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# 1 Dissolution Anisotropy of Pyroxenes: Role of Edges and Corners 2 Inferred from Stochastic Simulations of Enstatite Dissolution

3 Arnaud Bouissonnié,\* Damien Daval, and Philippe Ackerer



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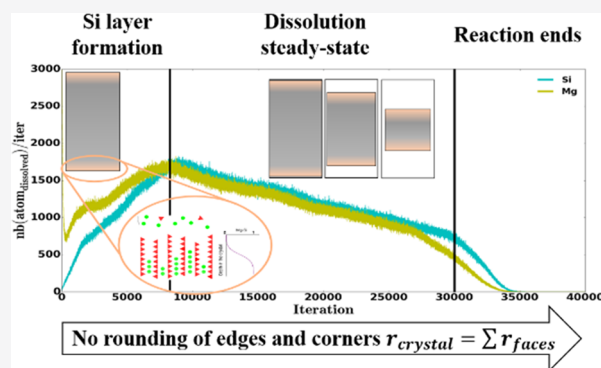
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4 **ABSTRACT:** Experimental studies exhibit a wide variety of dissolution  
 5 rates for a given mineral depending on the chemical conditions and also  
 6 on the type of experiment conducted. As a relevant example, studies  
 7 focused on face-specific dissolution and those focused on powder  
 8 dissolution can present differences of up to 1 order of magnitude.  
 9 Linking these two types of experiments is therefore relevant, since  
 10 experimental conditions can be almost entirely controlled throughout  
 11 the entire experiment. In this study, we use a stochastic dissolution  
 12 model based on hydrolysis of atomic bonds of enstatite, the magnesium  
 13 endmember pyroxene, to simulate the dissolution of different sizes and  
 14 aspect ratios of enstatite grains. This model, validated in a previous  
 15 study by a comparison with experimental (face-specific) rate data, is  
 16 used to understand the evolution of the dissolution rate with time, from

17 the beginning of the dissolution until the entire consumption of the crystal. We show that the behavior of the dissolution is  
 18 controlled mainly by the aspect ratio of the grain. A simple dissolution model based on face-specific dissolution is then used to  
 19 compare the results of the simulations obtained with those resulting from the grain dissolution model. The similarity between the  
 20 results points out that the contribution to the dissolution of edges and corners is only modest for very anisotropic silicates such as  
 21 pyroxenes, where silicate tetrahedrons are connected through chains running parallel to a given crystallographic axis. This simple  
 22 model is then extended using both face-specific experimental and model results and compared to existing powder dissolution results.  
 23 This comparison shows an excellent agreement between face-specific dissolution modeling and powder dissolution experiment,  
 24 indicating that, for anisotropic minerals such as pyroxenes, face-specific and powder dissolution experiments can be linked, which can  
 25 be of great interest for future dissolution studies.



## 1. INTRODUCTION

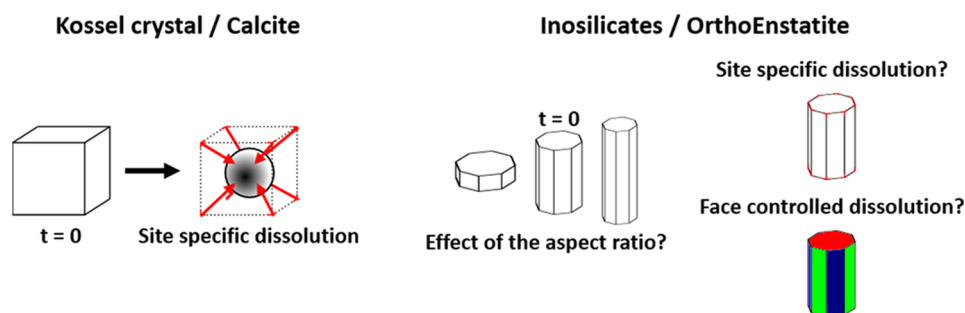
26 Dissolution kinetics is a key parameter to understand the Earth's  
 27 surface evolution and is crucial for several industrial and  
 28 environmental problems (cement dissolution, nutrient deple-  
 29 tion in soils, etc.). Over the last decades, numerous studies have  
 30 helped understand the processes that occur at the mineral–  
 31 water interface, as well as developing different methods to  
 32 measure their kinetics for a wide variety of minerals.<sup>1–9</sup> While  
 33 most of these studies are based on powder dissolution  
 34 experiments,<sup>2,10–12</sup> fewer studies succeeded to measure  
 35 dissolution rates on different faces of a given miner-  
 36 al.<sup>3,4,6,7,9,13–16</sup> This latter kind of studies has shown the  
 37 importance of the crystallographic structure (i.e., anisotropy)  
 38 on mineral dissolution kinetics. As a relevant example,  
 39 pyroxenes, which are strongly anisotropic due to their silica  
 40 tetrahedron chains, exhibit a strong dissolution anisotropy  
 41 consistent with the periodic bond chain theory.<sup>17</sup> However, the  
 42 comparison between the dissolution rates measured on single  
 43 faces and those measured on powder highlights a significant  
 44 difference (powder dissolution rates are generally higher than  
 45 face-specific dissolution rates<sup>18</sup>). This adds complexity to our

46 ability to upscale dissolution rates and to apply experimental  
 47 measurements on field studies without using empirical scaling  
 48 parameters that complicate reactive-transport simulations.

49 As suggested by different studies, this difference may result  
 50 from the amount of reactive sites present in each case.<sup>19–23</sup>  
 51 Indeed, considering face dissolution often means considering a  
 52 reactive surface which is not affected by the dissolution of  
 53 mineral's edges and corner. However, not only these sites are  
 54 the most reactive, as shown in Noiriél et al.,<sup>24,25</sup> they are also present  
 55 in greater proportions in powders than on centimeter-sized  
 56 single crystals (if one assumes a flat surface at the beginning of  
 57 the experiments). Therefore, studying the contribution of these  
 58 corners and edges to dissolution is essential. To do so, new

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**Figure 1.** Schematic representation of the objectives of this paper. Dissolution is often assumed to take place on reactive sites such as edges and corners. It has been demonstrated on Kossel crystal and calcite that, during the dissolution process, the shape of the crystal evolves, and edges and corners are rounded, leading to an almost spherical shape (for Kossel crystal, depending on the activation energy of the hydrolysis) when the primal material is a cube. In this study, we aim to determine whether these considerations are applicable on inosilicates, with a specific focus on enstatite. The study is based on simulations using a stochastic dissolution model applied at the atomic bond level and aims to explore different aspect ratios of the initial mineral parallelepipedal shape.

59 experimental setups have emerged, using analytical techniques  
60 such as X-ray tomography<sup>24–26</sup> or vertical scanning interferom-  
61 etry.<sup>27</sup> However, despite their increasing efficiency to study the  
62 processes that occur at finer scales (micrometer to nanometer  
63 scale), they often need to be combined with numerical studies to  
64 unravel what happens at the solid–fluid interface.

65 Numerical experiments have become a powerful tool to  
66 improve our understanding of processes occurring at the water–  
67 mineral interface, ranging from molecular dynamics to reactive-  
68 transport model used at pore scale.<sup>28–30</sup> The last decades have  
69 also seen the development of stochastic dissolution models, such  
70 as kinetics Monte Carlo models or Voronoï method.<sup>13,19,23,31–38</sup>

71 These models, based on a relation between the activation  
72 energies of individual processes (bond hydrolysis, for example)  
73 and their occurrence probability, allow for fast computation and  
74 the simulation of larger objects, which classical molecular  
75 dynamics is not able to deal with. These models, first applied on  
76 Kossel crystals, have brought or validated many important  
77 results. As an example, numerous studies applied on Kossel  
78 crystals validate the difference of reactivity between the crystal’s  
79 edges, corners, and surfaces.<sup>19</sup> The work of Zhang and Lutge<sup>35</sup>  
80 also mentioned these differences for feldspar dissolution.  
81 However, providing a generalization to other minerals, which  
82 is an intrinsic issue belonging to the field of physical chemistry, is  
83 important and may present a great interest to link laboratory and  
84 field observations, as mentioned by Noiriel et al.<sup>25</sup>

85 For several reasons, pyroxenes represent a relevant target to  
86 address these aspects. Indeed, not only do they have a strongly  
87 anisotropic structure (silica chains running parallel to a given  
88 crystallographic axis), but they are also present worldwide and  
89 represent a major group of minerals for reactive-transport  
90 models.<sup>39,40</sup> In two previous studies,<sup>16,41</sup> we described a  
91 stochastic dissolution model operating at atomic scale and  
92 applied to enstatite, the magnesian endmember of pyroxenes.  
93 This model, validated by a comparison between simulations and  
94 experimental results, has shown its ability to reproduce the  
95 dissolution anisotropy of enstatite as well as the surface features  
96 observed at the end of the experiments (etch pit morphology,  
97 and relative thickness of the silica layers developed on each  
98 face).<sup>16</sup> However, in these two studies, we focused on face-  
99 specific dissolution, neglecting the contribution of “macro-  
100 corners” and “macro-edges”, which can represent, for some  
101 minerals such as calcite, the most reactive sites.<sup>25</sup> In the present  
102 study, we propose to simulate the dissolution of enstatite  
103 rectangular parallelepipeds. Different sizes and aspect ratios are

modeled and analyzed, to understand if the dissolution of 104  
enstatite grains can be described mathematically using 105  
parameters related to the grain dimensions, as well as to 106  
understand if observations made on calcite<sup>25</sup> are expandable to 107  
enstatite, and more generally, to pyroxenes. Another objective 108  
deals with the impact of the aspect ratio of a grain on the 109  
dissolution rate. Powder experiments present a wide variety of 110  
grain morphologies resulting from the crushing of macro- 111  
crystals. These different shapes and sizes may affect the 112  
dissolution rate, since the dissolution rate is face-specific.<sup>3,15,16</sup> 113  
Furthermore, different grain sizes may imply a greater rate 114  
variability through the development of fast dissolving micro- 115  
facets at mineral’s edges and corners. These questions are 116  
summarized in Figure 1. 117 f1

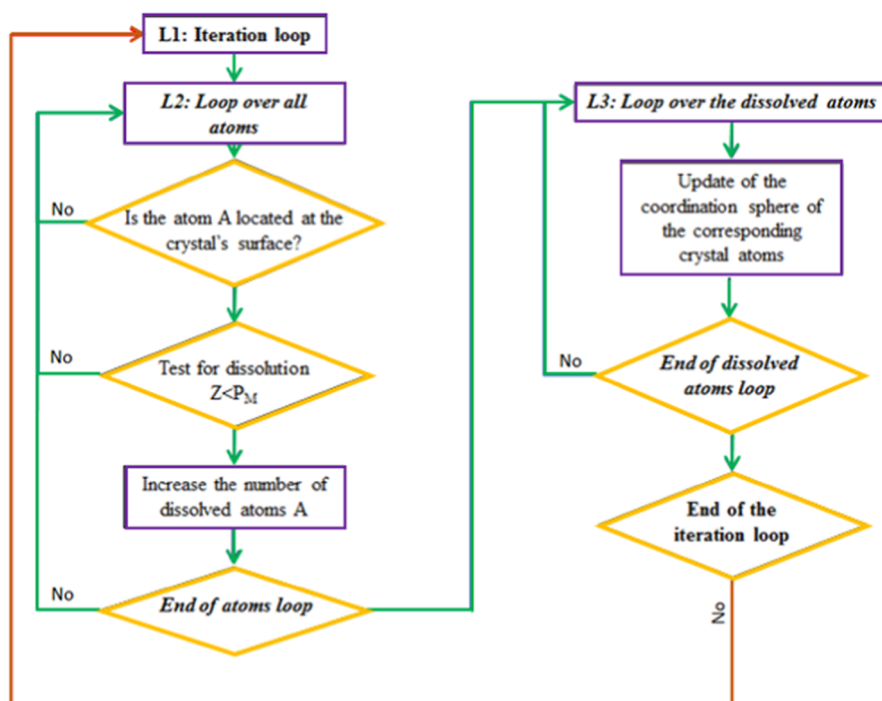
## 2. METHODS

**2.1. Model Description.** A complete description of the 118  
model is given in Bouissonnié et al.<sup>16</sup> Briefly, atoms contained in 119  
the enstatite cell are placed using *Pbca* space group symmetry 120  
elements, using the cell parameters ( $a = 18.233 \text{ \AA}$ ,  $b = 8.8191 \text{ \AA}$ , 121  
and  $c = 5.1802 \text{ \AA}$ ) and the coordinates given by Hugh-Jones and 122  
Angel.<sup>42</sup> Each magnesium and silicon atom is linked to oxygen 123  
according to their coordination. However, the dissolution of 124  
oxygen atoms is never considered in the dissolution model. 125  
Indeed, they are considered as bridging atoms<sup>13</sup> and the 126  
dissolution model is applied on  $M-O_{br}-M$  bonds ( $M$  being a 127  
 $Mg$  or  $Si$  atom). All atoms linked to another one via a bridging 128  
oxygen are part of its first coordination sphere.<sup>13</sup> Only the first 129  
coordination sphere is taken into account to compute the bond- 130  
breaking probabilities, since previous results showed that this 131  
strategy results in a satisfactory agreement between modeled and 132  
experimental results.<sup>16</sup> 133

