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1 **The Dissolution Anisotropy of Pyroxenes: A Surrogate Model for**
2 **Steady-State Enstatite Dissolution Resulting From Stochastic**
3 **Simulations of the Hydrolysis Process**

4

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25 Abstract

26 Over the past decades, the field of mineral dissolution kinetics has undergone a spectacular
27 evolution, with an increasingly detailed description of the atomic scale mechanisms of fluid-
28 solid interactions. The development of probabilistic dissolution models has played a
29 prominent role in this evolution, as they allow for bridging the outputs of *ab initio*
30 calculations to macroscopic observables such as dissolution rates and nanoscale surface
31 features. It is however admitted that these models cannot be easily adapted to simulate natural
32 systems at large space and time scales due to the restricted dimensions and durations that can
33 be simulated numerically. In the present study, we demonstrate that the steady-state outputs of
34 the face-specific stochastic treatment of enstatite dissolution, which was experimentally
35 validated in a previous paper, can be boiled down to a single analytical expression under the
36 form:

$$37 \quad r_{bulk}^{(hkl)} = k P_{Mg-O-Mg}^{\alpha} P_{Mg-O-Si}^{\beta} P_{Si-O-Si}^{\gamma}$$

38 where $r_{bulk}^{(hkl)}$ is the steady-state dissolution rate of a defect-free (*hkl*) face [$\text{\AA}/\text{iter}$], $P_{M-O-M'}$
39 stands for the bond-breaking probability of the M-O-M' bond, and k , α , β and γ are fitting
40 parameters adjusted following the outputs of the stochastic simulations. When dislocations
41 outcrop at the surface of a given (*hkl*) face of enstatite, the relation then becomes:

$$42 \quad r^{(hkl)} = r_{bulk}^{(hkl)} + r_{dislocation}^{(hkl)} \left(P_{Mg-O-Mg}, P_{Mg-O-Si}, P_{Si-O-Si} \right)$$

43 where $r_{dislocation}^{(hkl)}$ stands for the contribution of the dislocations to the overall dissolution rate.
44 The derivation of simple analytical expressions to get steady-state rate data that are similar to
45 those obtained using stochastic dissolution models, may contribute to parametrize efficiently
46 the bond-breaking probability of various atoms for pyroxene solid solutions, and raises the
47 question of the extension of such surrogate expressions to other silicate structures. Finally, the

48 development of surrogate models such as those reported here represents one of the possible
49 strategies for upscaling dissolution processes from the atomic scale to the micron scale.

50 **1. Introduction**

51 Many complementary approaches have been developed to predict the fate of water-
52 rock interactions, at various space and time scales. Historically, the conceptual framework
53 underpinning the corresponding models has been closely linked to the disciplinary field in
54 which they were developed.

55 When dealing with the Earth system, the first attempts to develop weathering rate laws
56 for large space (km²) and time (Myr) scales were undoubtedly phenomenological, and
57 strongly relied on empirical relations. The pioneering work of Berner and coworkers, aimed at
58 reconstructing the evolution of the CO₂ concentration in the atmosphere during the
59 Phanerozoic through the development of the BLAG¹ and GEOCARB²⁻⁴ codes, was based on
60 model weathering reactions, whose rates were largely parametrized according to empirical
61 rate-runoff, rate-pCO₂ and rate-temperature relations inferred from field measurements. Since
62 the early 90s, this approach has been gradually superseded by reactive transport models,
63 where the source-terms of the classical reaction-dispersion-advection equation are described
64 following kinetic rate laws derived from dissolution experiments conducted on powdered
65 single-crystals. Although the corresponding rate equations, which relate the dissolution rate to
66 fundamental parameters such as temperature, pH, surface area or solution saturation state,
67 were originally claimed to result from the transition state theory (TST)⁵⁻⁷, several studies
68 subsequently questioned the theoretical validity of the extension of TST to silicate dissolution
69⁸⁻⁹, the experimental validation of which being described as nothing more than a fitting
70 exercise with little physical basis by some authors¹⁰. More generally, a growing number of
71 experimental studies have underlined the limitations of TST-based relations, which fail to
72 accurately relate dissolution rates to solution saturation state¹¹⁻¹⁹, and are unable to account
73 for the variability (heterogeneity and anisotropy) of crystal dissolution rates²⁰⁻²⁸. With respect
74 to the relation between dissolution rate and fluid saturation state, the deviation from a TST-

75 behavior has often been attributed to the nucleation and opening of etch pits where
76 dislocations outcrop at the mineral's surface ^{11, 19, 23, 29-32}. Etch pits have been extensively
77 reported for a wide variety of minerals ^{22-23, 32-38}, when the fluid under saturation is large
78 enough and does not exceed a critical value of the Gibbs free energy. The efficiency of these
79 sites to enhance mineral dissolution rate has been showed both experimentally and
80 numerically, and is accounted for by the stepwave model ³¹. At the atomic-scale, the opening
81 of etch pits results in an increase of the density of kink and step sites. This process exposes
82 atoms with a lower coordination to the fluid which are, as a result, more rapidly dissolved.
83 More generally, the reactivity of minerals is highly heterogeneous, with hotspots of reactivity
84 such as kinks, steps (and ultimately crystal edges and corners) and can be accurately captured
85 by the "rate spectra" concept ^{20, 39}. Finally, several studies have pointed out that mineral
86 dissolution is anisotropic ^{19, 22-23, 38, 40-41}, resulting from the anisotropic distribution of atomic
87 positions in the crystal lattice. These observations have emphasized the need for deeper
88 experimental and theoretical studies of fluid-mineral interactions from the atomic- to the nm-
89 scale to unravel the dissolution mechanisms.

90 Precisely at the other end of the spatiotemporal spectrum, the advent of microscopic
91 and spectroscopic techniques of characterization of the fluid-mineral interface offered new
92 avenues to understand mineral reactivity ^{26, 42-53}. Studies dedicated to the molecular-scale
93 description of the silicate dissolution process following *ab initio* quantum mechanical
94 calculations and molecular dynamics (MD) models emerged some 20 years ago ⁵⁴⁻⁵⁹. These
95 studies provided essential theoretical insights into the dissolution process. Admittedly, the
96 corresponding studies have been of limited direct interest (and were not intended) to model
97 chemical weathering in natural settings, due to the restricted durations and dimensions of the
98 system that can be simulated numerically.

99 A first intermediate step in the upscaling process of dissolution reaction rates has been
100 successfully reached with the emergence of stochastic models of silicate and carbonate
101 dissolution^{25, 28, 36, 48, 53, 57, 60-69}, whose parametrization may strongly rely on the results of *ab*
102 *initio* calculations mentioned above, with considerable simplifications of the reaction details.
103 Such an approach dramatically increased the size of the studied systems from clusters of a few
104 atoms to nanocrystals of several tens of millions of atoms, simulating time scales of up to
105 several weeks^{41, 70}. However, implementing such models into reactive transport codes is not
106 an easy task since they usually do not provide the rate laws that are required by these codes to
107 predict the rates of water-rock interactions at large space and time scales⁷¹⁻⁷². Promising
108 strategies combining Monte Carlo simulations and Voronoi methods have been recently
109 developed to circumvent this issue^{39, 73}, offering the perspective to reach the next step in the
110 upscaling process, i.e., the continuum scale, where reactive transport can be applied. Such
111 recent breakthroughs emphasize the crucial importance of maintaining efforts to investigate
112 into more details the various theoretical and empirical emerging relations of stochastic
113 dissolution models, which represents one of the goals of the present paper.

114 In a previous study⁴¹, we developed a **probabilistic** model of enstatite dissolution
115 which successfully reproduced the measured anisotropy of enstatite dissolution rates and
116 associated surface features. In the present study, hundreds of simulations were conducted with
117 this model by varying the bond-breaking probabilities of the crystal-to explore the analytical
118 relation that may link together the detachment of individual atoms from the enstatite surface
119 to the overall face-specific dissolution rates. This work was in part motivated by the fact that
120 mineral dissolution kinetics is often treated by mixing macroscopic parameters with
121 microscopic ones, resulting in rate laws for which the theoretical basis remains questionable
122 (see discussion in e.g.⁹). Here we illustrate how overall rate constants may be derived from
123 atomic-scale parameters, considering especially the bond-breaking probability of hydrolysis

124 processes. In particular, we show that, at steady-state conditions, an analytical relation can be
125 derived to express the overall dissolution rate constant, whose parameters can be adjusted
126 following the outputs of numerical simulations performed at the atomic scale. We then show
127 that the resulting analytical relation can be used to predict the steady-state enstatite face-
128 specific dissolution rates over a wide range of bond-breaking probabilities. This relation is
129 then further extended from defect-free surfaces to defective surfaces impacted by screw
130 dislocations. Finally, we discuss the implications of such surrogate expressions, both from the
131 perspective of the mechanisms of pyroxene dissolution and for the upscaling of silicate
132 dissolution rates.

133

134 **2. Methods**

135 *2.1 Model description and algorithms*

136 A complete description of the model is given in Bouissonnié et al. ⁴¹. In short, the
137 positions of Mg, Si and O atoms provided by Hugh-Jones and Angel ⁷⁴ are used to create the
138 enstatite cell thanks to the symmetry elements of the *Pbca* space group. Mg and Si atoms are
139 then linked to the 6 and 4 nearest O atoms respectively. Since probabilistic dissolution models
140 generally consider the bond-breaking probabilities of M-O-M' bonds ^{30, 36, 69}, each Mg and Si
141 atom is connected to its first coordination sphere ³⁶.

