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1 Physical Properties of Interfacial Layers Developed  
2 on Weathered Silicates: a Case Study Based on  
3 Labradorite Feldspar

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19

20 ABSTRACT

21 Amorphous silica-rich surface layers (ASSLs) formed at the interface between silicate materials  
22 and reacting fluids are known to strongly influence, at least in some cases, the dissolution rates  
23 of silicate phases including soil minerals, glasses, and cements. However, the factors governing  
24 the formation of these ASSLs remain largely unknown. Here, we outline a novel approach that  
25 uses recent developments in vertical scanning interferometry (VSI) and in-situ synchrotron-based  
26 X-ray reflectivity (XRR) to directly follow the development of ASSLs, and the evolution of their  
27 physical properties, on a model silicate (labradorite feldspar). Our approach enabled  
28 independently probing the reactivities of the outer (bulk fluid/ASSL) interface and of the inner  
29 (ASSL/pristine mineral) interface *in-situ*, providing a detailed picture of the temporal evolution  
30 of the fluid-mineral interface. We investigated the effects of pH, SiO<sub>2</sub>(aq) concentration,  
31 crystallographic orientation, and temperature on the layer thickness, density, and reactivity as  
32 well as on the dissolution rate of the primary mineral. The dissolution rate of labradorite crystals  
33 increased with temperature, according to an apparent activation energy of ~57 kJ mol<sup>-1</sup> and  
34 showed no significant difference between crystallographic faces. Both labradorite and ASSL  
35 dissolution rates decreased as circum-neutral pH conditions were approached. High SiO<sub>2</sub>(aq)  
36 concentrations resulted in (i) decreased apparent dissolution rates, while far-from-equilibrium  
37 conditions with respect to labradorite were maintained in the bulk fluid, and (ii) an increasing  
38 ASSL density when combined with low temperature and close-to-neutral pH. Our results  
39 highlight the importance of ASSLs and their complex impact on the dissolution process. In  
40 particular, our results provide evidence of a discrepancy between bulk fluid conditions, generally  
41 probed and reported, and those actually operating at the interface with the dissolving primary

42 phase, which are of more direct relevance to the dissolution process but are still largely  
43 unknown.

44

45

## 46 INTRODUCTION

47 Amorphous silica-rich surface layers (ASSLs) are hydrated, nanoporous, metastable  
48 phases that form at the interface between reactive fluids and a variety of silicate materials  
49 including olivine<sup>1-4</sup>, wollastonite<sup>5-9</sup>, feldspars<sup>10-14</sup>, and glasses<sup>15-18</sup>. These layers, also called  
50 surface alteration layer (SAL), form ubiquitously from laboratory to field settings<sup>19-21</sup>. They play  
51 a key role in controlling the dissolution rates of silicate materials with important implications for  
52 several critical environmental and societal challenges including the degradation of cement  
53 infrastructure<sup>22</sup>, the long-term storage security of nuclear waste<sup>18,23</sup>, and the feasibility of  
54 enhancing silicate weathering as a large-scale CO<sub>2</sub> capture technology<sup>24,25</sup>.

55 While the existence of ASSLs has been known or hypothesized for at least 80 years<sup>26</sup>,  
56 the mechanisms underlying their formation and their influence on the dissolution rate of the  
57 primary material remain poorly understood. This lack of mechanistic understanding is illustrated  
58 by two fundamental disagreements. The first of these concerns whether ASSLs form by leaching  
59 of soluble elements (e.g., Ca, K, Mg, Na) from the primary mineral or, alternatively, by  
60 dissolution of the primary mineral followed by precipitation of an amorphous Si-rich phase. The  
61 first hypothesis (referred to as the “leached layer” hypothesis) has represented the prevailing  
62 paradigm for decades<sup>27,28</sup>. It is consistent with ion and photon probe results suggesting that the  
63 elemental profiles of reactive species and reaction products are anticorrelated within the ASSL  
64<sup>29-38</sup>. The alternative “dissolution-reprecipitation” hypothesis<sup>39</sup> is supported by transmission

65 electron microscopy observations that indicate an absence of compositional gradients within the  
66 ASSL<sup>13</sup> and atom-probe tomography measurements of altered glass samples that reveal an  
67 atomically sharp inner interface {Gin, 2017; Hellmann, 2015}, which has led to the suggestion  
68 that the compositional gradients observed in the ion and photon probe results may be artifacts  
69 associated with low lateral resolution<sup>20</sup>. It is also supported by indirect evidence, in some cases,  
70 of fluid-mineral interactions occurring through the layer and of mineral dissolution at the  
71 interface between the ASSL and the pristine mineral surface<sup>40</sup>, due to the presence of a thin fluid  
72 film at the inner interface {Hellmann, 2012}.

73         The second fundamental disagreement concerns the extent to which the ASSL behaves as  
74 a barrier to transport. The historical approach assumes that the dissolution rate of the pristine  
75 silicate mineral surface follows transition state theory (TST) and depends only on the chemistry  
76 of the bulk aqueous solution<sup>41</sup>. This “primary dissolution control” approach was based on  
77 studies where the presence of ASSLs had little or no effect on the dissolution rate or where  
78 evidence of diffusive processes was dismissed as experimental artefacts<sup>10,42-44</sup>. While challenged  
79 more than 20 years ago by both contradictory experimental results<sup>45,46</sup> and theoretical  
80 inconsistencies<sup>47,48</sup>, this hypothesis is still widely used in reactive transport codes. An important  
81 alternative (referred to as the “ASSL dissolution control” approach) consists in applying TST  
82 while treating the thermodynamic properties of the ASSL (rather than the primary mineral) as a  
83 driver of the overall weathering process<sup>45,49-53</sup>. In essence, this approach treats the ASSL as an  
84 activated complex in the sense of TST, the experimental verification of which is still a subject of  
85 debate<sup>54</sup>. A second important alternative (referred to as “primary dissolution and transport  
86 control”) suggests that, in addition to the dissolution of the primary mineral, transport limitations  
87 to the diffusion of reactive species across the ASSL must also be accounted for<sup>9,18,55-59</sup>.

88           One reason for the existence of competing modeling frameworks outlined above is the  
89 relatively limited availability of dissolution data relative to the vast range of conditions to be  
90 explored in terms of silicate mineral chemistry, aqueous chemistry, and temperature. For  
91 example, with the notable exception of results obtained on wollastonite over a wide pH range<sup>20</sup>,  
92 most studies supporting the hypothesis that chemical affinity between the bulk fluid and the  
93 primary mineral plays an important role were performed under low pH conditions, which favor  
94 the formation of non-passivating layers<sup>14</sup>, similar to the work by Lagache<sup>10</sup> more than 40 years  
95 ago. Similarly, parameters such as the redox potential of the solution that have not been  
96 systematically examined may have a direct impact on ASSL texture and resulting diffusivity<sup>60-</sup>  
97 <sup>62</sup>. In short, competing interpretations regarding the mechanism and impact of ASSL formation  
98 on the overall silicate dissolution rate for identical materials (e.g., Schott, et al.<sup>8</sup> vs. Ruiz-  
99 Agudo, et al.<sup>7</sup> or Hellmann, et al.<sup>63</sup> vs. Gin, et al.<sup>18</sup>) may simply reflect differences in reacting  
100 conditions combined with insufficient knowledge of the thermodynamic and transport properties  
101 of ASSLs.

102           The upshot of this is that an improved understanding of the fundamental properties of  
103 ASSLs is likely key to resolving the disagreements outlined above<sup>25,64</sup>. Existing data on the  
104 properties of ASSLs remains relatively limited for several reasons. First, standard dissolution  
105 experiments yield relatively low accuracy estimates of the growth rate of the ASSL as quantified  
106 indirectly from small deviations between the stoichiometric composition of released elements  
107 and that of the pristine solid. Second, reconstructions of mineral dissolution rates and ASSL  
108 thickness from elemental release data are challenged by uncertainties related to the specific  
109 surface area of the reactive interface, typically estimated as the Brunauer-Emmett-Teller (BET)  
110 surface area of the fresh mineral powder<sup>65</sup>. Such normalization may not account for the temporal

111 evolution of reactive surface area or spatial variability of the dissolution rate, while the surface  
112 area measurement itself may be inconsistent and carry large and often poorly constrained  
113 uncertainties <sup>66</sup>. Finally, the few existing detailed characterizations of ASSLS have been carried  
114 using destructive techniques and, therefore, they inherently do not reveal the time-dependence of  
115 ASSL properties.

116 To date, the transport properties of nanoporous surface layers developed on silicate  
117 materials have represented a recurrent topic for material scientists in general and have been  
118 addressed by theoretical and experimental studies beyond the field of Geosciences <sup>57,67-71</sup>.  
119 Importantly, such transport properties are critically inherited from the (yet to be determined)  
120 physicochemical evolution of the silica-rich surface layers, which represent some of the central  
121 insights to this study.

122 The aim of the present study is to utilize a novel combination of approaches to follow the  
123 evolution of the physical properties of ASSLS *in-situ*, providing direct information into ASSL  
124 thickness and density and indirect insights into the local physico-chemical conditions prevailing  
125 at the inner (pristine mineral/ASSL) interface. We use X-ray reflectivity (XRR) data to track the  
126 temporal evolution of ASSL thickness and density. Complementary vertical scanning  
127 interferometry (VSI) measurements are performed to track the evolution of the outer (ASSL/bulk  
128 solution) interface. Our methodology circumvents the aforementioned challenges and enables  
129 probing mineral reactivity and layer formation at low solid/fluid ratios ( $\sim 21 \text{ mm}^2$  for 800 ml of  
130 solution), ensuring that far-from-equilibrium conditions with respect to the dissolving crystal can  
131 be maintained. Layer thickness and surface retreat data are combined to determine the rate of  
132 retreat of the inner interface, enabling the calculation of the dissolution rate of the primary  
133 labradorite feldspar located underneath the ASSLS. Overall, this study provides a novel

134 characterization of the physicochemical properties of nanoporous surface layers developed on a  
135 reference silicate material (feldspar), with possible consequences for the dissolution kinetics of  
136 the underlying substrate.

137

## 138 METHODS

### 139 **Sample preparation**

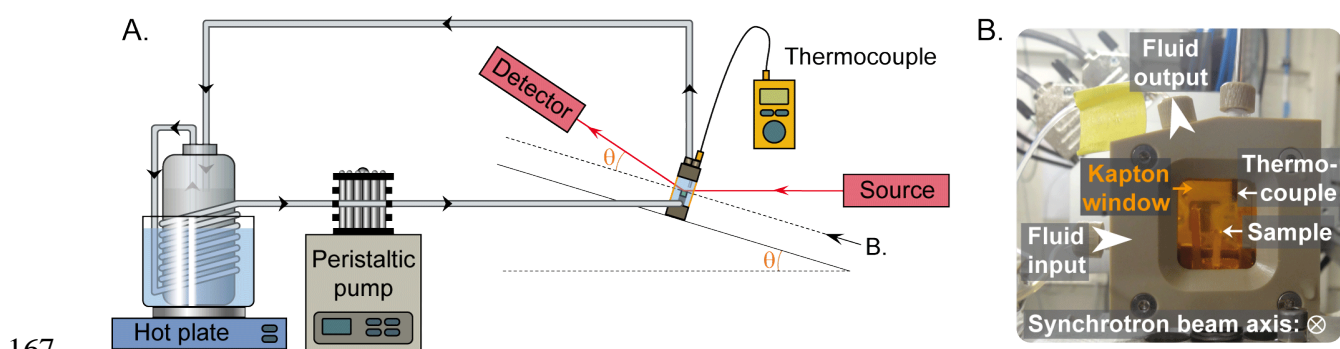
140 Labradorite single crystals from Nuevo Casas Grande, Chihuahua (Mexico) were  
141 provided by the Mineralogical & Geological Museum of Harvard University (Ref.  
142 MGMH#135998). They consist of transparent gem-grade crystals with a composition of  
143  $Ab_{39}An_{60}Or_1$ <sup>72</sup>. Samples of about 7 mm × 3 mm suited for XRR, VSI, and atomic force  
144 microscopy (AFM) measurements were prepared following standard procedures previously  
145 described<sup>14</sup>. Briefly, euhedral crystals were cut with a diamond saw following (001) preferential  
146 cleavage planes and polished down to the nanometer scale using colloidal silica polishing  
147 suspension. One (010) surface was also prepared. Their orientation was verified by indexing  
148 electron backscatter diffraction (EBSD) patterns obtained on a Tescan Vega 2 scanning electron  
149 microscope (SEM).