Usually, the probability attributed with one event (i.e., the 134  
bond-breaking probability) is written as follows<sup>38</sup> 135

$$P = e^{-E_a/k_B T} \quad (1) \quad 136$$

where  $P$  stands for the bond-breaking probability,  $E_a$  is the 137  
activation energy of the bond hydrolysis (J),  $k_B$  is the Boltzmann 138  
constant (J/K), and  $T$  is the temperature (K). In the present 139  
study, the greatest bond-breaking probability (i.e., the bond 140  
hydrolysis associated with the lowest activation energy,  $Mg-O-$  141  
 $Mg$ ) was arbitrarily set to 0.99 and the two other probabilities 142  
were scaled according to the differences between their 143  
corresponding activation energies following 144



**Figure 2.** Scheme of the dissolution algorithm used in the dissolution model. This scheme is adapted from Bouissonnié et al.<sup>41</sup>

$$\frac{P_A}{P_B} = e^{-(E_a^A - E_a^B)/k_B T} \quad (2)$$

where A and B represent two different bonds. According to the best agreement between modeled and experimental results developed in Bouissonnié et al.,<sup>16</sup> the other two probabilities were calculated as 0.4 and 0.0146 for Mg–O–Si and Si–O–Si respectively. The probability of backward reactions (i.e., the creation of a new bond, previously destroyed or not) is not considered here since the model is applied to reproduce experiments run at pH 0,<sup>16</sup> where these reactions can be neglected.

As it has been shown to successfully reproduce experimental data and observations, an “all-or-none” approach was used in this study.<sup>13,19,35–37,43,44</sup> This approach considers that an atom is released only if all bonds that connect it to the surface are simultaneously broken during a single iteration step. Hence, the numerical model works directly on the atoms, and not on the bonds. Then, the overall probability of an atom to be released into solution during one iteration is given by the product of all the probabilities corresponding to the different bonds it shares with other atoms

$$P_M = e^{-nE_{M-O-Mg}/k_B T} e^{-mE_{M-O-Si}/k_B T} = P_{M-O-Mg}^n P_{M-O-Si}^m \quad (3)$$

where  $n$  and  $m$  stand for the number of bonds that the considered atom shares with neighboring Mg and Si atoms, respectively.

**2.2. Dissolution Algorithm.** At each iteration step, all atoms located at the surface are scanned. An atom is considered at the surface if its first coordination sphere is incomplete. A random number  $Z$  is generated for each atom; if  $Z < P_M$ , the atom is released into the solution, if not, the scan of the atoms moves on. At the end of the iteration, i.e., after scanning all atoms located at the surface, the attributes of the atoms contained in the first coordination sphere of those which have been dissolved

during the iteration, are updated to consider this change, resulting in an increase of their departure probability at the next iteration. It is essential to update the attributes of the considered atoms only at the end of an iteration to avoid an “in cascade” dissolution, where the atoms would be released one after the other due to a direct change of the probabilities. A scheme of the algorithm is shown in Figure 2.

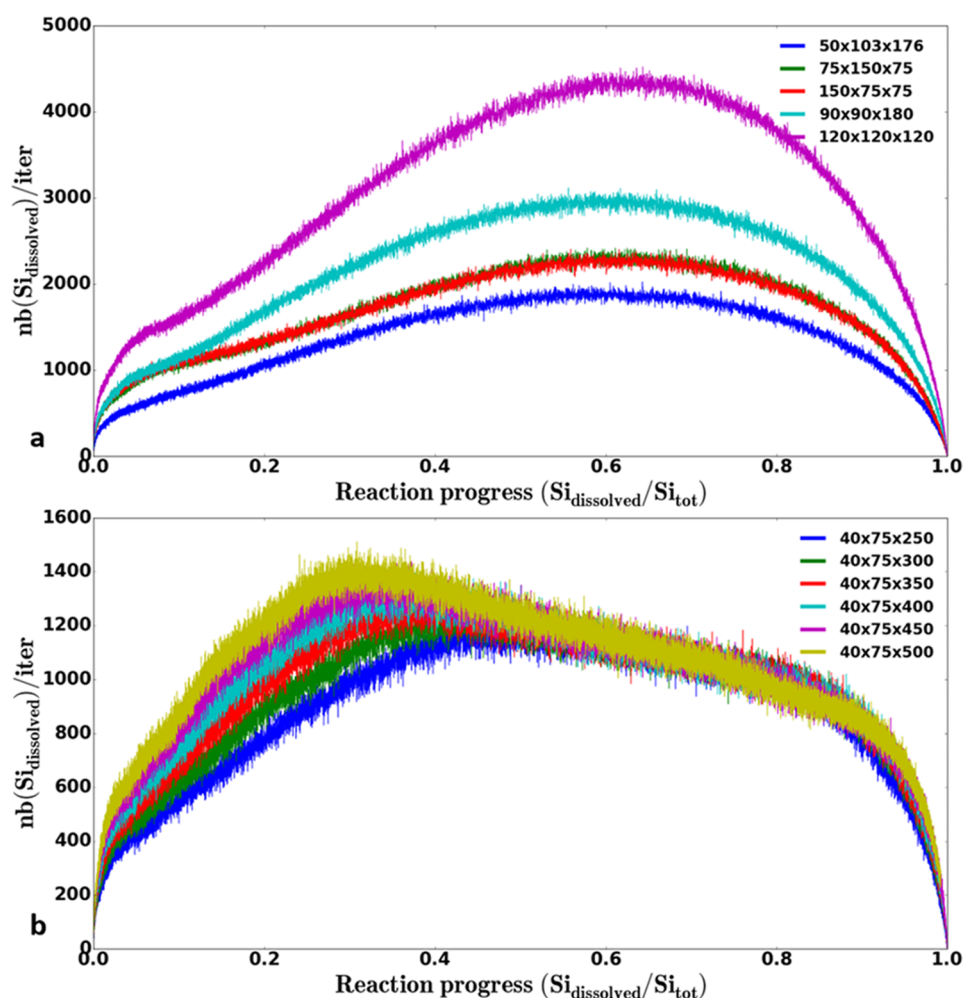
**2.3. Output of the Model.** The dissolution was monitored based on the release of Si atoms, as in classical studies dedicated to silicate dissolution kinetics. Note that because the dissolution at steady state (i.e., the dissolution rate can be considered to be constant) is stoichiometric,<sup>16</sup> this choice has no consequence on what will be described in the present study. However, the behavior of Mg release is important at the beginning of the dissolution process<sup>16</sup> and will be discussed in the section corresponding to this part of the dissolution timeline.

In the literature, the term “mineral dissolution rate” is usually used to refer to the release rate of atoms in the solution from a mineral surface, whether or not it is normalized to the contact surface between the fluid and the mineral. To avoid any confusion, in the following, we will use the term “dissolution rate” to refer to a velocity that is not normalized to the surface area (unit: mol/iteration) and “dissolution flux” to refer to dissolution rates normalized with respect to the surface area (unit: mol/m<sup>2</sup>/iteration). Both quantities are calculated at each iteration for any numerical simulation.

The cumulated number of released atoms has been used to calculate the total surface retreat during the simulations corresponding to the dissolution of single faces (i.e., only one face is considered to be in contact with the solution). The surface retreat is defined as the average height of material lost during the dissolution. It is calculated as follows

$$\Delta h_i^{(hkl)} = \frac{a^* b^* c}{16^* S_f} \sum_i^{n=1} n b(Si_{d,n}) \quad (4)$$





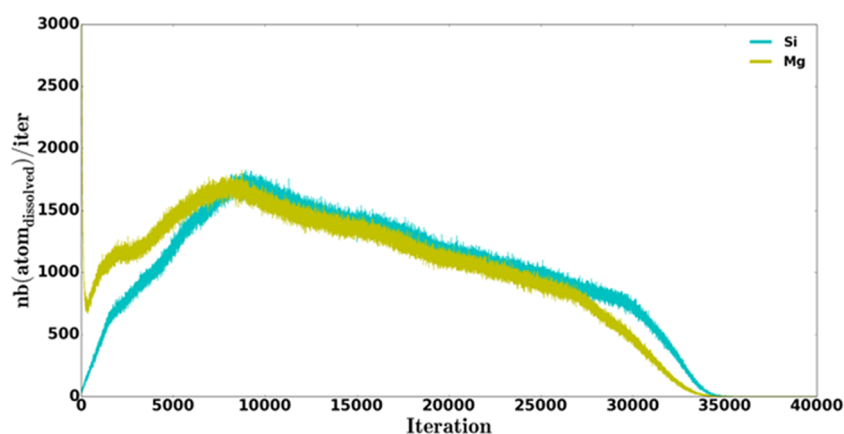
**Figure 3.** Results of the dissolution model showing the dissolution rate (defined as the number of Si atoms released per iteration) as a function of the reaction progress. Legends indicate how many times the crystal cell is multiplied in  $x$ ,  $y$ , and  $z$  directions. The results reported here represent sets of simulations applied on arbitrary parallelepiped sizes (i.e., not representative of the aspect ratio of natural enstatite). (a) First subgroup of simulations, with arbitrary rectangular parallelepiped dimensions. (b) Second subgroup: Length and width (parallel to the  $a$  and  $b$  axes of the enstatite cell) of the rectangular parallelepiped were kept constant while the height (parallel to the  $c$  axis) was modified in the different simulations. In both cases, a similar behavior is observed. (a) Simulations highlight a parabolic behavior of the dissolution. The maximum seems to be observed at similar values of the reaction progress. (b) Contrary to the first set, the simulations of the second set are different at the beginning of the dissolution. Here, the larger the crystal, the higher the maximum. After reaching the maximum, the number of Si atoms dissolved decreases linearly. The slope is the same for each simulation.

210 where  $\Delta h_i^{(hkl)}$  is the surface retreat at the  $i$ th iteration (m);  $a$ ,  $b$ ,  
 211 and  $c$  are the cell parameters (m);  $S_f$  is the surface area of the face  
 212 ( $m^2$ ); and  $nb(Si_{d,i})$  is the number of Si atoms dissolved at the  $i$ th  
 213 iteration. The number 16 corresponds to the number of Si atoms  
 214 in the enstatite cell. This method has been validated in  
 215 Bouissonnié et al.<sup>16</sup> and gives identical results to those obtained  
 216 if the mean coordinates in the direction normal to the surface  
 217 were used.

