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1 **The dissolution anisotropy of pyroxenes: Experimental validation**
2 **of a stochastic dissolution model based on enstatite weathering**

3

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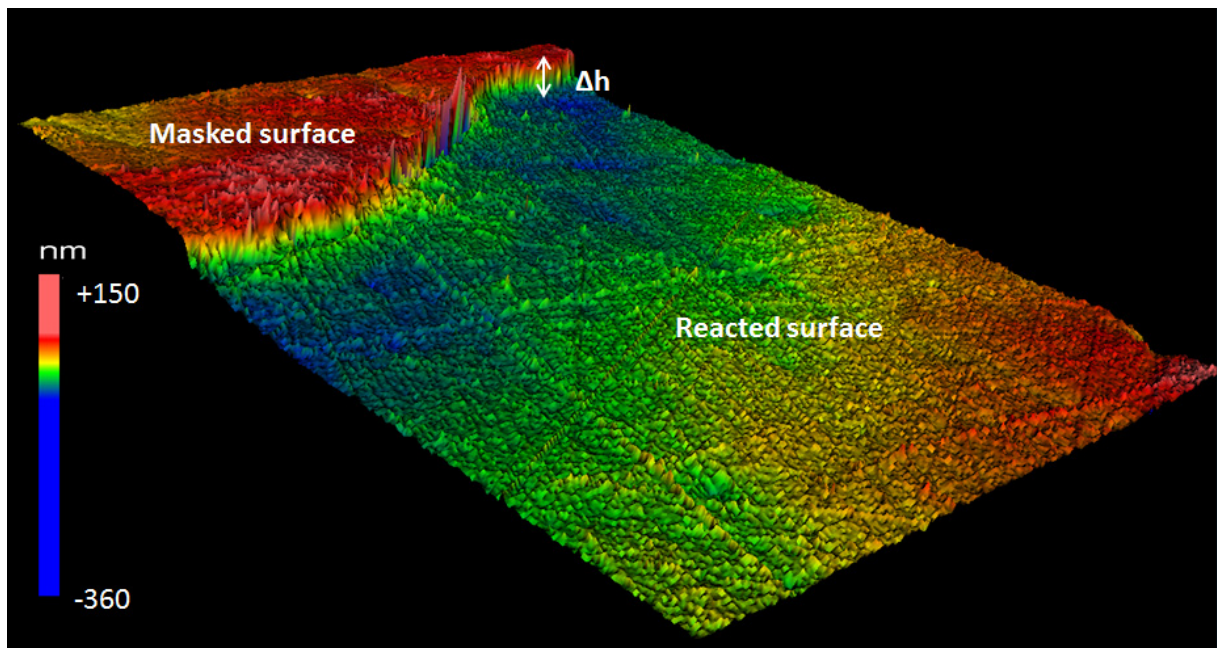
14

15 **Abstract**

16 The understanding of the atomic-scale mechanisms controlling silicate dissolution
17 represents a necessary prerequisite for the success of upscaling exercises aimed at predicting
18 the rates of water-silicate interactions over large space and time scales. In that respect, it has
19 been recently shown that physically-based stochastic models of crystal dissolution at the
20 atomic scale represent a promising alternative to the conventional treatment of silicate
21 dissolution rates, which consists in using empirical rate laws adjusted to the results of powder
22 dissolution experiments. However, most stochastic simulations conducted so far have been
23 based on simple cubic solid structure, and very few were directed to ascertaining the extent to
24 which the simulation outputs quantitatively compare to experimental measurements. In the
25 present study, we take advantage of the anisotropic crystallographic structure and reactivity of
26 chain silicates (pyroxenes) to tackle this issue. Face-specific enstatite dissolution experiments
27 conducted at pH 0 and 90 °C reveal that the face-specific dissolution rates observe the
28 following trend: $r^{(001)} \gg r^{(210)} > r^{(010)} \geq r^{(100)}$. Electron microscopy characterizations
29 additionally show that lenticular etch pits elongated following the c axis grow on $(hk0)$ faces,
30 and that nm-thick amorphous Mg-depleted layers cover the reacted enstatite surfaces. A
31 stochastic model was developed, and we show that simulations conducted with bond-breaking
32 probability ratios (and therefore, activation energy differences) that are consistent with the
33 existing literature regarding the hydrolysis of Mg-O-Mg, Mg-O-Si and Si-O-Si bonds can
34 quantitatively account for the measured dissolution rates. In addition, the lenticular shape, the
35 orientation and the symmetry of the pits generated numerically on $(hk0)$ faces are also
36 consistent with those observed experimentally, while predicting the formation of Mg-depleted
37 surface layers. As a consequence, this study provides a first milestone to the application of
38 stochastic simulations to investigate the dissolution of pyroxenes.

39 **Keywords:** stochastic model; pyroxene dissolution anisotropy; dissolution kinetics.

40 **Abstract graphic**



41
42

43 **1. Introduction**

44 The interactions between aqueous fluids and silicates play a central role in many major
45 geological, environmental and industrial processes. Silicate dissolution and precipitation
46 reactions control on various space and time scales many aspects of the continental surfaces
47 such as providing nutrients to living organisms¹, participating to the surface water chemistry,
48 mobilizing² or sequestering natural and anthropic contaminants³, shaping landscapes⁴ and
49 ultimately regulating the long-term carbon cycle and climate⁵⁻⁶. On an equal footing,
50 predicting the reactivity of silicate surfaces is further important for industrial purposes, such
51 as cement hydration⁷⁻⁸ and kinetics of catalyzed reactions⁹. As a consequence, the dissolution
52 rates of silicates have now been investigated for more than half a century, giving rise to a
53 dense body of literature (e.g. Brantley et al.¹⁰ for a review).

54 From a mechanistic standpoint, the conventional treatment of mineral reactivity has long
55 been based on the fundamental assumption that silicate dissolution may be described within
56 the framework of the transition state theory (TST), early developed by Eyring¹¹ for
57 elementary and homogeneous reactions. The extension of TST by Aagaard and Helgeson¹² to
58 heterogeneous fluid-solid reactions supposes that silicate dissolution reactions are controlled
59 by a unique rate-limiting step, implicitly requiring that the surface reactivity is homogeneous,
60 isotropic and immutable for a given fluid composition¹³. Although the resulting ‘kinetic rate
61 laws’ have been implemented into reactive transport codes for several decades, an increasing
62 number of studies has consistently challenged this conceptual framework:

63 First, it has been theoretically and experimentally demonstrated that mineral reactivity is
64 highly heterogeneous, resulting from the distribution of reactive sites at the fluid-solid
65 interface¹⁴. The ‘rate spectra’ concept¹⁵, which provides a measurement of the rate
66 distribution at the mineral surface in the spatial domain, was developed to indirectly capture
67 this energetic landscape.

68 Second, the advent of nanoscale imaging of surface topography has resulted in the
69 demonstration that crystal dissolution is a highly anisotropic process^{8, 16-24}. These studies
70 showed that the anisotropic reactivity of minerals results from the anisotropic distribution of
71 atomic positions in the crystal lattice, and may be described in the framework of the periodic
72 bond chain (PBC) theory²⁵. This theory suggests that crystal faces may be sorted following
73 the number of chains of energetically strong bonds (PBCs) they contain, with the faces
74 containing the largest numbers of PBCs dissolving slower, and vice versa. Pollet-Villard et
75 al.²¹ further proposed that the recognition of the anisotropy of crystal reactivity challenged the
76 idea of a unique relation between the overall dissolution rate of a crystal and the Gibbs free
77 energy of reaction (ΔG), which is constitutive of the TST formulation, while questioning the
78 existence of a unique intrinsic dissolution rate constant for crystals.

79 Finally, silicate dissolution is accompanied with gradual physicochemical and structural
80 modifications of their surface, resulting in the formation of nm- to μm -thick silica-rich surface
81 layers²⁶⁻³¹. Accounting for the transport properties of such layers, especially when developed
82 under mildly aggressive conditions (circum-neutral pH, low temperature), was also proposed
83 to be essential to develop reliable models of silicate dissolution^{23, 32}.

84 In a nutshell, all these studies converge towards the same conclusion: providing a better
85 theoretical description of mineral dissolution crucially requires gaining knowledge on the
86 relation between the atomic configuration of (and therefore, the energetic distribution at) the
87 dissolving mineral surface and the overall dissolution rate of a given crystal.

88 Driven by this assertion, studies dedicated to the molecular-scale description of the
89 silicate dissolution process following *ab initio* quantum mechanical calculations emerged
90 some 20 years ago³³⁻³⁸. Such studies shed light on essential theoretical information regarding
91 the dissolution process such as suggesting reaction paths, determining transition state
92 configurations (i.e., bond lengths and angles) and calculating activation energies of the

93 hydrolysis reactions in various pH domains. They also independently confirmed that the
94 dissolution process cannot be boiled down to the kinetics of a single surface reaction.
95 Actually, the large number of possible configurations of dangling atoms at the silicate surface
96 over the course of the dissolution translates into as many possible different hydrolysis
97 reactions, justifying the need for specific numerical simulations of the dissolution process at a
98 scale exceeding clusters of a few atoms. This was precisely one of the motivations for the
99 development of kinetic models using a Monte Carlo approach (often abbreviated as kMC)^{9, 22,}
100 ³⁹⁻⁴⁷, whose parametrization may strongly rely on the results of *ab initio* calculations
101 mentioned above. However, with the noticeable exception of a few recent studies^{9, 22, 45}, to
102 date, most of these modelling studies were conducted with simple Kossel crystals⁴⁸, making
103 difficult the direct comparison of the outputs of the simulations with experimental data.

104 In the present study, we combined experimental measurements of the anisotropy of
105 silicate dissolution (face-specific topographic features and dissolution rates) with stochastic
106 simulations to critically assess the validity of a simple dissolution model. Because of its very
107 anisotropic crystallographic structure made of chains of silica tetrahedrons running parallel to
108 one of the main crystallographic axes, pyroxene was chosen as a case study. It was previously
109 shown that the anisotropic structure of this family of silicates (also known as inosilicates)
110 resulted in a strong anisotropy of dissolution^{18, 23, 49}, intensifying the differences of reactivity
111 between the various faces that define their usual crystal habit. Owing to its simple chemical
112 composition (MgSiO_3) and structure (orthorhombic), enstatite was chosen as a model within
113 the pyroxene group.

114 After a brief description of the methods used and the ensuing information, we will
115 discuss the experimental results (i.e., the anisotropy of enstatite dissolution rates and surface
116 features observed using electron microscopy) in regard of pre-existing studies based on
117 pyroxene dissolution. These results will then be compared to the outputs of the simulations,

118 which will lead to a validation of the dissolution model and a discussion of the wider
119 implications and conclusions for pyroxene dissolution and dissolution mechanisms at the
120 fluid-silicate interface.

121

122 **2. Materials and methods**

123 *2.1 Starting materials and preparation*

124 The enstatite samples used in this study come from Kilosa (Tanzania), and were supplied
125 by Mawingu Gems Company. Negligible amounts of clinoenstatite (around a few wt. %) were
126 detected using X-ray diffraction (Fig. S1). Monolithic enstatite samples (up to several tens of
127 mm on a side) were cut with a diamond blade saw and polished down to the nanometer scale
128 through a multi-step abrasive sequence. The crystallographic orientation of each sample was
129 determined using an electron backscatter diffraction (EBSD) detector attached to a scanning
130 electron microscope (SEM) (TESCAN® Vega 2). The initial roughness of each surface was
131 measured at different scales with vertical scanning interferometer (VSI; ZYGO® NewView
132 7300). For each sample, the initial average arithmetic roughness (R_a), defined as the
133 arithmetic average of the absolute values of the roughness profile, ranged between 5 nm and
134 15 nm, and R_q (the roughness calculated with the root-mean-square of the vertical distance
135 between the surface elevation and the mean surface line) ranged between 19 nm and 70 nm.
136 These initial roughness parameters were measured on $270 \times 360 \mu\text{m}^2$ images obtained using
137 VSI.

138 *2.2 Dissolution experiments and analytical procedures*

139 Oriented samples were mounted in a passivated titanium support as designed by Daval et
140 al.¹⁸, where a Viton® disk held with a screw creates a non-wetted reference area. Partially
141 masked samples were dissolved in a synthetic acidic solution in 120 ml-PFA reactors at 90 °C

142 for durations ranging from 6 hours to 3 weeks to check for the linearity of the surface retreat
143 as a function of time.