### 150 **Labradorite dissolution and ASSL formation**

151 Labradorite samples were reacted in pH environments ranging from 1.5 to 4 and  
152 experiments were run for durations of about 1 hour to more than 35 days as required to form  
153 measurable (i.e., > 5 nm thick) ASSLs at the fluid-mineral interface. Samples were incubated at  
154 80°C using (PTFE) Savillex® reactors equipped with a custom PTFE stirring system<sup>14</sup>. Reactors  
155 were filled with a reacting fluid consisting of Milli-Q water whose pH had been previously  
156 adjusted with high-grade HCl (37%, ACS reagent) and, for some experiments, saturated with  
157 respect to amorphous silica using sodium metasilicate, nonahydrate (Sigma Aldrich®, >98%).



158 The pH was regularly controlled and adjusted if necessary. A summary of experiments and  
159 experimental conditions can be found in Tables S1-S6. The saturation indices for labradorite and  
160 amorphous silica at 80 °C were calculated using the Chess® software and the Chess® tdb  
161 database. After reaction, samples were briefly rinsed in Milli-Q water and kept at room  
162 temperature in aqueous solutions close to saturation with respect to amorphous silica until XRR  
163 measurement to avoid subsequent dehydration or dissolution. For experiments carried out over  
164 short durations (up to 94 hours), crystals were directly reacted *in-situ* over the course of the XRR  
165 measurements with an experimental setup enabling fluid circulation at controlled temperature in  
166 a custom flow-through cell with Kapton windows (Figure 1).



167  
168 **Figure 1.** overview of the experimental setup (A) and front view of the flow-through cell  
169 designed for *in-situ* experiments (B). Fluid temperature within the cell was verified with a  
170 thermocouple.

171

### 172 **Dissolution rate at the outer interface by vertical scanning interferometry**

173 The topography of each labradorite sample was measured on a Zygo New View 7300 VSI  
174 prior to reaction. A portion of the surface of samples summarized in Tables S5 and S6 was then  
175 masked with a room-temperature-vulcanizing (RTV) silicone glue spot in order to create a non-  
176 reacted reference by avoiding fluid-mineral contact at this specific location. After reaction, the

177 global retreat of the surface due to crystal dissolution was quantified using topography images  
178 recorded by VSI on reacted samples after removal of the mask. The absolute dissolution rate at  
179 the fluid/layer interface is estimated as  $r = (\Delta h / \Delta t) \times (1 / V_m)$ , where  $r$  stands for the absolute  
180 dissolution rate ( $\text{mol m}^{-2} \text{s}^{-1}$ ),  $\Delta h$  is the surface retreat (m),  $\Delta t$  is the alteration duration (s), and  
181  $V_m$  is the molar volume of labradorite ( $\text{m}^3 \text{mol}^{-1}$ )<sup>73</sup>. Topography images and profiles were  
182 analyzed using SPIP software.

183 The roughness of the outer interface,  $\sigma_{ex}$ , was determined based on AFM (Bruker  
184 Multimode AFM) and VSI measurements conducted on three representative portions of the  
185 surface with dimensions of  $1 \mu\text{m} \times 1 \mu\text{m}$  (AFM) and  $125 \mu\text{m} \times 125 \mu\text{m}$  (VSI). The roughness  
186 value was calculated using Gwyddion software<sup>74</sup> as the root mean square of the deviations in  
187 height  $z$  from the mean image data plane  $z_0$ . Nanoscope Analysis software and Gwyddion were  
188 used to visualize and process AFM data including particle size measurements.

### 189 **Internal properties of the ASSL by *in-situ* X-ray reflectivity experiments**

190 X-ray reflectivity measurements were performed at the European Synchrotron Radiation  
191 Facility (ESRF) at the French BM32 beamline (CRG-IF). 27 keV X-rays (wavelength,  $\lambda =$   
192 0.0459 nm) were used to ensure sufficient transmission ( $T \sim 68.5\%$ ) through the  $\sim 1$  cm thick  
193 solution in the cell. Reflectivity patterns were acquired for  $2\theta$  angles ranging between  $0^\circ$  and  $1^\circ$   
194 (corresponding to scattering vectors ranging between 0.0 and  $0.5 \text{\AA}^{-1}$ ). For the pre-reacted  
195 samples (i.e., samples reacted prior to the XRR measurement campaign), the dissolution  
196 experiments had different onset times and were all stopped one day prior to the XRR campaign,  
197 yielding samples altered for a range of desired time periods. The pre-reacted samples were then  
198 transported to the ESRF in a near-neutral pH solution (pH $\sim$ 6.5) saturated with respect to  
199 amorphous silica. Once at the ESRF, pre-reacted samples were analyzed in our custom cell

200 (Figure 1B) filled with Milli-Q water at room temperature. For the *in-situ* experiments, unreacted  
201 samples were placed in the same cells circulated with fluid of desired chemistry at 80°C and  
202 patterns were acquired every 5 to 15 min depending on the growth rate of the ASSL (Figure 1).

203 Reflectivity data were fitted using the analysis package Motofit<sup>75</sup>, which runs under the  
204 IGOR Pro environment. Interfacial roughness, layer density (initially set to that of pure  
205 amorphous silica), and layer thickness were refined to match the scattering length density (SLD)  
206 profile  $q(z)$  in the direction perpendicular to the mineral-water interface. The strategy used to fit  
207 the experimental XRR patterns involved the minimum number of layers required to obtain a  
208 satisfactory fit following Nelson<sup>75</sup>. Discrepancies between the model and data were quantified  
209 by the  $\chi^2$  parameter as defined by Nelson<sup>75</sup>, which was minimized by adjusting the thickness  
210 and SLD parameters of each layer as well as inner and outer roughness values following a two-  
211 step procedure including genetic optimization<sup>76</sup> and the Levenberg-Marquardt method<sup>77</sup>. As  
212 shown in Figure S1, some factors (for example, the existence of local minima) were found to  
213 have non-monotonic influence on fit quality as quantified by the  $\chi^2$  value. Hence, the reliability  
214 of data modeling was ensured by including genetic optimization as the first step of the fitting  
215 procedure. All possible solutions were analyzed manually and discarded if necessary (for  
216 instance in the case non-realistically high density values).

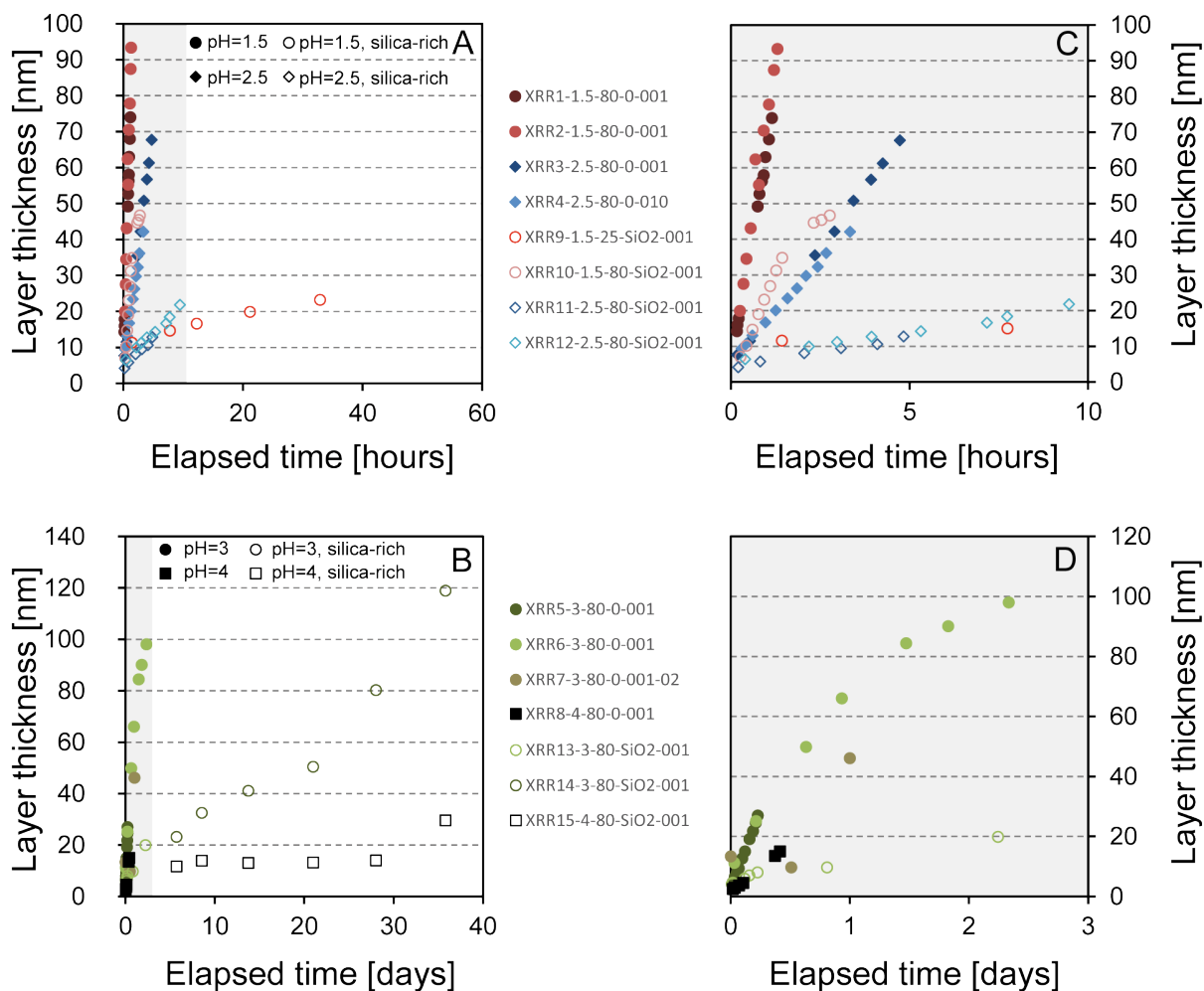
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## 218 RESULTS

### 219 **Formation of ASSLs and *in-situ* evolution of their physical properties**

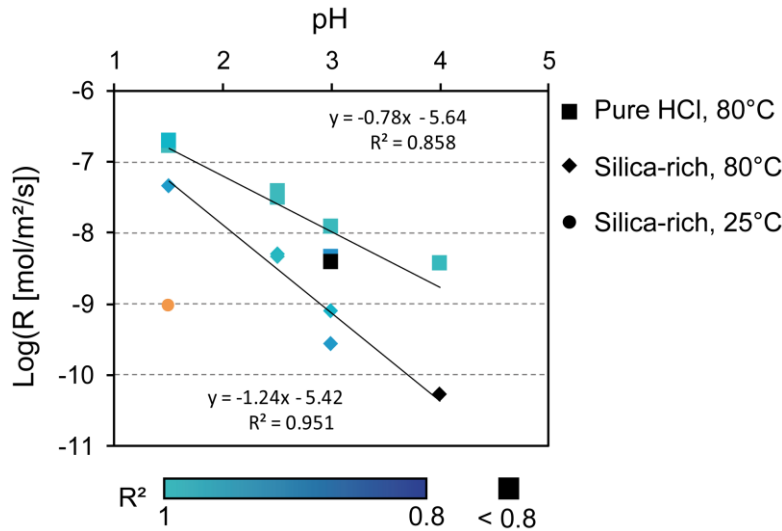
220 The formation of ASSLs at the fluid-mineral interface was observed by XRR for all  
221 tested conditions, i.e. pH = 1.5 to pH = 4, 80°C or 25°C, in aqueous solutions that were either  
222 saturated or not with respect to amorphous silica. As a general trend, ASSLs' growth rate

223 decreases for experiments conducted at higher pH values, in solutions saturated with respect to  
224 amorphous silica or at lower temperature, all other conditions being kept constant. The ASSL  
225 was found to grow at a nearly constant rate in most conditions as revealed by the linear trends in  
226 Figure 2, with the notable exception of the longest experiments conducted at pH = 3 and 4  
227 (duration  $\geq 1$  day). Comparison between results at different pH values revealed a near-linear pH-  
228 dependence of the logarithm of the growth rate (Figure 3). Use of a lower temperature (25 vs.  
229 80°C at pH = 1.5) in saturated solution led to a drop of the dissolution rate by a factor of ~50  
230 (orange symbol, Figure 3). Fluid saturation with respect to amorphous silica led to a decrease of  
231 the growth rate by a factor ranging from ~4 at pH = 1.5 to nearly 30 at pH = 4 (diamonds versus  
232 squares, Figure 3).