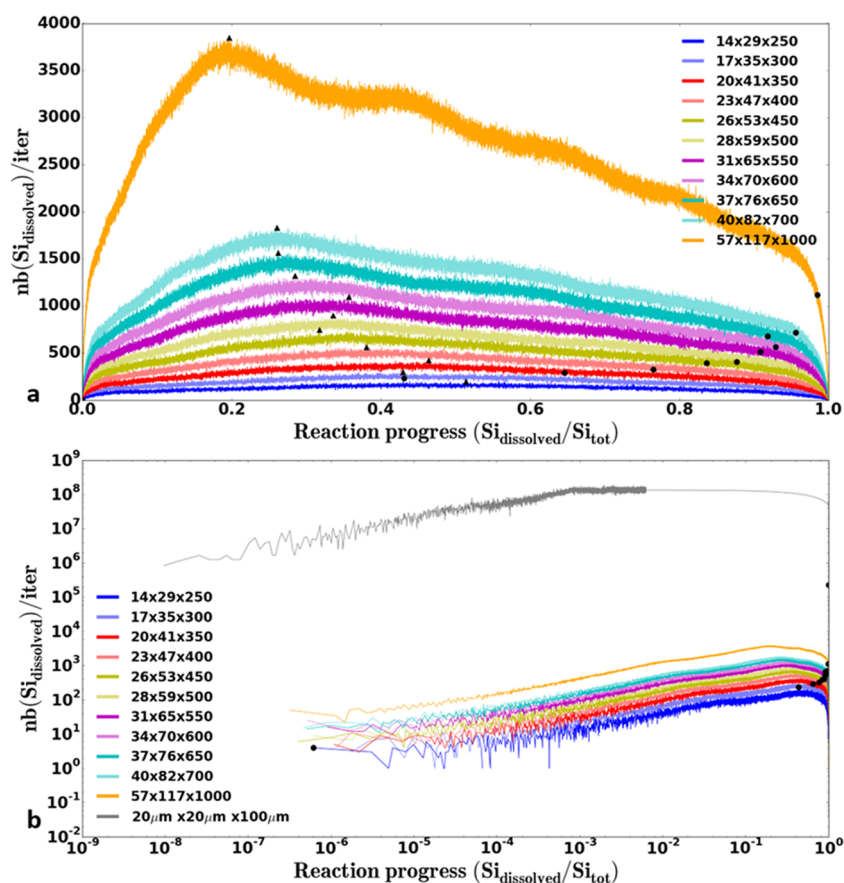
218 Finally, the last parameter used in this study is the  
 219 advancement of the dissolution reaction. It is defined as the  
 220 ratio between the number of Si atoms dissolved from the  
 221 beginning of the simulation and the initial number of Si atoms at  
 222 the beginning of the simulation.

223 **2.4. Assumptions and Limitations of the Model.** The  
 224 model has proven its ability to reproduce both experimental  
 225 dissolution rates and observed surface features evolutions.  
 226 However, several assumptions (all based on the studied  
 227 chemical condition) are considered and may impact the  
 228 model outputs and their upscaling to study natural environment:

- No backward reactions (i.e., formation of atomic bonds) 229  
 are implemented. This simplification was made because of the  
 very low pH of the studied solution (pH 0). This pH 231  
 makes the solution to be very far from the thermodynamic 232  
 equilibrium with respect to enstatite. Therefore, backward 233  
 reactions (i.e., formation of atomic bonds) are considered 234  
 unlikely to happen. 235
- The dissolution algorithm is applied on atoms rather than 236  
 atomic bonds. This method is commonly used in 237  
 stochastic dissolution studies, however, combined with 238  
 the first assumption, this precludes the formation of 239  
 amorphous silica layers resulting from interfacial dis- 240  
 solution–reprecipitation<sup>45</sup> or reorganization of dangling 241  
 bonds.<sup>46</sup> In the present study, such layers are suspected to 242  
 have no impact on the dissolution rate because their 243  
 passivating ability is thought to be pH-dependent<sup>14,47</sup> and 244  
 passivating layers are unlikely to form in strongly acidic 245  
 environments. Such conditions may limit the extension of 246  
 the conclusions of the study to less acidic environments. 247



**Figure 4.** Example of the results of a simulation conducted on a  $40a \times 82b \times 700c$  volume. This figure shows the dissolution rate (number of dissolved atoms per iteration) as a function of the number of iteration steps. The cyan curve represents Si atoms, and the dark yellow curve represents Mg atoms. Contrary to the Si curve, which increases continuously at the beginning of the simulation, the Mg curve is marked by a sharp decrease of the number of atoms released per iteration. This is explained by the fast depletion of superficial Mg, which have a high probability of departure. After reaching the maximum value of the amount of Si and Mg released per iteration (corresponding to the iteration where the silica layer reaches a constant thickness), the dissolution rate decreases continuously and the dissolution is stoichiometric.



**Figure 5.** (a, b) Results of the dissolution model showing the dissolution rate (defined as the number of Si atoms released per iteration) as a function of the reaction progress. Legends indicate how many times the crystal cell is multiplied in  $x$ ,  $y$ , and  $z$  directions or exact dimension (black line). Each panel represents Si dissolution rate as a function of the reaction progress for the set of simulations that observe realistic aspect ratios for the grains, plotted in standard and logarithmic scales, respectively. Black triangles indicate the reaction progress where the dissolution rate reaches its maximum. Black circles indicate the reaction progress where the volume of the enstatite grain is equivalent to that of the initial smallest simulated rectangular parallelepiped ( $14 \times 29 \times 250$ ). For each simulation, the dissolution rate increases at the beginning of the process, until reaching its maximum value. After the maximum value is reached, the dissolution rate decreases linearly until the reaction progress reaches  $\sim 95\%$ . The duration of the linear decreasing phase depends on the crystal size: the larger the crystal, the longer the linear phase.

248 However, the conclusions reached in the present study  
249 may remain valid even in conditions where the fluid is less

acidic, as long as the fluid is at far from equilibrium with 250  
respect to  $\text{SiO}_{2(\text{am})}$ , since presumptive passivating layers 251

would be unstable and therefore, would not be rate-controlling of the dissolution process.<sup>48</sup>

- The simulations correspond to conditions where the aqueous solution is continuously stirred, resulting in no local variations of the saturation index of the solution. Therefore, the saturation index is supposed to be constant (and far from equilibrium), both in space and time.

### 3. RESULTS

**3.1. Evolution of Si Dissolution.** A total of 22 different enstatite volumes have been simulated. In the following, each volume is named after the number of cells in the three spatial directions.

The first 11 simulations were conducted using arbitrary volumes to highlight potential similarities between their dissolution behaviors. The results of these simulations are given in Figure 3. This group of simulations can be separated into two main subgroups (Figure 3a,b). The first subgroup (Figure 3a) presents results of simulation runs with initial aspect ratios that have no particular relation to each other, unlike the second subgroup (Figure 3b), which contains simulations made on grains varying only in height (the length in the *x* and *y* directions having been kept constant).

The first subgroup is marked by a sharp increase of the amount of dissolved Si atoms within the first 3–5% of the reaction, which corresponds to an increase from 0 to 500–1400 Si atoms released into solution per iteration, depending on the initial volume. After this first step, the behavior of the release rate of Si differs from the simulated volume. Indeed, while smaller volumes ( $50 \times 103 \times 176$ ,  $75 \times 150 \times 75$  and  $150 \times 75 \times 75$ ) are characterized by a linear increase extending over almost 40% of the reaction, the others ( $90 \times 90 \times 180$  and  $120 \times 120 \times 120$ ) show a shorter linear evolution (only 20% of the total reaction). In each case, after the linear increase of the release rate of Si into solution, a slower increase is observed until the dissolution rate reaches its maximum, which occurs after a similar reaction progress (between 60 and 65%) for all volumes of this subgroup. The dissolution rate reaches ~1900, 2300, 2300, 2950, and 4350 Si atoms/iteration for the  $50 \times 103 \times 176$ ,  $75 \times 150 \times 75$ ,  $150 \times 75 \times 75$ ,  $90 \times 90 \times 180$ , and  $120 \times 120 \times 120$  volumes, respectively. After this maximum is reached, the dissolution rate of Si decreases until the reaction is complete, and all of the crystal has been dissolved. This step extends over the last 35–40% of the total reaction.

The second subgroup of simulations is composed of six different volumes. While these volumes differ in height (length in the *z* direction parallel to the *c* axis), the lengths in the *x* and *y* directions were kept constant. Hence, the surface area of (100) and (010) faces varied, unlike that of the (001) faces. The onset of the simulations exhibits a similar behavior to that described for the first subgroup: the first 3% of the reaction is characterized by a sharp increase (from 0 to 350–600 Si atoms/iteration) of the release rate of Si. This step is followed by a linear increase of the dissolution rate until it reaches its maximum. Contrary to the first subgroup of simulations, the advancement corresponding to this maximum depends on the size of the initial volume. Indeed, if the maximal dissolution rate is greater for the largest volume (1390 Si atoms/iteration for the volume  $40 \times 75 \times 500$ ) compared to the smallest one (1190 Si atoms/iteration for the volume  $40 \times 75 \times 250$ ), the advancement at which the maximum is reached is lower (0.30 against 0.45, respectively). Another difference between the first and second subgroups is the

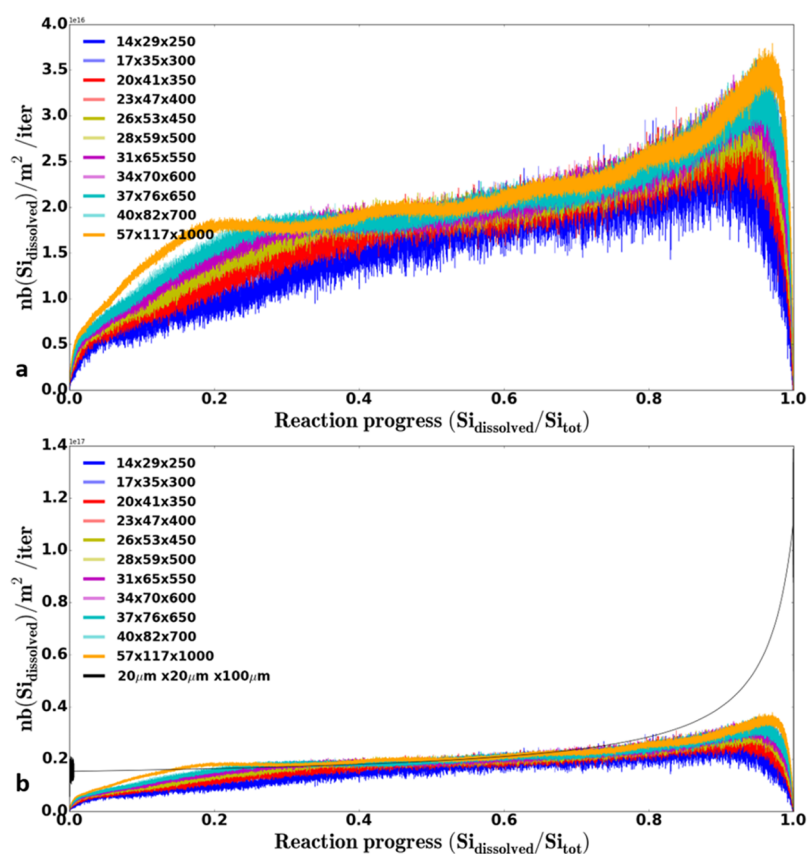
behavior of the dissolution after the maximum is reached. While, in the first case, the dissolution rate decreases sharply until the end of the reaction, in the second case, a slow and linear decrease is observed from an advancement of 30–45 to 85–90% depending on the considered volume. During this linear decrease, regardless of the volume, all simulation results are almost identical, showing the same dissolution rate of Si atoms at the same advancement of reaction. The last 10–15% of the reaction is characterized by a sharp decrease of the dissolution rate of Si atoms to finally reach 0 when the reaction is complete (Figure 4).

The second group of eleven simulations is shown in Figure 5. Contrary to the previous group of simulations, the aspect ratios which were used are representative of natural enstatite crystal habit. In spite of these differences, the evolution of the dissolution rate of Si atoms is almost identical to that described for the second subgroup of the first group described above, with the following steps: (1) a sharp increase of the Si dissolution rate during the first 3% of the dissolution, (2) a linear increase until the maximum is reached (from 145 to 3660 Si atoms released per iteration, reached after a reaction progress of 40–20% for the smallest and the largest volumes, respectively), (3) a linear decrease in the release rate of Si until 90–95% of the reaction, and finally (4) a sharp decrease in the release rate of Si over the last 5–10% of the reaction.

