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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, SiO₂(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⁻¹ 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 SiO₂(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 olivine¹⁻⁴, wollastonite⁵⁻⁹, feldspars¹⁰⁻¹⁴, and glasses¹⁵⁻¹⁸. These layers, also called
50 surface alteration layer (SAL), form ubiquitously from laboratory to field settings¹⁹⁻²¹. 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 infrastructure²², the long-term storage security of nuclear waste^{18,23}, and the feasibility of
54 enhancing silicate weathering as a large-scale CO₂ capture technology^{24,25}.

55 While the existence of ASSLs has been known or hypothesized for at least 80 years²⁶,
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^{27,28}. 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
64²⁹⁻³⁸. The alternative “dissolution-reprecipitation” hypothesis³⁹ is supported by transmission

65 electron microscopy observations that indicate an absence of compositional gradients within the
66 ASSL¹³ 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 resolution²⁰. 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 surface⁴⁰, 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 solution⁴¹. 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^{10,42-44}. While challenged
79 more than 20 years ago by both contradictory experimental results^{45,46} and theoretical
80 inconsistencies^{47,48}, 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^{45,49-53}. 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 debate⁵⁴. 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^{9,18,55-59}.

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 range²⁰,
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 layers¹⁴, similar to the work by Lagache¹⁰ 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 diffusivity⁶⁰⁻
97 ⁶². 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.⁸ vs. Ruiz-
99 Agudo, et al.⁷ or Hellmann, et al.⁶³ vs. Gin, et al.¹⁸) 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^{25,64}. 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 powder⁶⁵. 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 ⁶⁶. 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 ^{57,67-71}.
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

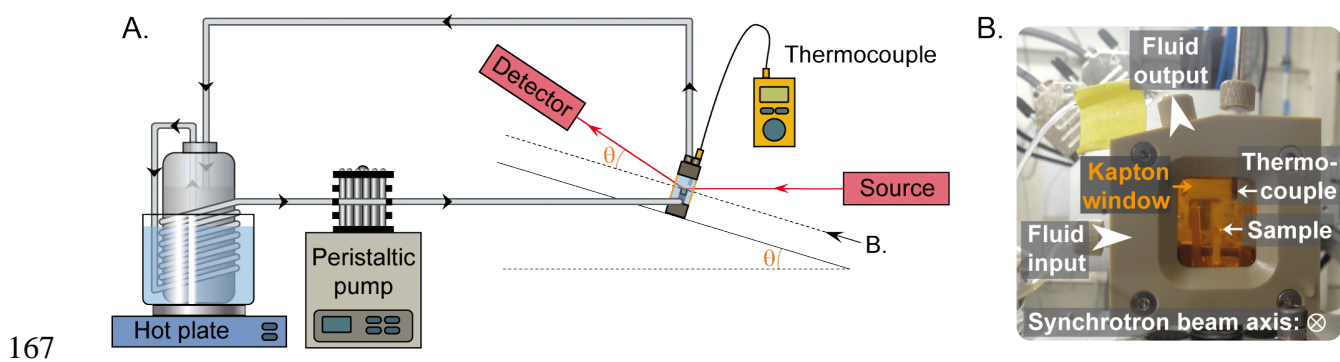
139 **Sample preparation**

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 $Ab_{39}An_{60}Or_1$ ⁷². 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 described¹⁴. 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 system¹⁴. 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 ($\text{mol m}^{-2} \text{s}^{-1}$), Δh is the surface retreat (m), Δt is the alteration duration (s), and
181 V_m is the molar volume of labradorite ($\text{m}^3 \text{mol}^{-1}$)⁷³. Topography images and profiles were
182 analyzed using SPIP software.

183 The roughness of the outer interface, σ_{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 software⁷⁴ 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 ~ 1 cm thick
193 solution in the cell. Reflectivity patterns were acquired for 2θ angles ranging between 0° and 1°
194 (corresponding to scattering vectors ranging between 0.0 and 0.5 \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 Motofit⁷⁵, 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 Nelson⁷⁵. Discrepancies between the model and data were quantified
209 by the χ^2 parameter as defined by Nelson⁷⁵, 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 optimization⁷⁶ and the Levenberg-Marquardt method⁷⁷. 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 χ^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).