144 The aqueous solutions were made with ultrapure deionized water (18.2 MΩ.cm) and
145 analytical grade nitric acid. The pH was adjusted to 0.0 ± 0.2 . Nitric acid was chosen to avoid
146 the dissolution of the titanium support that was observed in preliminary tests conducted with
147 hydrochloric acid under similar conditions. Solution sampling was regularly carried out for
148 the analyses of Si, Mg and Fe using ICP-AES (Thermo ICAP 6000). The CHESS code⁵⁰ was
149 used to determine the *in situ* pH and saturation indices with respect to enstatite and secondary
150 phases. It was verified that all solutions were undersaturated with respect to any secondary
151 phase.

152 For each orientation, at least two solid samples were analyzed for topography
153 measurements. While the first one was periodically recovered to perform the analyses and put
154 back in reactor, the second sample was left in the reactor all over the duration of the
155 experiment. This protocol was followed to make sure that the reactivity of samples that
156 experience wetting/drying cycles to get time-resolved topography measurements remains
157 similar to the reactivity of samples continuously immersed in solution. The topography
158 measurements were performed using VSI in stitching mode (magnification: $\times 5$) to estimate
159 the average changes in height between the unreacted reference surface and the reacted mineral
160 surface. For each oriented sample, dissolution rates were calculated according to the
161 following equation (see e.g. Lüttge et al.⁵¹):

$$r_{exp}^{(hkl)} = \frac{\Delta h}{\Delta t} \bar{V}^{-1} \quad (1)$$

162 where $r_{exp}^{(hkl)}$ ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) is the dissolution rate of the (hkl) face, Δh is the surface retreat (m),
163 Δt is the alteration duration (s) and \bar{V} ($\text{m}^3\cdot\text{mol}^{-1}$) is the molar volume of enstatite. As detailed
164 below, the minute lateral extension of etch pits (\sim a few tens of nm) prevented the
165 investigation of individual pits by VSI even at high magnification ($\times 100$; lateral resolution \sim

166 300 nm), rendering impossible more sophisticated treatment of the surface topography using
167 e.g. rate spectra.

168 After completion of the surface topography measurements, the formation of nm-thick,
169 amorphous Si-rich layers (ASSL) was verified to make sure that the layer thickness was
170 negligible compared to the corresponding surface retreat measured by VSI. The samples were
171 either platinum- or carbon-coated and thin sections perpendicular to the investigated faces
172 were prepared by focused ion beam (FIB) milling using the FEI Helios 600 Nanolab dual-
173 beam operating at CP2M (Marseille, France). The FIB Ga ion milling was carried out at an
174 ion beam voltage of 30 kV and with beam currents from 3 nA to 10 pA for the final steps.
175 Micrometer-thick sections were lifted out *in situ* using an Omniprobe 200 micromanipulator
176 and transferred to a half copper grid for final ion milling to electron transparency (final
177 thickness of about 100 nm). High-resolution transmission electron microscopy (HRTEM) and
178 scanning transmission electron microscopy (STEM) observations were performed on FIB
179 foils using a JEOL 2100F microscope operating at 200 kV, equipped with a field emission
180 gun. Energy dispersive X-ray (EDX) spectra were acquired in STEM mode to probe the
181 chemical compositions, with a focused electron beam (1 nm). When the FIB thin section
182 intersected etch pits (i.e., for the (100) and (010) samples), TEM was further used to
183 characterize their morphologies.

184 ***2.3 Modeling strategy***

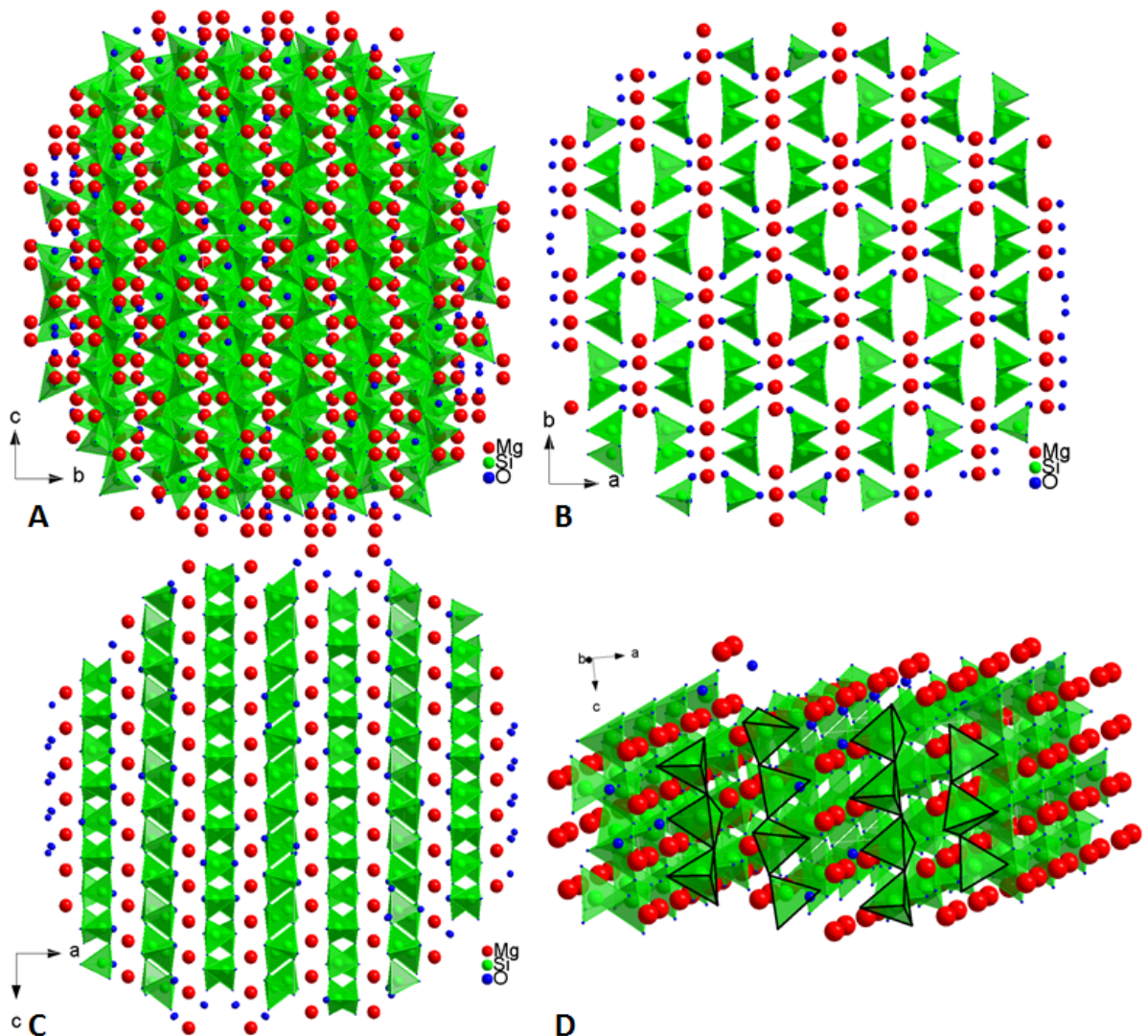
185 The stochastic approach for mineral dissolution studies has emerged in the mid-80's⁵².
186 Since then, numerous studies have used stochastic simulations to describe mineral dissolution
187 at the atomic scale, principally using simple Kossel crystals^{43, 47-48} (simple cubic crystal
188 lattice; 6-fold coordinated atoms) but some have also applied them on more complex mineral⁹,
189 ^{22, 41} and glass^{40, 44, 53} structures. These studies have shown the robustness of these models

190 through their ability to reproduce etch pit shapes^{9, 22} and sometimes, by comparing modeled
 191 and measured dissolution rates²².

192 These models are based on a simple relation that links the bond-breaking probability
 193 to the activation energy of the hydrolysis of this bond⁵²:

$$P = e^{\frac{-\Delta E_a}{k_B T}} \quad (2)$$

194 where P is the bond-breaking probability, ΔE_a , the activation energy (J), k_B , the Boltzmann
 195 constant (J/K) and T the temperature (K).



196
 197 **Fig. 1.** Projection of enstatite structure following [100] (A), [001] (B), [010] (C) zone axes and a rotation view of
 198 the enstatite volume (D) to highlight the chains of silicate tetrahedrons. The Mg, Si and O atoms are represented
 199 by red, green and blue spheres respectively. Si tetrahedrons are represented in light green.

200

201 2.3.1 Modeling enstatite crystal structure

202 Enstatite is an inosilicate made of chains of silicate tetrahedrons running parallel to the c -
203 axis. The crystal lattice of orthoenstatite (used in the present study) is orthorhombic and
204 belongs to the $Pbca$ space group. Hugh-Jones et al.⁵⁴ have provided the coordinates of the
205 atomic positions (Table 1) that allow forming the enstatite cell with the following relations
206 corresponding to the $Pbca$ system:

$$\begin{array}{ccc} x & y & z \\ \frac{1}{2} - x & \frac{1}{2} + y & z \\ x & \frac{1}{2} - y & \frac{1}{2} + z \\ \frac{1}{2} + x & y & \frac{1}{2} - z \\ -x & -y & -z \\ \frac{1}{2} + x & \frac{1}{2} - y & -z \\ -x & \frac{1}{2} + y & \frac{1}{2} - z \\ \frac{1}{2} - x & -y & \frac{1}{2} + z \end{array} \quad (3)$$

207 The lengths of the a , b and c axes are 18.233, 8.8191 and 5.1802 Å respectively and the
208 angles α , β and γ are equal to 90° (orthorhombic system).

209 The enstatite unit cell was created based on these parameters, and is composed of 16
210 atoms of magnesium, 16 atoms of silicon and 48 atoms of oxygen. The cell is then repeated
211 following the three space dimensions in order to get a simulated crystal of several tenths to
212 hundreds of nanometers on a side.

213 Mg and Si atoms were connected to O atoms according to the following rules: (i) Mg
214 atoms are located in octahedral sites and Si atoms in tetrahedral sites (i.e., Mg atoms are
215 connected to 6 O atoms and Si atoms are connected to 4 O atoms) and (ii) the closest O atoms
216 were considered to create the coordination spheres surrounding each cation. The resulting
217 modeled surfaces ((100), (010) and (001)) are shown in Fig. 1.

218

Atoms	x/a	y/b	z/c
Mg 1	0.3763	0.6541	0.8663
Mg 2	0.3769	0.4872	0.3589
Si 1	0.2715	0.3418	0.0506
Si 2	0.4736	0.3374	0.7981
O 1	0.1835	0.3407	0.0340
O 2	0.3114	0.5029	0.0430
O 3	0.3025	0.2224	0.8320
O 4	0.5622	0.3414	0.7980
O 5	0.4324	0.4836	0.6900
O 6	0.4483	0.1951	0.6030

219

220 **Table 1.** Atomic coordinates in enstatite cell⁵⁴ used in Eq. (3) to form the entire cell.

221

222 2.3.2 Bond-breaking probabilities

223 Most stochastic simulations performed at the atomic scale on silicate materials
 224 consider the cleavage of M-O-M bonds instead of single M-O bonds⁹. Hence, the oxygen
 225 atoms are only considered as bridges between two cations (O_{br}), and the cations connected to
 226 the oxygens of a specific Si or Mg atoms are referred to as their first coordination spheres⁹. In
 227 enstatite, three types of bonds exist: Mg-O_{br}-Mg, Mg-O_{br}-Si and Si-O_{br}-Si bonds.

228 Two different strategies may be considered to develop stochastic models: the former
 229 considers that the release of a cation results from the sequential cleavage of each bond which
 230 connects it to the surface, and the latter considers that the cation release results from the
 231 simultaneous cleavage of all these bonds at a given iteration step. The difference between the
 232 two methods stands in the number of information required to run a simulation (for a single
 233 enstatite cell, 160 bonds need to be considered following the first strategy whereas only 32
 234 atoms (16 Mg and 16 Si atoms; O atoms being considered as “bridges”) are required for the
 235 second strategy). For this reason, the second strategy is generally used and has previously
 236 proven successful^{9, 22, 41, 44, 53}. Accordingly, our simulations were run using the following
 237 probability for the release of Mg and Si atoms:

$$P_M = e^{\frac{-n\Delta E_{M-O-Mg}}{k_B T}} e^{\frac{-m\Delta E_{M-O-Si}}{k_B T}} \quad (4)$$

238 where $M = \text{Mg}$ or Si and n and m correspond to the number of Mg and Si atoms linked to the
 239 considered M atom, respectively. This equation, together with knowledge of the connectivity
 240 of each atom, represents the core description of the physical basis adopted for our stochastic
 241 simulations. Importantly, more sophisticated relations may be found in the literature, which
 242 attempt to account for various physical processes such as lattice resistance^{34, 45}, steric
 243 constraints⁹ or backward attachment reactions possibly resulting in self-healing of disrupted
 244 $\text{Si-O}_{\text{br}}\text{-Si}$ bonds^{34, 40-41, 44}. Importantly, even if the resulting stochastic models are physically
 245 more robust, they also introduce significant degrees of freedom in the parametrization of the
 246 resulting bond-breaking probabilities (see bond-breaking probability expressions and
 247 parametrization derived in, e.g.,^{9, 40}). In contrast, the present work was intended to assess the
 248 extent to which a stochastic approach with the simplest physical basis can satisfactorily
 249 account for the main face-specific features of enstatite dissolution, explaining why we used
 250 the simple relations provided by Eq. (4).