**3.2. Evolution of Mg Dissolution.** The behavior of Mg dissolution is similar to the one described above for Si dissolution (Figure 4). The main differences are observed at the very beginning and at the end of the simulations. Mg dissolution evolution has been studied only for simulated volumes representative of natural aspect ratios of enstatite. Because all simulations, as for Si atoms, exhibit a similar behavior, only one case is shown in Figure 4 ( $40 \times 82 \times 700$ ). The global trend of Mg dissolution evolution is as follows:

- A dramatic decrease of the dissolution rate at the beginning of the reaction (325 iterations for the volume shown in Figure 4).
- An increase of the dissolution rate from the 315th to the 8000th iterations. This increase is marked by two pulses for the volume presented in Figure 4.
- A linear, slow decrease of the dissolution rate, similar to the one observed in the case of Si dissolution. In the  $40 \times 82 \times 700$  volume, this step extends from the 8000th to the 26 990th iterations.
- A more pronounced decrease in the dissolution rate for the last iterations until all of the Mg atoms have been dissolved.

**3.3. Dissolution Normalized Per Surface Unit.** Because the most realistic cases treated in this study are those that observe the aspect ratio of pyroxenes, only the corresponding simulations were investigated with respect to a normalization per surface unit. The evolution of the surface area is not derived from direct outputs of the simulations. Instead, it is assumed that the surface decreases according to the retreat of each single face of the simulated volumes. In Bouissonnié et al.,<sup>16</sup> we investigated the surface retreat of (100), (010), and (001) faces, demonstrating that our model was able to reproduce observed experimental data. Similar simulations were then used to calculate the evolution of the surface area of the simulated crystals according to the following equation



**Figure 6.** Dissolution flux as a function of the reaction progress. Legends indicate how many times the crystal cell is multiplied in the  $x$ ,  $y$ , and  $z$  directions. (a) Results of the simulations. (b) Results of the simulations and modeled theoretical result for enstatite grain with realistic grain size (black curve). The black patch at the beginning of the realistic grain size dissolution corresponds to the stages 1 and 2 of Figure 9a,b. In each case, the dissolution flux increases at the beginning of the simulations. After reaching a given value of the reaction progress (corresponding to the 8000th iteration), the increase slows down and the dissolution flux can be considered as constant for few iterations (the larger the crystal, the longer the “steady-state” regime). Then, a moderate increase is observed until the dissolution reaches its maximum. After reaching its maximum, the dissolution flux decreases dramatically and reaches zero when all of the atoms have been dissolved.

$$A(i) = 2[(x_0 - 2\Delta h_i^{(100)})(y_0 - 2\Delta h_i^{(010)} + (y_0 - 2\Delta h_i^{(010)})(z_0 - 2\Delta h_i^{(001)} + (x_0 - 2\Delta h_i^{(100)})(z_0 - 2\Delta h_i^{(001)})] \quad (5)$$

where  $A(i)$  is the surface area at the  $i$ th iteration;  $x_0$ ,  $y_0$ , and  $z_0$  are the initial lengths in the  $x$ ,  $y$ , and  $z$  directions, respectively; and  $\Delta h_i^{(hkl)}$  is the surface retreat of the corresponding  $(hkl)$  face at the  $i$ th iteration, derived from the simulations performed on single faces where the edges were constrained to be nonreactive. This method, however, does not take into account a possible rounding of the edges, often observed in mineral dissolution experiments and modeling.<sup>23,25,49</sup> The number of Si atoms released at each iteration is then divided by the surface area at the corresponding iteration.

Results are shown in Figure 6. The trends followed by the dissolution fluxes differ from those obtained for dissolution rates. The first 3.5–1% of reaction is characterized by a sharp increase in the dissolution flux from 0 to  $5.4\text{--}6.2 \times 10^{15}$  Si atoms/( $\text{m}^2$  iteration) for the smallest and largest volumes, respectively. The increase in the dissolution flux is then less pronounced over the next 42.5–19% of the reaction. The Si dissolution flux reaches  $1.6 \times 10^{16}$  Si atoms/( $\text{m}^2$  iteration) at 47% of the reaction progress for the smallest volume against  $1.8 \times 10^{16}$  Si atoms/( $\text{m}^2$  iteration) at 20% for the largest one. After

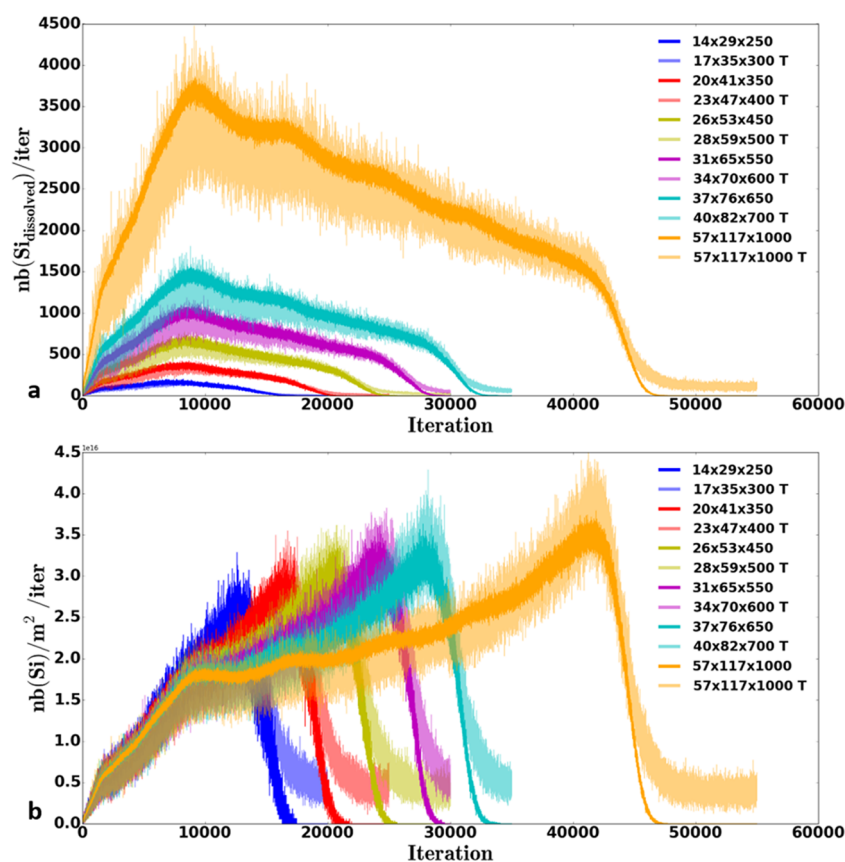
this period, the dissolution flux tends to stabilize for the three largest volumes but only over a short reaction progress (approximately 10% of the total reaction). After this phase, the dissolution flux of the largest volumes follows that of the smallest ones. The dissolution flux still increases, but the difference between each iteration is less pronounced until the reaction progress reaches 90–96% (where the dissolution flux reaches its maximum:  $(2.2\text{--}3.5) \times 10^{16}$  Si atoms/( $\text{m}^2$  iteration) for the smallest and largest volumes, respectively). Finally, from 90 to 96% of the dissolution, the Si dissolution flux decreases sharply to reach 0 when the volume has been completely consumed.

## 4. DISCUSSION

### 4.1. Evolution of Mg and Si Dissolution Rates.

**4.1.1. Evolution during the First 8000 Iterations.** Despite the differences in volumes used in the simulations, all simulation outputs are characterized by a sharp increase of the number of Si atoms released at the beginning of the dissolution. Figures 3a and 5b show this increase as a function of the advancement of the dissolution reaction. Depending on the volumes, the advancements corresponding to this stage are different. However, a clear pattern is highlighted when this evolution is considered as a function of the number of iteration steps (i.e., time) (Figure 7a). The dissolution rate is always at maximum around the same iteration ( $\approx 8000$ th) for the different volumes.





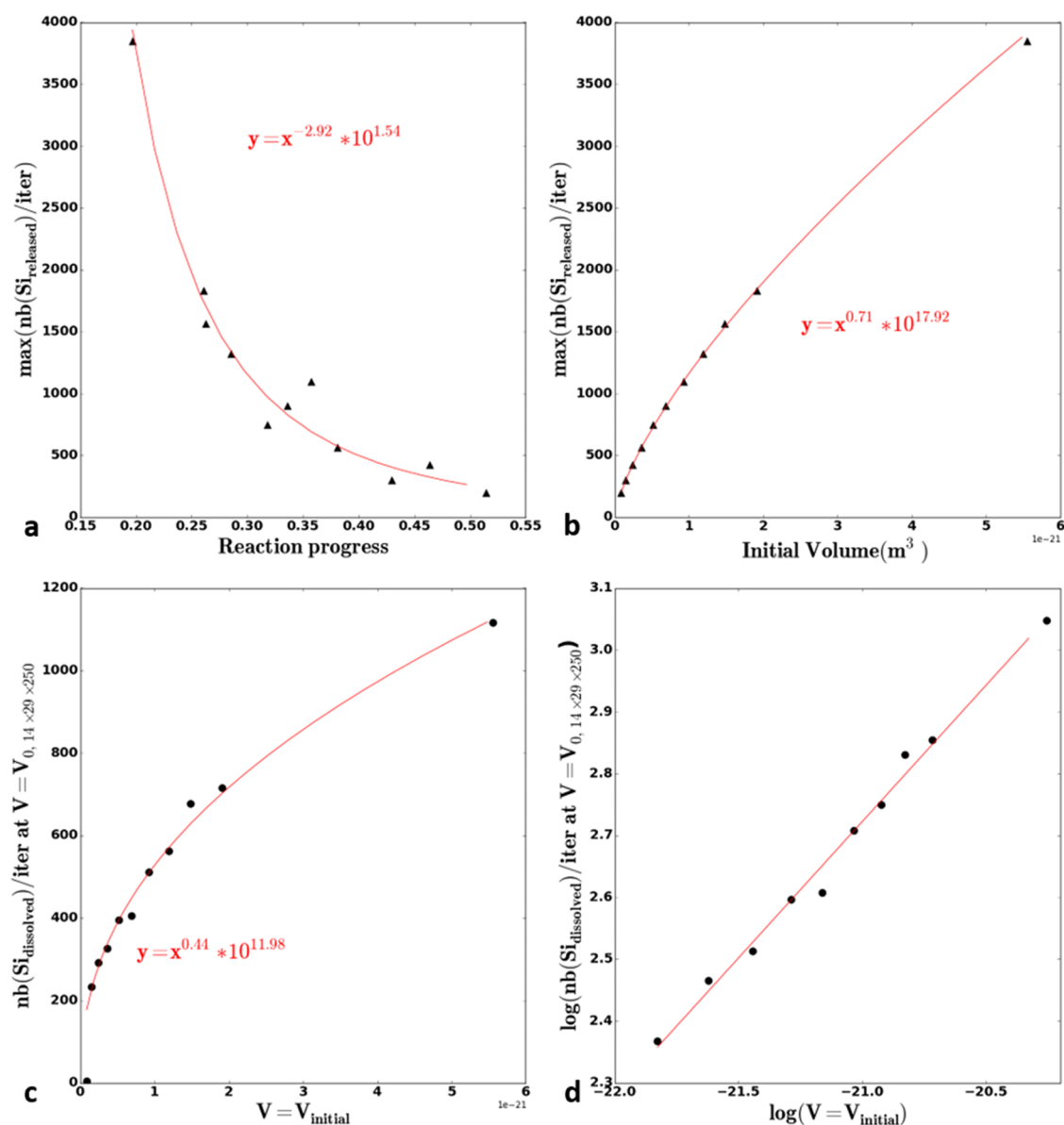
**Figure 7.** (a) Dissolution rate as a function of the total number of iteration steps (equivalent to time). Legends indicate how many times the crystal cell is multiplied in the  $x$ ,  $y$ , and  $z$  directions. Light-colored curves represent the evolution of the number of Si atoms released per iteration based on theoretical considerations developed in Section 4.2. Dark-colored curves represent the simulation results of the stochastic dissolution of rectangular parallelepipeds. (b) Dissolution flux as a function of the total number of iteration steps. Light-colored curves represent the evolution of the number of Si released per iteration and per surface unit based on theoretical considerations developed in Section 4.2. Dark-colored curves represent the simulation results of the stochastic dissolution of rectangular parallelepipeds. In each panel, the agreement between theory and simulation outputs highlights the slight effects of edges and corners on the global rate/flux. The difference between theory and simulation outputs at the end of the simulations is due to the assumptions underpinning the theoretical model (see text for details).