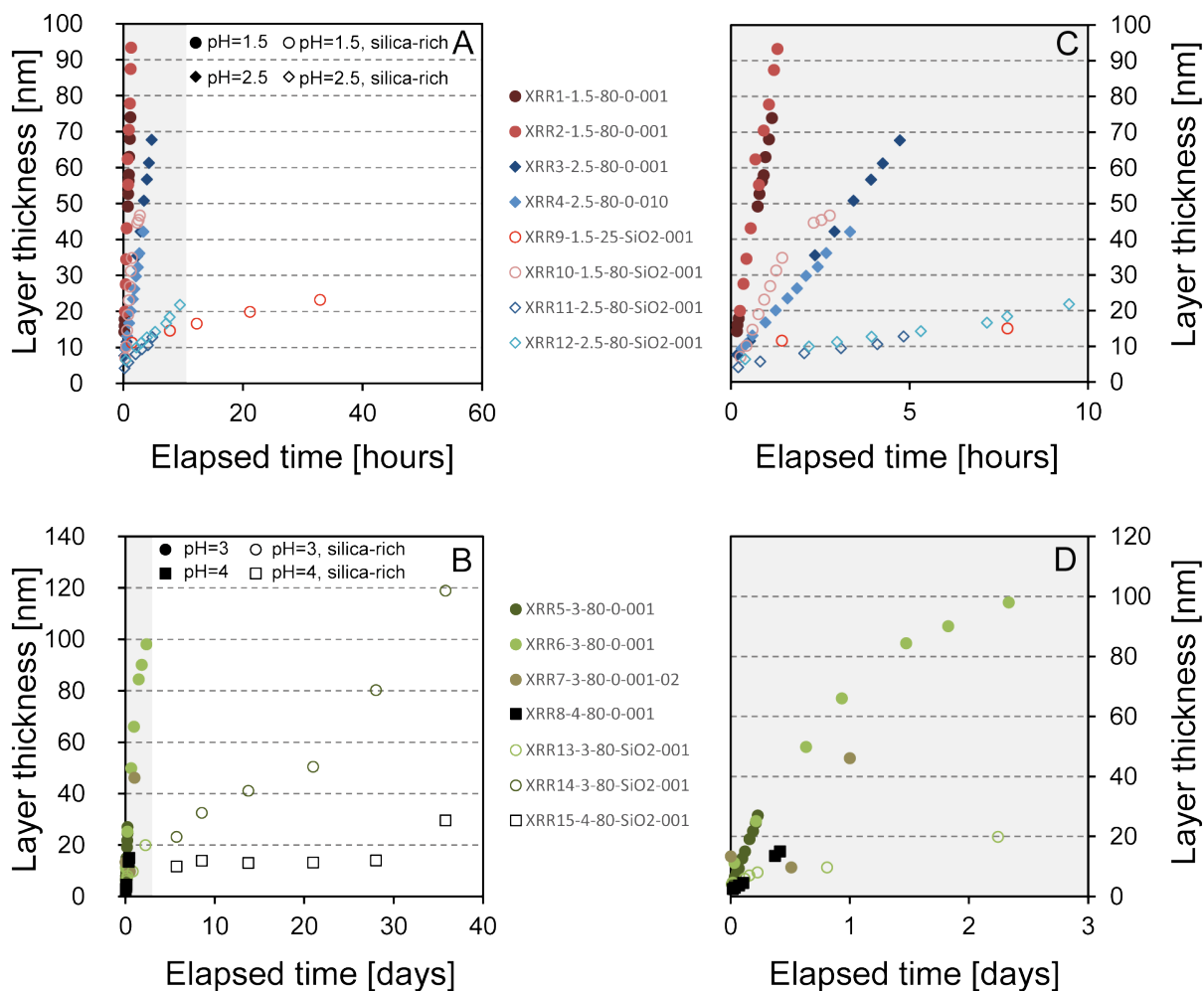
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218 RESULTS