251 Various algorithms may be used to run stochastic simulations. In the present study, we
 252 followed a strategy close to the “random select and test” approach previously described and
 253 used in e.g.^{40, 43} (see section 2.3.4). As described in these studies, this approach consists in
 254 scaling to unity the most probable event, and scaling accordingly the probabilities of all other
 255 events. Equation (4) then simply becomes:

$$P_M = P_{M-O-Mg}^n \times P_{M-O-Si}^m \quad (5)$$

256 with $0 < P_{M-O-Mg}, P_{M-O-Si} < 1$. According to *ab initio* and experimental studies, the most
 257 probable event is the detachment of an Mg atom bonded to the surface via a single Mg-O-Mg
 258 bond. The corresponding probability was then set to 0.99 and can be associated, by
 259 identification, to the Mg-O-Mg activation energy term in Eq. (4). The two other elementary
 260 probabilities ($P_{Mg-O-Si}$ and $P_{Si-O-Si}$) were calculated in order to observe the theoretical
 261 difference of activation energies between the hydrolysis of Mg-O-Mg and that of Mg-O-Si or

262 Si-O-Si, respectively. Considering the *ab initio* data from^{36, 38} for the activation energy of Si-
263 O-Si ($\Delta E_{Si-O-Si} = 69$ kJ/mol) and Mg-O-Si ($\Delta E_{Mg-O-Si} = 59$ kJ/mol) hydrolyses and the
264 experimental data from⁵⁵ for Mg-O-Mg hydrolysis ($\Delta E_{Mg-O-Mg} = 60 \pm 12$ kJ/mol), the
265 range of difference in activation energy that was explored is [0 ; 10 kJ/mol] for the {Si-O-Si ;
266 Mg-O-Si} pair and [0 ; 4 kJ/mol] for the {Mg-O-Mg; Mg-O-Si} pair.

267

268 **2.3.3 Dislocations**

269 Etch pits are known to nucleate at dislocations outcropping at crystal surfaces⁵⁶. In
270 order to compare the observed and simulated morphology of etch pits on each face, screw
271 dislocations were introduced in the model. The main dislocations for enstatite follow the
272 [001], [010] and [100] axes⁵⁷. Therefore, screw dislocations are perpendicular to the different
273 studied orientations, except for the (210) face. In order to propagate the dislocation in the
274 volume, the distances between the first atom (located at the center of the reactive surface) and
275 its neighbors in the xOy plan are calculated. The shortest distance defines the atom that will
276 be the next one belonging to the dislocation line. The same process is repeated until reaching
277 the opposite face of the simulated crystal. For the (210) face, a rotation of the volume is made
278 before applying these steps in order to respect the dislocation directions ([100] and [010]).
279 Finally, when all the atoms that belong to the dislocation line are identified, their bond-
280 breaking probabilities are set to 1^{9, 22}.

281

282 **2.3.4 Dissolution algorithm**

283 The “random select and test” (RST^{40, 43}) and “divide and conquer” approaches (DaC^{43,}
284 ⁵⁸) are two different algorithms commonly used in stochastic simulations. Nowadays, the DaC
285 algorithm is usually preferred because it requires less computer time. Furthermore, it provides
286 a correspondence between iteration and time⁹. However, DaC algorithms cannot reproduce

287 simultaneous events, and favor a “layer-by-layer” removal of atoms⁴¹. For these reasons, we
288 preferred using an approach close to the “primitive” RST despite its poor computation
289 efficiency. Moreover, time cannot be associated *a priori* to a number of iterations. This
290 relation has to be inferred using at least two experimental data sets (e.g., two dissolution rates
291 for two different faces). By measuring mean dissolution rates for 4 different faces, we made
292 sure that the problem was overconstrained, ensuring a well-established relationship between
293 time and simulation steps (iterations).

294 The crystal is described by the coordinates of the Mg and Si atoms and the
295 connectivity of each atom to its neighbors follows the rules described in Section 2.3.1. Only
296 the cations that have an incomplete first coordination sphere (incomplete connectivity), are
297 considered to be located at the crystal surface, and may experience dissolution. For each Mg
298 and Si atom, an integer number indicates the three possible states of the atom: (i) dissolved,
299 (ii) at the crystal surface, or (iii) inside the crystal. This indicator allows counting the number
300 of dissolved cations and their nature (Mg or Si) and identifying the atoms located at the
301 surface in an efficient way.

302 The algorithm for simulating the dissolution process is as follows:

- 303 1. At each iteration step k , all cations of the simulated crystal volume are scanned
304 sequentially (Loop 1 in Fig. S2).
- 305 2. For each surface cation, a random number Z uniformly distributed between 0
306 and 1 is generated. The probability of dissolution of that atom P_M is computed as
307 the product of the bond-breaking probabilities of the bonds that link it to the
308 crystal following Eq. (5). If $Z < P_M$, the atom is released (dissolved). If not, the
309 scan of the atoms is moving on (Loop 2 in Fig. S2).
- 310 3. When the scan of all atoms is completed, the first coordination spheres of the
311 remaining atoms are updated if necessary (i.e., when a removed atom was

312 belonging to the coordination spheres of one of the remaining atoms; cf. Loop 3 in
313 Fig. S2). Because the coordination spheres are modified, the probability of
314 dissolution P_M of the corresponding atoms are increased.

315 4. The number of released Si and Mg atoms at iteration k is saved for post-
316 processing.

317 5. The iteration number is incremented and the process continues step 1.

318 **2.3.5 Model outputs**

319 The outputs of the simulations were used to document face-specific features of
320 enstatite dissolution, such as (i) the mean dissolution rates at steady-state conditions, (ii) the
321 thickness of the Si-rich surface layer that may result from preferential leaching of Mg (if any)
322 and (iii) the etch pit morphology.

323 The dissolution rates may be calculated following two different approaches. First, the
324 list of surface cations after a given iteration is used to calculate the corresponding mean
325 elevation of the surface ($z_{surface} = \sum_{i=1}^{N_{atome,surface}} z_i / N_{atom,surface}$) and infer the
326 corresponding mean surface retreat rate ([nm/iteration]), which can be converted into a
327 surface normalized dissolution rate $r_{mod,topo}^{(hkl)}$ ([mol/m²/iter]) using Eq. (1) (in which the
328 number of iterations is substituted for time). When steady-state conditions are reached (i.e.,
329 when $r_{mod,topo}^{(hkl)}$ becomes constant), this approach can be related to the dissolution rates
330 estimated using VSI (see section 2.2). Of note, the difference in terms of surface areas
331 between the simulated (0.33 μm^2 for the largest) and measured (dozens of mm^2) surfaces
332 preclude any direct use of the rate spectra concept¹⁵, so that in the present study, only the
333 mean surface retreat rates were subsequently used as a criterion to assess the correspondence
334 between simulated and measured dissolution rates.

335 A second approach considers the amount of Mg and Si atoms released at each
 336 iteration, as could be determined experimentally using ICP-AES solution analyses. Distinct
 337 rates based on Mg ($r_{mod,Mg}^{(hkl)}$ ([mol/m²/iter])) and Si ($r_{mod,Si}^{(hkl)}$ ([mol/m²/iter])) release were
 338 calculated following:

$$r_{mod,Mg}^{(hkl)} = \frac{\sum_{i=1}^{it} N_{Mg,i} * V_{cell}}{it * N_{Mg,cell} * S * \bar{V}} \quad (6a)$$

$$r_{mod,Si}^{(hkl)} = \frac{\sum_{i=1}^{it} N_{Si,i} * V_{cell}}{it * N_{Si,cell} * S * \bar{V}} \quad (6b)$$

339 where *it* represents the iteration step at which the calculation is performed, $N_{M,i}$, the number of
 340 Mg or Si atoms released after the *i*th iteration, $N_{M,cell}$, the number of Mg or Si atoms in the cell
 341 (16), V_{cell} the enstatite cell volume, \bar{V} the molar volume of enstatite and *S*, the geometric
 342 surface area of the reactive surface.

343 While this approach eventually yielded results very close to the previous method, it
 344 further provided information regarding the stoichiometry of the dissolution by comparing the
 345 evolution of the departure of the Mg and Si atoms, and eventually, regarding the existence
 346 and thickness of a Si-rich surface layer, which was previously documented for inosilicates
 347 weathered experimentally^{18, 23, 59-61}. Since the model does not consider the backward reaction
 348 of Si attachment to the surface (see discussion in^{41, 62}), it only indicates a lower bound for the
 349 thickness of the layer resulting from cation depletion, ignoring possible Si re-deposition
 350 following an interfacial dissolution-precipitation mechanism.

351 Finally, for simulations run with dislocations, the resulting etch pits and surface
 352 retreats were calculated using Surfer©. The coordinates of the atoms at the surface were
 353 stored and used as an input file for Surfer. The minimum curvature method was used to
 354 calculate the mean surface retreat at a given iteration.

355

356 2.3.6 Linking time to iteration

357 As mentioned above, simulation results are normalized to the number of iterations
358 instead of elapsed time. However, in order to compare modeled and measured dissolution
359 rates, it is necessary to link a single iteration to a physical time increment. The
360 correspondence between time and iteration was determined following Eq. (7):

$$t = \left\langle \frac{r_{mod}^{(hkl)}}{r_{exp}^{(hkl)}} \right\rangle it \quad (7)$$

361

362 **3. Results**

363 *3.1 Face-specific dissolution rates of enstatite revealed experimentally*

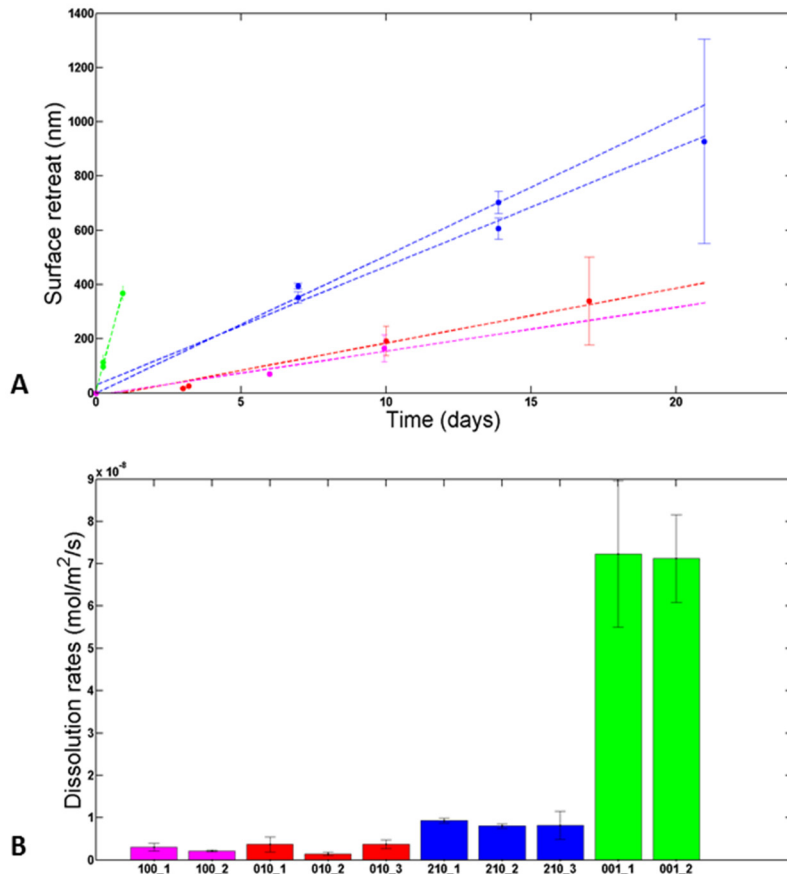
364 Fig. 2A shows the temporal evolution of the mean surface retreat measured using VSI.
365 Whereas the $(hk0)$ faces were reacted for durations of up to three weeks, the rapid increase of
366 the roughness of the (001) face prevented the measurements of surface topography for
367 durations exceeding a couple of days. The main results are as follows:

368 (i) the dissolution rate is constant through time (at least from the first experimental
369 measurements) for all of the four faces, within experimental uncertainties;

370 (ii) the dissolution rates of the samples left in the reactor all over the duration of the
371 experiments are similar to those that were periodically retrieved from the reactors;

372 (iii) enstatite dissolution is an anisotropic process (i.e., the slopes of the linear
373 regressions differ from one face to the other). The face-specific dissolution rates ($r_{exp}^{(hkl)}$)

374 observe the following trend: $r_{exp}^{(001)} \gg r_{exp}^{(210)} > r_{exp}^{(010)} \geq r_{exp}^{(100)}$. The mean values of
375 dissolution rates are 71.8 ± 13.9 , 8.5 ± 1.5 , 3.0 ± 1.0 and 2.6 ± 0.6 nmol/m²/s for the (001) ,
376 (210) , (010) and (100) faces, respectively (Fig. 2B).