233  
 234 **Figure 2.** Temporal evolution of layer thickness as measured by X-ray reflectivity. Layers'  
 235 growth was generally faster for experiments at  $\text{pH} \leq 2.5$  (A) compared to experiments at  $\text{pH} >$   
 236 2.5 (B), and slower for experiments conducted with fluids saturated with respect to amorphous  
 237 silica (open data points) compared to their non-saturated counterparts (filled data points). All  
 238 experiments were conducted at 80°C with the exception of experiment XRR10-1.5-25-SiO2-001  
 239 (red open circles in panel A), conducted at 25°C.

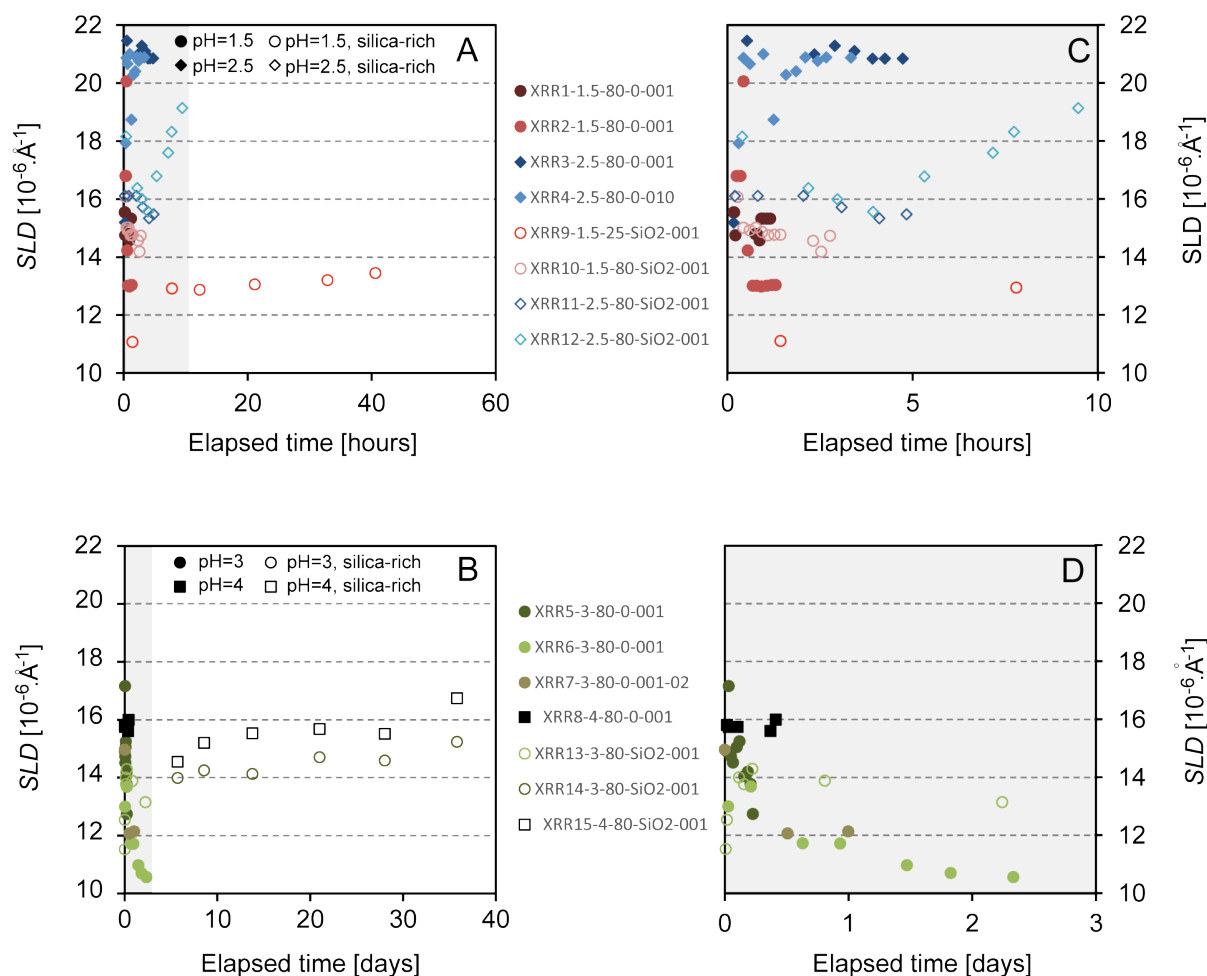
240



241  
 242 **Figure 3.** pH-dependence at 80°C of layer growth rate represented as moles of labradorite per  
 243 square meter converted each second into layer (*labradorite* → *layer*). Diamonds and squares  
 244 represent experiments where the fluid was saturated or not with respect to amorphous silica,  
 245 respectively. For each experiment represented here, the color quantifies the regression coefficient  
 246 associated to linear regression of the temporal evolution of the layer thickness (cf. Figure 2)  
 247 according to the color scale below the graph. The orange data point corresponds to the  
 248 experiment conducted at 25°C in a silica-rich fluid.

249  
 250  
 251 Measured SLD values ranged from 10.6 to 21.5  $10^{-6} \text{ \AA}^{-1}$ , which would correspond to  
 252 densities of  $\sim 1.25$  and  $2.53 \text{ g cm}^{-3}$  under the hypothesis that ASSL are composed of pure silica  
 253 ( $\text{SiO}_2$ ) (Figure 4). No significant SLD difference (within the uncertainty of  $\pm 5 \%$ ) was detected  
 254 between ASSLs grown on different crystallographic surfaces [(001) vs. (010)]. Experiments  
 255 conducted in fluids combining high Si concentrations ( $\sim 145 \text{ ppm}$ ) and weakly acidic pH or low  
 256 temperature (e.g. experiments XRR10-1.5-25-SiO<sub>2</sub>, XRR14-3-80-SiO<sub>2</sub>-001 or XRR15-4-80-  
 257 SiO<sub>2</sub>-001) tended to exhibit constant or increasing SLD trends over time, suggesting progressive

258 densification. Conversely, experiments conducted in fluids with low Si concentrations (< 200  
 259 ppb) exhibited decreasing, constant, or non-monotonous SLD trends. The experiment conducted  
 260 at 25°C in a silica-rich fluid at pH=1.5 exhibited a significantly lower mean SLD compared to its  
 261 counterpart conducted at 80°C ( $12.8 \pm 0.9$  vs.  $14.8 \pm 0.5$  respectively). Measurements performed  
 262 after completion of experiments XRR9-1.5-80-SiO2-001, XRR11-2.5-80-SiO2-001 and XRR13-  
 263 3-80-SiO2-001 revealed that layers dried and measured immediately after *in-situ* dissolution tend  
 264 to exhibit lower SLD values than previous measurements corresponding to their hydrated  
 265 counterparts (Table S3).



266  
 267 **Figure 4.** Temporal evolution of the scattering length density of ASSLs as measured by X-ray  
 268 reflectivity for experiments at  $\text{pH} \leq 2.5$  (A, C) and  $\text{pH} > 2.5$  (B, D). Open data points correspond

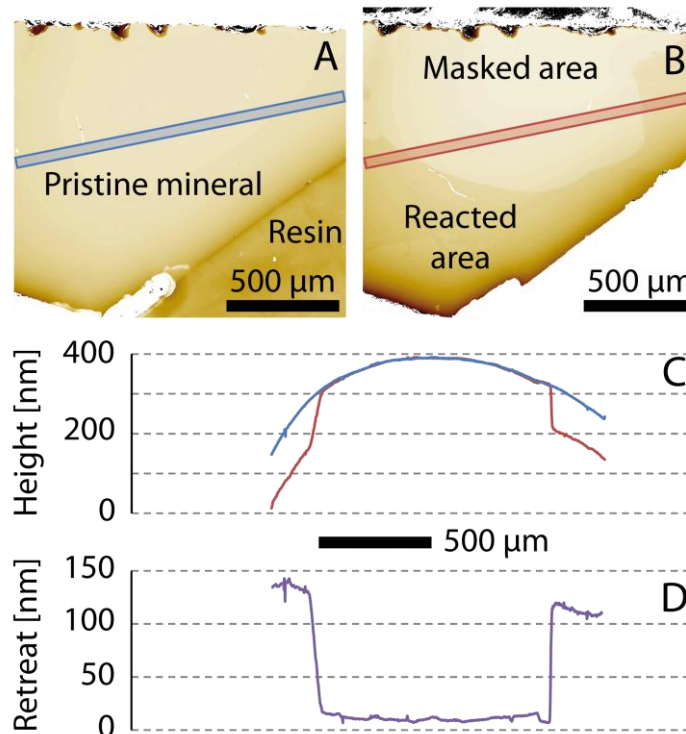
269 to experiments conducted with fluids saturated with respect to amorphous silica. C and D  
270 correspond to close-up views of the regions indicated by the shaded areas on plots A and B,  
271 respectively. All experiments were conducted at 80°C with the exception of experiment XRR10-  
272 1.5-25-SiO2-001 (red open circles in panel A), conducted at 25°C.

273

274

### 275 **Reactivity and evolution of the outer interface**

276 The global retreat of the outer surface compared to a masked reference (Figure 5), as  
277 measured using VSI, was used to probe the reactivity at the outer (ASSL/bulk solution) interface  
278 in all tested conditions (see Tables S5 and S6) on a set of samples distinct from those dedicated  
279 to XRR measurements.



280

281 **Figure 5.** Typical measurement of surface retreat based on topography maps acquired by VSI  
282 before (a) and after (b) the dissolution process (here a labradorite sample weathered for 35 days



283 at 80°C in a fluid at pH = 3 saturated with respect to amorphous silica). This specific sample was  
284 detached from the resin after reaction to facilitate VSI alignment. Height profiles recorded before  
285 (blue) and after (red) weathering through the non-reacted masked area are superimposed (c) and  
286 subtracted to highlight the overall surface retreat. Some variation on the retreat can be seen,  
287 which is consistent with literature on intrinsic variability of the dissolution rate and profile  
288 subtraction at the mm scale.