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

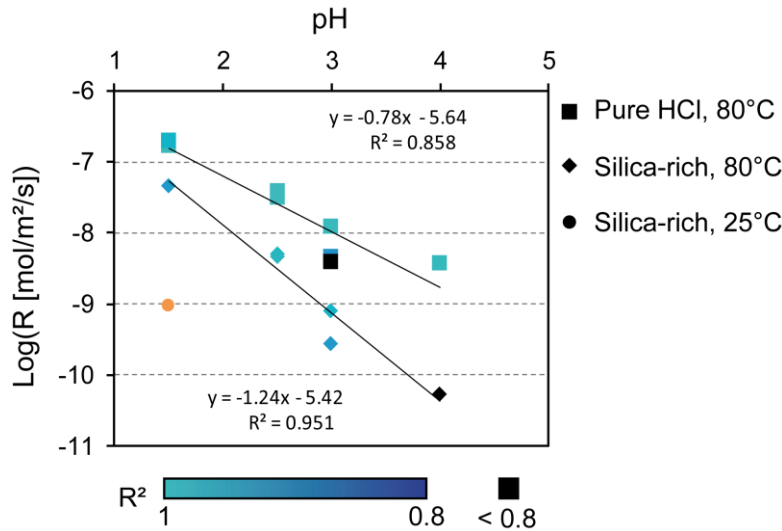
220 The formation of ASSLs at the fluid-mineral interface was observed by XRR for all
221 tested conditions, i.e. pH = 1.5 to pH = 4, 80°C or 25°C, in aqueous solutions that were either
222 saturated or not with respect to amorphous silica. As a general trend, ASSLs' growth rate

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 ≥ 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.

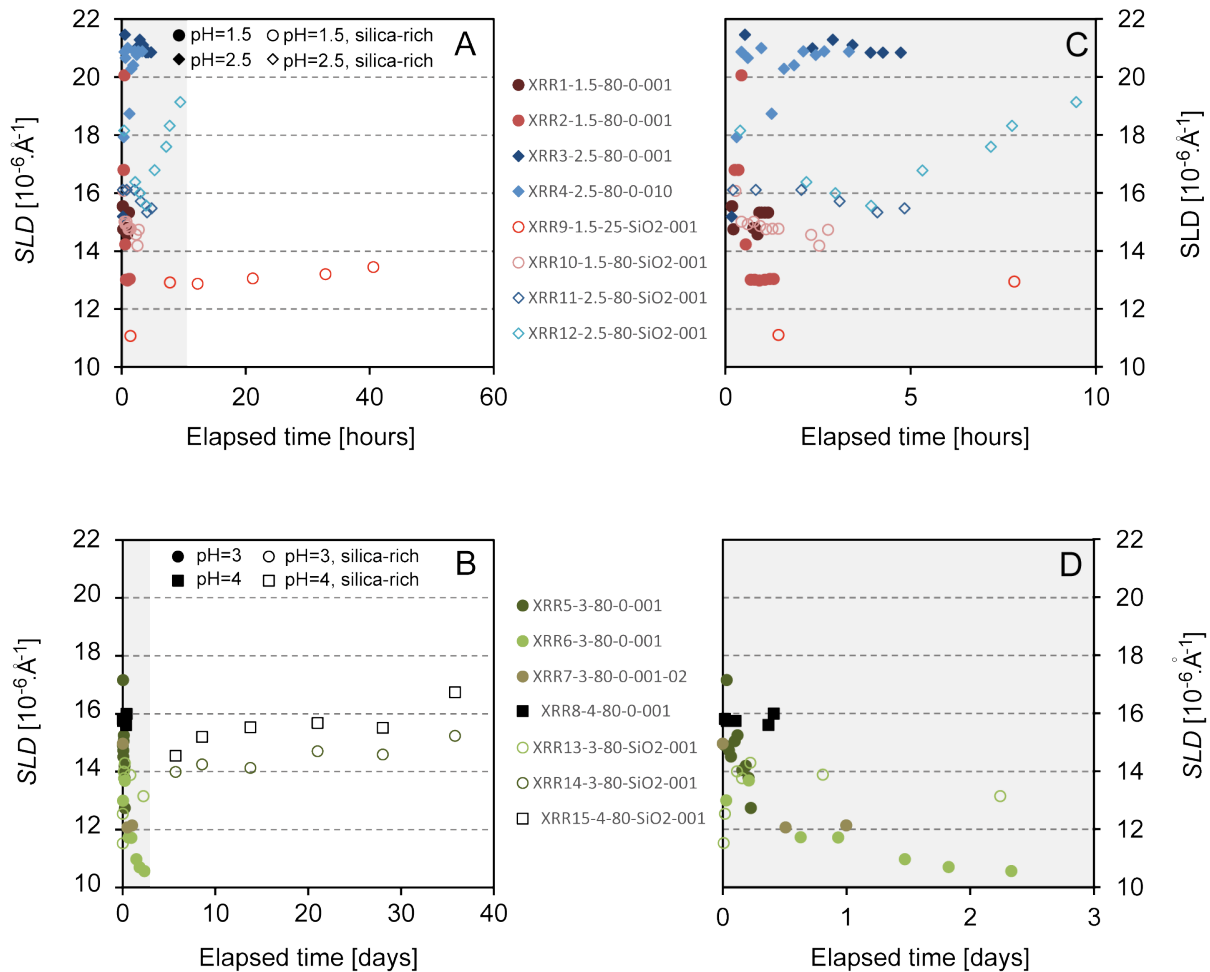
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241
 242 **Figure 3.** pH-dependence at 80°C of layer growth rate represented as moles of labradorite per
 243 square meter converted each second into layer (*labradorite* → *layer*). Diamonds and squares
 244 represent experiments where the fluid 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} \AA^{-1} , which would correspond to
 252 densities of ~ 1.25 and 2.53 g cm^{-3} under the hypothesis that ASSL are composed of pure silica
 253 (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-SiO₂, XRR14-3-80-SiO₂-001 or XRR15-4-80-
 257 SiO₂-001) 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 ± 0.9 vs. 14.8 ± 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