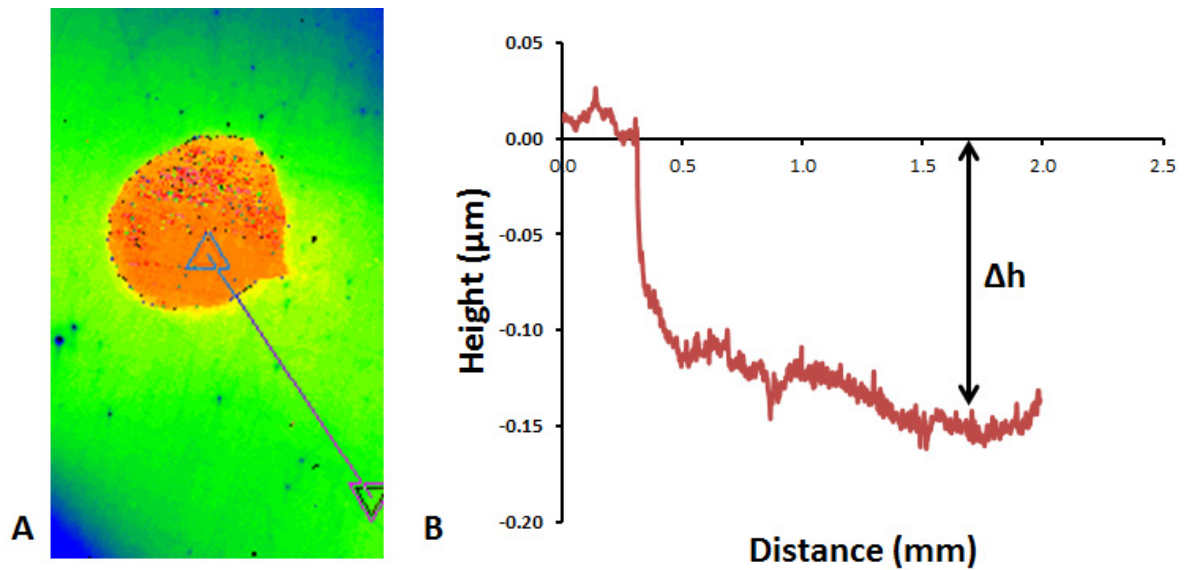
377

378 **Fig. 2.** A. Face-specific temporal evolution of the mean surface retreat measured with VSI and associated linear
 379 regressions. B. Measured face-specific dissolution rates. For both graphs, magenta, red, green and blue colors
 380 stand for the results obtained for (100), (010), (001) and (210) faces, respectively.

381

382 *3.2 Face-specific microstructural features revealed experimentally*

383 The etch pits possibly formed on each surface were too small to be properly
 384 investigated by VSI, whose resolution is close to 300 nm at the maximum 100x-
 385 magnification. Apart from the surface retreat between the masked and unmasked portions of
 386 the samples (Fig. 3), no specific topography feature could be evidenced using VSI.



387

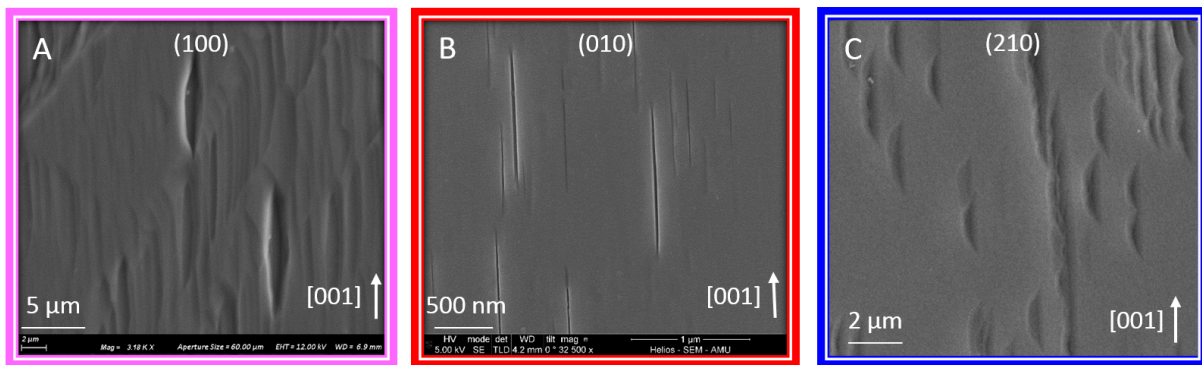
388 **Fig. 3.** A. Surface topography of the (001) surface dissolved for ~ 8h measured using VSI. The red spot
 389 represents the mask (non-reacted) area while the blue/green area represents the reacted surface. B. Topography
 390 of the surface (straight line in A) after dissolution. The upper part corresponds to mask area while the lower part
 391 corresponds to the reacted area.

392

393 SEM imaging of the reacted surfaces revealed that etch pits did nucleate on three of
 394 the four investigated faces (Fig. 4), and confirmed that their lateral extension was too modest
 395 to be imaged by VSI. The (100) and (010) faces exhibited similar lenticular pits elongated
 396 following the *c*-axis (the major axis is more than 6 times larger than the minor axis). The
 397 shape of the pits projected to the horizontal surface shows a central symmetry, consistent with
 398 the shape previously described in the literature for pyroxenes in general^{18, 60, 63-65}. Two types
 399 of pits are visible on the (210) face: while the former is similar to the ones observed on the
 400 (100) and (010) faces (with a small minor axis compare to the major axis), the latter, also
 401 elongated following the *c*-axis, presents a wider minor axis (3 times smaller than the major
 402 axis). In addition to this difference of minor-axis length, these pits differ from the ones
 403 observed on the other faces by their non-symmetrical, half-moon shape. Whereas the lowest
 404 points for the pits developed on the (100) and (010) faces are located at the center of the pits,

405 conversely, for pits developed on the (210) face, the lowest point is located at the center of the
406 major-axis but shifted on one edge of the minor-axis (Fig. 4C).

407 The dislocation density is also a function of crystallographic orientation. The number
408 of dislocations has been calculated on each face by counting the number of etch pits observed
409 by SEM on surface areas of $\sim 300 \mu\text{m}^2$. Of note, polishing scratches also represented an
410 important source of etch pits. Because they can contribute to the global dissolution rate by
411 exposing step sites, they have been taken into account in the calculation of the dislocation
412 density.



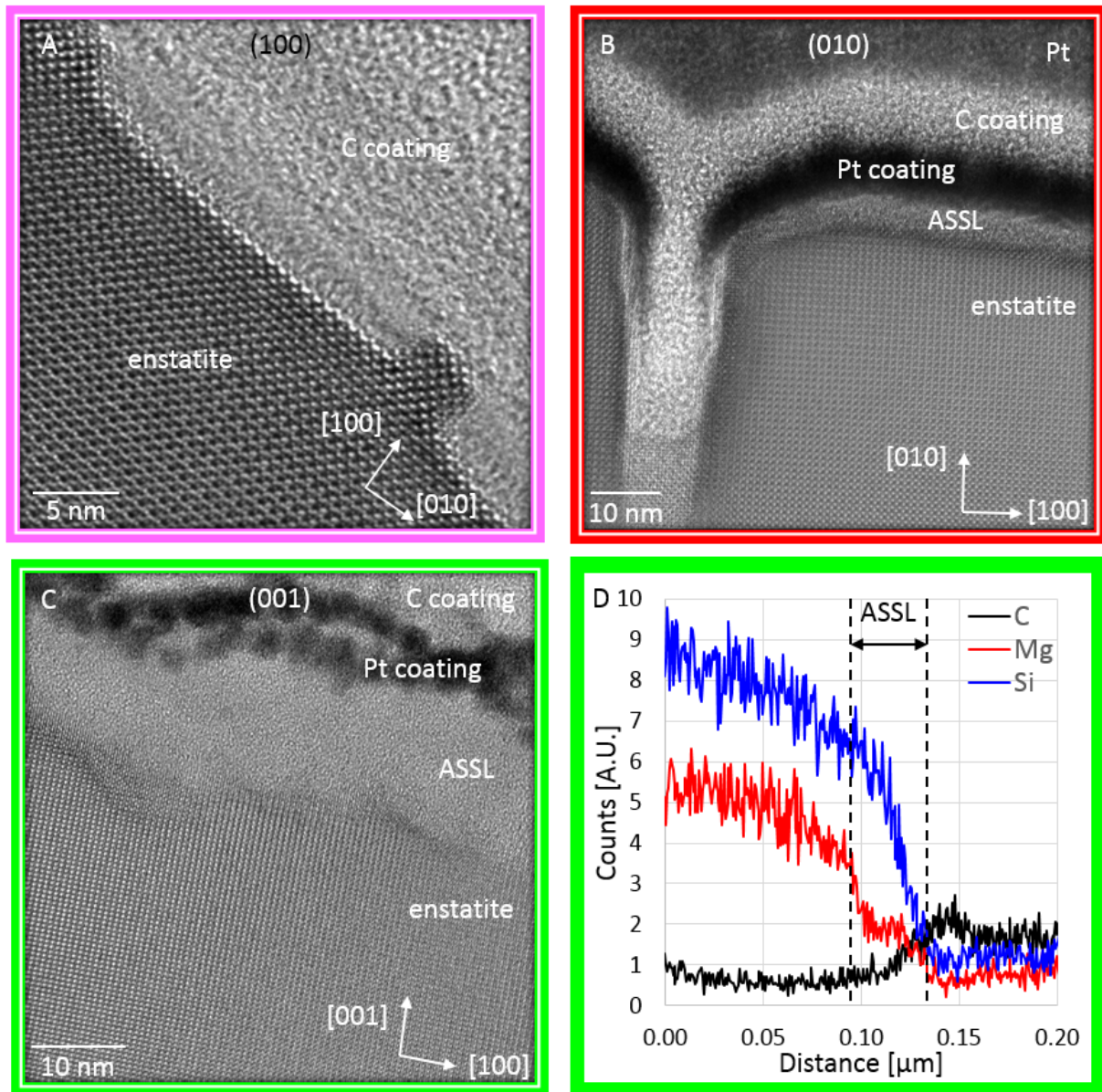
413
414 **Fig. 4.** SEM images of the surface of (001) (A), (010) (B) and (210) faces reacted at pH 0 for 7 to 21 days. The
415 images reveal the nucleation of lenticular etch pits elongated following the [001] direction. Note the asymmetric
416 shape of the pits nucleated on the (210) face, as opposed to those developed on the other two faces.

417
418 The dislocation density on the (100) and (210) faces was found to be similar (on the
419 order of $4.9 \pm 0.3 \times 10^8$ dislocations / cm^2), and is about two orders of magnitude greater than
420 that measured on the (010) face (9.8×10^6 dislocation / cm^2). The dislocation density on the
421 (001) face could not be determined because of the rapid roughening of the surface, which
422 impeded the identification of individual etch pits. These dislocation densities are in agreement
423 with other studies⁶⁶⁻⁶⁷, which reported dislocation densities ranging between 4.0×10^7 and 7.0
424 $\times 10^8$ dislocations / cm^2 . The close correspondence between the dislocation density calculated
425 for the (100) and the (210) faces may be explained by the main orientation of screw

426 dislocations for the enstatite structure. As mentioned in section 2.3.3, the main dislocations in
427 enstatite follow the [100], [010] and [001] directions⁵⁷. Therefore, outcropping dislocations at
428 the (210) surface should represent the sum of the dislocation outcropping at the (100) and the
429 (010) surfaces, which is consistent with our observations.