142 Usually, the probability attributed with one event (i.e. the bond-breaking probability)
143 is written as follows ³⁰:

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

144 where P stands for the bond-breaking probability, E_a for the activation energy of the bond
145 hydrolysis (J), k_B for the Boltzmann constant (J/K) and T for the temperature (K). In the
146 present study, the most likely bond-breaking probability (i.e., the bond hydrolysis associated

147 ~~to~~ with the lowest activation energy, Mg-O-Mg) was arbitrarily set to 0.99 and the two other
 148 probabilities were scaled according to the differences between their corresponding activation
 149 energies following:

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

150 where A and B represent two different bonds.

151 In agreement with previous studies^{48, 61-66}, an “all-or-none” approach has been used.
 152 This approach considers the hydrolysis of atoms instead of individual bonds. In other words,
 153 for a given simulated step, an atom is released only when all the remaining bonds that connect
 154 the atom to the surface of the crystal are broken simultaneously. Otherwise, the corresponding
 155 atom remains connected to the surface. The probability of an atom M to be released in the
 156 fluid depends on the number and type of atomic bonds present in its first coordination sphere.
 157 In the case of the enstatite, this probability can be written as follows:

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

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

160 The dissolution algorithm was described in details in Bouissonnié et al.⁴¹ and is
 161 schematically represented in Fig. 1. Such algorithms have previously proven successful to
 162 simulate the dissolution of silicate materials (e.g.^{41, 48, 61}). In short, a random number Z
 163 uniformly distributed between 0 and 1 is drawn for each atom at the surface defined by an
 164 incomplete coordination sphere (i.e. an atom at the crystal surface). If $Z < P_M$, all atomic
 165 bounds are broken and the atom is considered as dissolved (removed from the surface); if not,
 166 the atom stays at the surface. The first coordination spheres of the remaining atoms are then
 167 updated if necessary (i.e., when a removed atom was belonging to the coordination spheres of
 168 one of the neighboring remaining atoms). Because coordination spheres are modified, the

169 probability of dissolution P_M of the corresponding atoms increases. In such kinds of
170 algorithms, each iteration step corresponds to a given simulated duration, and the time-step is
171 therefore constant for all simulations. The proportionality factor to convert the number of
172 iterations into time is not known a priori, and can be determined by comparing the outputs of
173 a simulation with experimental data (see ⁴¹ for details). This aspect contrasts with kinetic
174 Monte Carlo algorithms based on a “divide and conquer” approach ^{36, 63}, which use an
175 adaptive time step that varies at each iteration as a function of the random number that is
176 drawn, corresponding to a specific surface site that is dissolved during the iteration. The main
177 strengths of the “divide and conquer” approach are that they allow for a direct link between
178 time and the number of iterations, while precluding the existence of “dead” iterations,
179 reducing accordingly the computing time required to simulate a given process. Conversely,
180 “dead” iterations may sometimes occur over the course of the algorithm that we used
181 (essentially, at the beginning of the simulations), but as opposed to the “divide and conquer”
182 approach, it allows for simultaneous events to occur over a given iteration (and time step).
183 Although both methods should ultimately provide identical results (see theoretical derivation
184 in ⁷⁵), to the best of our knowledge, a comparison between both types of algorithms has never
185 been proposed for mineral dissolution, and is out of the scope of the present study.

186 The impact of dislocation density has also been studied by running additional
187 simulations for the (100) face. Dislocations were introduced as lines running parallel to the
188 [100] axis, in agreement with previous observations ⁷⁶. To simulate the faster dissolution at
189 dislocation sites (placed at the center of the reactive surface), the bond-breaking probabilities
190 associated τ with the atoms belonging to the dislocation line were set to 1 following
191 Kurganskaya and LuttgeKurganskaya and Luttge ³⁶.

192 One of the goals of this study was to understand how the dissolution rate evolves as a
 193 function of the probabilities used as input parameters. To perform this sensitivity analysis,
 194 each of the three fundamental probabilities ($P_{Mg-O-Mg}$, $P_{Si-O-Mg}$, or $P_{Si-O-Si}$) was sampled in a
 195 given range while the other two remained constant.

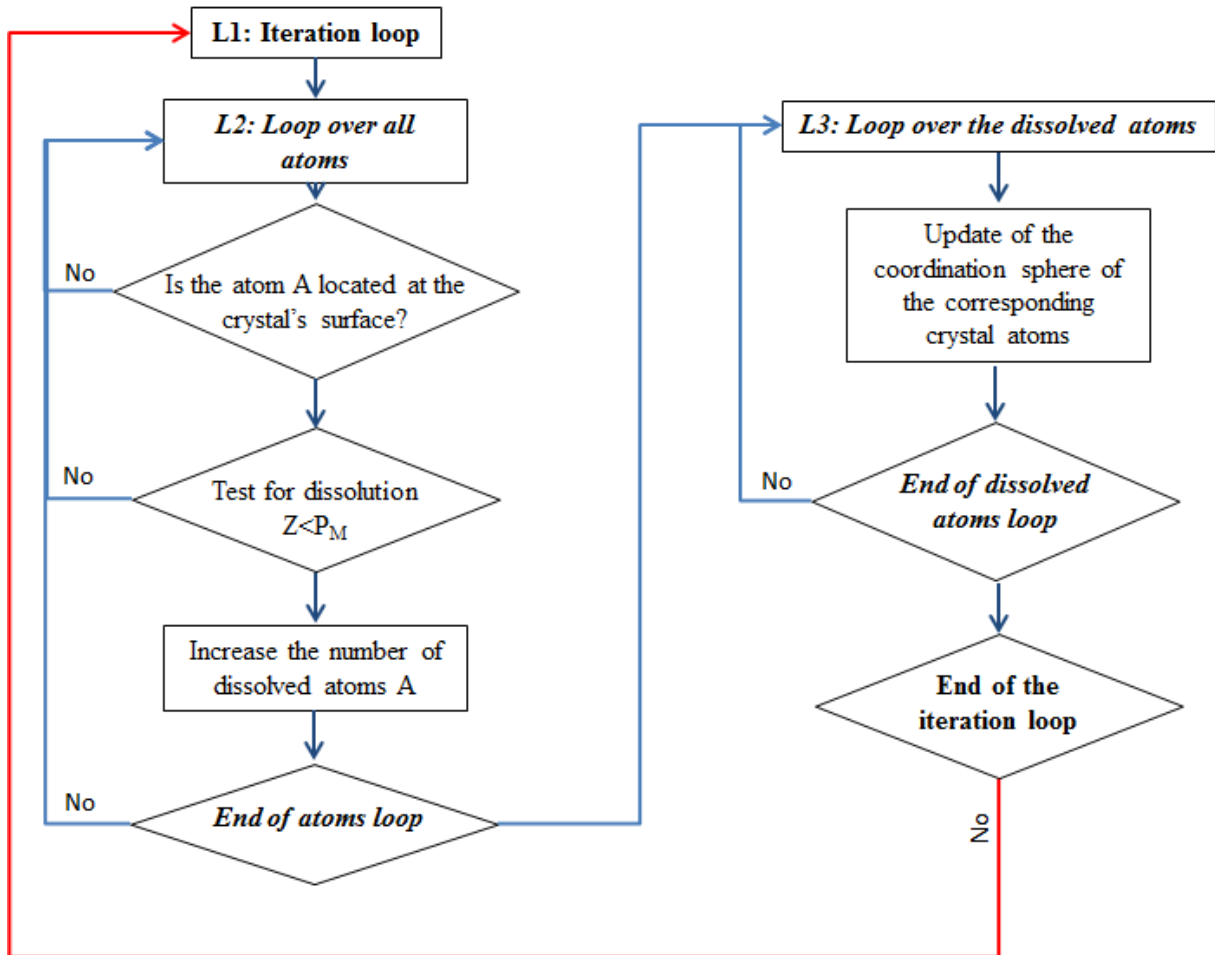


Figure 1 Scheme of the numerical algorithm of the probabilistic model.

196 Finally, the boundary conditions (BC) were set as follows: atoms that are part of the
 197 sides of the simulated volume cannot be dissolved. Since it can induce a dependence of the
 198 dissolution rate on the dimensions of the simulated surface, we verified that the simulated
 199 surface area was large enough to avoid any impact of the BC on the dissolution rate.

200

201 **2.2. Outputs of the model**

202 In order to determine the dissolution rate, the number of released Mg and Si atoms is
 203 stored at each step (iteration). In this study, the dissolution rate calculation is based on the
 204 release of Si atoms (equivalent to the one based on Mg atoms departure and mean surface
 205 height at steady-state conditions ⁴¹):

$$r^{(hkl)} = \frac{V_{cell}}{iter \times N_{Si,cell} \times S} \sum_{i=1}^{iter} N_{Si,i} \quad (4)$$

206 where $r^{(hkl)}$ stands for the dissolution rate ($\text{\AA}/\text{it}$) of a given face (here, either (100), (010) or
 207 (001)), $N_{Si,i}$ for the number of Si atoms released at each iteration i , $N_{Si,cell}$ for the number of Si
 208 atoms in enstatite cell (16), $iter$ for the total number of iterations, and S for the geometric
 209 surface area of the crystal face (\AA^2). The second output of the model is related to the chemical
 210 environment of the atoms when they are released from the surface. In particular, knowledge
 211 of the first coordination sphere of each atom that has been dissolved allows for the
 212 determination of the number of Mg and Si atoms that were connected to the released M
 213 atoms. As opposed to other similar numerical studies (e.g. ⁷⁷⁻⁷⁸), our study was not aimed to
 214 capture the intrinsic heterogeneous distribution of reaction rates at the simulated crystal
 215 surface. Instead, our primary goal was to provide an analytical expression for the overall face-
 216 specific steady state dissolution rate as a function of bond-breaking probabilities, which has to
 217 be achieved at the scale of a given face, echoing the face-specific dissolution rates frequently
 218 reported from dissolution experiments (see ^{39,79} for an overview).