417 Interestingly, this value corresponds to the one where the surface  
 418 retreat of the (001) face reaches the steady state when the set of  
 419 probabilities used is [0.99, 0.4, 0.0146] for [Mg–O–Mg, Si–  
 420 O–Mg, Si–O–Si] bonds respectively.<sup>16</sup> It was interpreted as  
 421 the moment when the dissolution becomes congruent.  
 422 Considering that the other faces reach their steady-state  
 423 dissolution regime before the (001) face,<sup>16</sup> the fact that the  
 424 dissolution rate of the simulated rectangular parallelepiped is at  
 425 maximum at the iteration corresponding to the attainment of a  
 426 steady state for face (001) may mean that the evolution of the  
 427 dissolution regime of a simulated rectangular parallelepiped  
 428 enstatite is controlled by the face for which this steady state is  
 429 reached the latest (after the largest number of iterations).  
 430 Alternatively, another explanation could be that the face (001)  
 431 being the fastest to dissolve, the amount of Si released from this  
 432 face is greater than those of the other faces. Hence, this relation  
 433 between a simulated rectangular parallelepiped enstatite and the  
 434 (001) face reaching their steady state at the same iteration may  
 435 come from the fact that a significant proportion of their  
 436 dissolution is supported by the (001) face.  
 437 Regarding the dissolution rate of Mg atoms, Figure 4 shows  
 438 that it decreases dramatically during the first few hundred  
 439 iterations (325 for the volume  $40 \times 82 \times 700$ ). This can be  
 440 explained by the fast departure of Mg atoms from the reactive  
 441 surface at the beginning of the simulations because of their

greater probability to be dissolved. This results in a fast leaching  
 442 step at the beginning of the reaction, when these atoms are  
 443 numerous. After a few iterations, the main coordination of Mg at  
 444 the surface increases prior reaching a constant value,<sup>41</sup> making  
 445 them more difficult to dissolve.  
 446

The fast decrease of Mg dissolution rate can also be linked to  
 447 the increase of Si dissolution rate. Indeed, the fewer the Mg–O–  
 448 Si bonds, the higher the Si departure probability. In other words,  
 449 when numerous Mg atoms are released into solution, the  
 450 dissolution of Si atoms is enhanced. This departure of Si atoms  
 451 resulting from the fast leaching of Mg atoms at the surface also  
 452 makes it easier for the “solution” to reach the Mg atoms located  
 453 deeper in the simulated crystals. These combined effects  
 454 possibly explain why, after a dramatic decrease, the Mg  
 455 dissolution rate increases with Si dissolution, until the maximum  
 456 is reached. After the maximum is reached, both Si and Mg  
 457 dissolution rates decrease. More importantly, these decreases  
 458 are almost identical (same slope), indicating that the dissolution  
 459 is stoichiometric.  
 460

**4.1.2. Parameters Controlling the Dissolution.** Although the  
 461 first set of simulated rectangular parallelepipeds was not  
 462 representative of the aspect ratio of natural enstatite grains,<sup>50</sup>  
 463 it allows highlighting some behaviors and parameters that may  
 464 control the dissolution. Indeed, the two subgroups presented in  
 465 Figure 3 have their own patterns that can help understand the  
 466



**Figure 8.** (a) Maximum dissolution rate as a function of the progress of the dissolution process for various initial volumes. Each triangle represents a different initial volume. The maximal value corresponds to the largest volume and the minimal to the smallest. (b) Maximum dissolution rate as a function of the initial volume. (c, d) Dissolution rate when the volume of the enstatite grain reaches the initial volume of the smallest simulated rectangular parallelepiped ( $14 \times 29 \times 250$ ) as a function of the initial simulated enstatite rectangular parallelepiped volume represented in standard and logarithmic scales, respectively.

467 two principal factors impacting the dissolution, namely, the  
 468 length of the rectangular parallelepiped in the z-direction and  
 469 the surface area of the (001) face. The most striking feature is the  
 470 one of the subgroup composed of rectangular parallelepipeds  
 471 varying only by their heights ( $40 \times 75 \times 250$ ,  $40 \times 75 \times 300$ ,  $40$   
 472  $\times 75 \times 350$ ,  $40 \times 75 \times 400$ ,  $40 \times 75 \times 450$ , and  $40 \times 75 \times 500$ ).  
 473 While the beginning of the dissolution differs depending on the  
 474 volume, the stage depicting a decreasing reactivity is  
 475 characterized by a similar trend and value of Si dissolution  
 476 rates for all simulations (Figure 3b). Therefore, it can be  
 477 assumed that this stage is controlled mostly by the surface area of  
 478 the (001) faces. Then, the surface area of the (100) and (010)  
 479 faces would only affect the reaction progress required to reach  
 480 this stage (the greater these surfaces, the longer the preliminary  
 481 stage).

This assumption can be verified with the second subgroup of 482  
 simulated rectangular parallelepipeds ( $50 \times 103 \times 176$ ,  $75 \times 150$  483  
 $\times 75$ ,  $150 \times 75 \times 75$ ,  $90 \times 90 \times 180$ , and  $120 \times 120 \times 120$ ). 484  
 Indeed, the only simulations presenting the same (001) surface 485  
 area are those conducted with the  $75 \times 150 \times 75$  and  $150 \times 75 \times$  486  
 $75$  volumes. These two rectangular parallelepipeds have the 487  
 same dissolution behavior throughout the entire reaction 488  
 (Figure 3a). While this similarity supports that the dissolution 489  
 is primarily controlled by the face (001), it also suggests that the 490  
 other two faces have only a minor contribution to the overall 491  
 dissolution rate of enstatite grains. This is further supported by 492  
 the differences in reaction rates between the three faces ((100), 493  
 (010), and (001)). The dissolution rate of the (001) face is more 494  
 than 1 order of magnitude higher than those of faces (100) and 495  
 (010). To have a significant impact on the total dissolution rates, 496  
 the surface area of the (100) and (010) faces should be at least 497

498 10 times greater than that of the (001) face, which was never  
499 investigated in this study due to computational capacities and  
500 our commitment to perform simulations that observe as much as  
501 possible the aspect ratios of enstatite grains encountered in  
502 natural environments.

503 The difference in shape between the released Si curves of the  
504 two subgroups (Figure 3a vs Figure 3b) is more difficult to  
505 explain. The main difference in the simulation parameters  
506 resides in the dimensions of the simulated volumes and mainly,  
507 their heights. Indeed, the heights (length in the  $z$  direction) of  
508 the subgroup composed of the  $50 \times 103 \times 176$ ,  $75 \times 150 \times 75$ ,  
509  $150 \times 75 \times 75$ ,  $90 \times 90 \times 180$ , and  $120 \times 120 \times 120$  rectangular  
510 parallelepipeds are smaller than those of the volumes of the  
511 second subgroup. It is therefore possible that the former  
512 volumes are consumed before reaching a stage where the Si  
513 dissolution rate decreases linearly, which would explain this  
514 difference in behavior. If the overall dissolution is mainly  
515 controlled by the dissolution of the (001) faces, it is indeed  
516 possible that these volumes cannot reach this dissolution stage  
517 because their height is too short. This is consistent with the  
518 evolution of the dissolution rate of the other subgroup for which  
519 the smaller the volume, the shorter the linear stage. It can be  
520 reasonably assumed that rectangular parallelepipeds with a very  
521 short height never reach a stage where the dissolution rate  
522 decreases linearly.

523 To conclude, the simulations shown in Figure 3 provide  
524 important information regarding the global dissolution of a  
525 rectangular parallelepiped enstatite: the dissolution rate seems  
526 mainly controlled by that of the (001) faces.

527 The simulations conducted with the second set of rectangular  
528 parallelepipeds, more representative of the natural crystal habit  
529 of pyroxenes, also exhibit specific patterns. Indeed, while the  
530 amount of Si atoms released at each iteration varies from one  
531 volume to another, trends and shapes are identical (Figure 5).  
532 This could indicate that the overall evolution of the dissolution is  
533 directly controlled by the shape of an enstatite grain. For the  
534 same aspect ratio, the initial volume only influences the absolute  
535 amount of released atoms.

536 This simulation set allows focusing on a quantity that  
537 delineates a transition in the evolution of the dissolution rate  
538 of a rectangular parallelepiped enstatite, namely, the maximum  
539 value this latter can reach (black triangles in Figure 5a). While it  
540 is obvious that the bigger the volume of a rectangular  
541 parallelepiped, the greater the instantaneous Si dissolution  
542 rate, interestingly, it is possible to link these two quantities  
543 mathematically (Figure 8b). In the same way, it is possible to  
544 link this maximum rate to the reaction progress (Figure 8a). The  
545 corresponding relations are given by

$$\begin{aligned} \max(\text{Si}_{\text{released}}) &= 10^{17.9} \times V_0^{0.71} \\ \max(\text{Si}_{\text{released}}) &= 10^{1.54} \times \xi^{-2.92} \end{aligned} \quad (6)$$

547 where  $V_0$  is the initial volume ( $\text{m}^3$ ) and  $\xi$  is the reaction progress.  
548 Combining these two relations allows predicting the reaction  
549 progress corresponding to the maximal dissolution rate as a  
550 function of the initial volume.

$$\xi_{\max(\text{Si})} = 10^{-5.61} \times V_0^{-0.24} \quad (7)$$

552 Based on this equation, it is theoretically possible to estimate  
553 the time at which the release of Si is maximal when knowing the  
554 initial volume of an enstatite grain. Such empirical relations are  
555 very relevant for experimental works and practical applications

because it corresponds to the attainment of the steady-state  
regime of the dissolution (see Section 4.5).

4.1.3. *Variability of Dissolution Rates for a Given Grain Size.* A long-standing concern in mineral/water interaction deals with the uniqueness of the dissolution rate.<sup>18,51</sup> While the variability of the dissolution rate is known to be significant when the geochemical conditions are changed, it is often assumed, particularly in reactive-transport studies, that the intrinsic dissolution rate constant remains unchanged when the fluid chemistry and the temperature are constant. However, several studies tend to show that this assumption may be too simplistic, as the dissolution rate may vary with time. While some studies highlight a monotonic decrease of the dissolution rate with time which can be associated with several factors such as the development of amorphous silica-rich layers,<sup>52</sup> others emphasize a complex evolution of the dissolution rate resulting from the gradual modification of the crystal habit,<sup>15,23,53</sup> the inherited history of the crystal reactivity<sup>54,55</sup> or the microstructural differences (e.g., defect density) between two individual crystals of a same mineral.<sup>3,5,18,23,56–58</sup> Therefore, it is central to understand if two minerals placed under the same biogeochemical conditions but differing in their history (one being fresh and the other one being aged for example) will have the same dissolution rate; hence, if two minerals of the same volume have the same unique dissolution rate.