430 TEM investigations performed on FIB thin sections prepared on the reacted samples
431 revealed the occurrence of amorphous surface layers on (010), (210) and (001) samples, with
432 a thickness specific to the surface orientations (Fig. 5). The thickest layers were evidenced on
433 (001) samples (15-20 nm; cf. Figs. 5C-D). The layers developed on (210) and (010) samples
434 have similar thickness (≤ 4 nm; cf. Fig. 5B), whereas no surface layer could be clearly
435 evidenced on (100) samples (Fig. 5A). The layers developed on (001) samples were thick
436 enough to analyze their chemical composition with STEM-EDX, which revealed that they are
437 Si-rich and Mg-depleted (Fig. 5D). The similarity of these results with those reported by
438 Daval et al.¹⁸ for diopside dissolved at pH 1 is noteworthy. Finally, it was possible to
439 determine the cross-section morphology of etch pits nucleated on the (100) and (010) faces, as
440 the FIB thin sections were realized in locations where etch pits were particularly abundant.
441 Regarding the (010) face, TEM images revealed that the pit geometry observes an axial
442 symmetry with respect to the [010] axis, and that the pit walls are particularly steep, forming
443 an angle of $93^\circ \pm 2^\circ$ with the (010) surface (Fig. 5B). Similarly, the walls of the pits
444 developed on the (100) face formed an angle of $97^\circ \pm 5^\circ$ with the (100) surface, although the
445 pits appear to be flat-bottomed (Fig. 5A). Overall, these results confirmed that profilometry
446 techniques such as atomic force microscopy or vertical scanning interferometry would have
447 failed to reveal the 3D-geometry of such etch pits.

448



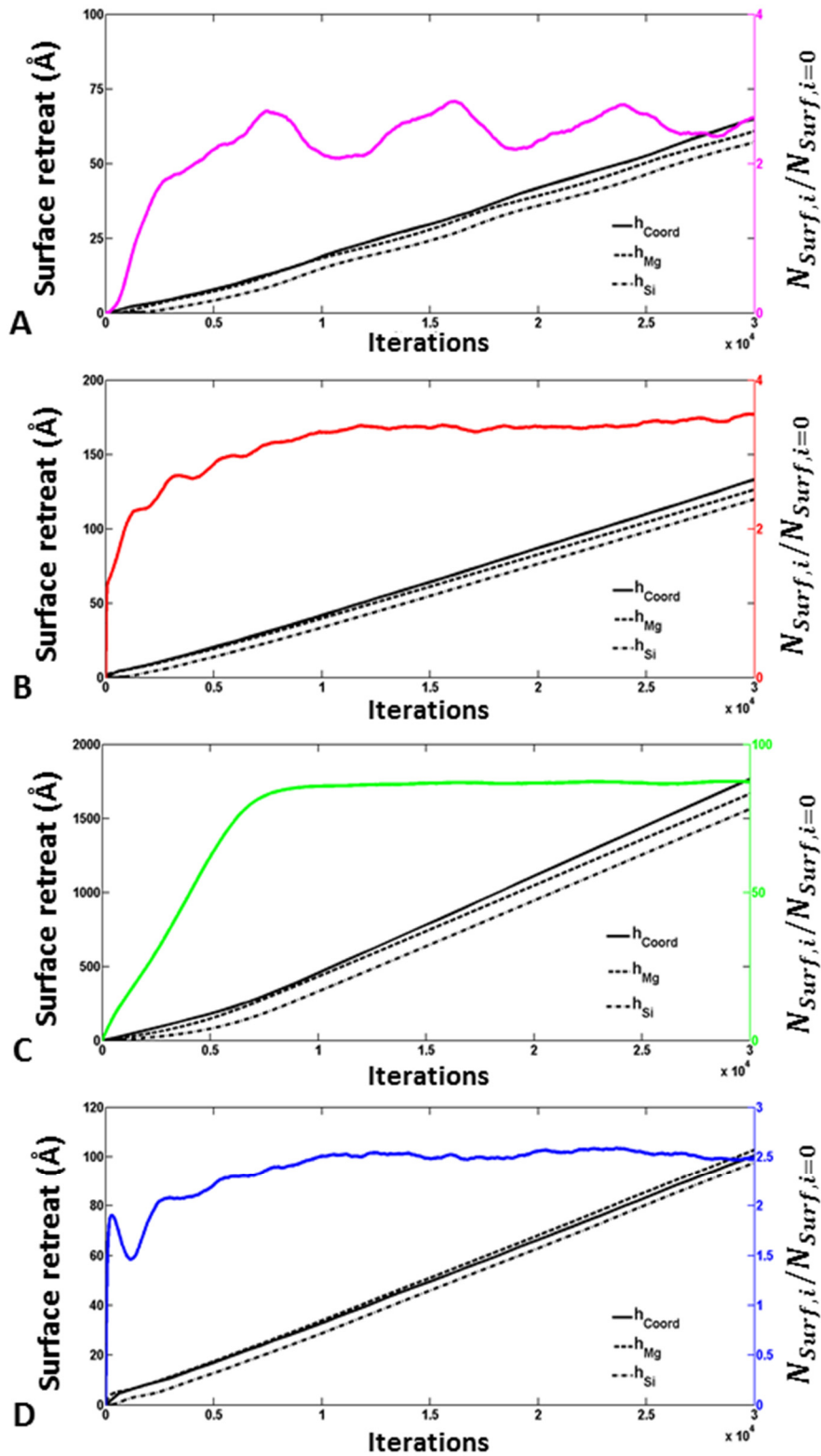
449

450 **Fig. 5.** TEM characterizations of FIB thin sections prepared on (100) (A), (010) (B), and (001) (C and D) reacted
 451 surfaces. HRTEM images in (B) and (C) reveal the formation of a nm-thick amorphous layer formed on the
 452 surface, with a sharp crystallographic boundary between enstatite and the surface layer. For the FIB thin section
 453 realized on (001) surface, STEM-EDX profiles measured parallel to the [001] direction reveal that the surface
 454 layer is Si-rich and Mg-depleted (D).

455

456 **3.3 Model outputs**

457 **3.3.1 Dissolution stoichiometry and steady-state dissolution rates**



458

459 **Fig. 6.** Outputs of the simulations conducted with the bond-breaking probabilities corresponding to the best

460 agreement between measured and modeled dissolution rates (see text for details) for (100) (A), (010) (B), (001)

461 (C) and (210) (D) faces. The evolution of the modeled surface retreat calculated following three different

462 methods (see text) is depicted with black lines. The color lines stand for the evolution of the number of surface

463 cations, normalized to the initial number of cations at the enstatite surface. Note that the increase of the number
464 of surface atoms is much greater for (001) face (about an 80-fold factor) than for the other ($hk0$) faces (between a
465 2.5- and 3.8-fold factor).

466

467 A common trait to all of the simulation outputs, irrespective to the set of bond-
468 breaking probabilities that have been tested, is the attainment of a steady-state dissolution
469 regime, which is characterized by a congruent release of Mg and Si cations and a constant
470 dissolution rate (Fig. 6). This steady-state regime was found to result from the attainment of a
471 constant number of atoms at the surface of each face, as illustrated in Fig. 6 (color lines).

472 During the initial transient period, Mg is released preferentially, and enstatite dissolution
473 rate based on Si release increases gradually. The duration and the shape of the transient period
474 depend on the set of bond-breaking probabilities that are used to run the simulations and is a
475 function of surface orientation. In a general manner, the steady-state regime is achieved
476 earlier for the ($hk0$) faces than for the (001) face, for which the initial non-congruence of the
477 dissolution is also more pronounced (Fig. 6). As a consequence, thicker ASSLs are expected
478 to build up on the (001) face, compared to the ($hk0$) faces. When one considers the set of
479 bond-breaking probabilities that allows for the best agreement between the modeled and
480 measured steady-state face-specific dissolution rates (see below), the modeled thickness of
481 ASSL is on the order of 1-2 atomic monolayers for all ($hk0$) faces, as opposed to ~ 10 nm for
482 the ASSL developed on the (001) face.

483 The modeled absolute values of steady-state dissolution rates and the relative differences
484 between the reactivity of the four faces depend on the set of bond-breaking probabilities that
485 were used to conduct the simulations. Considering a range of probabilities that is consistent
486 with the literature (see section 2.3.2) and the dislocation density determined experimentally
487 for each face, the modeled face-specific dissolution rates $r_{mod}^{(hkl)}$ observe the following trend:
488 $r_{mod}^{(001)} \gg r_{mod}^{(hk0)}$. The relative differences between the modeled dissolution rates for the

489 various ($hk0$) faces depend on the set of probabilities used to run the simulations. The best
490 agreement between modeled and measured steady-state dissolution rates is obtained for P_{Mg-O}
491 $P_{Mg-O-Si} = 0.99$; $P_{Mg-O-Si} = 0.4$ and $P_{Si-O-Si} = 0.0146$ (i.e., $\Delta E_{Si-O-Si} - \Delta E_{Si-O-Mg} = 10$ kJ/mol
492 and $\Delta E_{Mg-O-Mg} - \Delta E_{Si-O-Mg} = 2.7$ kJ/mol), for which the modeled face-specific
493 dissolution rates $r_{mod}^{(hkl)}$ observe the following trend: $r_{mod}^{(001)} \gg r_{mod}^{(010)} > r_{mod}^{(210)} > r_{mod}^{(100)}$.
494 Whereas the amplitude of the reactivity measured between the fastest and slowest dissolving
495 face is well reproduced by the model, one can note that it slightly overestimates the reactivity
496 of the (010) face (or slightly underestimates the reactivity of the (210) face).

497

498 3.3.2 Morphology of modeled etch pits

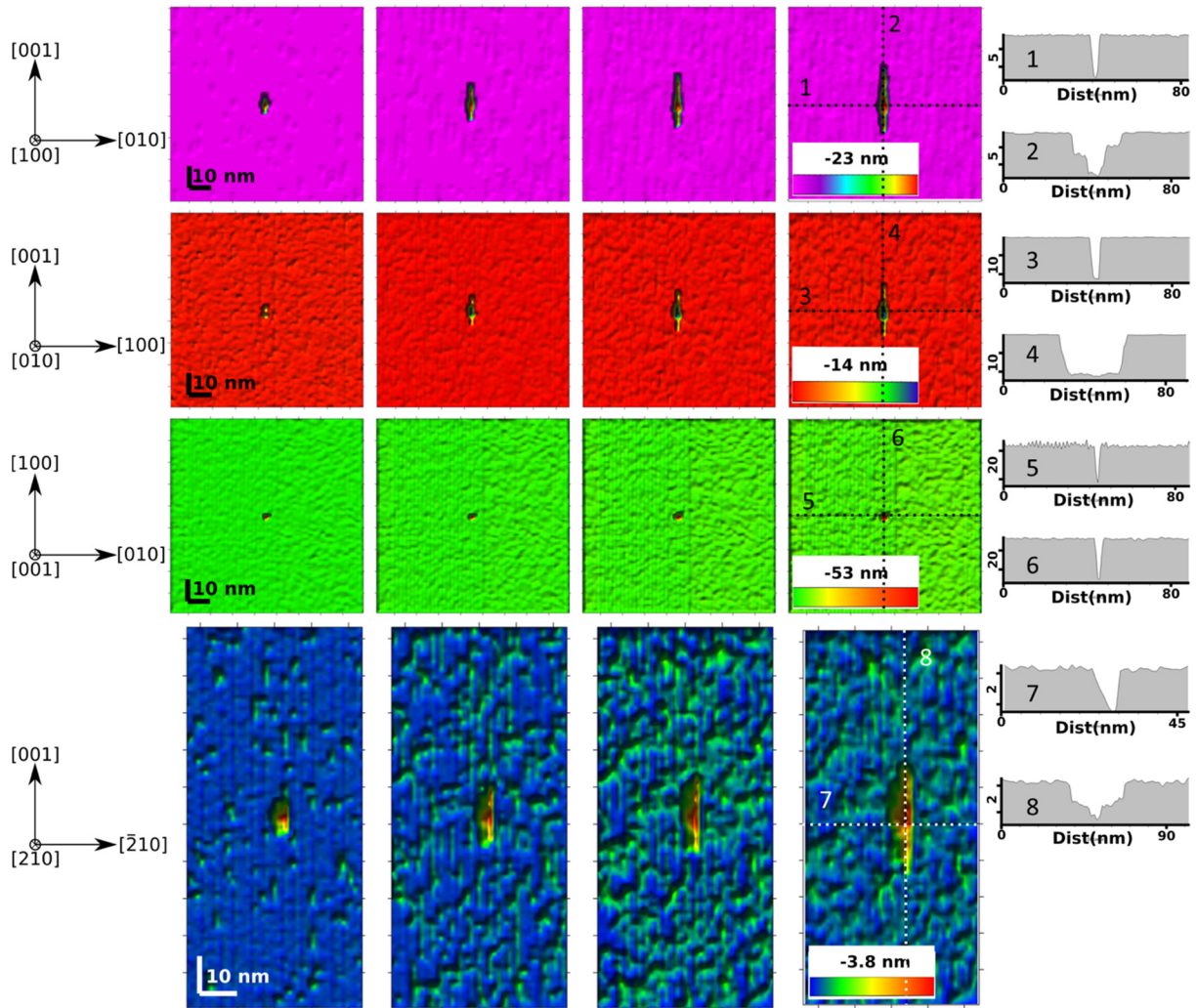
499 The implementation of dislocation lines in the simulated crystals allowed to document
500 the morphology of etch pits for the four investigated faces. Fig.7 depicts the modeled surface
501 evolution of the four studied faces, centered on an outcropping dislocation line, for
502 simulations ranging from 0 to 2,000 iterations. Screw dislocation orientations were chosen
503 following those determined by Skrotzki⁵⁷ for enstatite: [100] for (100) and (210) faces, [010]
504 for the (010) face and [001] for the (001) face. These results were obtained using the set of
505 bond-breaking probabilities corresponding to the best agreement between the modeled and
506 measured steady-state face-specific dissolution rates.