219

220 **3. Results**

221 *3.1. Dissolution rate evolution as a function of bond-breaking probabilities*

222

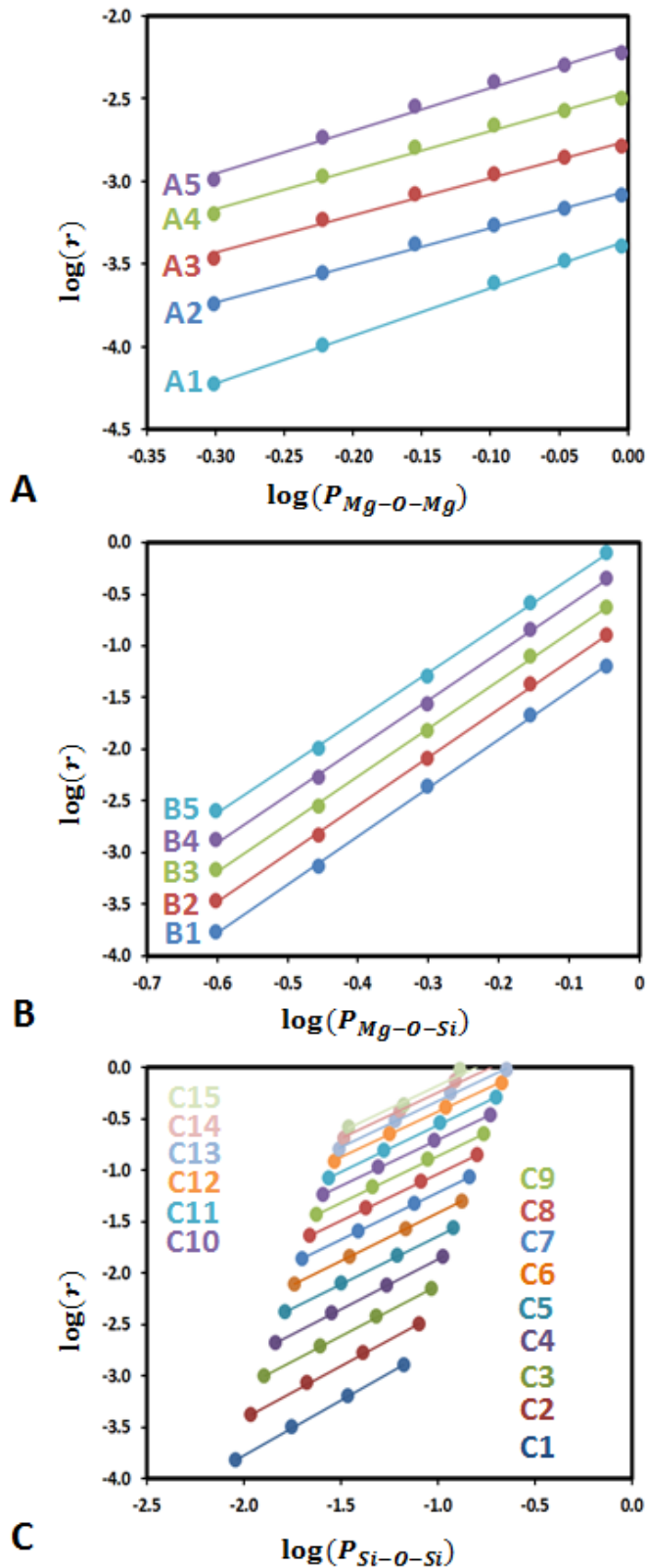


Fig.2. Results of the different simulations for the (100) face. Each graph represents the evolution of the steady-state dissolution rate as a function of the logarithm of: (A) $P_{Mg-O-Mg}$, (B) $P_{Mg-O-Si}$ and (C) $P_{Si-O-Si}$. Each color represents a different ΔE_a between the two other probabilities which remains fixed. Slopes and intercepts are listed in Table 1. Legends correspond to the code indicated for each group of simulations. These codes are used in Table 1 to indicate which simulation corresponds to which groups of data.

| | $P_{Mg-O-Mg}$ | $P_{Mg-O-Si}$ | $P_{Si-O-Si}$ | ΔE (Mg-O-Mg-Mg-O-Si) (kJ/mol) | ΔE (Mg-O-Si-Si-O-Si) (kJ/mol) | ΔE (Mg-O-Mg-Si-O-Si) (kJ/mol) | a | b | R ² | Fig 2 code |
|-------|---------------|---------------|-----------------|---|---|---|------|-------|----------------|---------------|
| | 0.99 - 0.50 | 0.30 | 0.01 | - | 10.0 | - | 2.87 | -3.36 | 1.00 | A1 |
| | 0.99 - 0.60 | 0.30 | 0.02 | - | 8.0 | - | 2.23 | -3.06 | 1.00 | A2 |
| | 0.99 - 0.70 | 0.30 | 0.04 | - | 6.0 | - | 2.26 | -2.75 | 0.99 | A3 |
| | 0.99 - 0.80 | 0.30 | 0.08 | - | 4.0 | - | 2.37 | -2.46 | 0.99 | A4 |
| | 0.99 - 0.90 | 0.30 | 0.15 | - | 2.0 | - | 2.59 | -2.18 | 0.99 | A5 |
| | 0.99 | 0.90 - 0.25 | 0.01 | - | - | 14.0 | 4.68 | -0.97 | 1.00 | B1 |
| | 0.99 | 0.90 - 0.26 | 0.02 | - | - | 12.0 | 4.67 | -0.68 | 1.00 | B2 |
| (100) | 0.99 | 0.90 - 0.27 | 0.04 | - | - | 10.0 | 4.62 | -0.41 | 1.00 | B3 |
| | 0.99 | 0.90 - 0.28 | 0.07 | - | - | 8.0 | 4.59 | -0.15 | 1.00 | B4 |
| | 0.99 | 0.90 - 0.29 | 0.14 | - | - | 6.0 | 4.53 | 0.10 | 1.00 | B5 |
| | 0.99 | 0.25 | 0.0665 - 0.0091 | 4.2 | - | - | 1.06 | -1.64 | 1.00 | C1 |
| | 0.99 | 0.30 | 0.0798 - 0.0109 | 3.6 | - | - | 1.02 | -1.37 | 1.00 | C2 |
| | 0.99 | 0.35 | 0.0930 - 0.0128 | 3.1 | - | - | 0.98 | -1.14 | 1.00 | C3 |
| | 0.99 | 0.40 | 0.1063- 0.0146 | 2.7 | - | - | 0.97 | -0.90 | 1.00 | C4 |

| | | | | | | | | | |
|------|------|-----------------|-----|---|---|------|-------|------|-----|
| 0.99 | 0.45 | 0.1196 - 0.0164 | 2.4 | - | - | 0.94 | -0.70 | 1.00 | C5 |
| 0.99 | 0.50 | 0.1329 - 0.0182 | 2.1 | - | - | 0.93 | -0.49 | 1.00 | C6 |
| 0.99 | 0.55 | 0.1462 - 0.2000 | 1.8 | - | - | 0.92 | -0.29 | 1.00 | C7 |
| 0.99 | 0.60 | 0.1595 - 0.0219 | 1.5 | - | - | 0.92 | -0.12 | 1.00 | C8 |
| 0.99 | 0.65 | 0.1728 - 0.0237 | 1.3 | - | - | 0.91 | 0.05 | 1.00 | C9 |
| 0.99 | 0.70 | 0.1861 - 0.0255 | 1.0 | - | - | 0.90 | 0.20 | 1.00 | C10 |
| 0.99 | 0.75 | 0.1994 - 0.0273 | 8.4 | - | - | 0.90 | 0.34 | 1.00 | C11 |
| 0.99 | 0.80 | 0.2127 - 0.0292 | 6.4 | - | - | 0.89 | 0.45 | 1.00 | C12 |
| 0.99 | 0.85 | 0.2260 - 0.0310 | 4.6 | - | - | 0.90 | 0.57 | 1.00 | C13 |
| 0.99 | 0.90 | 0.2393 - 0.0328 | 2.9 | - | - | 0.90 | 0.66 | 1.00 | C14 |
| 0.99 | 0.95 | 0.2526 - 0.0346 | 1.2 | - | - | 0.89 | 0.72 | 0.99 | C15 |

| | $P_{Mg-O-Mg}$ | $P_{Mg-O-Si}$ | $P_{Si-O-Si}$ | ΔE (Mg-O-Mg-Mg-O-Si) (kJ/mol) | ΔE (Mg-O-Si-Si-O-Si) (kJ/mol) | ΔE (Mg-O-Mg-Si-O-Si) (kJ/mol) | a | b | R ² |
|-------|---------------|---------------|-----------------|---|---|---|------|-------|----------------|
| | 0.99 - 0.50 | 0.30 | 0.01 | - | 10.0 | - | 2.18 | -3.08 | 1.00 |
| | 0.99 - 0.60 | 0.30 | 0.02 | - | 8.0 | - | 2.24 | -2.83 | 1.00 |
| | 0.99 - 0.70 | 0.30 | 0.04 | - | 6.0 | - | 2.24 | -2.60 | 1.00 |
| | 0.99 - 0.80 | 0.30 | 0.08 | - | 4.0 | - | 2.21 | -2.39 | 1.00 |
| | 0.99 - 0.90 | 0.30 | 0.15 | - | 2.0 | - | 2.21 | -2.18 | 1.00 |
| | 0.99 | 0.90 - 0.25 | 0.01 | - | - | 14.0 | 4.48 | -0.78 | 1.00 |
| (010) | 0.99 | 0.90 - 0.26 | 0.02 | - | - | 12.0 | 4.48 | -0.54 | 1.00 |
| | 0.99 | 0.90 - 0.27 | 0.04 | - | - | 10.0 | 4.72 | -0.19 | 1.00 |
| | 0.99 | 0.90 - 0.28 | 0.07 | - | - | 8.0 | 4.79 | 0.72 | 1.00 |
| | 0.99 | 0.90 - 0.29 | 0.14 | - | - | 6.0 | 4.79 | 0.29 | 1.00 |
| | 0.99 | 0.25 | 0.0665 -0.0091 | 4.2 | - | - | 0.75 | -1.92 | 1.00 |
| | 0.99 | 0.30 | 0.0798 - 0.0109 | 3.6 | - | - | 0.82 | -1.48 | 1.00 |
| | 0.99 | 0.35 | 0.0930 - 0.0128 | 3.1 | - | - | 0.75 | -1.23 | 1.00 |