289

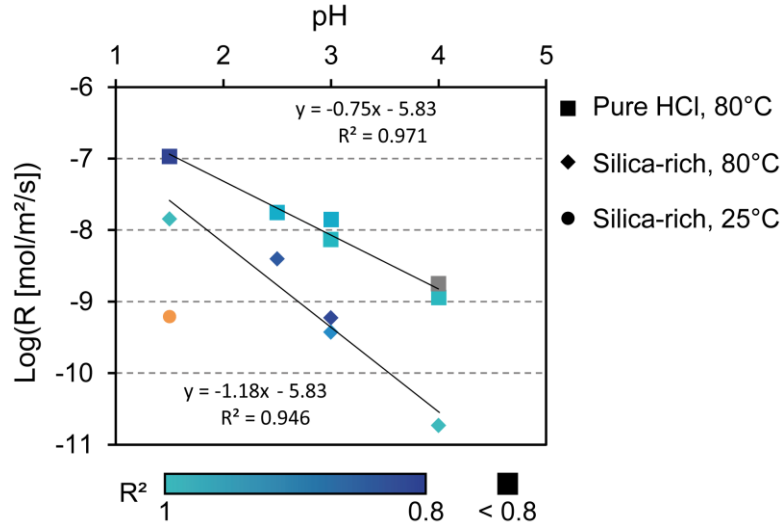
290 Assuming isovolumetric weathering, dissolution rates of the outer interface were reconstructed  
291 from VSI data and showed a significant decrease with increasing pH (Figure 6). Dissolution rates  
292 were smaller when the bulk fluid was saturated with respect to amorphous silica, indicating a  
293 decreased reactivity of the ASSL at the outer interface by a factor of 4 to 80. The high vertical  
294 resolution of the VSI measurements (down to a few nm) enabled estimating the apparent  
295 activation energy ( $E_a$ ) of the ASSL dissolution process based on kinetic data collected at  $T_1 =$   
296 80°C and  $T_2 = 25^\circ\text{C}$  for experiments with a fluid at pH = 1.5 saturated with respect to amorphous  
297 silica, as:

$$E_a = R \frac{T_1 T_2}{T_1 - T_2} \ln \left( \frac{r_1}{r_2} \right) \quad (1)$$

298

299 where  $r$  is the dissolution rate of ASSL. In these conditions, the ~23-fold decrease in ASSL  
300 dissolution rate between 80°C and 25°C corresponds to an  $E_a$  value of 50 kJ mol<sup>-1</sup>.

301



302

303 **Figure 6.** pH-dependence of layer dissolution rate (*layer*→*dissolved species*) at 80°C.

304 Diamonds and squares represent experiments where the fluid was saturated or not with respect to

305 amorphous silica, respectively. For each experiment represented here, the color quantifies the

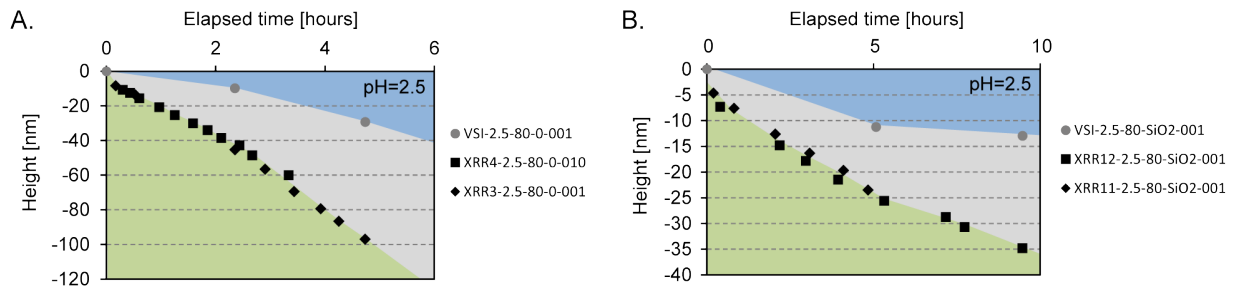
306 regression coefficient associated to linear regression of the temporal retreat of the outer

307 fluid/layer interface (cf. Figure 7) according to the color scale below the graph. Grey square:

308 based on 2 retreat values. The orange data point corresponds to the experiment conducted at

309 25°C in a silica-rich fluid.

310



311

312 **Figure 7.** Temporal evolution of ASSL thickness (grey) at the interface between mineral (green)

313 and fluid (blue) for experiments conducted at 80°C, pH=2.5), using a fluid that was saturated

314 (SiO<sub>2</sub>, panel B) or not (0, panel A) with respect to amorphous silica. Grey dots correspond to VSI

315 measurements of the surface retreat compared to a non-reacted reference (zero height) and track  
316 the reactivity of the outer interface. Black diamonds and squares correspond to X-ray reflectivity  
317 data corrected for surface retreat and track the temporal evolution of the inner interface. Colored  
318 background is used to guide the eye. All experiments were conducted on (001) labradorite faces  
319 with the exception of one experiment conducted on (010) (A). A summary of all experimental  
320 conditions tested in this study can be found in Figure S3.

321

322

323 The roughness of the outer interface of a sample reacted at pH=3 was measured before  
324 and after dissolution on AFM and VSI data<sup>14,78</sup>. Both techniques yield roughness values of  
325 similar order of magnitude, the VSI measurements being nevertheless systematically higher than  
326 those from AFM. During the experiments, roughness increased from  $\sigma_{ex}^{VSI} = 17$  nm and  $\sigma_{ex}^{AFM} = 7$   
327 nm to  $\sigma_{ex}^{VSI} = 65$  nm and  $\sigma_{ex}^{AFM} = 36$  nm as measured using VSI and AFM, respectively. AFM  
328 measurements further showed the formation of a nanoscale botryoidal texture of the outer  
329 interface exhibiting spherical particles with an average radius of  $9.8 \pm 1.2$  nm (Figure S2). In  
330 order to estimate a maximal porosity formed by the silica beads constituting the layer (as  
331 opposed to a dense packing of these particles), their arrangement at the outer interface was  
332 studied based on AFM data. The intersection of particles with a plane located 9.8 nm below the  
333 highest point of a representative portion of the fluid/layer interface yields a pore/particle ratio of  
334 3.2, which yields a rough estimate of  $\sim 0.76$  as an upper bound on the porosity of the ASSL.

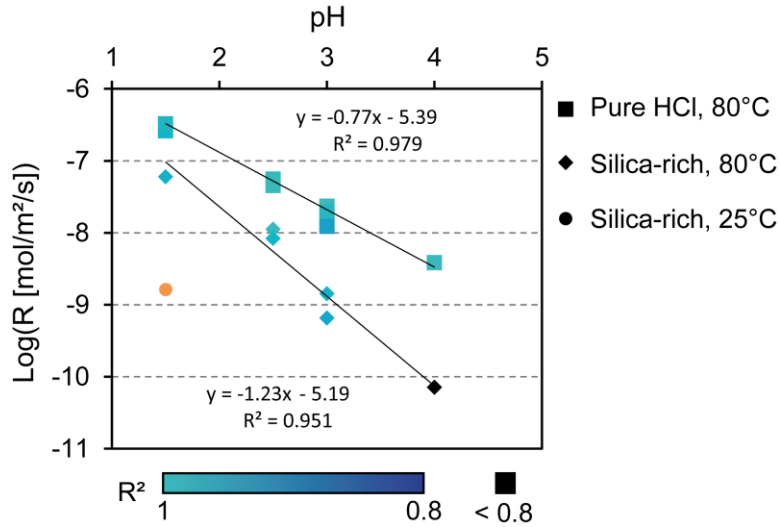
335

336 **Temporal evolution of the fluid-silicate interface and labradorite reactivity**

337 VSI and XRR data were combined to provide one of the first accurate representations of  
338 the temporal evolution of the fluid-silicate interface during dissolution and layer formation  
339 (Figure 7, Figure S3). In particular, the surface retreat  $z_{out}$  measured by VSI was combined with  
340 the ASSL thickness  $\Delta z$  determined from XRR data to evaluate the absolute height of the inner  
341 interface  $z_{in}$  (black squares and diamonds, Figure 7) at each timestep  $t$ :

$$z_{in}(t) = -\Delta z(t) - \frac{z_{out}(t_{+1}) - z_{out}(t_{-1})}{t_{+1} - t_{-1}} * t \quad (2)$$

342  
343 In equation 2,  $\Delta z(t)$  is evaluated at time  $t$  by XRR, while  $z_{out}(t_{+1})$  and  $z_{out}(t_{-1})$  correspond to  
344 absolute values of the surface retreat at the closest VSI measurement before and after XRR  
345 measurement respectively. In most cases, the temporal evolution of the inner interface was linear  
346 or made up of linear portions of curves, which indicates constant dissolution rate at given  
347 experimental conditions. Linear regression of  $z_{in}$  vs. time was used as a proxy to estimate the  
348 overall reactivity of labradorite (i.e., the dissolution rate of the primary mineral). Of note, this  
349 approach considers the ASSL/mineral boundary as a single interface since the two reaction fronts  
350 located on each side of the thin fluid film often reported at the inner interface {Hellmann, 2012},  
351 could not be resolved by XRR. The resulting retreat rates of the inner interface revealed a near  
352 logarithmic dependence of the dissolution rate on pH (Figure 8). Saturation of the solution with  
353 respect to amorphous silica decreased the dissolution rate by a factor ranging from ~5 at pH =  
354 1.5 to ~50 at pH = 4. A temperature decrease from 80°C to 25°C at pH = 1.5 yielded a 37-fold  
355 drop in dissolution rate corresponding to an apparent energy of activation of about 57 kJ mol<sup>-1</sup>.  
356



357

358 **Figure 8.** pH-dependence at 80°C of labradorite dissolution rate  
 359 (*labradorite* → *layer* + *dissolved species*). Diamonds and squares represent experiments where  
 360 the fluid was respectively saturated or not with respect to amorphous silica. For each experiment  
 361 represented here, the color quantifies the regression coefficient associated to linear regressions of  
 362 the temporal retreat of the inner layer/mineral interface (cf. Figure 7) according to the color scale  
 363 below the graph. The orange data point corresponds to the experiment conducted at 25°C in a  
 364 silica-rich fluid.

365

366

### 367 **Fluid saturation state**

368 To verify that all our experiments were conducted at far-from-equilibrium conditions  
 369 with respect to labradorite dissolution (*i.e.*, in the region where the dissolution rate is invariant  
 370 with saturation state, which defines the dissolution rate plateau), we used the final surface retreat  
 371 and layer thickness, along with the known sample geometric surface area ( $\sim 2.8 \times 10^{-5} \text{ m}^2$ ) and  
 372 labradorite density ( $\sim 9.8 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ ), to estimate the maximum possible fluid saturation state  
 373 with respect to labradorite at the end of our experiments. We note that rough samples edges

374 resulting from diamond saw cutting were washed and covered with RTV glue prior to  
375 experiment, which limited their contribution to cation release to the solution composition. As  
376 shown in Table S1, Gibbs free energy ( $\Delta G_r$ ) values were all below the  $\Delta G_r$  threshold value of -  
377 41.8 kJ mol<sup>-1</sup> where labradorite dissolution should be invariant with saturation as reported by  
378 Taylor, et al.<sup>46</sup>.

379

## 380 DISCUSSION

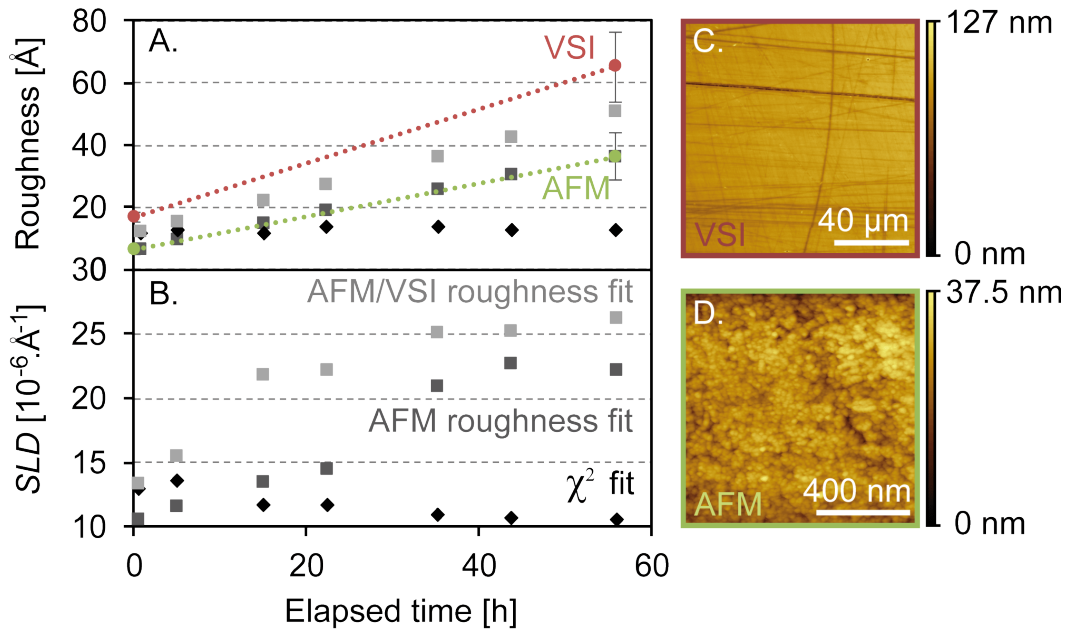
### 381 **Fitting X-ray reflectivity data**

382 During the XRR fitting procedure, four parameters describing the ASSL were adjusted to  
383 match the reflectivity data. These parameters include the layer thickness, density, as well as its  
384 inner and outer roughness. Since the thickness of the layer primarily affects the periodicity of the  
385 signal, which is not significantly impacted by density or roughness, this parameter can be  
386 independently assessed with a high degree of confidence. The three other parameters are  
387 somewhat correlated, so that the choice of a “best fit” solely based on the  $\chi^2$  minimization  
388 criterion is non-trivial (see e.g. Figure S1) and sometimes implicitly corresponds to favoring the  
389 fitting of one portion of the curve relative to another. Indeed, since the  $\chi^2$  value depends on the  
390 proportion of data points accurately fitted by the model, it is possible to get a lower  $\chi^2$  value with  
391 a less relevant fit if parts of the curve containing little information (as opposed to “features of  
392 interest” such as critical angle or well-defined oscillation region), account for a large proportion  
393 of the considered data points.