507 Etch pits growing on the (100) face were found to be lenticular and symmetric with
508 respect to the b - and c -axes, respectively (cross-sections 1 and 2). Their aspect ratio evolves
509 as a function of the reaction progress, as their length following the c -axis increases faster than
510 along the b -axis. In addition, they exhibit a single lower point that may result from a slow step
511 propagation (and thus, difficult pit opening), as suggested by the shape of their bottom along
512 the c -axis. The bottom of the pits developed on the (100) face are surrounded by steep pit
513 walls ($\theta \approx 93^\circ \pm 1^\circ$ between the surface and pit walls).

514 The morphology of etch pits growing on the (010) face displays similar features
515 (elongated following the c -axis, and symmetric with respect to the a - and c -axes, with similar
516 length and width (≈ 5 -10 nm) after 2,000 iterations), although the pits are deeper (≈ 20 nm
517 against ≈ 10 -15 nm after 2,000 iterations) and thinner than those developed on the (100) face.
518 Of note, their growth rate is lower than that of pits developed on the (100) face. The bottom of
519 the pits developed on the (010) face is surrounded by steep pit walls ($\theta \approx 95^\circ$ between the
520 surface and pit walls).

521 The morphology of etch pits growing on the (210) face is similar to that of etch pits
522 developed on (100) and (010) faces. However, their lenticular shape is not as well defined and
523 approaches that of a half-moon: indeed, one edge of the pit subparallel to the c -axis is
524 straighter than the other, which is more curvilinear. In addition, whereas the deepest point of
525 pits modeled on (100) and (010) faces is located at the center of the pit, the pits developed on
526 the (210) face are asymmetric (see cross- section 7) and the deepest point (3-4 nm) is located
527 at the center of the pit following the c -axis, but shifted on one edge of the minor-axis ($[-210]$).

528 Finally, although no etch pit could be evidenced experimentally on (001) faces, the
529 model predicts that small (≈ 10 nm) and deep (> 40 nm) subcircular etch pits may grow on the
530 (001) face if screw dislocations parallel to the c -axis are implemented. However, unlike the
531 other faces, etch pits developed on the (001) face reach a stable radius or tend to vanish, as a
532 result of the increasing roughness of the surrounding surface, possibly explaining why such
533 etch pits remained out of reach of our analytical characterizations.



534

535 **Fig. 7.** Evolution of modeled etch pits and associated cross-sections following the directions depicted by the
 536 dotted lines. For all pictures, magenta, red, green and blue colors stand for the results obtained for (100), (010),
 537 (001) and (210) faces.

538

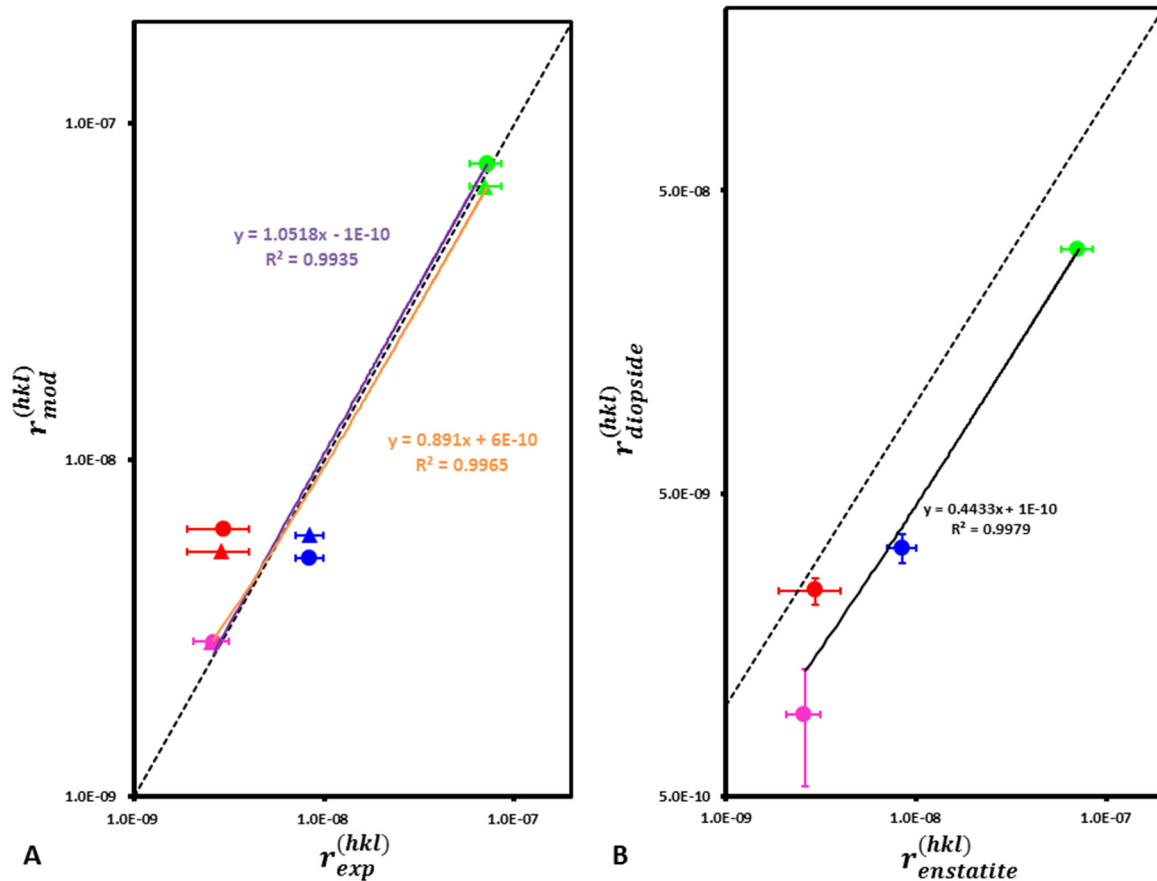
539 4. Discussion

540 4.1 Factors influencing the face-specific dissolution rates of enstatite and comparison 541 with previous studies

542 As reported above, the face-specific dissolution rates of enstatite range between 2.6
 543 and 71.8 nmol/m²/s at pH 0 and $T = 90$ °C. These values are between one and two orders of
 544 magnitude lower than expected using the dissolution rate law derived from powder

545 dissolution experiments conducted by Oelkers⁶⁸ (between 730 and 973 nmol/m²/s), which
546 represents the largest enstatite dissolution kinetics dataset that we are aware of. Such
547 discrepancies may either be ascribed to the contribution of edges and corners, whose
548 reactivity is much greater than that of faces^{13, 46} and which are overrepresented when using
549 powders. It may also be due to the very low pH investigated in the present study, which may
550 result in a saturation of proton surface sites⁶⁹, possibly leading to a weaker pH-dependence of
551 silicate dissolution rate than expected in the extreme acidic pH domain. In any case, the
552 present study illustrates the unsuitability of isotropic dissolution rate laws derived from
553 powder dissolution experiments to predict the amplitude and absolute values of face-specific
554 dissolution rates, as pointed out in previous studies^{15, 21, 70}.

555 The results show that the dissolution rate of the (001) face is about one order of
556 magnitude greater than that of the other investigated (*hk0*) faces. Among these latter faces, the
557 dissolution rates of the (100) and (010) faces are similar within uncertainties, and are about
558 three times slower than that of the (210) face. If one considers the crystallographic similarities
559 existing between the (110) face of diopside and the (210) face of enstatite (both faces
560 correspond to the cleavage plane of these minerals, and intersect the highest density of Mg-O-
561 Si bonds), these results are in excellent agreement with those obtained on diopside
562 (Ca_{0.5}Mg_{0.5}SiO₃)¹⁸, which also belongs to the pyroxene group (Fig. 8B). Note however that
563 the anisotropic reactivity of enstatite seems to be less pronounced than that of diopside. This
564 is likely due to the presence of Ca ions in the diopside structure, which offers more
565 combinations for the bond-breaking probabilities (and therefore, detachment rates) of Mg and
566 Si atoms. Indeed, the hydrolysis rates of Ca-O-Si and Ca-O-Ca bonds are faster than that of
567 Mg-O-Si and Mg-O-Mg bonds, as demonstrated experimentally⁷¹ and indirectly confirmed
568 theoretically following *ab initio* calculations³⁸.



569

570 **Fig. 8.** A. Best agreement between modeled and measured face-specific enstatite dissolution rates. The triangles
 571 and circles stand for simulations conducted with and without dislocations, respectively. Note that the modeled
 572 dissolution rate of the (001) face is also affected because the time for one iteration changes as a function of the
 573 mean ratio between experimental and modeled dissolution rates (Eq. 7). B. Comparison between enstatite and
 574 diopside¹⁸ face-specific dissolution rates. For both graphs, magenta, red, green and blue colors stand for the
 575 results obtained for (100), (010), (001) and (210) faces, respectively.

576

577 The factors that are most frequently invoked to account for the anisotropy of silicate
 578 dissolution include (i) the crystallographic bonding structure and in particular, the
 579 connectedness of silicate tetrahedrons^{18, 23, 72} (ii) the dislocation density and orientation^{18, 21, 23,}
 580 ⁷³⁻⁷⁴ and (iii) the formation of ASSLs, whose transport properties may differ as a function of
 581 the crystallographic orientation^{18, 20, 23}.

582 Considering the conditions that are thought be required for the development of
583 passivating ASSLs (i.e., oxic conditions and mildly acidic pHs, see [20, 23, 75-76](#)), the latter factor
584 (iii) can be safely ruled out in the present study.

585 Unravelling the relative contributions of factors (i) and (ii) to the observed anisotropic
586 reactivity may benefit from the comparison between the outputs of the simulations and the
587 experimental results. When the simulations are run without implementing any dislocation in
588 the enstatite structure, the reactivity of the (001) face is strikingly greater than that of the other
589 ($hk0$) faces, as observed experimentally (Fig. 6). Therefore, this suggests that the
590 connectedness of silicate tetrahedrons dictates the anisotropic reactivity of enstatite at first
591 order: as previously pointed out by Daval et al.¹⁸, the release of Si atoms from the (001) face
592 to the solution requires the cleavage of one Si-O-Si bond only, while it would require the (less
593 likely) simultaneous cleavage of two Si-O-Si bonds on the ($hk0$) faces, which are parallel to
594 the silicate tetrahedron chains.

595 The connectedness of SiO_4 tetrahedrons cannot be invoked to distinguish between the
596 reactivity of the three other investigated ($hk0$) faces, because it is the same for all of them.
597 However, because the outputs of the simulations show that the dissolution rates of these three
598 faces are different even without implementing any dislocation, this suggests that the
599 crystallographic bonding structure also exerts a strong control on the face-specific reactivity.
600 As it can be seen in Fig. 1, the Mg and Si atoms are organized following planes that are
601 parallel to the (100) face. If one supposes that the detachment rate of Si atoms connected to
602 two other Si atoms is lower than that of Mg atoms (in agreement with the respective
603 activation energies for the hydrolysis of Si-O-Si, Si-O-Mg and Mg-O-Mg bonds, see section
604 2.3.1), it can be assumed that the progression of the dissolution in the [100] direction will be
605 hampered by the sluggishness of the dissolution of these Si-rich planes. Conversely, the
606 detachment of accessible Mg atoms located below the first atomic plane of the (010) face may

607 contribute to destroying the first coordination spheres of the topmost Si atoms, which
608 eventually increase their probability of detachment. In turn, this explanation would account
609 for the fact that the slowest dissolving face is (100), and the dissolution rates inferred from the
610 simulations therefore observe the following trend: $r_{mod}^{(100)} < r_{mod}^{(210)} < r_{mod}^{(010)} \ll r_{mod}^{(001)}$, the
611 (210) face representing an intermediate configuration between the (100) and (010) faces.