| | | | | | | | | |
|------|------|-----------------|-----|---|---|------|-------|------|
| 0.99 | 0.40 | 0.1063 - 0.0146 | 2.7 | - | - | 0.76 | -0.94 | 1.00 |
| 0.99 | 0.45 | 0.1196 - 0.0164 | 2.4 | - | - | 0.77 | -0.68 | 1.00 |
| 0.99 | 0.50 | 0.1329 - 0.0182 | 2.1 | - | - | 0.79 | -0.45 | 1.00 |
| 0.99 | 0.55 | 0.1462 - 0.2000 | 1.8 | - | - | 0.79 | -0.25 | 1.00 |
| 0.99 | 0.60 | 0.1595 - 0.0219 | 1.5 | - | - | 0.79 | -0.06 | 1.00 |
| 0.99 | 0.65 | 0.1728 - 0.0237 | 1.3 | - | - | 0.78 | 0.10 | 1.00 |
| 0.99 | 0.70 | 0.1861 - 0.0255 | 1.0 | - | - | 0.78 | 0.25 | 1.00 |
| 0.99 | 0.75 | 0.1994 - 0.0273 | 8.4 | - | - | 0.77 | 0.38 | 0.99 |
| 0.99 | 0.80 | 0.2127 - 0.0292 | 6.4 | - | - | 0.74 | 0.47 | 0.99 |
| 0.99 | 0.85 | 0.2260 - 0.0310 | 4.6 | - | - | 0.71 | 0.54 | 0.98 |
| 0.99 | 0.90 | 0.2393 - 0.0328 | 2.9 | - | - | 0.66 | 0.59 | 0.97 |
| 0.99 | 0.95 | 0.2526 - 0.0346 | 1.2 | - | - | 0.60 | 0.60 | 0.94 |

| | $P_{Mg-O-Mg}$ | $P_{Mg-O-Si}$ | $P_{Si-O-Si}$ | ΔE (Mg-O-Mg-Mg-O-Si) (kJ/mol) | ΔE (Mg-O-Si-Si-O-Si) (kJ/mol) | ΔE (Mg-O-Mg-Si-O-Si) (kJ/mol) | a | b | R ² |
|-------|---------------|---------------|-----------------|---|---|---|------|-------|----------------|
| | 0.99 - 0.50 | 0.30 | 0.01 | - | 10.0 | - | 7.46 | -1.72 | 1.00 |
| | 0.99 - 0.60 | 0.30 | 0.02 | - | 8.0 | - | 6.77 | -1.77 | 1.00 |
| | 0.99 - 0.70 | 0.30 | 0.04 | - | 6.0 | - | 6.64 | -1.73 | 0.99 |
| | 0.99 - 0.80 | 0.30 | 0.08 | - | 4.0 | - | 5.88 | -1.74 | 0.98 |
| | 0.99 - 0.90 | 0.30 | 0.15 | - | 2.0 | - | 5.05 | -1.73 | 0.96 |
| | 0.99 | 0.90 - 0.25 | 0.01 | - | - | 14.0 | 4.09 | 0.39 | 1.00 |
| (001) | 0.99 | 0.90 - 0.26 | 0.02 | - | - | 12.0 | 4.20 | 0.46 | 1.00 |
| | 0.99 | 0.90 - 0.27 | 0.04 | - | - | 10.0 | 4.23 | 0.48 | 1.00 |
| | 0.99 | 0.90 - 0.28 | 0.07 | - | - | 8.0 | 4.21 | 0.49 | 1.00 |
| | 0.99 | 0.90 - 0.29 | 0.14 | - | - | 6.0 | 4.23 | 0.51 | 1.00 |
| | 0.99 | 0.25 | 0.0665 -0.0091 | 4.2 | - | - | 0.17 | -1.81 | 0.99 |
| | 0.99 | 0.30 | 0.0798 - 0.0109 | 3.6 | - | - | 0.15 | -1.52 | 0.97 |
| | 0.99 | 0.35 | 0.0930 - 0.0128 | 3.1 | - | - | 0.13 | -1.27 | 0.98 |

| | | | | | | | | |
|------|------|-----------------|-----|---|---|------|-------|------|
| 0.99 | 0.40 | 0.1063- 0.0146 | 2.7 | - | - | 0.12 | -1.04 | 0.99 |
| 0.99 | 0.45 | 0.1196 - 0.0164 | 2.4 | - | - | 0.15 | -0.80 | 0.99 |
| 0.99 | 0.50 | 0.1329 - 0.0182 | 2.1 | - | - | 0.12 | -0.63 | 0.99 |
| 0.99 | 0.55 | 0.1462 - 0.2000 | 1.8 | - | - | 0.12 | -0.45 | 0.99 |
| 0.99 | 0.60 | 0.1595 - 0.0219 | 1.5 | - | - | 0.11 | -0.30 | 0.99 |
| 0.99 | 0.65 | 0.1728 - 0.0237 | 1.3 | - | - | 0.12 | -0.14 | 1.00 |
| 0.99 | 0.70 | 0.1861 - 0.0255 | 1.0 | - | - | 0.14 | 0.02 | 1.00 |
| 0.99 | 0.75 | 0.1994 - 0.0273 | 8.4 | - | - | 0.14 | 0.14 | 0.99 |
| 0.99 | 0.80 | 0.2127 - 0.0292 | 6.4 | - | - | 0.14 | 0.26 | 0.99 |
| 0.99 | 0.85 | 0.2260 - 0.0310 | 4.6 | - | - | 0.14 | 0.35 | 0.98 |
| 0.99 | 0.90 | 0.2393 - 0.0328 | 2.9 | - | - | 0.15 | 0.44 | 0.98 |
| 0.99 | 0.95 | 0.2526 - 0.0346 | 1.2 | - | - | 0.16 | 0.51 | 0.95 |

Table 1. Different ΔE_a values used in this study (the “-” symbol indicates that ΔE_a varies). The slope (a), intercept (b) and correlation coefficient (R^2) of the linear regression of $\log(r) = f(\log(P))$ are given in the last three columns (see text for details). When $P_{Mg-O-Mg}$ was left constant, its value was set to 0.99. This value allows for minimizing the simulation time required while having the possibility to associate a corresponding physical ΔE_a value. When the relation between dissolution rate and $P_{Mg-O-Mg}$ was studied, $P_{Mg-O-Si}$ was arbitrarily set to 0.3. Finally, the chosen probabilities were constrained by $P_{Mg-O-Mg} > P_{Mg-O-Si} > P_{Si-O-Si}$.

224 In total, 345 simulations have been conducted (115 per face) to explore a wide range
 225 of activation energies. Over these 115 simulations, 30 were dedicated to unravelling the
 226 dependence of the dissolution rate evolution on $P_{Mg-O-Mg}$, 25 on $P_{Mg-O-Si}$, and 60 on $P_{Si-O-Si}$.