394 In an attempt to alleviate the issue identified above, we constrained our estimate of the  
395 roughness of the outer interface using roughness values measured on the same sample before and  
396 after dissolution. We note that these independent roughness measurements had to be performed

397 *ex-situ*, which prevented the acquisition of a time-series during the experiment. We associated as  
398 a first approximation  $\sigma_{ex}^{XRR}$  either to the linear interpolation of initial and final AFM-based  
399 roughness ( $\sigma_{ex}^{AFM}$ , cf. dark grey squares, Figure 9) or to the interpolation of the initial and final  
400 averages between VSI- ( $\sigma_{ex}^{VSI}$ ) and AFM- ( $\sigma_{ex}^{AFM}$ ) based roughness (cf. light grey squares, Figure  
401 9). Reflectivity measurements performed on dried layers (Table S3) were used to verify that any  
402 observed discrepancy between  $\sigma_{ex}^{XRR}$  and  $\sigma_{ex}^{VSI}$  or  $\sigma_{ex}^{AFM}$  was unlikely due to dehydration of  
403 ASSLs. After applying this constraint, the best fit to the XRR data for both methods (referred to  
404 as “AFM/VSI roughness fit” and “AFM roughness fit” and shown as light and dark grey squares  
405 in Figure 9B) based on the two remaining parameters (ASSL density and the roughness of the  
406 inner interface) suggested that the density of the ASSL invariably increases with time, in contrast  
407 with the conclusions reached from the analysis solely based on the  $\chi^2$  minimization criterion.  
408 However, the resulting density values exceeded those of pure amorphous silica ( $\sim 20.6 \times 10^{-6} \cdot \text{A}^{-2}$ )  
409 and even those of unreacted labradorite ( $23.5 \times 10^{-6} \cdot \text{A}^{-2}$ ). This likely unphysical result suggests  
410 that the roughness values derived by both AFM and VSI overestimate the roughness reflected by  
411 the XRR results. Consequently, we decided to rely on the well-documented “ $\chi^2$  fit” approach<sup>75</sup>,  
412 which also enables direct comparison of our data with literature<sup>9,56</sup>. We note however that  
413 surface roughness may artificially lower the layer apparent density and that further research  
414 should be directed at better characterizing the *in-situ* evolution of surface roughness with  
415 relevant experimental probes.

416



417

418 **Figure 9.** Temporal evolution of roughness (A) and SLD (B) for experiment XRR6-3-80-0-001.

419 Black diamonds correspond to the best fits determined using the lowest  $\chi^2$  value as the criterion

420 to assess the validity of the fit, grey squares correspond to best fits obtained using the lowest  $\chi^2$

421 value after imposing at each temporal step the roughness at the outer interface based on

422 topography measurements. In that case, the roughness at the inner interface and the density of the

423 layer were the only adjustable parameters of the model (see text for details). For the “AFM

424 roughness fit” (dark grey squares), the evolution of the outer interface is assimilated to a linear

425 interpolation of AFM roughness measurements acquired before and after experiment. For the

426 “AFM/VSI roughness fit” (light grey squares), the evolution of the outer interface is associated

427 to the mean value between VSI and AFM measurements, their evolution being supposed linear

428 (see text). The sample roughness measured before and after experiment by VSI and AFM is

429 reported in red and green respectively in panel A. Typical fields of view are represented in

430 panels C and D.

431



432        **Reactivity and physicochemical properties of the fluid/solid interface inferred from**  
433        **XRR and VSI measurements**

434        Traditionally, the mechanisms and rates of mineral dissolution have been indirectly  
435        monitored through the evolution of fluid composition <sup>79,80</sup>. In these studies, the non-  
436        stoichiometry of elemental release was used to indirectly probe the formation of ASSLs at the  
437        fluid-mineral interface<sup>10,28,31</sup>. As mentioned in the introduction, this indirect approach suffers  
438        from high uncertainties when it comes to determining the evolution of ASSL thickness and  
439        density, particularly at low dissolution rates, principally due to the difficulty of accurately  
440        determining the stoichiometry of the small elemental release and, also, of constraining the  
441        evolving reacting surface area. Our results show that this challenge can be circumvented, to some  
442        extent, by using a combination of XRR and VSI measurements to characterize the rate of ASSL  
443        formation at the labradorite-water interface. We were able to detect the formation of ASSLs at  
444        the surface of labradorite in all tested conditions, in agreement with previous results on a variety  
445        of silicate minerals including feldspars <sup>20</sup>. We also probed independently the reactivity of the  
446        outer fluid/layer interface and of the inner layer/mineral interface *in-situ*. This provided an  
447        accurate picture of the temporal evolution of the fluid-mineral interface (Figure 7, Figure S3),  
448        which enabled unravelling the reaction kinetics. Our results indicate a reaction order with respect  
449        to hydrogen ion (corresponding to the power to which the activity of this ion is raised, see eq. 3  
450        and Figure 8) of about 0.77 for the overall dissolution process of labradorite occurring at the  
451        inner interface, which is slightly higher than values previously reported for this mineral—  
452        typically 0.6—but consistent with the expected range within the feldspar series, typically up to  
453        1.0 for bytownite <sup>80</sup>. Slight differences with previously published data are expected since the

454 protocol used here investigates the reactivity of single cleavage planes, which is known to differ  
455 from that of bulk mineral powders <sup>78</sup>.

456 Most of the mean density values of ASSLs estimated from XRR data fall between 1.29  
457  $\text{g}\cdot\text{cm}^{-3}$  and  $1.89 \text{ g}\cdot\text{cm}^{-3}$ . These measured density values are consistent with the theoretical values  
458 for a medium composed of spheres of pure amorphous silica organized within an aqueous  
459 medium with either a “dense packing” (face-centered cubic) or a “minimal packing” (estimated  
460 from 2D analysis, see “Reactivity and evolution of outer interface” section), corresponding to  
461 water-silica mass ratios of 63:10 and 10:14, respectively. They may alternatively be associated  
462 with a homogeneous product of hydrated silica. Analysis of samples “XRR3-2.5-80-0-001” and  
463 “XRR4-2.5-80-0-010” yielded XRR density estimates exceeding the value reported for bulk  
464 anhydrous  $\text{SiO}_2$  ( $2.2 \text{ g}\cdot\text{cm}^{-3}$ , cf. Iler <sup>81</sup>). Such high values may arise from samples with curved  
465 interfaces causing total reflection intensity to be detected at angles exceeding the actual critical  
466 angle <sup>9</sup> and are therefore not further discussed. Overall, our results indicate that the ASSL is  
467 either hydrated or accommodates significant porosity, which, together with the botryoidal texture  
468 of the outer interface, is consistent with the hypothesis that ASSL formation involves significant  
469 dissolution-reprecipitation <sup>20,59</sup>.

470 Our experiments show that the dissolution rate of the pristine mineral is impacted by the  
471 saturation state of the solution with respect to amorphous silica (Figure 6). From a pure  
472 thermodynamic standpoint, only the dissolution rate of the ASSL (and not labradorite) should be  
473 impacted by the aqueous silica concentration, because the experiments were conducted at far-  
474 from-equilibrium conditions with respect to labradorite. This result indicates that the intrinsic  
475 dissolution rate of ASSL significantly modulates the reactivity of labradorite (see section  
476 “Passivation by surface layers” below).

477           The dissolution rate of the ASSL was not directly probed by our XRR measurements,  
478 which only probed ASSL thickness. However, the need for frequent z-axis realignment  
479 throughout the dissolution experiment to match perfect  $\theta$ - $2\theta$  reflection conditions at the surface  
480 of the sample provides additional evidence of the progressive retreat of the outer interface, which  
481 was tracked more precisely by VSI on separate samples. Our VSI results indicate that the mean  
482 ASSL dissolution rate ranged from  $1.07 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$  at pH = 1.5 to  $1.46 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$   
483 at pH = 4 at 80°C in silica-poor solutions. These values are in good agreement with the  
484 dissolution rate of amorphous silica observed in other studies. For example, linear extrapolation  
485 of our experimental  $\text{Log}(\text{rate})=f(\text{pH})$  model is consistent (within a factor of 0.5 log unit) with the  
486 results of Icenhower and Dove (2000)Icenhower and Dove<sup>82</sup> for dilute solutions at pH = 5.7 at  
487 80°C and also (within the same 0.5 log units factor) with estimates based on Rimstidt and Barnes  
488 (2000)Rimstidt and Barnes<sup>83</sup> at a pH comprised between 6.5 and 7.1 at 80°C. In addition, our  
489 dissolution rates are consistently 2 to 3 orders of magnitude greater than that of quartz<sup>84</sup>, as  
490 expected for amorphous SiO<sub>2</sub>.

491           Finally, the observation of surface layer dissolution with a fluid at saturation with respect  
492 to amorphous silica supports previous hypothesis suggesting either an enhanced solubility of the  
493 ASSL formed on silicates such as wollastonite compared to pure amorphous silica, or that  
494 ASSLs dissolve by a different mechanism than amorphous silica<sup>6</sup>. This result however is at odds  
495 with observations conducted on ASSLs formed on diopside<sup>85</sup>, where the solubility of the ASSLs  
496 was suggested to be close to that of  $\alpha$ -cristobalite.

497           In summary, our results suggest that ASSLs formed on labradorite have slightly higher  
498 solubility than amorphous SiO<sub>2</sub> but similar dissolution rates. Since the solubility of hydrated  
499 amorphous silica would theoretically be decreased compared to pure amorphous silica according

500 to <sup>81</sup>, we conclude that the presence in our system of a homogenous layer of hydrated amorphous  
501 silica is unlikely. Instead, a layer composed of a rather dense packing of silica-rich spheres  
502 surrounded by aqueous solution may form, which would be consistent with a mechanism  
503 whereby a botryoidal texture propagates through the layer. Whether the packing, size, or  
504 composition of the spheres changes through time still needs to be determined.

505 As shown in Figure 5, the dissolution rate of ASSL in an acidic solution is also pH-  
506 dependent, meaning that hydrogen ions are involved, to some extent, in the dissolution reaction.  
507 This feature is generally unexpected for pure amorphous silica <sup>82</sup>. This supports the hypothesis  
508 that ASSLs formed on labradorite at pH > 1.5 may not consist of pure hydrated SiO<sub>2</sub> <sup>14</sup>. In  
509 addition, when the fluid is saturated with respect to amorphous silica (aqueous silica  
510 concentrations typically of 5.2 ×10<sup>-3</sup> M), the reaction order with respect to hydrogen ion is  
511 reduced, showing a reduced impact of the layer on the dissolution rate at more acidic pH values  
512 (Figure 8). This is consistent with the formation of different layer-forming phases depending on  
513 the pH conditions, the passivating effect of which would be enhanced at conditions closer to  
514 neutrality.