612 Finally, these simple crystallographic considerations do not account for the
613 observation that the dissolution rate of the (210) face is greater than that of the (010) face.
614 Interestingly, running the simulations with the appropriate dislocation density measured
615 experimentally allows to obtain a global trend for the face-specific reactivity of enstatite
616 which matches exactly to that measured experimentally, with $r_{mod,exp}^{(100)} < r_{mod,exp}^{(010)} < r_{mod,exp}^{(210)}$
617 $\ll r_{mod,exp}^{(001)}$ (see details in section 4.2). These results confirm the critical contribution of
618 dislocations to mineral dissolution rates (e.g., 9, 21, 74, 77-78).

619 To sum up, both the crystallographic bonding structure and the presence of crystal
620 defects (and in particular, dislocations) contribute to the observed anisotropic reactivity of
621 enstatite, in agreement with previous studies dedicated to the face-specific dissolution rates of
622 minerals.

623

624 ***4.2 Assessing the agreement between measured and simulated rate data***

625 A total of 45 sets of activation energies for the thermally activated probabilities of
626 breaking Mg-O-Mg, Mg-O-Si and Si-O-Si bonds were tested to cover the possible range of
627 hydrolysis described in section 2.3.2. Three different complementary metrics were used to
628 evaluate quantitatively the agreement between simulation outputs and experimental results:
629 classical metrics such as the relative root mean square error (*RRMS*) and the relative mean
630 error (*RME*), and an additional original metrics (*Sal*) based on a linear combination of the

631 slope and the intercept of the line of best fit, i.e., the line obtained through linear regression
 632 between modeled dissolution rates vs. measured dissolution rates. These metrics are defined
 633 by:

$$RRMS = \frac{1}{N_E} \sqrt{\sum_{n=1}^{N_E} \left(\frac{r_{mod}^{(hkl)n} - r_{exp}^{(hkl)n}}{r_{exp}^{(hkl)n}} \right)^2}$$

$$RME = \frac{1}{N_E} \sum_{n=1}^{N_E} \frac{r_{mod}^{(hkl)n} - r_{exp}^{(hkl)n}}{r_{exp}^{(hkl)n}} \quad (8)$$

$$Sal = abs(1 - a) + abs\left(\frac{b}{\langle r_{exp}^{(hkl)} \rangle}\right)$$

634 where $r_{exp}^{(hkl)}$ (resp. $r_{mod}^{(hkl)}$) is the dissolution rate for face (hkl) estimated experimentally (resp.
 635 by the model), N_E is the number of experimental values (4 in our case), a is the slope of the
 636 best fit line, b is the intercept of the best fit line and $\langle r_{exp}^{(hkl)} \rangle$ the average of all
 637 experimental dissolution rates.

638 The *RRMS* index indicates how spread out are the differences between the modelled
 639 values and the observed values or how close are, in average, these differences around the line
 640 of best fit. The *RME* index allows detecting possible bias, i.e., if *RME* is significantly greater
 641 than 0 (resp. lower than 0), the model overestimates (resp. underestimates) the observed
 642 values. The information provided by the best fit line is gathered in the *Sal* index. Because of
 643 differences in units (a is dimensionless, b has the dimension of the dissolution rate), the
 644 second term of *Sal* is divided by $\langle r_{exp}^{(hkl)} \rangle$. We used this reference for model performance
 645 comparisons because it is a common reference for all data.

646 *RRMS-RME* indices and the *Sal* index provide different kinds of information. Any set
 647 of probabilities (or their corresponding activation energies) that minimizes the *RRMS* and
 648 *RME* indices does not necessarily minimizes the *Sal* index as well (e.g., the set of

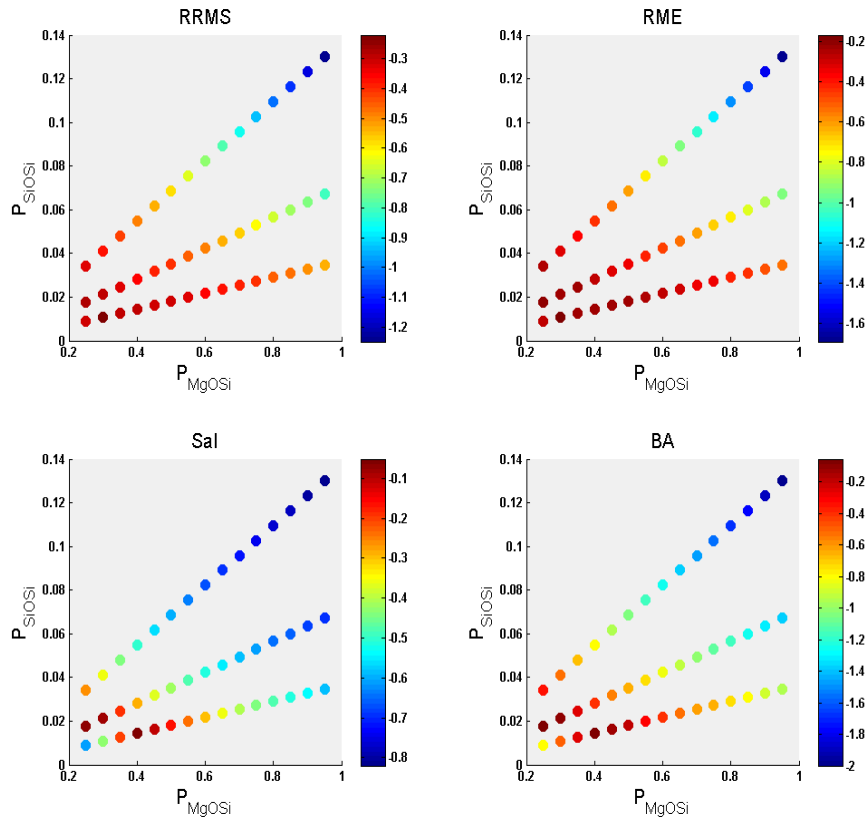
649 probabilities that minimizes the *RRMS* and *RME* indices is [$P_{MgOMg} = 0.99$, $P_{SiOMg} = 0.3$ and
650 $P_{SiOSi} = 0.0109$] ($RRMS = 22\%$ and $RME = 17\%$), whereas it overestimates the dissolution rate
651 anisotropy ($SaI = 0.52$). On the other hand, the set that allows for the best SaI is [$P_{MgOMg} =$
652 0.99 , $P_{SiOMg} = 0.40$ and $P_{SiOSi} = 0.0146$] ($SaI = 0.06$), corresponding to *RRMS* and *RME* of
653 30% and 22% , respectively). In order to compare the 45 sets of probabilities, we finally
654 defined a composite metric that we called best agreement (*BA*) for each set i by the following
655 formulation:

$$BA_i = \frac{1}{2} \left(\frac{RRMS_i - \min(RRMS)}{\max(RRMS) - \min(RRMS)} + \frac{RME_i - \min(RME)}{\max(RME) - \min(RME)} \right) + \frac{SaI_i - \min(SaI)}{\max(SaI) - \min(SaI)} \quad (9)$$

656 In this formulation, the three metrics are scaled by their max-min values, and we balanced the
657 classical metrics *RRMS* and *RME* with the new metric SaI . Other formulations could have
658 been used for *BA* but we privileged the balanced linear formulation that is more robust than
659 other formulations based on single values like min-max values. Due to the small number of
660 experimental data, more sophisticated composite metrics would have been questionable.
661 Following this formulation, the smallest the *BA*, the better is the agreement between
662 experimental dissolution rates and simulated dissolution rates.

663 Based on the *BA* metric, only a narrow range of probabilities provided a satisfactory
664 agreement between simulation outputs and experimental data (Fig. 9) and one set of
665 probabilities ($[P_{MgOMg} = 0.99$, $P_{SiOMg} = 0.4$; $P_{SiOSi} = 0.0146]$) yielded the lowest value of *BA*
666 ($BA = 0.05$). This set has been selected to further discuss the outputs of the simulations below,
667 although it is noteworthy that a couple of sets of probabilities also returns similarly low *BA*
668 values (e.g., the two sets of probabilities [$P_{MgOMg} = 0.99$, $P_{SiOMg} = 0.25$; $P_{SiOSi} = 0.0177$] and
669 [$P_{MgOMg} = 0.99$, $P_{SiOMg} = 0.3$; $P_{SiOSi} = 0.0212$] correspond to *BA* values of 0.07 and 0.09,

670 respectively), pointing towards the existence of a narrow range of possible P_{MgOSi} and P_{SiOSi}
 671 (and therefore, of $\Delta E_{Si-O-Si} - \Delta E_{Si-O-Mg}$ and $\Delta E_{Mg-O-Mg} - \Delta E_{Si-O-Mg}$) values.



672
 673 **Fig. 9.** Color maps of the agreement between modeled and measured dissolution rates in regards to the sets of
 674 probabilities that have been tested. The browner the color, the better agreement. See section 4.2 for a description
 675 of the *RRMS*, *RME*, *Sal* and *BA* indices.

676
 677 The discrepancies between the results of the simulations conducted with and without
 678 dislocations are shown in Fig. 8A. As mentioned above, the main impact of the
 679 implementation of the right dislocation density for the (100), (010) and (210) faces consists in
 680 an inversion between the reactivities of the (210) and (010) faces. Whereas the face-specific
 681 dissolution rates observe the following trend without dislocations : $r_{mod}^{(100)} < r_{mod}^{(210)} < r_{mod}^{(010)} \ll$
 682 $r_{mod}^{(001)}$, it becomes $r_{mod}^{(100)} < r_{mod}^{(010)} < r_{mod}^{(210)} \ll r_{mod}^{(001)}$ when dislocations are added, in good
 683 agreement with the experimental measurements. In detail, the implementation of dislocations
 684 increased the dissolution rates of the (210) and (100) faces, while the reactivity of the (010)

685 face remains unaffected, probably because of the low dislocation density observed on this
686 face. Finally, the outcropping of dislocations at the surface of the (001) face has not been
687 considered, since it was not possible to evidence etch pits on the corresponding samples. Of
688 note, the implementation of dislocations also has an impact on the agreement between
689 simulation outputs and experimental results. Whereas the implementation of dislocations tend
690 to minimize the *RRMS* and *RME* values (*RRMS* = 22% and *RME* = 13% with dislocations vs.
691 *RRMS* = 30% and *RME* = 22% without dislocations), this also results in a modest increase of
692 the *SaI* (*SaI* = 0.11 vs. *SaI* = 0.05), implying that the dissolution rate anisotropy becomes
693 slightly underestimated. Overall, it can be concluded that adding dislocations to the model
694 slightly improves the general agreement between simulation outputs and experimental results
695 in terms of *RRMS* and *RME* but slightly degrades the account for the anisotropy of dissolution
696 rates (increase of the *SaI* value). However, the *BA* index remains unaffected (*BA* = 0.06 in
697 both cases), which indicates that for this set of probabilities, the simulations conducted with
698 dislocations are statistically equivalent to those run without dislocations.

699 To sum up, the model satisfactorily accounts for enstatite face-specific dissolution
700 rates measured experimentally, using bond-breaking probabilities consistent with what can be
701 inferred from literature. Moreover, adding dislocations to the simulations in proportions that
702 are consistent with the analytical characterizations allows one to reproduce the order of the
703 face-specific dissolution rates observed experimentally.

704 ***4.3 Comparison between observed and modeled etch pits and related implications for*** 705 ***enstatite dissolution mechanisms***

706 The improvement of the agreement between modeled and experimental dissolution
707 rates is not the only interesting output resulting from the implementation of dislocations in the
708 simulated crystals. It also offers the possibility to compare the morphology of simulated etch
709 pits developed at the dislocation outcrop to their counterparts revealed by electron microscopy

710 on the different faces of enstatite (Fig. 4). This represents an aspect of great interest, as it is
711 regularly searched for as a tracer of weathering conditions⁷⁸⁻⁸⁰.