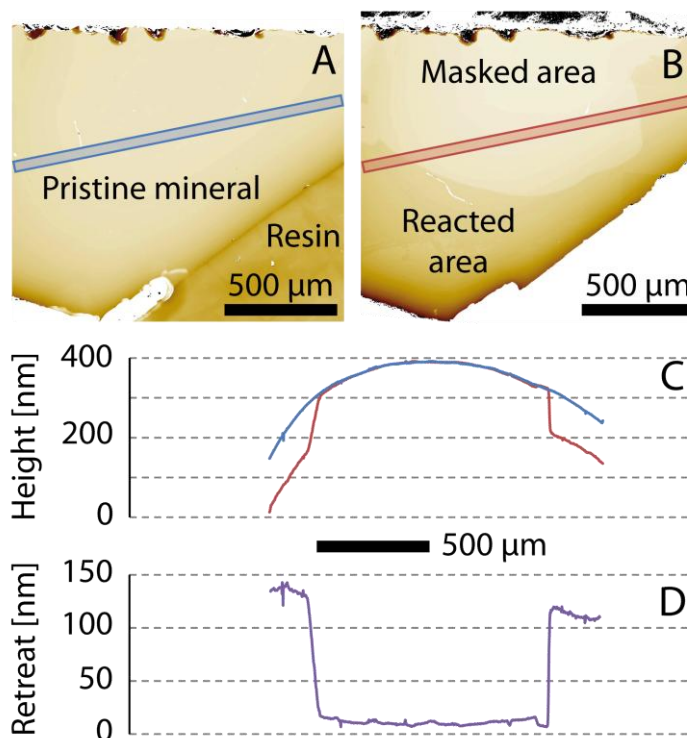
269 to experiments conducted with fluids saturated with respect to amorphous silica. C and D
270 correspond to close-up views of the regions indicated by the shaded areas on plots A and B,
271 respectively. All experiments were conducted at 80°C with the exception of experiment XRR10-
272 1.5-25-SiO2-001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

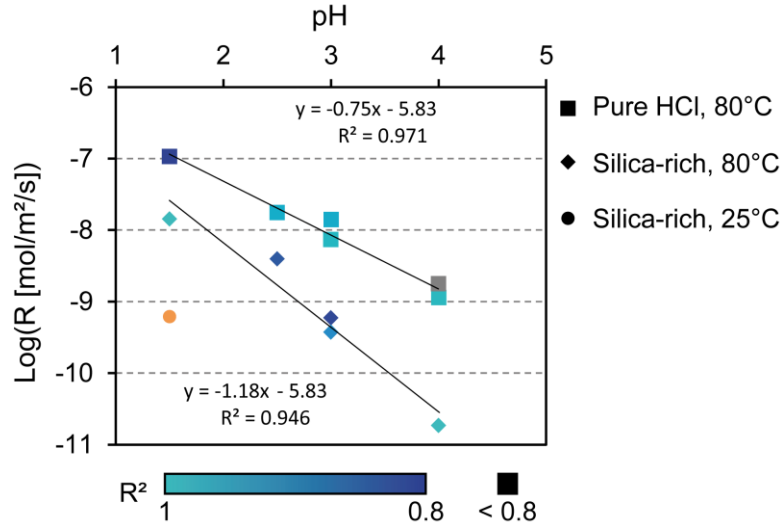
283 at 80°C in a fluid at pH = 3 saturated with respect to amorphous silica). This specific sample was
284 detached from the resin after reaction to facilitate VSI alignment. Height profiles recorded before
285 (blue) and after (red) weathering through the non-reacted masked area are superimposed (c) 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⁻¹.