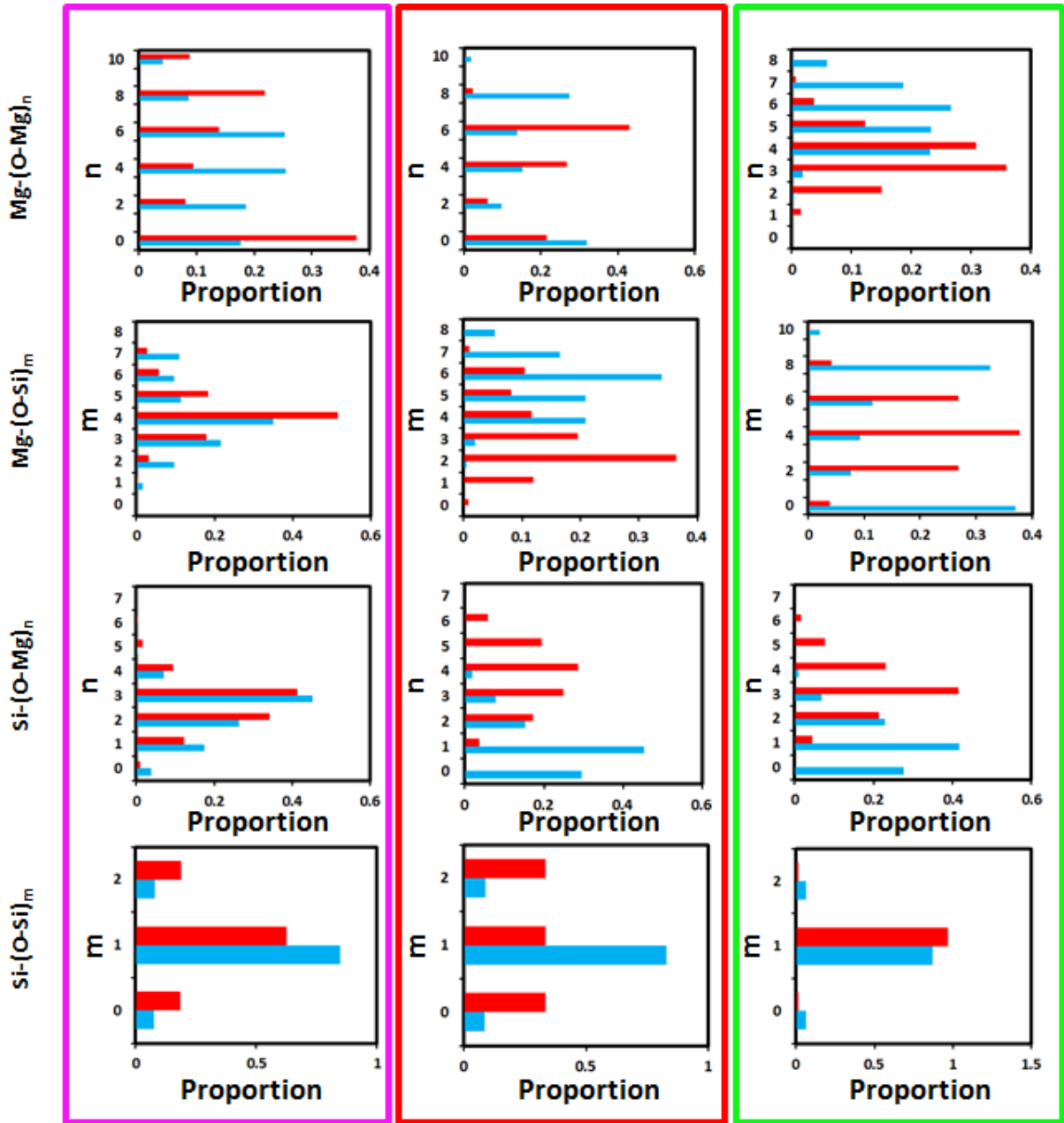


Fig.3. Distribution of the different coordination spheres of an atom right before its dissolution. The first two lines depict Mg atoms, and the following two lines, Si. The proportion is defined by the number of atoms at the surface having m or n bounds divided by the total number of atoms, so that the sum of all modes is 1. Blue and red bars correspond to a set of low ($P_{Mg-O-Mg} = 0.5$, $P_{Mg-O-Si} = 0.3$ and $P_{Si-O-Si} = 0.0109$) and high ($P_{Mg-O-Mg} = 0.99$, $P_{Mg-O-Si} = 0.3$ and $P_{Si-O-Si} = 0.1547$) probability values, respectively. Magenta, red and green rectangle stand for the simulations on (100), (010) and (001) faces respectively.

227 As an illustration, the treatment of the outputs of the simulation conducted with the (100) face
228 is depicted in Fig. 2. As expected, the simulations with the lowest probabilities correspond to
229 those resulting in the lowest steady-state dissolution rates. The different datasets of
230 probabilities (one set corresponds to one value of $P_{Mg-O-Mg}$, $P_{Mg-O-Si}$ and $P_{Si-O-Si}$ as the master
231 variable, all else being constant) have been sorted into different groups according to their
232 fixed ΔEa value. A total of 25 groups per face were analyzed (5 groups of 6 datasets, 5 groups
233 of 5 datasets and 15 groups of 4 datasets for the $r = f(P_{Mg-O-Mg})$, $r = f(P_{Mg-O-Si})$ and
234 $r = f(P_{Si-O-Si})$ cases respectively). These different groups and the full dataset are listed in
235 the Table 1.

236 A linear relationship between the logarithm of the dissolution rate and the logarithm of
237 the bond-breaking probabilities can be observed for the different simulations (see Fig. 2). This
238 linear model matches results from numerical simulations quite satisfactorily. Moreover, the
239 slope remains constant when changing the activation energy for the hydrolysis of one bond,
240 whatever the difference in the activation energy of the two other bonds (i.e. the slopes are the
241 same for the results shown in each Fig. 2A, 2B and 2C). Slopes, intercepts and R^2 of these
242 linear regressions are listed in Table. 1.

243

244 ***3.2. Mean first coordination sphere of released atoms***

245 The attainment of a mean surface configuration when steady-state dissolution rates are
246 reached represents a common trait of all simulations. The corresponding mean first
247 coordination spheres of the M atoms at the iteration step of their detachment from the surface
248 are depicted in Fig. 3. The coordination spheres will be referred as $M-(O-Mg)_n$ or $M-(O-Si)_m$
249 in the following (n and m standing for the number of Mg and Si neighbors, respectively).
250 Whereas the coordination of $Si-(O-Si)_m$ is dominated by a single mode for which $m = 1$,
251 others are more dispersed around one or more principal modes. Regarding $Mg-(O-Mg)_n$, n is

252 always an even number, regardless of the set of probabilities, consistent with the structure of
 253 enstatite. The value of the principal modes of $\text{Mg}-(\text{O-Mg})_n$, $\text{Mg}-(\text{O-Si})_m$, and $\text{Si}-(\text{O-Mg})_m$
 254 depends on the probability and differs from one face to another, as illustrated in Fig. 3, where
 255 the blue and red bars corresponds to two distinct sets of probabilities ($[P_{\text{Mg-O-Mg}} = 0.99, P_{\text{Mg-O-}}$
 256 $\text{Si} = 0.3, P_{\text{Si-O-Si}} = 0.0109]$ and $[P_{\text{Mg-O-Mg}} = 0.7, P_{\text{Mg-O-Si}} = 0.3$ and $P_{\text{Si-O-Si}} = 0.1547]$) selected
 257 from the slowest and fastest range of dissolution rates respectively. However, these
 258 distributions also reveal that the mean coordination spheres remain constant, regardless of the
 259 set of probabilities used to run the simulation or the face that is considered (4.02 ± 0.01 ; 6.64
 260 ± 0.02 and 1.002 ± 0.002 for Mg-O-Mg; Mg-O-Si+Mg-O-Si and Si-O-Si bonds, respectively).

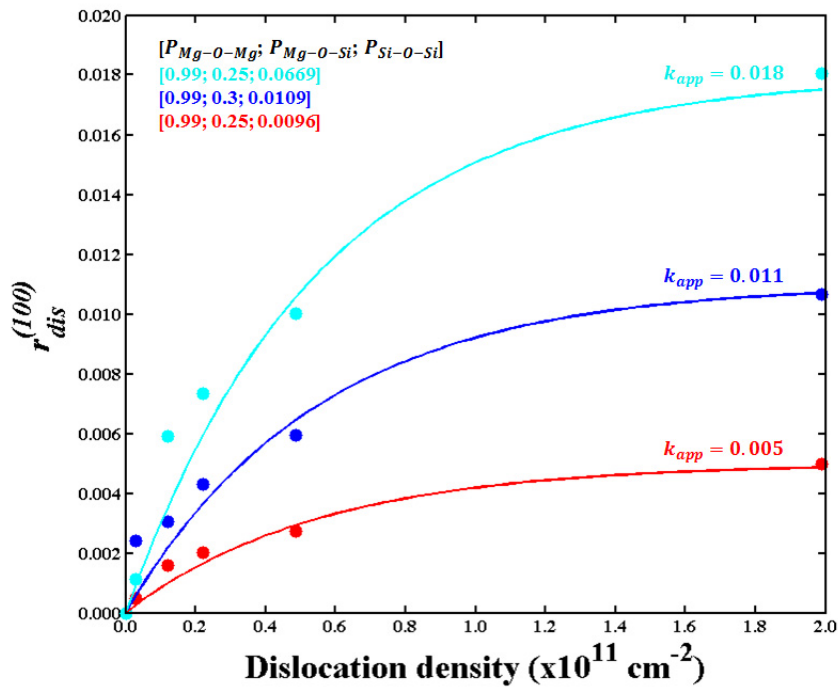


Fig 4. Contribution of dissolution rate specific to dislocations ($r_{dislocation}^{(100)}$) to the total dissolution rate ($r_{\square}^{(100)}$) as a function of the dislocation density. The filled circles represent the results of the different simulations and lines, the application of Eq. 16 using the parameters that allow for the best fit of all the simulations. Colors represent different $[P_{\text{Mg-O-Mg}}; P_{\text{Mg-O-Si}}; P_{\text{Si-O-Si}}]$ input probabilities: $[0.99; 0.25; 0.0669]$, $[0.99; 0.3; 0.0109]$ and $[0.99; 0.25; 0.0096]$ for the cyan, blue and red lines respectively. Values of k_{app} are 0.018, 0.011 and 0.005 for the cyan, blue and red lines respectively.

262 **3.3. Dislocation density**

263 The results of simulations conducted with dislocations are reported in Fig. 4. The
264 dislocation density has been investigated by varying the surface area (i.e., all simulations were
265 conducted using a single dislocation line, while varying the simulated surface area).
266 Simulations containing dislocations have been conducted on the (100) face. The presented
267 result show the relation between the dissolution rate and the dislocation density after
268 subtraction of the “bulk” contribution to the overall dissolution rate (i.e., $r_{dislocation}^{(hkl)} = r^{(hkl)} -$
269 $r_{bulk}^{(hkl)}$). The results highlight an asymptotic relationship between dissolution rate and
270 dislocation density.