712 Interestingly, both the lenticular shape, the orientation and the symmetry of the pits
713 generated numerically on (100) and (010) faces using the best set of probabilities (see
714 previous section) are consistent with those observed experimentally. The simulated and
715 experimentally observed pits are very elongated along the *c*-axis and their minor-axes follow
716 either the [010] (for pits developed on (100) faces) or the [100] (for pits developed on the
717 (010) faces) direction, respectively. These directions also represent symmetry axes for the
718 pits, resulting in the existence of a symmetry point at their center. The TEM characterizations
719 performed on the FIB thin section realized on the altered (010) and (100) faces further
720 indicate that the angle formed by the pit walls with the surface are in good agreement with the
721 outputs of the simulations.

722 A noticeable difference revealed by the model between the pits developed on the (100)
723 and (010) faces consists in the shape of their bottoms following the *c*-direction (Fig. 7). These
724 differences may be ascribed to the crystallographic structure of enstatite. Indeed, while the
725 deepening of pits formed on the (100) face requires to sequentially intersect Si-rich and Mg-
726 rich planes, the deepening of pits formed on the (010) face entails that the dissolution takes
727 place in a single plane, resulting in a faster opening of the corresponding pits. This may
728 explain why modeled etch pits formed on the (010) face are flat-bottomed in the *c*-direction,
729 as opposed to the pits formed on the (100) face, since the propagation of the dissolution
730 following the *c*-axis will be easier in the case of the (010) face than the one of the (100) face.
731 Supporting this assertion, the sequential removal of Mg atoms from Mg-planes, which are
732 readily accessible for pits formed on (010) faces, will result in lowering the coordination of Si
733 atoms in the Si-planes, thereby accelerating the global propagation of the pit along the *c*-axis.
734 Such a mechanism is not possible for pits developed on the (100) face, where the widening of

735 a pit involves dissolving Mg- and Si-rich planes sequentially. Finally, it is noteworthy that
736 these differences in terms of pit morphology, which follow from the anisotropic structure of
737 enstatite, also result in a difference of reactivity of the pits themselves, with pits developed on
738 the (010) faces being more effective to enhance enstatite dissolution than those developed on
739 the (100) faces. Finally, TEM observations reveal that etch pits nucleated on the (100) face
740 are flat-bottomed following their minor axis ($[010]$), a feature that is not accurately
741 reproduced by the model. Possible explanations for this observation include the fact that etch
742 pits revealed experimentally may have investigated at a greater reaction progress than the
743 modeled ones, which result in a widening of the pit in the b -direction.

744 Regarding the modeled pits formed on the (001) face, their main features consist in
745 their narrow subcircular shape (5 nm) and important depth (> 20 nm). As reported above, the
746 simulations reveal that the diameter of the simulated pits never exceeds 5 nm because of the
747 gradual and global roughening of the surface, which may explain why no etch pits were
748 observed by VSI, SEM or TEM on the (001) samples altered experimentally. The absence of
749 a continued lateral growth of the pits in the (001) plane also suggests that dislocation etch pits
750 form on the (001) face (if any) have a negligible contribution to the dissolution rate of this
751 face.

752 The pits that have been simulated on the (210) face are different from the ones
753 simulated on the (100) and (010) faces. Their shape approaches that of a crescent, with one
754 straight edge along the c -axis on one side and a curvilinear edge on the other side. This shape
755 is consistent with that revealed experimentally for (210) samples (see Fig. 4), and very similar
756 to the one observed for pits developed on the (110) and $(1\bar{1}0)$ faces of diopside by Daval et
757 al.¹⁸. The topography profile of the pits following the c -axis is similar to the one observed on
758 the (100) face, with a deepest point ($\approx 2.0 - 2.5$ nm) located at the center of the pit. The main
759 difference between the pits simulated on this face and those simulated on the (100) and (010)

760 faces is revealed when considering the topography profile of the pit following the minor-axis,
761 which is strongly asymmetric. Whereas the angle between the (210) surface and the pit wall at
762 the straight edge is very steep ($\theta \approx 95^\circ$), the other one is much less sharp ($\theta \approx 113^\circ$). Although
763 it was not possible to get a FIB foil across a single etch pit nucleated on the (210) face, it is
764 worth mentioning that this asymmetry was also observed for pits developed on the (110) face
765 of diopside (see atomic force microscopy (AFM) measurements in ¹⁸). This asymmetry is due
766 to the fact that the direction of the dislocation is not orthogonal to the (210) face. An
767 interesting consequence of this specific geometry is that the entire simulated pit is not visible
768 in Fig. 7, since part of the pit is located below the surface of the face. Such features may
769 correspond to the so-called “etch tubes”⁷⁷ or “etch tunnels”⁸¹ sometimes reported in the
770 literature, which cannot be imaged using classical surface sensitive techniques such as VSI or
771 AFM.

772 Finally, the pit geometry revealed by the numerical simulations also has broader
773 consequences for the practical measurement of crystal dissolution rates. As can be seen in Fig.
774 6D, the dissolution rate of the (210) face based on Mg release exceeds that calculated using
775 the overall surface topography. Such a “hidden” contribution to crystal reactivity may help
776 explain why face-specific mineral dissolution rates determined from solution chemistry
777 measurements sometimes overestimate dissolution rates estimated using surface sensitive
778 techniques, such as VSI²⁴. Furthermore, considering that the dislocation network in crystals
779 can be connected to the surface as a result of pit opening, intra-crystalline dissolution may
780 occur. A detailed understanding of the solution chemistry within single pits then becomes
781 crucial, since concentration gradients can affect the reactivity of the etch pit⁷⁸.

782 To sum up, the etch pits modeled on (100), (010) and (210) are very similar to the
783 ones observed on enstatite samples. The orientation, shape, and symmetry of the pits are

784 correctly predicted by the model, and result from the crystallographic structure of enstatite
785 and orientation of dislocation lines.

786 *4.4 Relation between the dissolution regime and the formation of Si-rich surface layers*

787 As shown in Fig. 6, the transient regime, which is characterized by a non-
788 stoichiometric release of Mg and Si atoms and a variable dissolution rate, spans over 7,500 to
789 8,250 iterations (depending on the considered face) corresponding to 2.7 ± 1.0 to 2.9 ± 1.0
790 days, when the best set of probabilities is selected (section 2.3.6). This result suggests that the
791 dissolution rates estimated experimentally for the (100), (010) and (210) faces were actually
792 measured during the steady-state regime, where the dissolution is stoichiometric and the rate
793 is constant, and may explain why the very first VSI measurements of surface retreats
794 conducted on the (100) and (010) faces fall slightly below the regression trend line.
795 Conversely, part of the measurements carried out on the (001) faces might have been
796 performed during the transient regime, although this assertion is not supported
797 experimentally, since the measured surface retreats observe a linear temporal trend. This
798 result is not totally surprising, considering the expected modest evolution of the dissolution
799 rate with time inferred from the numerical outputs of the simulation for this face (Fig. 6),
800 which would imply that any deviation from the linear trend would fall within experimental
801 uncertainties.

802 From a physical standpoint, the model outputs suggest that the transient regime
803 corresponds to the period where the number of surface atoms increases. The number of atoms
804 at the surface increases by a 2.5-, 2.8-, 3.5-, and 80 fold-factor for the (100), (210), (010) and
805 (001) faces, respectively. After this transient regime, the number of each surface cation
806 reaches a constant value, resulting in a steady-state dissolution rate. Prior to reaching the
807 steady-state regime, the dissolution rates based on Mg or Si release have opposite trends:

808 while the Mg release rate decreases, enstatite dissolution rate based on Si release increases
809 with time.

810 The attainment of a steady-state regime thereby appears intimately connected to the
811 dynamics of Si release, which can be explained by the large differences existing between the
812 detachment rates of Mg and Si atoms: the preferential detachment of Mg atoms will result in a
813 depletion of the first coordination sphere of Si atoms, in turn increasing their release rates.
814 The simultaneous attainment of a constant dissolution rate and a constant number of Si
815 surface atoms for the 4 faces further suggests that the mean coordination of Si surface atoms
816 also reached a steady-state after the transient regime.

817 This divergence in the dynamics of Si and Mg release has another important
818 consequence: during the transient regime, the simulations predict that the preferential release
819 of Mg atoms results in the formation of an Mg-depleted / Si-rich surface layer. According to
820 the simulation outputs, the thickness of the leached layer is 3.8, 6.0, 6.9 and 107 Å for (100),
821 (210), (010), and (001) faces, respectively. Interestingly, the model therefore predicts that
822 thick surface layers should develop on the (001) face, whereas they should be much thinner
823 on (*hk*0) faces, which is consistent with the TEM results described in section 3.3, and the
824 results reported by Daval et al.¹⁸ for diopside dissolution. However, the model systematically
825 underestimates the actual thickness of the layer, which may be ascribed to the fact that it
826 neither accounts for (i) the spontaneous reorganization of the Mg-depleted layer, such as the
827 condensation of silanol groups, which may be associated to a global variation of the volume
828 of the surface layers, as suggested in previous studies (e.g. ⁸²⁻⁸³); nor for (ii) the backward
829 reactions of Si attachment to the surface layer, following the alternative interfacial
830 dissolution-reprecipitation mechanism^{26, 60-61, 84}. Here, and as emphasized in previous kMC
831 studies⁶², the outputs of the model indirectly support that the preferential alkali / alkaline earth

832 depletion during silicate dissolution is limited to the topmost layers of the minerals, and that
833 ASSL formation should, *at least partly*, result from Si redeposition²³.

834 To sum up, the comparison between the experimental data and the simulation outputs
835 suggests that the duration of the transient period is reasonably well reproduced by the model.
836 In addition, the model predicts the formation of Mg-depleted / Si-rich layers, although their
837 actual thickness remains underestimated. This latter result indirectly reveals that certain
838 mechanisms that are not accounted for by the model (e.g. Si attachment reactions;
839 condensation of silanol groups) actually occur over the course of enstatite dissolution.

840

841 **5. Conclusions and perspectives**

842 In this study, we focused on the agreement between the outputs of stochastic atomic-
843 scale dissolution simulations and the results obtained on face-specific enstatite dissolution
844 experiments carried out at 90 °C and pH 0 (rate data and structural observations of the faces).
845 Nearly 200 simulations were conducted to demonstrate that the anisotropy of enstatite
846 dissolution rate can be satisfactorily reproduced using bond-breaking probability ratios (and
847 therefore, activation energy differences) that are consistent with the existing literature
848 regarding the hydrolysis of Mg-O-Mg, Mg-O-Si and Si-O-Si bonds. On the same footing, the
849 model also correctly predicts various face-specific features, such as the orientation, symmetry,
850 and shape of dislocation etch pits. From a physical chemistry standpoint, this agreement gives
851 rise to the following two perspectives with respect to silicate dissolution and the silicate-water
852 interface:

853 (i) Nowadays, *ab initio* calculations are generally used to feed kMC simulations (e.g. ^{9,}
854 ^{22, 45}). Conversely, our study suggests that kMC simulations have the ability to be a powerful
855 tool to constrain a range of activation energies for the hydrolysis of bonds that are not

856 available in the current literature, and/or to validate the values resulting from *ab initio*
857 calculations. For instance, the value of $\Delta E_{Mg-O-Mg}$ we used was selected from an experimental
858 work⁵⁵, because to the best of our knowledge, no study provided a theoretical value for this
859 parameter. If the agreement between modeled and simulated rates and etch pit geometry is
860 taken for granted, it could be immediately transposed to the diopside structure, for which far-
861 from-equilibrium rate data already exist¹⁸, making possible the determination of a possible
862 range for parameters such as $\Delta E_{Mg-O-Ca}$, $\Delta E_{Ca-O-Ca}$ or $\Delta E_{Ca-O-Si}$ (note that *ab initio* data already
863 exist for this latter parameter, see ³⁸). This will be the subject of an upcoming paper.

864 (ii) On the same footing, a similar approach could be usefully transposed to other
865 silicate structures for which rate data already exist (see ⁷¹, which report far-from-equilibrium
866 rate data for a series of eight endmember orthosilicate minerals (M_2SiO_4) which varied only
867 by the nature of the divalent cation M they contain).

868 Conversely, we showed that the model underestimates the thickness of ASSLs formed
869 on the various faces of enstatite. In itself, this result already provides insights into the
870 dynamics of the dissolution process, as previously pointed out by Zhang and Lüttge⁶²: thick
871 (i.e., several 10s of nm) ASSLs cannot be formed by a pure leaching mechanism only. This
872 indicates where future kMC efforts should be directed, as the formation, growth and
873 maturation of such layers are regularly suggested to influence the reactivity of the underlying
874 substrate, at least in $SiO_2(aq)$ rich solutions and mildly acidic pHs^{20, 31, 75-76}.

875

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882

883 **References**

884

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