515 The estimate for the activation energy of labradorite dissolution in the present  
516 experiments is ~58 kJ mol<sup>-1</sup>, which is similar to those typically reported for labradorite, at ~42 kJ  
517 mol<sup>-1</sup> <sup>80</sup>. Finally, no difference was detected between the layer growth rate recorded on (001) and  
518 (010) faces (Figure 7A). Since no anisotropy of dissolution is expected from amorphous phases  
519 such as those constituting the ASSL, we conclude that no compelling evidence of dissolution  
520 anisotropy for labradorite could be evidenced here.

521

522 **Effect of drying on ASSL properties**

523 Our approach, involving a continuously hydrated fluid-mineral interface, is not  
524 completely analogous to environmental settings where minerals, glasses, and concrete materials  
525 experience drying/wetting cycles. The effect of drying was therefore investigated at three pH  
526 conditions (experiments XRR9-1.5-80-SiO2-001, XRR11-2.5-80-SiO2-001, and XRR13-3-80-  
527 SiO2-001). As reported in Table S3, drying of ASSLs tends to decrease their apparent density,  
528 while having no clear impact on their thickness or roughness. The porosity, defined as the  
529 volume proportion of fluid or air in the ASSL, was estimated from SLD values measured *in-situ*  
530 or after drying, respectively. The layer was considered to a first approximation as a porous  
531 amorphous silica phase, as suggested by its reactivity (cf. previous section). This analysis  
532 suggests a drop in the porosity during drying for the experiment conducted under acid conditions  
533 (pH=1.5) and an increase of the density at milder pH (pH>1.5) (Table 1). Such behavior cannot  
534 be explained by a prospective collapse or dilatation of the porous network during drying since no  
535 significant evolution of the thickness of the ASSL could be observed. Alternatively, precipitation  
536 of distinct phases from the poral solution, depending on its pH, could explain either the sealing  
537 of the porosity by growth and coalescence of the particles forming the layer at pH=1.5 (which  
538 can bear higher concentrations of dissolved species), while the precipitation of platelet-like  
539 phases could open-up the porosity of layers formed at milder conditions, which are suspected to  
540 exhibit higher Al-content<sup>14</sup>. This hypothesis is supported by the larger discrepancy existing  
541 between the porosity measured *in-situ* and after drying for the experiment at pH=3 (22.5%) than  
542 at pH=2.5 (10.5%). The preliminary results obtained with our approach open interesting avenues  
543 for the investigation of dry/wet cycles on ASSL textural properties that still need to be explored  
544 in depth.  
545

Measurement <i>Experiment</i>	<i>In-situ</i>		dried	
	<i>SLD Layer</i> [10 <sup>-6</sup> .Å <sup>-2</sup> ]	<i>Porosity</i> %Water (Vol.)	<i>SLD Layer</i> [10 <sup>-6</sup> .Å <sup>-2</sup> ]	<i>Porosity</i> %Air (Vol.)
XRR9-1.5-80-SiO2-001	14.7	43	14.0	25
XRR11-2.5-80-SiO2-001	15.5	34	10.3	45
XRR13-3-80-SiO2-001	13.2	60	3.4	82

546

547 **Table 1:** Scattering length densities (SLD) and associated estimate of layer's porosity measured

548 *in-situ* or after drying.

549

### 550 **Passivation by surface layers**

551 The passivating effect of ASSLs, which results in the reduction of the dissolution rate of  
552 primary silicates, has been evidenced in a variety of geological or geochemical contexts<sup>2,9,14,21,61</sup>.

553 In the present study, lower dissolution rates were observed on a reference silicate material  
554 (labradorite feldspar) during experiments conducted with silica-rich solutions compared to those  
555 that used silica-poor solutions at equivalent pH values. Such contrasting behavior cannot be  
556 explained using current analysis approaches, which consist of relating physico-chemical  
557 properties of the bulk fluid (e.g.  $T$ , pH, and other ion activities) to the overall dissolution rate of  
558 the silicate materials ( $R_{min}$ ), following:

$$R_{min} = \left[ \sum_i A_{i,min} \cdot \exp\left(\frac{-E_{a,min}^i}{RT}\right) \cdot a_i^{n_{i,min}} \right] \left( 1 - \exp\left(\frac{S * \Delta Gr}{RT}\right) \right) \quad (3)$$

559 where  $A_{i,min}$  is an Arrhenius pre-exponential factor;  $E_{a,min}^i$ ,  $a_i$ , and  $n_{i,min}$  are the activation

560 energy, activity, and reaction order with respect to reactive species  $i$ ;  $R$  is the ideal gas constant;

561  $T$  is absolute temperature; and  $\Delta Gr$  and  $S$  are the Gibbs free energy of the dissolution reaction

562 and a dimensionless empirical factor. According to the classical theoretical framework of

563 mineral dissolution kinetics, the affinity term  $\left( 1 - \exp\left(\frac{S * \Delta Gr}{RT}\right) \right)$  equals  $\sim 1$  in our experiments

564 since the aqueous solutions were at far-from-equilibrium conditions with respect to the  
565 dissolution of the primary phase ( $\Delta G_r < -41.8 \text{ kJ mol}^{-1}$ , Table S1). Note that this statement holds  
566 true even if more sophisticated empirical functions are used, such as the one determined by  
567 Taylor, et al.<sup>46</sup> for labradorite. Moreover, in acidic conditions ( $\text{pH} \leq 4$ ), the only reactive species  
568 to be considered is  $\text{H}^+$ . In short, no effect of the activity of dissolved  $\text{SiO}_2$  is anticipated for our  
569 system, which is at odds with labradorite dissolution rate in silica-rich solutions being 5 to 50  
570 times lower compared with silica-poor solutions as described above. Therefore, we conclude that  
571 the composition of the solution at the inner (labradorite/ASSL) interface must be different from  
572 that of the bulk solution, consistent with other recent studies<sup>86</sup>. In particular, since temperature  
573 was maintained constant, we conclude that the two remaining parameters able to influence the  
574 kinetic dissolution rate (namely pH and/or ion concentration) might be significantly higher at the  
575 inner interface than in the fluid at least for the silica-rich experiments, and that this discrepancy  
576 is higher for experiments conducted in silica-rich fluid than for silica-poor experiments. This  
577 hypothesis is supported by the fact that the rate drop observed when saturating the fluid with  
578 respect to amorphous silica is more marked for experiments conducted at higher pH, where fluid  
579 composition is more sensitive to proton consumption and cation release by the dissolution  
580 process. Of note, at  $\text{pH} = 4$  with high background concentrations of dissolved silica, pore fluid  
581 can only accommodate about 30 ppb of  $\text{Al}^{3+}$  and  $\text{Ca}^{2+}$  before reaching the close-to-equilibrium  
582 regime domain with respect to labradorite dissolution defined by Taylor, et al.<sup>46</sup>. These  
583 conclusions may be related to the overall increase of density observed for most experiments  
584 conducted in silica-rich solutions, which may indicate a decrease in the ASSL's porosity and,  
585 possibly, transport properties as previously reported for the dissolution of wollastonite<sup>9</sup>.  
586 Decreasing density observed for XRR9 and XRR11 experiments suggests however that density

587 may not fully explain transport properties inside ASSLs and that other parameters controlling the  
588 spatial organization of the porous network (e.g. tortuosity) may need to be investigated in future  
589 using microscopy and surface-sensitive scattering techniques coupled with numerical modeling.

590 In summary, we hypothesize that the decrease of the dissolution rate of labradorite  
591 minerals in silica-rich fluids was due to the passivation by ASSLs formed under these conditions,  
592 which decreased the transport properties of reactive species and reaction products through the  
593 layer, ultimately leading to higher local pH and/or ion concentration at the inner layer/mineral  
594 interface.

595 On the contrary, for experiments conducted in silica-poor fluids, no clear evidence of  
596 passivation and ASSL densification was noted. Two possible explanations can be put forward to  
597 explain this observation, in contrast with previous data where passivation could be directly  
598 observed<sup>14,21</sup>. First, it is likely that the emergence of passivating properties requires a certain  
599 minimal duration for the layer to densify, also called “maturing time”<sup>87</sup>. Analogous time-  
600 dependent processes have been previously observed for amorphous phases such as pregibbsite  
601 gels<sup>88</sup>. Of note, no clear temporal decrease of the dissolution rate was seen on the timescale of  
602 our experiments. Secondly, it is possible that elemental release from accessory phases included  
603 in a given primary mineral or assemblage, and especially iron-containing minerals, plays an  
604 important role in the buildup of passivating layers. Indeed, formation of a hematite-amorphous  
605 silica assemblage, exhibiting passivating properties due to strong Fe(III)-Si chemical interactions  
606<sup>62,89</sup> is one of the few clearly identified mechanism of silicate passivation to date. Contrary to the  
607 present study, both in Wild, et al.<sup>14</sup> and Daval, et al.<sup>21</sup> where passivation effect could be  
608 observed, the labradorite used contained Fe-bearing mineral inclusions. Such hypothesis,



609 however, would still need to be demonstrated, especially regarding transport of iron from  
610 accessory phases to the iron-free silicate surface.

611 Existing dissolution rate laws are based almost exclusively on laboratory experiments  
612 consisting in immersing mineral grains in reactive fluids at high temperature and low pH  
613 conditions and recording dissolution through elemental release into solution. The methodology  
614 developed here provides complementary data that can help shed light on silicate dissolution in  
615 natural settings. In particular, we were able to precisely quantify two properties critical to  
616 extrapolating laboratory results to natural settings and larger time and spatial scales: the rates of  
617 dissolution of the pristine mineral and of the ASSL and their associated activation energies. In  
618 addition, we provided indirect evidence for changes in the pore fluid chemistry of the ASSL,  
619 possibly related to the apparent transport properties of this phase. With regards to implications  
620 for silicate weathering in field conditions, our results suggest that circum-neutral pH values,  
621 silica-rich fluids, the presence of complex mineralogical assemblages including Fe-rich phases,  
622 long time scales, and drying-wetting cycles all tend to favor the formation of ASSLs with  
623 reduced porosity and transport properties. The methodology developed here should therefore  
624 enable to better characterize the physicochemical evolution of the silica-rich surface layers on a  
625 wide range of silicate materials, enabling to relate the dissolution rates of silicate materials  
626 observed at the macroscale to the transport properties of nanoporous silica-rich layers, which  
627 have been extensively studied both from theoretical and experimental perspectives<sup>57,67-71</sup>.

628

## 629 CONCLUSIONS

630 The present study tested a novel methodology to probe *in-situ* the formation and  
631 properties of amorphous silica-rich surface layers (ASSLs) developed at a fluid-silicate interface.

632 Our approach enabled precise quantification of the formation of ASSLs on labradorite feldspar, a  
633 silicate mineral representative of the continental crust. We quantified ASSL density, thickness,  
634 and roughness by X-ray reflectivity while independently probing ASSL reactivity by vertical  
635 scanning interferometry. Our results suggest that the ASSLs have a significant effect on the  
636 dissolution rate of the primary mineral: our experiments revealed a drop in the dissolution rate of  
637 labradorite in silica-rich solutions compared to silica-poor solutions, where both conditions were  
638 far-from equilibrium with respect to the dissolution of this primary phase in the bulk fluid. Our  
639 results suggest that ASSLs formed in silica-rich fluids have distinct transport properties resulting  
640 in either higher ion activities, higher pH, or both in the pore solution controlling the dissolution  
641 of the primary phase.

642 Overall, our findings underline the need for an improved understanding of the processes  
643 controlling local physico-chemical parameters at the interface with the dissolving silicate, which  
644 may differ from those recorded in bulk fluid. The methodology developed here is a valuable tool  
645 for investigating silicate dissolution. In addition to complementary from bulk fluid analysis, it  
646 has the potential to enable the determination of the relevant parameters (e.g. local fluid pH and  
647 saturation conditions actually driving the dissolution process at the inner layer-silicate interface)  
648 for onsite applications and important industrial processes.