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

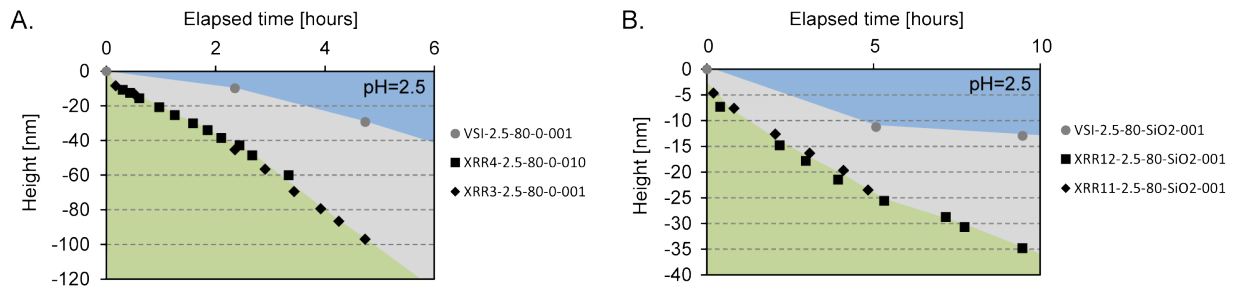
306 regression coefficient associated to linear regression of the temporal retreat of the outer

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 (SiO₂, 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^{14,78}. 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 ± 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 ~ 0.76 as an upper bound on the porosity of the ASSL.

335

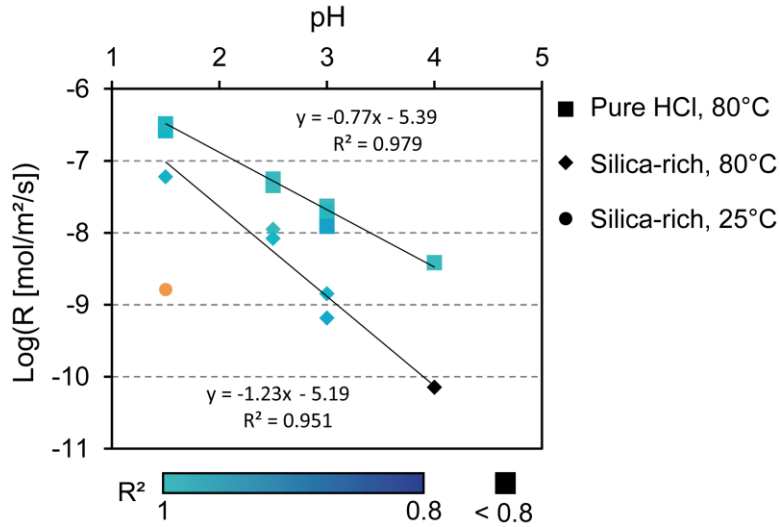
336 **Temporal evolution of the fluid-silicate interface and labradorite reactivity**

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 Δz 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⁻¹.

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 (ΔG_r) values were all below the ΔG_r threshold value of -
377 41.8 kJ mol⁻¹ where labradorite dissolution should be invariant with saturation as reported by
378 Taylor, et al.⁴⁶.