To investigate this question using the dissolution model, it has been decided to focus on the dissolution rate of the rectangular parallelepipeds when their volume reaches a volume equivalent to that of the smallest simulated crystal ( $14 \times 29 \times 250$ ). The remaining volume is calculated with the number of atoms that are still in the rectangular parallelepiped at each iteration following

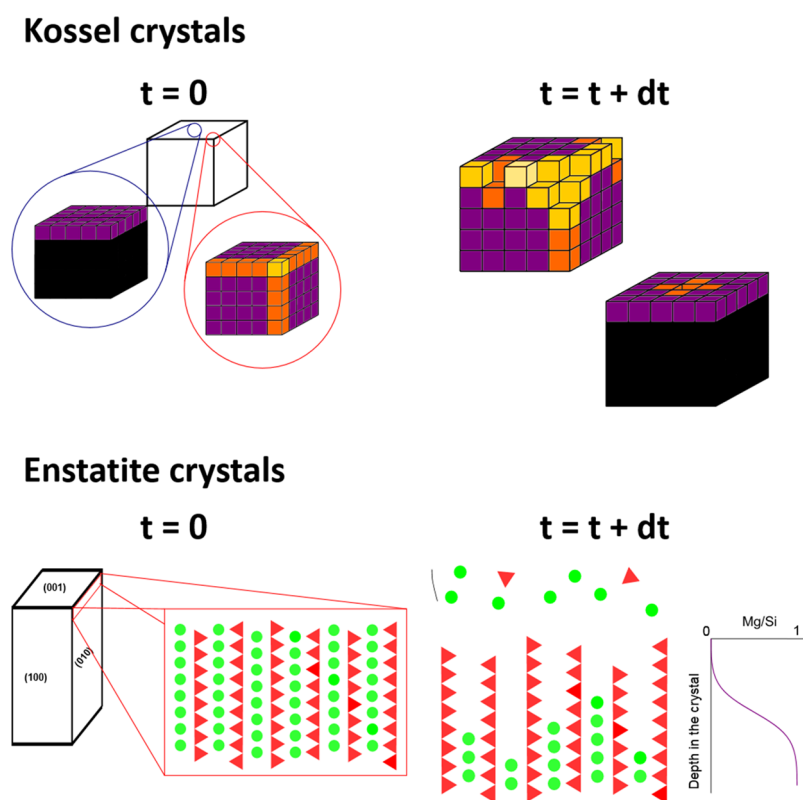
$$V_i = \frac{a^*b^*c}{16} \left( N_0 - \sum_i^{n=0} N_n \right) \quad (8)$$

with  $V_i$  the volume at the  $i$ th iteration;  $a$ ,  $b$ , and  $c$  the cell parameters (m);  $N_0$  the number of Si atoms in the enstatite parallelepiped at the beginning of the simulation; and  $N_n$ , the total number of Si released until the  $i$ th iteration. This mass balance is divided by 16 since the enstatite cell is formed by 16 atoms of Si. The attainment of the volume corresponding to the smallest crystal is indicated by the black circles in Figure 5, and the dissolution rates at  $V = V_{14 \times 29 \times 250}$  (named  $\text{Si}_{\text{released}, V=V_{14 \times 29 \times 250}}$ ) as a function of the initial volume are shown in Figure 8c,d. Interestingly, a relation between the initial volume and the dissolution rates for  $V = V_{14 \times 29 \times 250}$  exists

$$\text{Si}_{\text{released}, V=V_{14 \times 29 \times 250}} = 10^{12.0} \times V_0^{0.44} \quad (9)$$

This kind of relationships means that for a given volume, different values of dissolution rates exist depending on the initial size of the minerals.

**4.2. Simple Mathematical Model of Si Dissolution Rate.** The evolution of Si dissolution rates and fluxes has a specific behavior as described above. If this behavior seems difficult to reproduce with a theoretical model, it is possible to test hypotheses on how the dissolution evolves: here, we suggest testing the assumption that the overall enstatite grain dissolution simply corresponds to the sum of the contribution of the various single faces delineating the enstatite volume. This assumption may be true if, contrary to what is often proposed in the literature, the edges and corners do not have a strong impact on



**Figure 9.** Scheme of the mechanism driving the dissolution of Kossel and enstatite crystals. Kossel: Black cubes represent atoms that are not at the mineral reactive surface. Purple, orange, and yellow cubes represent surface-, edge-, and corner-site atoms, respectively. During the dissolution, the atoms with fewer neighbors have a higher probability to be dissolved. This leads to the formation of rounded corners and edges. The atoms at the surface with only one neighbor missing (purple) are particularly difficult to dissolve compared to the others. Enstatite: at the beginning of the dissolution, Mg atoms are dissolved first. This is particularly visible on the (001) face where they exhibit a less populated first coordination sphere, leading to Mg depletion of the surface and the formation of a Si-enriched layer with a thickness not exceeding a few atomic layers. Because silica chains are not connected to each other, the probability of departure of Si atoms is the same on the entire (001) face, making it unlikely to exhibit rounded edges and corners.

614 the dissolution rate/flux and thus, if these sites do not lead to an  
 615 excessive rounding of the crystal. In this case, a simple cross-  
 616 multiplication would be able to reproduce the evolution of the  
 617 dissolution rate/flux.

618 To model the dissolution of Si atoms, the first step is to  
 619 consider the volume ( $\Delta V_i$ ) that is dissolved during an iteration

$$620 \quad \Delta V_i = V_{i-1} - V_i \quad (10a)$$

$$621 \quad V_i = (x_0 - 2\Delta h_i^{(100)})(y_0 - 2\Delta h_i^{(010)})(z_0 - 2\Delta h_i^{(001)}) \quad (10b)$$

622 If the dissolved volume is known, the number of Si atoms  
 623 released per iteration can easily be calculated knowing the  
 624 volume of the enstatite cell and the number of Si atoms it  
 625 contains (16)

$$626 \quad \text{Si}_{\text{released},i} = \frac{16\Delta V_i}{abc} \quad (11)$$

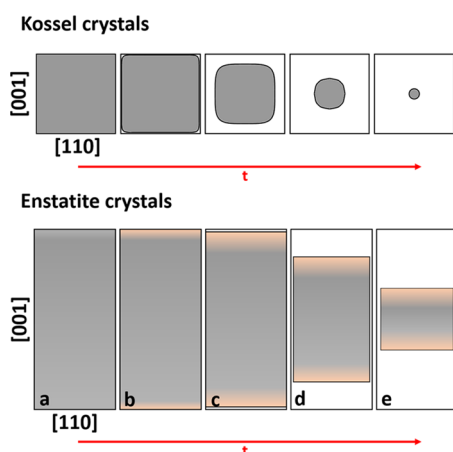
627 Modeling the release rate of Si requires to know the values of  
 628  $\Delta h_i^{(hkl)}$  at each iteration step  $i$ , which requires to know the face-  
 629 specific dissolution rate of enstatite both at steady state and  
 630 during the transient states, i.e., at the beginning and at the end of  
 631 the simulations. To the best of our knowledge, while an  
 632 analytical expression has been developed in Bouissonnié et al.<sup>41</sup>  
 633 for the steady state, a similar expression does not exist for  
 634 transient phases. To model the dissolution of the rectangular  
 635 parallelepipeds used in the different simulations, we first

performed three additional face-specific simulations (i.e., 636  
 simulations where only the atoms belonging to the face ( $hkl$ ) 637  
 are allowed to react, thus excluding atoms belonging to edges, 638  
 corners, and all other ( $h'k'l'$ ) faces), with a depth equivalent to 639  
 half the depth of the volume in a given direction. The evolution 640  
 of the surface retreats as a function of time for the (100), (010), 641  
 and (001) faces were then retrieved and implemented in eq 10b 642  
 to model the dissolution of a rectangular parallelepiped and 643  
 determine the evolution of the release rate of Si atoms as a 644  
 function of time. The results of this dissolution model are 645  
 presented in Figure 7 (light-colored curves) and compared to 646  
 the outputs of the simulations conducted with rectangular 647  
 parallelepipeds (dark-colored curves). The agreement between 648  
 both models is striking, with a sharp increase of the dissolution 649  
 rate observed during the first 8000 iterations, followed by a slow 650  
 decrease of the dissolution rate and a sharper decrease at the end 651  
 of simulations. 652

**4.3. Comparison between Results of the Simulation 653  
 and Modeled Dissolution.** Figure 7 shows that the results 654  
 derived from theoretical dissolution and modeled dissolution 655  
 are almost identical. With the exception of the very end of the 656  
 dissolution, the results of the simulations performed with 657  
 rectangular parallelepipeds and those derived from face-specific 658  
 dissolution are superimposed. However, contrary to the results 659  
 of the simulations performed with rectangular parallelepipeds, 660  
 those derived from face-specific dissolution exhibit a greater 661  
 standard variation around the mean value of the curves. This 662



663 observation stems from the fact that stochastic variations in the  
 664 instantaneous dissolution rate of each single face are cumulated,  
 665 increasing the overall standard variation artificially. Interestingly,  
 666 when one looks at the variation of the dissolution rate as a  
 667 function of the number of elapsed iterations (Figure 7a), the  
 668 mean value of the results derived from the face-specific approach  
 669 is slightly lower than the one derived from the simulations  
 670 performed with rectangular parallelepipeds. This slight differ-  
 671 ence may be explained by the contribution of corners and edges  
 672 to the dissolution rate/flux. However, contrary to other  
 673 minerals, the dissolution of these surface sites seems to have a  
 674 negligible impact. A scheme exhibiting the difference between  
 675 enstatite and a Kossel crystal<sup>9,19,36,37,59–61</sup> dissolution, for which  
 676 the contribution of edges and corners was shown in previous  
 677 studies to be significant, is depicted in Figures 9 and 10 to



**Figure 10.** Scheme of the effect of dissolution through time on Kossel and enstatite crystals. Kossel: the high probability of departure of edge and corner sites leads to a rounding of the corresponding locations. This modifies significantly the crystal shape during the dissolution, which evolves from a cubic to a spherical shape. Black squares represent the crystal shape at  $t = 0$ . The gray area represents a section of the crystal. Enstatite: At the beginning of the dissolution, Mg atoms are preferentially dissolved due to their particularly incomplete first coordination sphere, leading to the formation of a Si-enriched layer (orange area) on the (001) face (a–c). The Si-enriched layer reaches its constant depth (b, c) and the dissolution becomes stoichiometric. Both Si and Mg atoms are dissolved preferentially on the (001) face, but a few are dissolved on the (100) and (010) faces (c–e). This dissolution behavior makes the rounding of the crystals unlikely.

678 explain this counterintuitive result. These schemes are based on  
 679 the periodic bond chain theory,<sup>17</sup> which governs silicate  
 680 dissolution. In a Kossel crystal, the volume is composed of a  
 681 unique component (“atom”), leading to the existence of a single  
 682 type of bond. By nature, a Kossel crystal will have specific surface  
 683 sites (adatoms, steps, and kinks) with a high probability of  
 684 departure, leading to the rounding of the simulated crystals over  
 685 time. In the case of enstatite, the anisotropic nature of pyroxenes  
 686 makes this morphological evolution simpler. As opposed to, e.g.,  
 687 tectosilicates, which have a three-dimensional framework of  
 688 silica tetrahedrons, inosilicates are composed of silica chains  
 689 oriented following a specific direction (parallel to the  $c$ -axis in  
 690 enstatite). In enstatite, Mg and Si atoms are also organized in  
 691 planes parallel to the (100) face. This particular organization  
 692 explains the anisotropy of dissolution of enstatite, as discussed in  
 693 Bouissonnié et al.,<sup>16</sup> and likely explains why macro steps and  
 694 corners do not play an essential role in the evolution of the

dissolution rate with time. Indeed, as shown in Figure 9, most of  
 695 enstatite dissolution flux is supported by (001) faces. This is due  
 696 to the fact that the release of Si from ( $hk0$ ) faces requires the  
 697 simultaneous cleavage of two Si–O–Si bonds, while the release  
 698 of Si from (001) faces requires the cleavage of one Si–O–Si  
 699 bond only.  
 700

This specific anisotropic structure also explains why the  
 701 model depicted in Section 4.2 successfully matches the outputs  
 702 of the simulations run with enstatite parallelepipeds, indirectly  
 703 suggesting that no rounding of the crystals occurs with time. The  
 704 greater probability to release Mg atoms to the solution results in  
 705 the formation of a Mg-depleted zone at the mineral surfaces  
 706 during the first iterations (Figure 4), where the mineral–  
 707 solution interface is only composed of chains of Si atoms (Figure  
 708 9). This process is more pronounced at the surface of the (001)  
 709 faces, where Mg atoms have the greater departure probabilities.  
 710 This is fully consistent with the experimentally observed thicker  
 711 amorphous silica layers on (001) faces. If the (001) faces exhibit  
 712 a Mg-depleted mineral–solution interface, then it means that it  
 713 is composed essentially on silica chains, not connected between  
 714 them (Figure 9). These silica chains will be present throughout  
 715 the entire surface of the (001) face but, as their topmost Si atoms  
 716 all exhibit the same departure probability, a rounding of the  
 717 edges and kinks is unlikely to happen.  
 718