649

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655 The manuscript was written through contributions of all authors. All authors have given approval  
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667

#### 668 ABBREVIATIONS

669 ASSLs, amorphous silica-rich surface layers; VSI, vertical scanning interferometry; XRR, X-ray  
670 reflectivity;

671 TST, transition state theory; BET, Brunauer-Emmett-Teller; AFM, atomic force microscopy;

672 EBSD, electron backscatter diffraction; SEM, scanning electron microscope; PTFE,

673 polytetrafluoroethylene; RTV, room-temperature-vulcanizing; ESRF, European synchrotron

674 radiation facility; SLD, scattering length density; Ab, Albite ( $\text{NaAlSi}_3\text{O}_8$ ); An, Anorthite ( $\text{CaAl}_2$

675  $\text{Si}_2\text{O}_8$ ); Or, Orthoclase ( $\text{KAlSi}_3\text{O}_8$ ).

676

677 SUPPORTING INFORMATION AVAILABLE

678 Summary of experiments conducted in this study, tables of best fit parameters associated to  
679 reflectivity data, Table of surface retreat measured by VSI, example of treatment of reflectivity  
680 data, AFM topography of a reacted portion of labradorite.

681

682 REFERENCES

- 683 1 Bearat, H., McKelvy, M. J., Chizmeshya, A. V. G., Gormley, D., Nunez, R., Carpenter,  
684 R. W., Squires, K. & Wolf, G. H. Carbon sequestration via aqueous olivine mineral carbonation:  
685 Role of passivating layer formation. *Environ. Sci. Technol.* 40, 4802-4808 (2006).
- 686 2 Daval, D., Sissmann, O., Menguy, N., Saldi, G. D., Guyot, F., Martinez, I., Corvisier, J.,  
687 Garcia, B., Machouk, I., Knauss, K. G. et al. Influence of amorphous silica layer formation on  
688 the dissolution rate of olivine at 90°C and elevated pCO<sub>2</sub>. *Chem. Geol.* 284, 193-209 (2011).
- 689 3 Johnson, N. C., Thomas, B., Maher, K., Rosenbauer, R. J., Bird, D. & Brown Jr, G. E.  
690 Olivine dissolution and carbonation under conditions relevant for in situ carbon storage. *Chem.*  
691 *Geol.* 373, 93-105 (2014).
- 692 4 Maher, K., Johnson, N. C., Jackson, A., Lammers, L. N., Torchinsky, A. B., Weaver, K.  
693 L., Bird, D. K. & Brown Jr, G. E. A spatially resolved surface kinetic model for forsterite  
694 dissolution. *Geochim. Cosmochim. Acta* 174, 313-334 (2016).
- 695 5 Daval, D., Martinez, I., Corvisier, J., Findling, N., Goffe, B. & Guyot, F. Carbonation of  
696 Ca-bearing silicates, the case of wollastonite: Experimental investigations and kinetic modeling.  
697 *Chem. Geol.* 265, 63-78 (2009).
- 698 6 Weissbart, E. J. & Rimstidt, D. J. Wollastonite: Incongruent dissolution and leached layer  
699 formation. *Geochim. Cosmochim. Acta* 64, 4007-4016 (2000).

700 7 Ruiz-Agudo, E., Putnis, C. V., Rodriguez-Navarro, C. & Putnis, A. Mechanism of  
701 leached layer formation during chemical weathering of silicate minerals. *Geology* 40, 947-950  
702 (2012).

703 8 Schott, J., Pokrovsky, O. S., Spalla, O., Devreux, F., Gloter, A. & Mielczarski, J. A.  
704 Formation, growth and transformation of leached layers during silicate minerals dissolution: The  
705 example of wollastonite. *Geochim. Cosmochim. Acta* 98, 259-281 (2012).

706 9 Daval, D., Bernard, S., Rémusat, L., Wild, B., Guyot, F., Micha, J. S., Rieutord, F.,  
707 Magnin, V. & Fernandez-Martinez, A. Dynamics of altered surface layer formation on dissolving  
708 silicates. *Geochim. Cosmochim. Acta* 209, 51-69 (2017).

709 10 Lagache, M. New data on the kinetics of the dissolution of alkali feldspars at 200°C in  
710 CO<sub>2</sub> charged water. *Geochim. Cosmochim. Acta* 40, 157-161 (1976).

711 11 Casey, W. H., Westrich, H. R., Massis, T., Banfield, J. F. & Arnold, G. W. The surface of  
712 labradorite feldspar after acid hydrolysis. *Chem. Geol.* 78, 205-218 (1989).

713 12 Casey, W. H., Westrich, H. R., Banfield, J. F., Ferruzzi, G. & Arnold, G. W. Leaching  
714 and reconstruction at the surface of dissolving chain-silicate minerals. *Nature* 366, 253-256  
715 (1993).

716 13 Hellmann, R., Penisson, J.-M., Hervig, R. L., Thomassin, J.-H. & Abrioux, M.-F. An  
717 EFTEM/HRTEM high-resolution study of the near surface of labradorite feldspar altered at acid  
718 pH: evidence for interfacial dissolution-reprecipitation. *Physics and Chemistry of Minerals* 30,  
719 192-197 (2003).

720 14 Wild, B., Daval, D., Guyot, F., Knauss, K. G., Pollet-Villard, M. & Imfeld, G. pH-  
721 dependent control of feldspar dissolution rate by altered surface layers. *Chem. Geol.* 442, 148-  
722 159 (2016).

723 15 Cailleateau, C., Angeli, F., Devreux, F., Gin, S., Jestin, J., Jollivet, P. & Spalla, O. Insight  
724 into silicate-glass corrosion mechanisms. *Nature Materials* 7, 978-983 (2008).

725 16 Verney-Carron, A., Gin, S., Frugier, P. & Libourel, G. Long-term modeling of alteration-  
726 transport coupling: Application to a fractured Roman glass. *Geochim. Cosmochim. Acta* 74,  
727 2291-2315 (2010).

728 17 Geisler, T., Nagel, T., Kilburn, M. R., Janssen, A., Icenhower, J. P., Fonseca, R. O. C.,  
729 Grange, M. & Nemchin, A. A. The mechanism of borosilicate glass corrosion revisited.  
730 *Geochim. Cosmochim. Acta* 158, 112-129 (2015).

731 18 Gin, S., Jollivet, P., Fournier, M., Angeli, F., Frugier, P. & Charpentier, T. Origin and  
732 consequences of silicate glass passivation by surface layers. *Nat. Commun.* 6, 6360 (2015).

733 19 Nugent, M. A., Brantley, S. L., Pantano, C. G. & Maurice, P. A. The influence of natural  
734 mineral coatings on feldspar weathering. *Nature* 395, 588-591 (1998).

735 20 Hellmann, R., Wirth, R., Daval, D., Barnes, J.-P., Penisson, J.-M., Tisserand, D., Epicier,  
736 T., Florin, B. & Hervig, R. L. Unifying natural and laboratory chemical weathering with  
737 interfacial dissolution–reprecipitation: A study based on the nanometer-scale chemistry of fluid–  
738 silicate interfaces. *Chem. Geol.* 294–295, 203-216 (2012).

739 21 Daval, D., Calvaruso, C., Guyot, F. & Turpault, M.-P. Time-dependent feldspar  
740 dissolution rates resulting from surface passivation: Experimental evidence and geochemical  
741 implications. *Earth and Planetary Science Letters* 498, 226-236 (2018).

742 22 Monteiro, P. J. M., Miller, S. A. & Horvath, A. Towards sustainable concrete. *Nature*  
743 *Materials* 16, **698** (2017).

744 23 Gin, S., Collin, M., Jollivet, P., Fournier, M., Minet, Y., Dupuy, L., Mahadevan, T.,  
745 Kerisit, S. & Du, J. Dynamics of self-reorganization explains passivation of silicate glasses. *Nat.*  
746 *Commun.* 9, 2169 (2018).

747 24 Park, A.-H. A. & Fan, L.-S. CO<sub>2</sub> mineral sequestration: physically activated dissolution  
748 of serpentine and pH swing process. *Chemical Engineering Science* 59, 5241-5247 (2004).

749 25 Noiriél, C. & Daval, D. Pore-scale geochemical reactivity associated with CO<sub>2</sub> storage:  
750 new frontiers at the fluid–solid interface. *Accounts of Chemical Research* 50, 759-768 (2017).

751 26 Correns, C. W. & von Engelhardt, W. Neue Untersuchungen über die Verwitterung des  
752 Kalifeldspates. *Naturwissenschaften* 26, 137-138 (1938).

753 27 Luce, R. W., Bartlett, R. W. & Parks, G. A. Dissolution kinetics of magnesium silicates.  
754 *Geochim. Cosmochim. Acta* 36, 33-50 (1972).

755 28 Paces, T. Chemical characteristics and equilibration in natural water-felsic rock-CO<sub>2</sub>  
756 system. *Geochim. Cosmochim. Acta* 36, 217-240 (1972).

757 29 Muir, I. J., Michael Bancroft, G. & Wayne Nesbitt, H. Characteristics of altered  
758 labradorite surfaces by SIMS and XPS. *Geochim. Cosmochim. Acta* 53, 1235-1241 (1989).

759 30 Petit, J.-C., Dran, J.-C., Schott, J. & Mea, G. D. New evidence on the dissolution  
760 mechanism of crystalline silicates by MeV ion beam techniques. *Chem. Geol.* 76, 365-369  
761 (1989).

762 31 Hellmann, R., Eggleston, C. M., Hochella, M. F. J. & Crerar, D. A. The formation of  
763 leached layers on albite surfaces during dissolution under hydrothermal conditions. *Geochim.*  
764 *Cosmochim. Acta* 54, 1267-1281 (1990).

765 32 Inskeep, W. P., Nater, E. A., Bloom, P. R., Vandervoort, D. S. & Erich, M. S.  
766 Characterization of laboratory weathered labradorite surfaces using X-ray photoelectron

767 spectroscopy and transmission electron microscopy. *Geochim. Cosmochim. Acta* 55, 787-800  
768 (1991).

769 33 Muir, I. J. & Nesbitt, H. W. Effects of aqueous cations on the dissolution of labradorite  
770 feldspar. *Geochim. Cosmochim. Acta* 55, 3181-3189 (1991).

771 34 Shotyk, W. & Nesbitt, H. W. Incongruent and congruent dissolution of plagioclase  
772 feldspar - effect of feldspar composition and ligand complexation. *Geoderma* 55, 55-78 (1992).

773 35 Shotyk, W. & Metson, J. B. Secondary ion mass spectrometry (SIMS) and its application  
774 to chemical weathering. *Reviews of Geophysics* 32, 197-220 (1994).

775 36 Schweda, P., Sjöberg, L. & Sodervall, U. Near-surface composition of acid-leached  
776 labradorite investigated by SIMS. *Geochim. Cosmochim. Acta* 61, 1985-1994 (1997).

777 37 Chen, Y. & Brantley, S. L. Dissolution of forsteritic olivine at 65°C and 2 <math>pH</math> <math>< 5</math>. *Chem.*  
778 *Geol.* 165, 267-281 (2000).

779 38 Nesbitt, H. W. & Skinner, W. M. Early development of Al, Ca, and Na compositional  
780 gradients in labradorite leached in pH 2 HCl solutions. *Geochim. Cosmochim. Acta* 65, 715-727  
781 (2001).

782 39 Putnis, C. V., Tsukamoto, K. & Nishimura, Y. Direct observations of pseudomorphism:  
783 compositional and textural evolution at a fluid-solid interface. *Am. Miner.* 90, 1909-1912 (2005).

784 40 Jordan, G., Higgins, S. R., Eggleston, C. M., Swapp, S. M., Janney, D. E. & Knauss, K.  
785 G. Acidic dissolution of plagioclase: in-situ observations by hydrothermal atomic force  
786 microscopy. *Geochim. Cosmochim. Acta* 63, 3183-3191 (1999).

787 41 Aagaard, P. & Helgeson, H. C. Thermodynamic and kinetic constraints on reaction-rates  
788 among minerals and aqueous solutions. 1. Theoretical considerations. *American Journal of*  
789 *Science* 282, 237-285 (1982).



790 42 Berner, R. A. & Holdren, G. R. Mechanism of feldspar weathering - some observational  
791 evidence. *Geology* 5, 369-372 (1977).