271

272 **4. Discussion**

273 **4.1 Bulk dissolution rate evolution as a function of bond-breaking probabilities**

274 From the numerical experiments described in Section 3.1, the steady state dissolution
275 rates of enstatite (defined as congruent and constant dissolution rates with time) are
276 proportional to each individual bond-breaking probability raised at a given power inferred
277 from the linear regressions depicted in a log-log diagram (Fig. 2). Moreover, since the slope
278 of the linear regression between $\text{Log}(P_i)$ (i stands for Mg-O-Mg or Mg-O-Si or Si-O-Si) and
279 $\text{Log}(r)$ is constant whatever the difference between the two other involved probabilities; a
280 more general function of the dissolution rate can be written as:

$$r_{bulk}^{(hkl)} = k P_{Mg-O-Mg}^{\alpha} P_{Mg-O-Si}^{\beta} P_{Si-O-Si}^{\gamma} \quad (5)$$

281 where k is a constant and α, β, γ are the corresponding slopes listed in Table 2 for the various
282 regressions. The parameter k is then obtained using equation 5 and is constant for each face.
283 The different parameter values are summarized in Table 2, the α, β, γ values are obtained by

284 taking the average values of the corresponding slopes and the dissolution rates calculated with
 285 the surrogate model (Eq. 5) are compared with the simulated one in Fig. 5.

| Face | k | α | β | γ |
|-------|------|----------|---------|----------|
| (100) | 8.87 | 2.46 | 4.62 | 0.94 |
| (010) | 7.80 | 2.22 | 4.65 | 0.75 |
| (001) | 4.72 | 6.36 | 4.19 | 0.14 |

286 **Table 2.** Values of the different face-specific parameters of the surrogate model.

287

288 If the parameter α can be considered as constant for (100) and (010) faces (Table 1), the slope
 289 that corresponds to a variation of $P_{Mg-O-Mg}$ decreases from 7.46 to 5.05 when the difference
 290 between $E_{Mg-O-Si}$ and $E_{Si-O-Si}$ decreases, i.e., when $E_{Mg-O-Si}$ gets closer to $E_{Si-O-Si}$. For these
 291 cases, the assumptions used in the concept of the surrogate model may not be fulfilled (e.g., k
 292 is constant and does not depend on the different probabilities). This assumption will be
 293 discussed in the next section. Despite this approximation and the apparent trend for the (001)
 294 face, the proposed model described by Eq. 5 is capable of satisfactorily estimating the
 295 simulated dissolution rates (Fig. 5) for the three different faces. Note that Eq. (5) has been
 296 derived from simulations where only the first coordination sphere of surface atoms is
 297 considered for expressing the dissolution probability of individual atoms. Several studies^{36, 64}
 298 have shown that second coordination sphere may also play a role in the dissolution, and may
 299 impact the shape of the developed etch pits. However, we showed that considering only the
 300 first coordination sphere is enough to reproduce satisfactorily the face-specific shape of etch
 301 pits observed on enstatite⁴¹, explaining why we stick to this model in the present study.
 302 Considering the impact of the second coordination sphere would make Eq. 5 more
 303 sophisticated, since it would probably incorporate specific terms related to the second
 304 coordination spheres.

4.2. Theoretical interpretation of the surrogate model

The development of the surrogate expression given in Eq. 5 is derived from a statistical analysis of the outputs of the stochastic simulations of enstatite dissolution, with no preconception of the mathematical form that should be used to relate the steady-state dissolution rates to the individual bond-breaking probabilities describing enstatite hydrolysis. In the present section, we provide a possible theoretical explanation of Eq. 5.

The dissolution rate can be defined as the derivative of the number of atoms that are dissolved with time:

$$r = \frac{dN_{M,d}}{dt} \quad (6)$$

where $N_{M,d}$ stands for the amount of dissolved atoms belonging to the M species during the time interval dt . Arguably, $N_{M,d}$ should depend on two parameters: the amount of atoms located at the mineral surface ($N_{M,S}$) and the intrinsic detachment rate of these atoms. Importantly, classical theories of dissolution kinetics suggest that at steady-state conditions, $N_{M,S}$ is constant and proportional to the considered surface area⁶. This aspect was numerically verified in our previous study⁴¹ where we showed that the amount of surface atoms level to a plateau as soon as the dissolution becomes congruent and the dissolution rate is constant.

At steady state, the number of dissolved atoms of Mg or Si is given by:

$$N = \hat{N}_{Mg} P_{Mg} = \hat{N}_{Si} P_{Si} \quad (7)$$

where N is the number of dissolved atoms of Mg or Si, \hat{N}_A is the number of atoms A (Mg or Si) at the mineral surface, P_A is the probability that atom A is dissolved. Following the previous equation, N can be rewritten as:

$$N = \sqrt{\hat{N}_{Mg} P_{Mg} \hat{N}_{Si} P_{Si}} \quad (8)$$

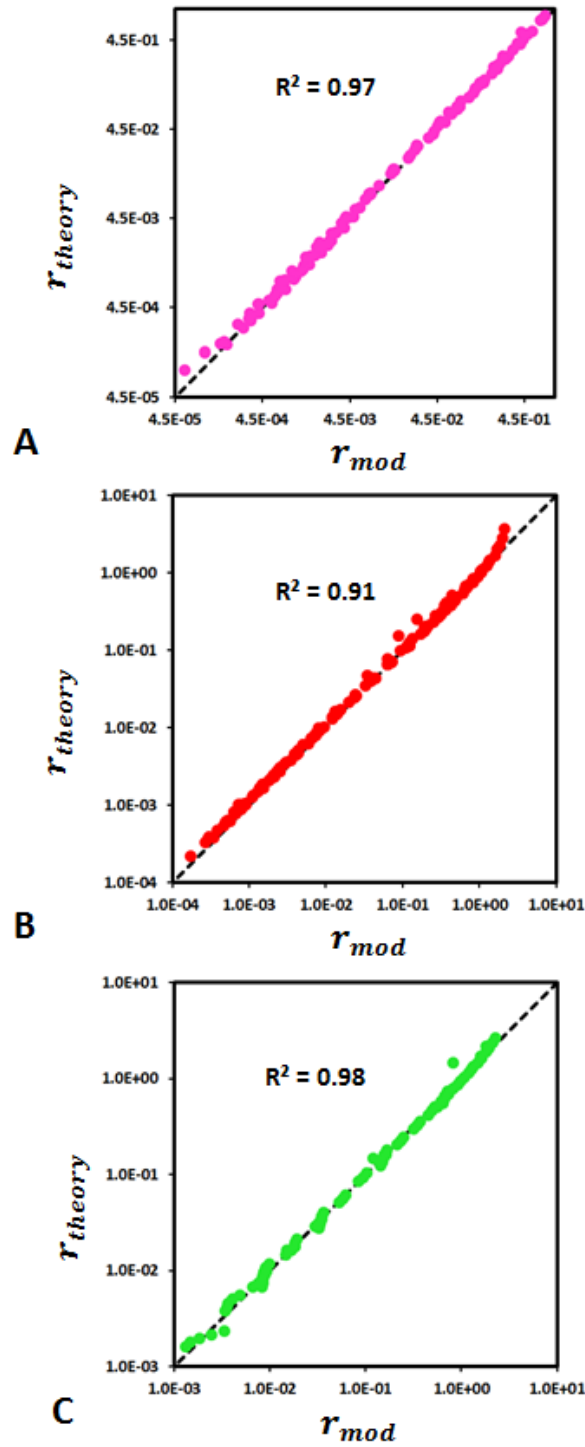


Fig 5. Comparison between the dissolution rates estimated with the surrogate model (r_{theory} ; Eq. 5) and dissolution rates provided by the numerical simulations (r_{mod}) for faces (100) (A), (010) (B) and (001) (C). The comparison is made for all the different simulations listed in Table 1. For instance, (A) presents all the simulations shown in Fig. 2, and the rate variability results from the corresponding bond-breaking probabilities that are reported in Table 1.

324 The dissolution of an A atom for a given coordination sphere i is given by:

$$P_{A,i} = P_{A-A}^{\alpha_i} P_{A-B}^{\beta_i} \quad (9)$$

325 where α_i and β_i are the number of bonds connecting the considered A atom to another A or
 326 to a B atom (Si or Mg accordingly), respectively. At the solid surface, we consider that there
 327 are N_C different coordination spheres and n_i atoms with a coordination sphere i . Therefore,
 328 the probability to dissolve the atom A over the mineral face is:

$$P_A = \frac{1}{\hat{N}_A} \sum_{i=1}^{N_C} n_i P_{A-A}^{\alpha_i} P_{A-B}^{\beta_i} \quad \text{and} \quad \hat{N}_A = \sum_{i=1}^{N_C} n_i \quad (10)$$

329 Or

$$P_A = \frac{1}{\hat{N}_A} \left(\sum_{i=1}^{N_C} n_i P_{A-A}^{\alpha_i - \alpha_A} P_{A-B}^{\beta_i - \beta_A} \right) P_{A-A}^{\alpha_A} P_{A-B}^{\beta_A} = k_A P_{A-A}^{\alpha_A} P_{A-B}^{\beta_A} \quad (11)$$

330 with

$$k_A = \frac{1}{\hat{N}_A} \sum_{i=1}^{N_C} n_i P_{A-A}^{\alpha_i - \alpha_A} P_{A-B}^{\beta_i - \beta_A} \quad (12)$$

331 and the number of dissolved atoms is:

$$\begin{aligned} N &= \sqrt{\hat{N}_{Mg} \hat{N}_{Si}} \sqrt{k_{Mg} P_{MgOMg}^{\alpha_{Mg}} P_{MgOSi}^{\beta_{Mg}} k_{Si} P_{SiOSi}^{\alpha_{Si}} P_{MgOSi}^{\beta_{Si}}} \\ &= \sqrt{\hat{N}_{Mg} k_{Mg} \hat{N}_{Si} k_{Si}} P_{MgOMg}^{\alpha} P_{MgOSi}^{\beta} P_{SiOSi}^{\gamma} \end{aligned} \quad (13)$$

332 with $\alpha = \alpha_{Mg}$, $\beta = \beta_{Mg} + \beta_{Si}$, $\gamma = \alpha_{Si}$.

