsic crystal reactivity. Increased reactivity was found at edges  
772 and corners due to the high concentration of kink sites at these surface features (Bollermann and  
773 Fischer, 2020; Noiriél et al., 2019). **Figure 11** shows a schematic overview of the crystal surface  
774 and explains the heterogeneous reactivity at flat surfaces, etch pits and edges. The increased  
775 edge reactivity can be captured with the slope parameterization, as the rounded edges exhibit an  
776 increased slope in comparison to the flatter surfaces they connect. Due to their inherent reactivity,  
777 the highest rates remain at the edges. In contrast, the crystal surfaces have, on average, lower  
778 concentrations of reactive sites and therefore lower dissolution rates.

779 This difference is visible in case (II) and is similar to the measurement of Noiriél et al. (2019). The  
780 main cause of high dissolution rates on the surface are etch pits that open up as the reaction time  
781 progresses and consequently produce large steps of high reactivity that move across the surface  
782 in both simulation and experiment (Noiriél et al., 2019). This behavior cannot be reproduced with  
783 the classical rate equation, where the structures of the surface topography do not play any role in  
784 the dissolution reaction. Therefore, such a model introduces errors in predicting the evolution of  
785 the fluid-mineral interface over time, which can affect surface-sensitive processes such as the  
786 adsorption of species onto the surface. It may also affect the evolution of pore geometries in  
787 natural rock systems in terms of parameters such as shape and connectivity.

788  
789 The overall lower dissolution rates when SSF\* is included also result in a slower volume loss of  
790 the crystal (**Fig. S1** in the Supporting Information). After three days, the difference between the  
791 two cases is about 2% of the initial volume, and the difference increases with time. This can lead  
792 to large differences in simulations on long time scales. A linear extrapolation of the volume loss in  
793 our two cases shows that crystal reaches half of its volume after 340 days without SSF\*  
794 parameterization, while it requires 420 days when the SSF\* is included. Large differences in  
795 predicted dissolved volume affect the available pore space, pore geometries, and permeability of  
796 the simulated rock sample. This can be illustrated by a simple calculation based on a sandstone  
797 with 15% calcite cement and 2% porosity described by Heidsiek et al. (2020). Using our simple  
798 volume loss extrapolation, the porosity of the sandstone increases after 340 days to 9.5% without  
799 the SSF\* and to 7.9% with the SSF\* parameterization. The difference in predicted porosity is 1.5%,  
800 which may have a significant effect on the hydrodynamic conditions in the sandstone, especially  
801 for permeability-determining volumes at pore throats. A precise description of the pore structures  
802 is needed to model and predict the evolution of geological environments as they play a critical role

803 in controlling the physical properties and processes in the rock (Anovitz and Cole, 2015).  
804 Therefore, to achieve an accurate prediction of future hydrodynamic conditions in the rock, a  
805 precise approximation of mineral surface reactivity is required.  
806



**Figure 11:** Schematic representation of the crystal surface before ( $S_0$ ) and after ( $S_1$ ) dissolution. Exemplary rate spectra based on block removal are shown for specific surface sections, including a flat area, an etch pit wall, and the crystal corner. The flat surface shows only the general height retreat and an uniform dissolution rate. At the etch pit, more blocks are removed due to the higher reactivity at the steps. Thus, the dissolution rates increase and show a more heterogenous pattern due to differences in the concentration and rate of the reactive sites. The crystal corner has the highest concentration of reactive sites. Here, the most material is removed, resulting in the highest observed dissolution rates.

807

## 808 **5. Summary and conclusions**

809 We have confirmed the conclusion from previous publications that the current rate equation  
810 approach in pore-scale reactive transport models cannot reproduce the experimentally derived  
811 dissolution rates for mineral surfaces (Agrawal et al., 2021; Karimzadeh and Fischer, 2021).  
812 Surface reactivity is a material-inherent parameter that needs to be considered, especially for  
813 surface controlled transport conditions. Based on the approach by Karimzadeh and Fischer (2021)  
814 to use the surface slope as an approximation for first-order reactivity, we further improved the rate  
815 equation based on the surface slope parametrization. The improved SSF\* can be applied to  
816 datasets with a larger field of view, larger height variation, and longer reaction times. The SSF\*  
817 approach significantly improves the agreement between model and experimental results with  
818 respect to the components of the dissolution rate spectrum. This improved fit increases the  
819 predictive capabilities of reactive transport models regarding porosity and permeability evolution  
820 of natural rock samples. Our parameterization can be applied to pore network scale simulations,  
821 e.g., derived from  $\mu$ -CT datasets. The parameter can be applied to any mineral by fitting the SSF\*  
822 normalization to the respective experimental rate spectra. Once an SSF\* normalization is derived,  
823 it can be used for any future simulation with surfaces of the same mineral. In this study, we have  
824 shown a pathway to incorporate a first-order approximation for surface reactivity into large pore-  
825 scale models to obtain an accurate description of the mineral dissolution and thus the evolution of  
826 the pore network, flow field, and permeability.

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829 models and interpretation of the results. We thank the German Federal Ministry of Education  
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831 funding.

832

833 **Research Data**

834 Research Data associated with this article can be accessed at <https://rodare.hzdr.de/>.



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