792 43 Berner, R. A. & Holdren, G. R. Mechanism of feldspar weathering .2. Observations of  
793 feldspars from soils. *Geochim. Cosmochim. Acta* 43, 1173-1186 (1979).

794 44 Holdren, G. R. & Berner, R. A. Mechanism of feldspar weathering. 1. Experimental  
795 studies. *Geochim. Cosmochim. Acta* 43, 1161-1171 (1979).

796 45 Oelkers, E. H., Schott, J. & Devidal, J.-L. The effect of aluminum, pH, and chemical  
797 affinity on the rates of aluminosilicate dissolution reactions. *Geochim. Cosmochim. Acta* 58,  
798 2011-2024 (1994).

799 46 Taylor, A. S., Blum, J. D. & Lasaga, A. C. The dependence of labradorite dissolution and  
800 Sr isotope release rates on solution saturation state. *Geochim. Cosmochim. Acta* 64, 2389-2400  
801 (2000).

802 47 Nagy, K. L., Blum, A. E. & Lasaga, A. C. Dissolution and precipitation kinetics of  
803 kaolinite at 80 degrees C and pH 3; the dependence on solution saturation state. *American*  
804 *Journal of Science* 291, 649-686 (1991).

805 48 Lasaga, A. C. in *Chemical weathering rates of silicate minerals* Vol. 31 (eds Art F.  
806 White & Susan L. Brantley) 23-86 (1995).

807 49 Grambow, B. & Muller, R. First-order dissolution rate law and the role of surface layers  
808 in glass performance assessment. *J. Nucl. Mater.* 298, 112-124 (2001).

809 50 Bourcier, W. L., Peiffer, D. W., Knauss, K. G., McKeegan, K. D. & Smith, D. K. A  
810 Kinetic model for B\borosilicate glass dissolution based on the dissolution affinity of a surface  
811 alteration layer. *MRS Online Proceedings Library Archive* 176, 1-10 (1989).

812 51 Oelkers, E. H. & Schott, J. Experimental study of anorthite dissolution and the relative  
813 mechanism of feldspar hydrolysis. *Geochim. Cosmochim. Acta* 59, 5039-5053 (1995).

814 52 Daux, V., Guy, C., Advocat, T., Crovisier, J. L. & Stille, P. Kinetic aspects of basaltic  
815 glass dissolution at 90°C: role of aqueous silicon and aluminium. *Chem. Geol.* 142, 109-126  
816 (1997).

817 53 Oelkers, E. H. General kinetic description of multioxide silicate mineral and glass  
818 dissolution. *Geochim. Cosmochim. Acta* 65, 3703-3719 (2001).

819 54 Lüttge, A. Crystal dissolution kinetics and Gibbs free energy. *Journal of Electron  
820 Spectroscopy and Related Phenomena* 150, 248-259 (2006).

821 55 Devreux, F., Ledieu, A., Barboux, P. & Minet, Y. Leaching of borosilicate glasses. II.  
822 Model and Monte-Carlo simulations. *J. Non-Cryst. Solids* 343, 13-25 (2004).

823 56 Rebiscoul, D., Van der Lee, A., Rieutord, F., Ne, F., Spalla, O., El-Mansouri, A., Frugier,  
824 P., Ayral, A. & Gin, S. Morphological evolution of alteration layers formed during nuclear glass  
825 alteration: new evidence of a gel as a diffusive barrier. *J. Nucl. Mater.* 326, 9-18 (2004).

826 57 Gin, S. p., Guittonneau, C., Godon, N., Neff, D., Rebiscoul, D., Cabié, M. & Mostefaoui,  
827 S. Nuclear glass durability: new insight into alteration layer properties. *The Journal of Physical  
828 Chemistry C* 115, 18696-18706 (2011).

829 58 Gin, S., Neill, L., Fournier, M., Frugier, P., Ducasse, T., Tribet, M., Abdelouas, A.,  
830 Parruzot, B., Neeway, J. & Wall, N. The controversial role of inter-diffusion in glass alteration.  
831 *Chem. Geol.* 440, 115-123 (2016).

832 59 Ruiz-Agudo, E., King, H. E., Patiño-López, L. D., Putnis, C. V., Geisler, T., Rodriguez-  
833 Navarro, C. & Putnis, A. Control of silicate weathering by interface-coupled dissolution-  
834 precipitation processes at the mineral-solution interface. *Geology* 44, 567-570 (2016).

835 60 Sissmann, O., Daval, D., Brunet, F., Guyot, F., Verlaguet, A., Pinquier, Y., Findling, N.  
836 & Martinez, I. The deleterious effect of secondary phases on olivine carbonation yield: Insight  
837 from time-resolved aqueous-fluid sampling and FIB-TEM characterization. *Chem. Geol.* 357,  
838 186-202 (2013).

839 61 Saldi, G. D., Daval, D., Morvan, G. & Knauss, K. G. The role of Fe and redox conditions  
840 in olivine carbonation rates: an experimental study of the rate limiting reactions at 90 and 150 °C  
841 in open and closed systems. *Geochim. Cosmochim. Acta* 118, 157-183 (2013).

842 62 Saldi, G. D., Daval, D., Guo, H., Guyot, F., Bernard, S., Le Guillou, C., Davis, J. A. &  
843 Knauss, K. G. Mineralogical evolution of Fe–Si-rich layers at the olivine-water interface during  
844 carbonation reactions. *Am. Miner.* 100, 2655-2669 (2015).

845 63 Hellmann, R., Cotte, S., Cadel, E., Malladi, S., Karlsson, L. S., Lozano-Perez, S., Cabié,  
846 M. & Seyeux, A. Nanometre-scale evidence for interfacial dissolution–reprecipitation control of  
847 silicate glass corrosion. *Nat Mater* 14, 307-311 (2015).

848 64 Casey, W. H. Glass and mineral corrosion dynamics and durability. *Nature Materials* 7,  
849 930-932 (2008).

850 65 White, A. F. & Brantley, S. L. The effect of time on the weathering of silicate minerals:  
851 why do weathering rates differ in the laboratory and field? *Chem. Geol.* 202, 479-506 (2003).

852 66 Fischer, C., Arvidson, R. S. & Lüttge, A. How predictable are dissolution rates of  
853 crystalline material? *Geochim. Cosmochim. Acta* 98, 177-185 (2012).

854 67 Cailleteau, C., Devreux, F., Spalla, O., Angeli, F. & Gin, S. Why do certain glasses with  
855 a high dissolution rate undergo a low degree of corrosion? *The Journal of Physical Chemistry C*  
856 115, 5846-5855 (2011).

857 68 Bourg, I. C. & Steefel, C. I. Molecular dynamics simulations of water structure and  
858 diffusion in silica nanopores. *The Journal of Physical Chemistry C* 116, 11556-11564 (2012).

859 69 Rébiscoul, D., Cambedouzou, J., Matar Briman, I., Cabié, M., Brau, H. P. & Diat, O.  
860 Water dynamics in nanoporous alteration layer coming from glass alteration: an experimental  
861 approach. *The Journal of Physical Chemistry C* 119, 15982-15993 (2015).

862 70 Neeway, J. J., Kerisit, S. N., Liu, J., Zhang, J., Zhu, Z., Riley, B. J. & Ryan, J. V. Ion-  
863 exchange interdiffusion model with potential application to long-term nuclear waste glass  
864 performance. *The Journal of Physical Chemistry C* 120, 9374-9384 (2016).

865 71 Collin, M., Gin, S., Dazas, B., Mahadevan, T., Du, J. & Bourg, I. C. Molecular dynamics  
866 simulations of water structure and diffusion in a 1 nm diameter silica nanopore as a function of  
867 surface charge and alkali metal counterion identity. *The Journal of Physical Chemistry C* 122,  
868 17764-17776 (2018).

869 72 Hövelmann, J., Austrheim, H. & Putnis, A. Cordierite formation during the experimental  
870 reaction of plagioclase with Mg-rich aqueous solutions. *Contributions to Mineralogy and  
871 Petrology* 168, 1063 (2014).

872 73 Arvidson, R. S., Beig, M. S. & Lüttge, A. Single-crystal plagioclase feldspar dissolution  
873 rates measured by vertical scanning interferometry. *Am. Miner.* 89, 51-56 (2004).

874 74 Nečas, D. & Klapetek, P. Gwyddion: an open-source software for SPM data analysis.  
875 *Central European Journal of Physics* 10, 181-188 (2012).

876 75 Nelson, A. Co-refinement of multiple-contrast neutron/X-ray reflectivity data using  
877 MOTOFIT. *Journal of Applied Crystallography* 39, 273-276 (2006).

878 76 Bowen, D. K., Tanner, B. K., Wormington, M., Panaccione, C., Matney Kevin, M. &  
879 Bowen, D. K. Characterization of structures from X-ray scattering data using genetic algorithms.

880 Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical  
881 and Engineering Sciences 357, 2827-2848 (1999).

882 77 Marquardt, D. An Algorithm for least-squares estimation of nonlinear parameters.  
883 Journal of the Society for Industrial and Applied Mathematics 11, 431-441 (1963).

884 78 Pollet-Villard, M., Daval, D., Ackerer, P., Saldi, G. D., Wild, B., Knauss, K. G. & Fritz,  
885 B. Does crystallographic anisotropy prevent the conventional treatment of aqueous mineral  
886 reactivity? A case study based on K-feldspar dissolution kinetics. Geochim. Cosmochim. Acta  
887 190, 294-308 (2016).

888 79 Schott, J., Pokrovsky, O. S. & Oelkers, E. H. The link between mineral  
889 dissolution/precipitation kinetics and solution chemistry. Thermodynamics and Kinetics of  
890 Water-Rock Interaction 70, 207-258 (2009).

891 80 Palandri, J. L. & Kharaka, Y. K. A compilation of rate parameters of water-mineral  
892 interaction kinetics for application to geochemical modeling. 70 (U.S. Geological Survey, Open  
893 File Report, 2004).

894 81 Iler, R. K. The chemistry of silica : solubility, polymerization, colloid and surface  
895 properties, and biochemistry / Ralph K. Iler. (Wiley, 1979).

896 82 Icenhower, J. P. & Dove, P. M. The dissolution kinetics of amorphous silica into sodium  
897 chloride solutions: effects of temperature and ionic strength. Geochim. Cosmochim. Acta 64,  
898 4193-4203 (2000).

899 83 Rimstidt, J. D. & Barnes, H. L. The kinetics of silica-water reactions. Geochim.  
900 Cosmochim. Acta 44, 1683-1699 (1980).

901 84 Tester, J. W., Worley, W. G., Robinson, B. A., Grigsby, C. O. & Feerer, J. L. Correlating  
902 quartz dissolution kinetics in pure water from 25 to 625°C. *Geochim. Cosmochim. Acta* 58,  
903 2407-2420 (1994).

904 85 Daval, D., Hellmann, R., Saldi, G. D., Wirth, R. & Knauss, K. G. Linking nm-scale  
905 measurements of the anisotropy of silicate surface reactivity to macroscopic dissolution rate  
906 laws: New insights based on diopside. *Geochim. Cosmochim. Acta* 107, 121-134, (2013).

907 86 Geisler, T., Dohmen, L., Lenting, C. & Fritzsche, M. B. K. Real-time in situ observations  
908 of reaction and transport phenomena during silicate glass corrosion by fluid-cell Raman  
909 spectroscopy. *Nature Materials* (2019).

910 87 Bottero, J. Y., Cases, J. M., Fiessinger, F. & Poirier, J. E. Studies of hydrolyzed  
911 aluminium-chloride solutions. 1. Nature of aluminium species and composition of aqueous  
912 solutions. *J. Phys. Chem.* 84, 2933-2939 (1980).

913 88 McHardy, W. J. & Thomson, A. P. Conditions for the formation of bayerite and gibbsite.  
914 *Mineralogical magazine* 38, 358-368 (1971).

915 89 Schott, J. & Berner, R. A. X-Ray Photoelectron studies of the mechanism of iron silicate  
916 dissolution during weathering. *Geochim. Cosmochim. Acta* 47, 2233-2240 (1983).

917