333 The statistical analysis of the numerical experiments provides some values of the parameters

334 k , α , β , γ (see Table 2). Surprisingly, the parameter k does not depend on the probabilities

335 P_{A-A} and P_{A-B} in the range of the numerical values used for the experiments. An appropriate

336 choice of (α_A, β_A) may explain this property. Assuming that $\alpha_A = \alpha_j$ and $\beta_A = \beta_j$, the

337 constant k_A can be rewritten as:

$$k_A = \frac{n_j}{\hat{N}_A} + \frac{1}{\hat{N}_A} \sum_{i=1, i \neq j}^{N_C} n_i P_{A-A}^{\alpha_i - \alpha_j} P_{A-B}^{\beta_i - \beta_j} \quad (14)$$

338 Therefore, k_A can be a constant value if $n_j \gg \sum_{i=1, i \neq j}^{N_c} n_i P_{A-A}^{\alpha_i - \alpha_j} P_{A-B}^{\beta_i - \beta_j}$ which is possible when
 339 $\alpha_i > \alpha_j$ and/or $\beta_i > \beta_j$, for having positive exponents for the probabilities P_{A-A} and/or P_{A-B} .
 340 Given that the exponents are positive, considering k as a constant is a reasonable assumption
 341 if the difference between P_{A-A} and P_{A-B} is significant. The validity of this condition is
 342 difficult to appreciate if P_{A-A} and P_{A-B} are close, as it is the case for the simulations run for
 343 (001) face (see section 4.1 and Table 1). Finally, this demonstrates that the dissolution rate is
 344 therefore compatible with Eq. 5:

$$r = W \frac{N}{dt} = W \frac{k P_{Mg-O-Mg}^{\alpha} P_{Mg-O-Si}^{\beta} P_{Si-O-Si}^{\gamma}}{dt} \text{ with } W = \frac{V_{cell}}{iter \times N_{cmx} \times S} \quad (15)$$

345 with N_{cmx} standing for the number of "complexes" (see 4.4) in the enstatite cell.

346

347 **4.3. Accounting for the impact of dislocation density on the dissolution rates**

348 Dislocations have a measurable impact on the dissolution rate, whatever the set of
 349 probabilities that was tested (Fig 6C). This result is consistent with numerical and
 350 experimental studies that showed that the presence of dislocations outcropping at mineral
 351 surfaces globally increases the dissolution rate when the nucleation of etch pits is
 352 thermodynamically favorable (i.e., at far-from-equilibrium conditions ^{11, 14, 16, 23, 31, 37}).
 353 However, when dealing with natural samples, the dislocation density remains a parameter
 354 impossible or difficult to control *a priori*, which complicates the prediction of its impact on
 355 dissolution rate. Furthermore, several studies showed that the mineral dissolution rate is not a
 356 strictly increasing function of the dislocation density ^{31, 37, 80} since above a given threshold, the
 357 dissolution rate no longer varies with the dislocation density.

358 To qualitatively comply with the above-mentioned studies, the results for the (100)
 359 face (Fig. 4) were fitted using the following empirical relation between dislocation density

360 and the additional dissolution rate resulting from etch pit opening at dislocation outcrop (see
 361 Section 3.3.), which verifies that the dissolution rate levels to a plateau value when the
 362 dislocation density tends towards infinity:

$$r_{dislocation}^{(100)} = k_{app} \left(1 - e^{-\frac{\rho_d}{\omega}} \right) \quad (16)$$

363 where k_{app} and ω ($\approx 5.51 \times 10^{10}$) are empirical parameters that were obtained by calibration
 364 on the outputs of the simulations, and ρ_d is the dislocation density. Whereas ω does not seem
 365 to vary with the probabilities used as input parameters, it clearly appears that k_{app} (Fig. 4)
 366 depends on the individual bond-breaking probabilities. From a physical standpoint, this
 367 observation may result from the fact the first coordination spheres of atoms in the vicinity of a
 368 dislocation line differ from those of atoms considered for defect-free surface.

369 Considering this apparent relationship between k_{app} and the probabilities, a first
 370 tentative to link the global rate to the probabilities and the dislocation density was performed
 371 using the same exponent for each probability as the “bulk” case. Since the global rate is
 372 equivalent to $r^{(hkl)} = r_{dislocation}^{(hkl)} + r_{bulk}^{(hkl)}$, it is possible to assume the following relation:

$$r^{(hkl)} = \left[k + k_{dis} \left(1 - e^{-\frac{\rho_d}{\omega}} \right) \right] P_{Mg-O-Mg}^{\alpha} P_{Mg-O-Si}^{\beta} P_{Si-O-Si}^{\gamma} \quad (17)$$

373 A comparison between this relation and the experimental results is given in Fig. 6A and the
 374 value of k_{dis} is given in Table 3. Although the relationship between the surrogate model and
 375 the results of the simulations was proven efficient to simulate the dissolution of defect-free
 376 surfaces ($R^2 > 0.9$ in all cases), it is not the case when using Eq. 17, for which $R^2 = 0.76$.

377 In order to improve the agreement between the surrogate model of the global rate and
 378 the results of the simulations, numerical experiments were run for face (100) with dislocations
 379 similarly to Section 4.1. The dissolution rates were fitted using the following function:

$$r_{dislocation}^{(hkl)} = k_{dis} k P_{Mg-O-Mg}^{\alpha_{dis}} P_{Mg-O-Si}^{\beta_{dis}} P_{Si-O-Si}^{\gamma_{dis}} \left(1 - e^{-\frac{\rho_d}{\omega}} \right) \quad (18)$$

380 The values of $\alpha_{dis}, \beta_{dis}, \gamma_{dis}$ are lower than those obtained in the “bulk” (defect-free) case
 381 (Table 3), which makes sense since the coordination spheres of atoms are arguably lower in
 382 the vicinity of the dislocation line, resulting in greater measured dissolution rates.

383

| k_{dis} | α_{dis} | β_{dis} | $\gamma_{dis} \gamma$ | R^2 |
|--------------|----------------|---------------|-----------------------|-------|
| 227.9 | 2.46 | 4.62 | 0.94 | 0.72 |
| 44.7 | 2.09 | 4.09 | 0.67 | 0.86 |

384 **Table 3.** Values of the parameters of the model described by Eq. 17 and Eq. 18 and the correlation coefficient
 385 R^2 . The bold characters represent the fitted parameters.
 386

387 The global dissolution rate of enstatite can then be calculated by summing $r_{bulk}^{(hkl)}$ and
 388 $r_{dislocation}^{(hkl)}$, resulting in the following relation:

$$r^{(hkl)} = k P_{Mg-O-Mg}^{\alpha} P_{Mg-O-Si}^{\beta} P_{Si-O-Si}^{\gamma} + k_{dis} P_{Mg-O-Mg}^{\alpha_{dis}} P_{Mg-O-Si}^{\beta_{dis}} P_{Si-O-Si}^{\gamma_{dis}} \left(1 - e^{-\frac{\rho_d}{\omega}} \right) \quad (19)$$

389 Therefore, the agreement between the results of the simulations and the surrogate model is
 390 improved and its correlation coefficient increases from 0.72 to 0.86 (Fig. 6B).

391 If this type of relations can be extended to other minerals and other types of defects
 392 (e.g. vacancies), they may represent an interesting method to link together dissolution rates
 393 derived from considerations at the atomic scale and those derived from observations at the
 394 mineral scale. This type of relations can also represent a significant progress for reactive
 395 transport models that simulate steady-state dissolution reactions. Indeed, even though the
 396 present work represents a preliminary step to link relations at the atomic scale to macroscopic
 397 dissolution rates, it shows promise as a mean to express face-specific steady-state dissolution
 398 rates as a function of the bond-breaking probabilities (and therefore, of the activation energies
 399 of hydrolysis) of the different types of bonds that exist for a given mineral. While some
 400 studies have questioned the possibility to use the outputs of Monte Carlo simulations in

401 reactive-transport codes because of the limited space- and time-scales investigated following
 402 such stochastic treatments of the dissolution process, here we show that steady-state
 403 dissolution rates may be satisfactorily calculated from considerations at the atomic scale. As a
 404 consequence, rate equations similar to Eq. 17 or Eq. 19 may be simply implemented in
 405 reactive transport codes as the rate-constant of the source term of the classical reaction-
 406 advection-diffusion equation. This may be of interest for modeling processes for which the
 407 fluid composition can be considered as unchanged over the considered simulated time, such
 408 as chemical weathering in rivers or in some aquifers with a constant fluid velocity, or fluid
 409 circulation in deep fractured geothermal reservoirs, where the fluid composition is
 410 approximately constant and poorly affected by geothermal power plant functioning (e.g. ⁸¹).
 411 More work remains however needed to assess whether this result is limited to enstatite or the