In summary, the dissolution of a Kossel crystal can be  
 719 described as follows: (i) Initial fast release of atoms from the  
 720 kinks and edges of the minerals; (ii) Through time, the Kossel  
 721 crystal habit evolves from a cubic to an almost spheroidal shape.  
 722 Conversely, the dissolution behavior of enstatite and more  
 723 generally, of pyroxenes, can be summarized as follows: (i) Rapid  
 724 depletion of the topmost Mg atoms from the (001) faces; (ii)  
 725 stabilization of the thickness of the corresponding silica layer;  
 726 and (iii) propagation of the dissolution front mainly from the  
 727 (001) faces. These mechanistic explanations are summarized in  
 728 Figures 9 and 10. Also, as mentioned in Section 2.4, the model is  
 729 not able to reproduce the amorphous silica layer. Then, the  
 730 interface mainly composed of Si atoms remains “crystalline”  
 731 with only disconnected silica chains. This may present a  
 732 limitation to the mechanisms developed above as, in natural  
 733 environment, a thicker amorphous silica layer may impact the  
 734 crystal shape evolution. Extending this discussion to other  
 735 minerals requires a specific treatment of other classes of  
 736 minerals, which is out of the scope of this study. However, it  
 737 is likely that many minerals, which highlight an anisotropy  
 738 similar to pyroxenes could observe a similar dissolution  
 739 mechanism. One could argue that many minerals are more  
 740 anisotropic than enstatite because of its orthorhombic Bravais  
 741 lattice, which has a high symmetry level. However, the notion of  
 742 anisotropy here refers to the organization of the Si tetrahedrons.  
 743 In this regard, orthorhombic inosilicates are less isotropic than,  
 744 e.g., triclinic tectosilicates, which have a three-dimensional  
 745 framework of silica tetrahedrons, even though the symmetry  
 746 level of the orthorhombic system is higher than that of the  
 747 triclinic system.  
 748

Finally, the main discrepancy between model’s outputs and  
 749 theoretical results is observed at the end of the simulations.  
 750 While the dissolution rates calculated using the simulations run  
 751 with rectangular parallelepipeds reach 0 at the end of the  
 752 reaction, indicating that all of the material is consumed, it is not  
 753 the case for the rates calculated based on face-specific  
 754 dissolution rates and using eqs 10a and 10b. This observation  
 755 is an artifact resulting from the mathematical construction of the  
 756 model. While faces (100), (010), and (001) are considered, the  
 757

dissolution is mainly controlled by the sole (001) face. Equation 10b implies that all faces dissolve independently so that when the length of the parallelepiped following the z-axis reaches 0, it is not the case for the two other axes. Therefore, following eq 10b, a plan of enstatite contained in the two-dimensional (2D) (xOy) plan still exists and continues to fuel the dissolution. Conversely, in the real world (and in the simulations run with rectangular parallelepipeds), the dissolution stops when the crystal is completely dissolved.

**4.4. Comparing Modeled Dissolution Fluxes and Experimental Results.** **4.4.1. Comparison Based on Dissolution Experiments Conducted with Powdered vs Single-Face Enstatite.** In the previous section, it has been shown that it is possible to reproduce the grain dissolution behavior with a simple mathematical model considering the dissolution fluxes of the faces in contact with the fluid. However, this good agreement was obtained using simulation results only. While, theoretically, the model used in the present study is also able to reproduce experimental data,<sup>16</sup> the corresponding validation has been previously based on a comparison with measured face-specific dissolution fluxes only, and not with results from powder experiments. This missing comparison is therefore attempted hereafter. As a first step, we use below the additivity property of single-face dissolution fluxes illustrated in Section 4.3 to compare the results of dissolution experiments previously conducted with single faces with those conducted with powdered enstatite.

In their study, Oelkers and Schott<sup>11</sup> have determined the dissolution flux of enstatite powder over a wide range of pH and temperature. Using the reaction order with respect to  $[H^+]$  and the activation energy derived from their study, the dissolution flux of enstatite powder at 90 °C and pH 0 (the chemical conditions simulated in this study) should be around  $2.35 \times 10^{-8}$  mol/(m<sup>2</sup> s). In our previous study, the different dissolution fluxes of the four main faces naturally exposed in enstatite have been determined to yield  $5.22 \times 10^{-9}$ ,  $5.92 \times 10^{-9}$ ,  $1.7 \times 10^{-8}$ , and  $1.44 \times 10^{-7}$  mol/(m<sup>2</sup> s) for the faces (100), (010), (210), and (001) respectively<sup>16</sup> (note that the results of Bouissonnié et al.<sup>16</sup> were corrected by a 2-fold factor, as they considered Mg<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> as the chemical formula for enstatite, whereas Oelkers and Schott used MgSiO<sub>3</sub>). The main cleavage plan of enstatite is {210}<sup>62</sup> and is likely to be the most abundant when enstatite is crushed prior to run powder dissolution experiments. If one assumes that, in enstatite powders, mostly (210) and (001) faces are present, then based on the results of the previous section, the dissolution flux of the powder can be calculated following:

$$r = \frac{4 * S_{(210)} * r^{(210)} + 2 * S_{(001)} * r^{(001)}}{S_0} \quad (12)$$

where  $S_{(hkl)}$  is the surface area of the (hkl) face (m<sup>2</sup>),  $r^{(hkl)}$  is the dissolution flux (mol/(m<sup>2</sup> s)) of the (hkl) face, and  $S_0$  is the initial surface area (m<sup>2</sup>). Depending on the size of the grains used in this calculation ( $10 \times 10 \times 100$  or  $20 \times 20 \times 100$  μm<sup>3</sup>, consistent with the grain size range reported in the Oelkers and Schott study), the dissolution flux is estimated to be  $2.85 \times 10^{-8}$  and  $2.31 \times 10^{-8}$  mol/(m<sup>2</sup> s) for  $20 \times 20 \times 100$  and  $10 \times 10 \times 100$  μm<sup>3</sup> crystals, respectively. These values are in excellent agreement with the dissolutions flux calculated based on the study of Oelkers and Schott (hereafter referred to as  $r_{OS}$ ) ( $2.35 \times 10^{-8}$  mol/(m<sup>2</sup> s)). This agreement further supports that edges and corners must negligibly contribute to the dissolution flux of enstatite grains, consistent with the previous section.

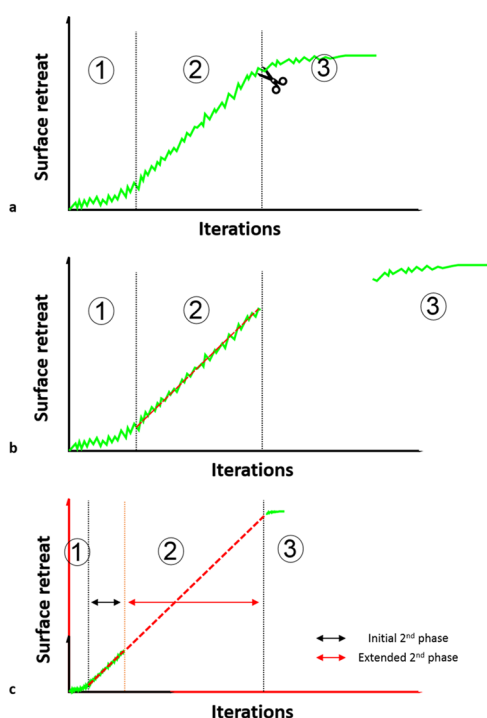
**4.4.2. Testing Different Methods to Upscale Dissolution Fluxes from Face-Specific Simulations to Powder Dissolution Experiments.** The ability of the model to reproduce dissolution fluxes derived from powder experiments with dissolution fluxes derived from face-specific simulations and experiments has been shown in Sections 4.3 and 4.4.1, respectively. However, simulating directly the dissolution of entire crystals with dimensions of typical grains used in laboratory experiments remains out of reach with current numerical methods. Indeed, our computational capabilities allow us to simulate the dissolution of crystals up to  $0.1 \times 0.1 \times 1$  μm<sup>3</sup>, whereas the typical enstatite grain size for powder dissolution experiments<sup>11,50</sup> is on the order of  $10 \times 10 \times 100$  μm<sup>3</sup>.

To circumvent this problem, a solution is to consider the good agreement between the results of the simulations run with rectangular parallelepipeds and the results calculated using face-specific dissolution (eq 10a). As the surface retreat does not depend on the considered surface area, each of the three main phases of the dissolution of a given face (i.e., initial transient regime, steady-state regime, i.e., linear increase of the surface retreat with iterations, and terminal regime) extends over a similar number of iterations, whatever the surface area considered. We used this property to simulate the dissolution of crystals with dimensions approaching those of grains used in classical powder dissolution experiments (see Figure 11). This process is repeated for all faces to simulate the dissolution of an entire parallelepiped. The results of the simulations conducted with this large volume are shown in Figures 5b and 6b (black curves). This process allows studying the evolution of the dissolution behavior over a wide range of volumes and also to understand how such systems evolve. Ultimately, the simulation of such large volumes allows comparing modeled and experimental data.

The first important highlight is that no real steady state is reached for dissolution rate/flux (Figures 5b and 6b). Indeed, the dissolution rate and flux steadily increase over the course of the simulation. This may be due to the evolution of the surface area that is not correctly captured, as the calculation does not consider its intrinsic variability over the entire surface (intrinsic reactivity and etch pits formation for example). However, the increase is slow and not significant (below 14 nmol/s, which would remain out of reach of conventional techniques used to measure dissolution fluxes in the laboratory), and this regime can therefore be approximated to a steady state. This pseudo-steady state corresponds to a mean dissolution flux of approximately  $1.8 \times 10^{16}$  Si atoms/(m<sup>2</sup> iteration) which yields  $2.62 \times 10^{-8}$  mol/(m<sup>2</sup> s), if one applies the time/iteration relationship calculated by Bouissonnié et al.<sup>16</sup> ( $r(\text{mol}/(\text{m}^2 \text{ s})) = 0.876 \times r(\text{mol}/(\text{m}^2 \text{ iteration}))$ ). This value is in very good agreement with that determined by Oelkers and Schott ( $\sim 1.11 r_{OS}$ ).

Three additional upscaling methods are tested and compared with  $r_{OS}$ .

The first method consists of considering the dissolution fluxes determined with single-face dissolution experiments:<sup>16</sup> (a) with faces (100), (010), and (001) and (b) with faces (210) and (001)



**Figure 11.** Scheme of the method followed to get the dissolution flux of enstatite rectangular parallelepipeds with a size comparable to those used in Oelkers and Schott.<sup>11</sup> (a) Surface retreat simulated as a function of the iterations is used for each considered face (e.g., (100), (010), and (001)). It is divided into three different phases: (1) the transient regime, (2) the steady-state regime, and (3) the terminal regime, corresponding to the consumption of the remaining atoms in the materials. A cut is operated between the second and third phases. (b) A linear regression (dashed red line) is applied, based on the results of the steady-state phase starting from the transition between the first and second phases and ended between the second and third phases. (c) Linear regression is used to increase the size of the parallelepiped to reach the size used by Oelkers and Schott. The third phase is then added at the end of the extended second phase.

$$r = \frac{16^* \Delta V(\Delta t)}{a^* b^* c^* \Delta t^* S_0^* N_A}$$

$$\Delta V(\Delta t) = V_t - (x_t - 2\Delta h_{\Delta t}^{(100)|(210)})(y_t - 2\Delta h_{\Delta t}^{(010)|(210)})(z_t - 2\Delta h_{\Delta t}^{(001)})$$

875

876 where  $r$  is the dissolution flux ( $\text{mol}/(\text{m}^2 \text{ s})$ ),  $\Delta t$  is the time  
877 interval considered for the calculation (s),  $S_0$  is the initial surface  
878 ( $\text{m}^2$ ),  $N_A$  is the Avogadro number ( $\text{mol}^{-1}$ ),  $\Delta V(\Delta t)$  is the  
879 difference of volumes over the time interval  $\Delta t$  ( $\text{m}^3$ ), and  $\Delta h_{\Delta t}^{(hkl)}$   
880 is the surface retreat of the  $(hkl)$  face over the time interval  $\Delta t$ .