379

380 DISCUSSION

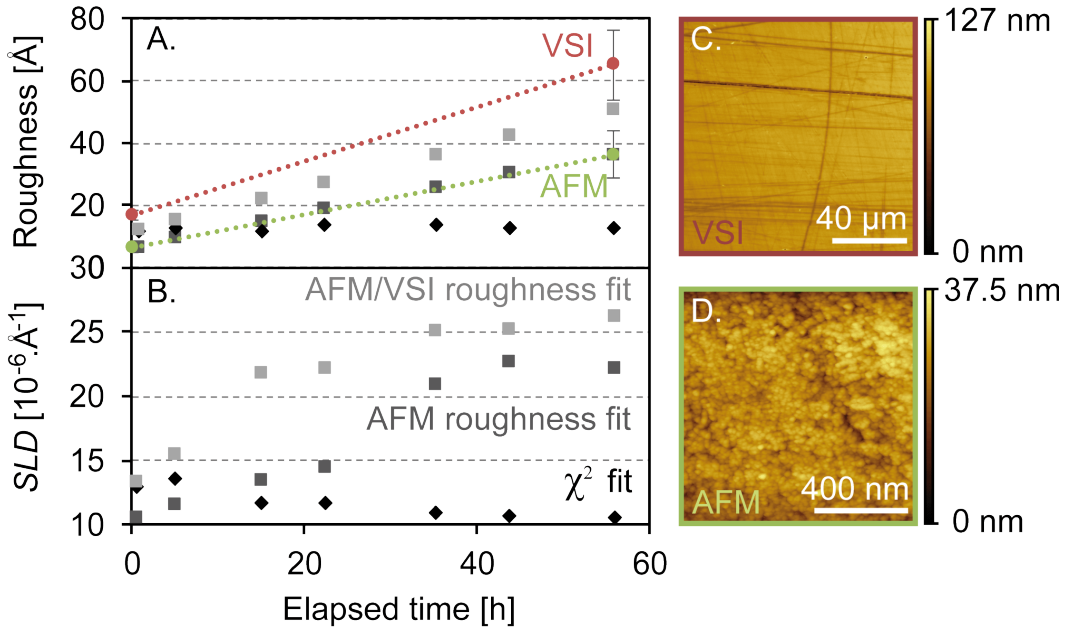
381 **Fitting X-ray reflectivity data**

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 χ^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 χ^2 value depends on the
390 proportion of data points accurately fitted by the model, it is possible to get a lower χ^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 σ_{ex}^{XRR} either to the linear interpolation of initial and final AFM-based
399 roughness (σ_{ex}^{AFM} , cf. dark grey squares, Figure 9) or to the interpolation of the initial and final
400 averages between VSI- (σ_{ex}^{VSI}) and AFM- (σ_{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 σ_{ex}^{XRR} and σ_{ex}^{VSI} or σ_{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 χ^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 “ χ^2 fit” approach⁷⁵,
412 which also enables direct comparison of our data with literature^{9,56}. 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 χ^2 value as the criterion

420 to assess the validity of the fit, grey squares correspond to best fits obtained using the lowest χ^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 ^{79,80}. 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^{10,28,31}. 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 ²⁰. 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 ⁸⁰. 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 ⁷⁸.

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 SiO_2 ($2.2 \text{ g}\cdot\text{cm}^{-3}$, cf. Iler ⁸¹). 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 ⁹ 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 ^{20,59}.

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 θ - 2θ 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 Dove⁸² 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 Barnes⁸³ 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 quartz⁸⁴, as
490 expected for amorphous SiO₂.

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 silica⁶. This result however is at odds
495 with observations conducted on ASSLs formed on diopside⁸⁵, where the solubility of the ASSLs
496 was suggested to be close to that of α -cristobalite.

497 In summary, our results suggest that ASSLs formed on labradorite have slightly higher
498 solubility than amorphous SiO₂ but similar dissolution rates. Since the solubility of hydrated
499 amorphous silica would theoretically be decreased compared to pure amorphous silica according

500 to ⁸¹, 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 ⁸². This supports the hypothesis
508 that ASSLs formed on labradorite at pH > 1.5 may not consist of pure hydrated SiO₂ ¹⁴. In
509 addition, when the fluid is saturated with respect to amorphous silica (aqueous silica
510 concentrations typically of 5.2 ×10⁻³ 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⁻¹, which is similar to those typically reported for labradorite, at ~42 kJ
517 mol⁻¹ ⁸⁰. 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-content¹⁴. 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 ⁻⁶ .Å ⁻²]	<i>Porosity</i> %Water (Vol.)	<i>SLD Layer</i> [10 ⁻⁶ .Å ⁻²]	<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^{2,9,14,21,61}.

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 ΔGr 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 ~ 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.⁴⁶ for labradorite. Moreover, in acidic conditions ($\text{pH} \leq 4$), the only reactive species
568 to be considered is H^+ . In short, no effect of the activity of dissolved 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 studies⁸⁶. 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 Al^{3+} and Ca^{2+} before reaching the close-to-equilibrium
582 regime domain with respect to labradorite dissolution defined by Taylor, et al.⁴⁶. 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 wollastonite⁹.
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^{14,21}. 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”⁸⁷. Analogous time-
600 dependent processes have been previously observed for amorphous phases such as pregibbsite
601 gels⁸⁸. 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^{62,89} is one of the few clearly identified mechanism of silicate passivation to date. Contrary to the
607 present study, both in Wild, et al.¹⁴ and Daval, et al.²¹ 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^{57,67-71}.

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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654 **Author Contributions**

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 (CaAl_2

675 Si_2O_8); Or, Orthoclase (KAlSi_3O_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

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