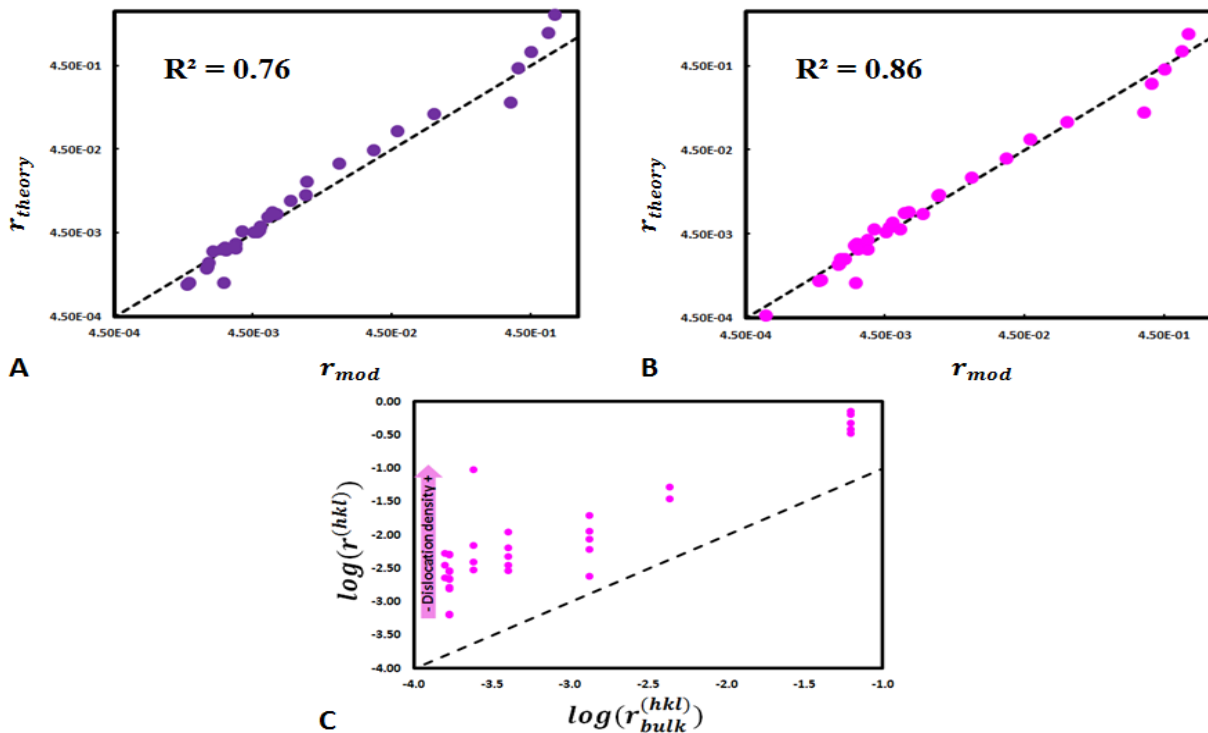


Figure 6. Comparison of experimental dissolution rates (r_{mod}) and dissolution rates determined with the surrogate model (r_{theory}) with the presence of one dislocation (dislocation density is changed by varying the surface area). Agreement using (A) Eq. 17 and (B) Eq. 19. (C) Comparison between dislocation-driven dissolution and bulk (dislocation-free) dissolution. The presence of dislocations increases dissolution rates for all the simulations. The data points represent the simulations conducted using sets of probabilities and dislocation densities given in Table 4.

412 pyroxene group (there is a priori no reason to think so), as well as expanding the relation to
 413 the transient regime, where the dissolution rate is neither stoichiometric nor constant. As long
 414 as this latter task remains not fulfilled, alternate approaches such as the use of Voronoi
 415 distance maps ^{39, 73} probably represents the most promising compromise to upscale kinetic
 416 Monte Carlo simulations. This strategy nonetheless remains far more complicated than just
 417 using a surrogate expression as proposed above.

| Dislocation density | MgOMg | MgOSi | SiOSi |
|---------------------|-------------|-------------|---------------|
| 1.99E+11 | 0.99 | 0.3 | 0.0109 |
| 1.99E+11 | 0.99 | 0.25 | 0.0096 |
| 1.99E+11 | 0.99 | 0.9 | 0.0096 |
| 1.99E+11 | 0.99 | 0.25 | 0.0091 |
| 1.99E+11 | 0.99 | 0.25 | 0.0669 |
| 4.88E+10 | 0.99 | 0.3 | 0.0109 |
| 4.88E+10 | 0.99 | 0.25 | 0.0096 |
| 4.88E+10 | 0.99 | 0.9 | 0.0096 |
| 4.88E+10 | 0.99 | 0.25 | 0.0091 |
| 4.88E+10 | 0.99 | 0.25 | 0.0669 |
| 2.21E+10 | 0.99 | 0.3 | 0.0109 |
| 2.21E+10 | 0.99 | 0.25 | 0.0096 |
| 2.21E+10 | 0.99 | 0.9 | 0.0096 |
| 2.21E+10 | 0.99 | 0.25 | 0.0091 |
| 2.21E+10 | 0.99 | 0.25 | 0.0669 |
| 1.21E+10 | 0.99 | 0.3 | 0.0109 |
| 1.21E+10 | 0.99 | 0.25 | 0.0096 |
| 1.21E+10 | 0.99 | 0.9 | 0.0096 |
| 1.21E+10 | 0.99 | 0.25 | 0.0091 |
| 1.21E+10 | 0.99 | 0.25 | 0.0669 |
| 3.00E+09 | 0.99 | 0.3 | 0.0109 |
| 3.00E+09 | 0.99 | 0.25 | 0.0096 |
| 3.00E+09 | 0.99 | 0.9 | 0.0096 |
| 3.00E+09 | 0.99 | 0.25 | 0.0091 |
| 3.00E+09 | 0.99 | 0.25 | 0.0669 |
| 1.9899E+11 | 0.99 | 0.5 | 0.0096 |
| 1.9899E+11 | 0.8 | 0.3 | 0.0109 |
| 1.9899E+11 | 0.7 | 0.3 | 0.0109 |
| 4.8773E+10 | 0.99 | 0.5 | 0.0096 |
| 4.8773E+10 | 0.8 | 0.3 | 0.0109 |
| 4.8773E+10 | 0.7 | 0.3 | 0.0109 |
| 2.211E+10 | 0.99 | 0.5 | 0.0096 |
| 2.211E+10 | 0.8 | 0.3 | 0.0109 |
| 2.211E+10 | 0.7 | 0.3 | 0.0109 |

418

419 **Table 4.** Dislocation densities and probabilities used in the simulations used for Fig. 5. Bolded lines represent
420 the input parameters used in the simulations shown in Fig. 3.

421

422 ***4.4. Relation between the coordination of atoms leaving the surface and the*** 423 ***surrogate expression***

424 Interestingly, when atoms are released from the mineral surface, they seem to have a
425 specific average coordination. This assertion is supported by the analysis of the environment
426 of Mg and Si when they leave the surface, since the mean values of Mg-O-Mg, Mg-O-Si+Mg-
427 O-Si and Si-O-Si bonds remain constant and unaffected by the set of probabilities used to run
428 the simulations for all faces (see Section 3.2). However, the numerical values of the
429 parameters used in the surrogate expression of the dissolution rate are face-specific. This
430 apparent paradox can be easily explained by recalling that the histograms reported in Fig. 3
431 actually take into account all atoms leaving the surface, including those whose departure is
432 not rate-limiting of the dissolution process.

433 By analogy with Eq. 3, the surrogate expression given by Eq. 17 or Eq. 19 may reflect
434 the average coordination of atoms that control the dissolution process, as kink sites would do.
435 The fact that the numerical values of α , β and γ are face-specific indicates that this average
436 rate-controlling configuration is not unique for a given mineral. Most likely, this result
437 reflects the fact that kink sites, which are much more difficult to define using a real crystal
438 lattice than simplified isotropic cubic Kossel crystals, differ from one face to another when
439 dealing with anisotropic structures. This explanation would in turn be consistent with the
440 observed anisotropic reactivity of the pyroxene structure.

441

442 **5. Conclusion**

443 In this study, we presented the results of hundreds of probabilistic simulations of
444 enstatite dissolution to link the overall dissolution rate to the bond-breaking probabilities used

445 as input parameters. By varying independently each probability, we showed that it is possible
446 to build a surrogate model that links the different probabilities to the dissolution rate
447 following a power law. This result contributes to the general effort of upscaling of mineral
448 dissolution kinetics, since this surrogate expression is based on a mechanistic approach
449 developed from considerations at the atomic-scale, from which the resulting dissolution rate
450 constants can be used as a source term in reactive transport simulations. However, the relation
451 remains valid at steady-state conditions only, and the transient regime must be treated
452 following other upscaling approaches, such as the use of Voronoï distance maps^{39,73}.

453 The various simulations conducted with dislocations have shown that it is possible to
454 link the dissolution rate to the dislocation density by introducing an exponential factor to the
455 global $r = f(\prod_i P_i^{z_i})$ relation. This relation further extends the interest of probabilistic
456 simulations of mineral dissolution to account for the impact of some important parameters
457 that are hardly controlled in experimental studies. In addition, in case of a bond hydrolysis
458 with significant higher activation energy than the others, the dissolution rate is strongly
459 correlated to this activation energy, and the surrogate model may be used to estimate the value
460 of this parameter.

461 However, the surrogate model also presents some limitations, particularly when M-O-
462 Si and Si-O-Si hydrolysis probabilities are getting close to each other (where M is a divalent
463 cation, i.e., Mg in the case of enstatite). In this specific case, the results may be out of the
464 limits of the theoretical framework that supports the development of the surrogate expression.
465 Of note, such cases are however those for which the input parameters are physically
466 unrealistic, as the activation energy of Si-O-Si hydrolysis is admitted to be much lower than
467 any other M-O-Si bond.

468 Finally, this study represents a first step towards the development of surrogate
469 expressions of mineral dissolution rates. Its application to natural environment, its extension
470 to other groups of minerals as well as its extension to transient state still have to be explored.

471

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476

477 **7. References**

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685 **TOC Graphic**

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