881 The second method uses the surrogate relation between the  
882 dissolution flux and the probabilities (i.e., activation energies)  
883 determined in Bouissonnié et al.<sup>41</sup>

$$\frac{\Delta h_{(hkl)}}{\Delta t} 0.876 \left[ \begin{array}{l} k P_{\text{Mg-O-Mg}}^{\alpha} P_{\text{Mg-O-Si}}^{\beta} P_{\text{Si-O-Si}}^{\gamma} + \\ k_{\text{dis}} P_{\text{Mg-O-Mg}}^{\alpha_{\text{dis}}} P_{\text{Mg-O-Si}}^{\beta_{\text{dis}}} P_{\text{Si-O-Si}}^{\gamma_{\text{dis}}} (1 - e^{-\rho_d/\omega}) \end{array} \right]$$

884

885 with  $k$ ,  $k_{\text{dis}}$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\alpha_{\text{dis}}$ ,  $\beta_{\text{dis}}$ ,  $\gamma_{\text{dis}}$ , and  $\omega$  being empirical  
886 parameters and  $\rho_d$  the dislocation density. The left-hand side of  
887 the sum referred to the “bulk” dissolution flux, while the right-  
888 hand side referred to the contribution etch pits at dislocation

outcrops. The values of these parameters were determined in  
Bouissonnié et al.<sup>41</sup> and are listed in Table 1. 889 890 t1

**Table 1.** Numerical Values of the Parameters in Equation 12 and Taken from Bouissonnié et al.<sup>41</sup>  $\alpha$

face	(100)	(010)	(001)
$k$ ( $\text{\AA}/\text{it}$ )	8.87	7.8	4.72
$\alpha$	2.46	2.22	6.36
$\beta$	4.62	4.65	4.19
$\gamma$	0.94	0.75	0.14
$k_{\text{dis}}$ ( $\text{\AA}/\text{it}$ )	44.7	44.7*	
$\alpha_{\text{dis}}$	2.09	2.09*	
$\beta_{\text{dis}}$	4.09	4.09*	
$\gamma_{\text{dis}}$	0.67	0.67*	
$\omega$	$5.51 \times 10^{10}$	$5.51 \times 10^{10}$ *	
$\rho_d$ ( $/\text{cm}^2$ )	$4.9 \times 10^8$	$9.8 \times 10^6$	0

$\alpha$ ,  $\beta$ , and  $\gamma$  represent fitting parameters for bulk dissolution rate (without the presence of dislocation).  $\alpha_{\text{dis}}$ ,  $\beta_{\text{dis}}$ , and  $\gamma_{\text{dis}}$  represent fitting parameters for dissolution rate impacted by the presence of dislocations. The parameters  $k$  and  $k_{\text{dis}}$  represent the dissolution constant for bulk dissolution rate and dissolution rate impacted by the dislocation, respectively.  $\omega$  is a fitting parameter, and  $\rho_d$  is the dislocation density measured in Bouissonnié et al.<sup>16</sup> (\*) Parameters corresponding to the presence of dislocation on the (010) face were not studied. For this study, it has been assumed that they were equal to those of the (100) face.

The last method considers the modeled face-specific  
dissolution fluxes given in Bouissonnié et al.<sup>16</sup> 891 892

The three methods were applied on  $20 \times 20 \times 100$  and  $10 \times$   
 $10 \times 100 \mu\text{m}^3$  rectangular parallelepipeds (considered as a  
model shape and size for the grains used in Oelkers and  
Schott<sup>11,50</sup>), and the results are summarized in Table 2. Overall,  
all methods exhibit a satisfactory agreement with the results  
obtained experimentally, with discrepancies never exceeding  
50%. Of note, a better agreement is obtained when the {210}  
face is considered. This observation may confirm that enstatite  
grains were mainly shaped with {210} face in the powder used

**Table 2.** Numerical Values of the Steady-State Dissolution Flux of an Enstatite Grain Considering the Simple Relation between Face-Specific Dissolution Flux and Powder Dissolution Flux Following Several Methods<sup>a</sup>

method	crystal size ( $\text{m}^3$ )	dissolution flux ( $r = \text{mol}/(\text{m}^2 \text{ s})$ ) ( $\times 10^{-8}$ )	$r/r_{\text{OS}}$
surface retreat of (100), (010), and (001) <sup>16</sup>	$20 \times 20 \times 100 \mu\text{m}^3$ $10 \times 10 \times 100 \mu\text{m}^3$	1.78 1.18	0.76 0.50
surface retreat of (210) and (001) <sup>16</sup>	$20 \times 20 \times 100 \mu\text{m}^3$ $10 \times 10 \times 100 \mu\text{m}^3$	2.75 2.17	1.17 0.92
surrogate model <sup>41</sup>	$20 \times 20 \times 100 \mu\text{m}^3$ $10 \times 10 \times 100 \mu\text{m}^3$	2.22 1.62	0.94 0.69
this study	$20 \times 20 \times 100 \mu\text{m}^3$	2.62	1.11
single-face-modeled results <sup>16</sup>	$20 \times 20 \times 100 \mu\text{m}^3$ $10 \times 10 \times 100 \mu\text{m}^3$	1.88 1.35	0.8 0.57

<sup>a</sup>The agreement (evaluated by the  $r/r_{\text{OS}}$  ratio) between powder dissolution experiments of Oelkers and Schott<sup>11</sup> and results obtained from face-specific dissolution experiments and modeling taken from Bouissonnié et al.<sup>16,41</sup> are reported in the last column. Crystal size has been chosen according to that reported in Oelkers and Schott, and an aspect ratio consistent with Dana.<sup>50</sup>



902 by Oelkers and Schott, which is consistent with the fact that  
903 {210} represents the main cleavage plan of enstatite.

904 **4.5. Relevance for Mineral Dissolution Studies and**  
905 **Limitations.** Both experimental results obtained with face-  
906 specific dissolution measurements and those obtained with the  
907 stochastic dissolution model run with rectangular parallelepi-  
908 peds succeed to reproduce the dissolution rates/fluxes measured  
909 during powder dissolution experiment. Here, we showed that  
910 face-specific and powder dissolution rates can be linked using a  
911 simple relation. However, this may be only true in the case of  
912 very anisotropic minerals such as enstatite (and pyroxenes)  
913 because edges and corners contribute negligibly to the  
914 dissolution flux. This conclusion does not hold for calcite, for  
915 example, as Noiriél et al.<sup>25</sup> showed that corners dissolve faster  
916 than (104) cleavage plans. In our opinion, our results would  
917 justify investigating the dissolution of other minerals according  
918 to the methods reported here to determine the crystallographic  
919 structures for which dissolution obeys relations similar to those  
920 evidenced for enstatite.

921 The results presented here may also be useful to model silicate  
922 weathering in natural environments. Subsurface environments  
923 present a wide diversity of textures, from porous to fractured  
924 media. Although fractured media should involve a preferential  
925 water/solid interaction of a limited number of mineral cleavage  
926 planes, porous media can exhibit a greater variety of mineral  
927 faces in contact with water. Actually, as a first approximation,  
928 micrometer-wide enstatite grains may be simplified as  
929 rectangular parallelepipeds made of (210) and (001) faces  
930 only, for which the length of the crystal in the z-direction is 5–10  
931 times greater than in the other directions leading to consider the  
932 dissolution rate given by eq 12. This result may still hold true in  
933 less acidic environment as long as the fluid is far from  
934 equilibrium with respect to  $\text{SiO}_{2(\text{am})}$ .<sup>48</sup> The fact that face-  
935 specific and powder dissolution studies can be linked through a  
936 simple relation for anisotropic minerals may imply that face-  
937 specific dissolution studies offer a greater interest than those  
938 conducted with powders for minerals presenting an anisotropy  
939 similar to the one of enstatite. In addition, our study shows the  
940 prevalence of fast dissolving faces over the others, suggesting  
941 that face-specific dissolution studies should target in priority  
942 such faces. Overall, the agreement between the outputs of the  
943 model and the theoretical results detailed in Section 4.2 shows  
944 how important it is to consider the evolution of the reactive  
945 surface area in geochemical/reactive-transport studies/models.  
946 The evolution of the aspect ratio was shown to be important in  
947 both cases when the reaction progress reaches approximately  
948 80%. Indeed, at this step, the aspect ratio has evolved enough so  
949 that the reaction flux is characterized by a sharp increase. This  
950 may be of great interest to model chemical weathering in the  
951 regolith, where primary materials are altered into secondary  
952 minerals and may be the main contributors of dissolved  
953 elements in springs and rivers.

954 Interestingly, the simulated instantaneous release rates of Mg  
955 and Si atoms as a function of time (Figure 4) exhibit a specific  
956 shape that corresponds in every way to the calorimetry curves  
957 depicting the progress of cement hydration (cf. Figures 2–4 in  
958 Luc et al.<sup>63</sup>), for which the rate-limiting step is supposed to be  
959 the dissolution of silicate minerals such as alite. It is noteworthy  
960 that such a shape has puzzled the materials sciences community  
961 for a couple of decades, since it reveals a strong nonlinearity of  
962 the dissolution rate with time, which is at odds with existing  
963 models of mineral reactivity.<sup>64</sup> While previous attempts did not  
964 succeed to fully account for such observations,<sup>65,66</sup> the present

study suggests that the anisotropic dissolution of silicates may  
indeed result in a general dissolution pattern consistent with  
previous measurements of cement hydration, representing  
relevant new avenues to be investigated in greater details.

Finally, among the main limitations of our study, the  
development of amorphous silica-rich surface layers through  
silica redeposition or surface network reorganization was not  
considered, as the impact of such layers is suspected to be  
nonsignificant in the experimental conditions investi-  
gated<sup>3,47,67,68</sup> by Bouissonnié et al.<sup>16</sup> (i.e., very acidic pH and  
low concentrations of aqueous silica). The implementation in  
the stochastic dissolution code of backward reactions of Si  
attachment, as described in, e.g., Zhang and Lüttge<sup>69</sup> or the  
consideration of M–O hydrolysis instead of M–O–M  
hydrolysis would be required to ultimately get closer to  
conditions operating in natural settings.

## 5. CONCLUSIONS

In this work, we simulated the dissolution of enstatite grains with  
a stochastic dissolution model developed at the atomic scale. By  
varying the size of the simulated grains, we showed that the main  
factor impacting the temporal evolution of the dissolution rate is  
the aspect ratio. A similar evolution of the dissolution rate  
through time is observed for grains with the same aspect ratio.  
Furthermore, different parameters such as the maximum  
dissolution rate, initial volume, dissolution at a given volume,  
and reaction progress were linked together through empirical  
functions.

One of the main outcomes of this study was provided by  
comparing the outputs of the stochastic grain dissolution with a  
theoretical dissolution model based on the sole contribution of  
face-specific dissolution, neglecting the contribution of edges  
and corners. The very good agreement between the two  
methods highlights the modest effects of edges and corners  
during enstatite dissolution, and probably, during the dis-  
solution of other very anisotropic minerals as well (i.e., minerals  
where the stronger atomic bonds are aligned in a specific  
direction).

The comparison between modeled and experimental results  
obtained by Oelkers and Schott<sup>11</sup> on powder dissolution also  
revealed an excellent agreement. This led to the conclusion that  
powder dissolution results from the specific contribution of each  
face in a very simple way, making it possible to link the different  
experimental works performed in a laboratory.

Finally, this study shows the importance of fast dissolving  
faces. Indeed, almost the entire dissolution rate relies on the  
dissolution of the face (001). However, if the dissolution rates of  
the fastest dissolving faces are prominent, the overall dissolution  
rate is strongly correlated to the surface area of the other slower  
faces. This result supports the idea that reactive surface is one of  
the most important parameters in water/mineral interactions  
studies and that one must be aware, particularly in reactive-  
transport studies, of what is the reactive surface and how it  
should be taken into account.

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1035 **Notes**

1036 The authors declare no competing financial interest.

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