Supporting Information for

The role of pH, temperature and NH_4^+ during mica weathering

Daniel LAMARCA-IRISARRI¹, Alexander E.S. VAN DRIESCHE^{2,*} Guntram JORDAN³,
Chiara CAPPELLI⁴, and F. Javier HUERTAS¹

¹ *Instituto Andaluz de Ciencias de la Tierra (CSIC-University of Granada), Avda. de las Palmeras 4, 18100 Armilla, Granada, Spain*

² *Université Grenoble Alpes, Université Savoie Mont Blanc, CNRS, IRD, IFSTTAR, ISTerre, F-38000, Grenoble, France.*

³ *Department für Geo- und Umweltwissenschaften, Ludwig-Maximilians-Universität München, Theresienstr, 41, 80333 München, Germany*

⁴ *Department of Geological Sciences, The University of Alabama, 201 7th Ave 2003 Bevill Building 35487 Tuscaloosa, AL, USA.*

This PDF file includes:

- 1. Supporting Table S1**
- 2. Supporting Figures S-1 to S-9**

1. Supporting Tables

Table S1. Experimental conditions and replicates of in-situ HAFM experiments.

Mica type	Solution*	pH*	Temp. (°C)	N° of replicates*
Biotite	0.1 M NH_4^+	6.8	100 and 120	27
Biotite	HCl + KCl	1.0 – 2.0	80 and 100	18
Biotite	HCl + KCl	1.0 – 2.0	25	4
Biotite	HCl + KCl	3.0 – 4.0	100	13
Muscovite	0.1 M NH_4^+	6.8	100 and 120	10
Muscovite	HCl + KCl	1.0 – 2.0	80 and 100	3
Muscovite	HCl + KCl	3.0 – 4.0	100	2
Phlogopite	0.1 M NH_4^+	6.8	100	3
Phlogopite	HCl + KCl	1.0 – 2.0	100	3
Phlogopite	HCl + KCl	3.0 – 4.0	100	3

*Observation with deionized water (pH 5.8) were conducted for all experimental runs, since this was the solution used to stabilize (heat/pressurize) the HAFM.

2. Supporting Figures

Figure S1. pH 2 solutions were used to dissolve the bulges taking advantage that areas affected by bulging are easier to dissolve. The pit produced was 7 nm deep (lower profile), indicating that only 7 biotite layers were involved in the bulge of 112 nm (upper profile).

Figure S2. *In-situ* AFM images of surface processes induced by pH variation. A) After 1 hour and 30 min at 120 °C in contact with pH 5.8 solution, swelling fronts with an average height of 0.5 nm are formed on the surface. However, in some areas these bands overlap and reached a height of ~1 nm (blue dashed line). The same cross-sections (orange dashed line), after 3 hours in contact with a pH 6.8 solution leads to a partial collapse of the swelled areas (1) and the formation of a 2 nm high bulge from 1 nm high swelling band (2 and green arrow in the picture B).

Figure S3. In-situ AFM deflection images of the effect of different solutions on the basal plane of biotite at 120 °C. A) During interaction with a pH 5.8 solution, a swelling front and a bulge (red arrow) are visible. B) After 10 min of reaction with a pH 6.8 solution, the bulge shown in image (A) has collapsed and a relict area has formed (red arrow). C) After 90 min of reaction with a pH 6.8 solution, several relict areas and precipitates (e.g. below red arrow) are visible on the surface. D) After 60 min at pH 2, most precipitates dissolved (e.g. below red arrow). E) After 75 min of deionized water treatment, the surface started to swell back to the original surface (green areas) shown in (A). F) After 120 min of deionized water treatment, large areas of the surface (central part) have swelled back to the original surface. G) After 5 minutes interacting with ammonium solution, all swelled surfaces have collapsed and a general decomposition of the surface is evident.

Figure S4. In-situ AFM deflection (left) and height (right) images of swelling patterns formed on the basal plane of biotite reacted for 53 min at pH 6.8 and 100 °C. Insets show zoomed areas of swelling patterns in deflection (A) and height (B) imaging modes. A cross-section of a typical swelling structure (green line in A) shows a height of ~ 0.6 nm.

Figure S5. Development of dissolution fronts initiating at bulges (A, B, C: deflection images; A', B', C': height images) in pH 2 solutions at 100 °C. A and A') Initial surface. B and B') After 30 min at 100 °C, bulging and swelling (red arrows) patterns as well as a dissolution channel (green arrow) are evident. C and C'). After 90 min at 100 °C, step retreatment (red arrows) and spreading and deepening of the dissolution channel (green arrow).

Figure S6. Compositional differences between different areas of the basal surface of biotite altered at pH 6.8 and 50 °C in a flow-through system for 22 days. Spectrums 92 and 95 show areas enriched in Si, probably due to the formation of leached layers. No etch pits were observed. Inset: ternary plot which shows that the surface layer of reacted samples is enriched in tetrahedral cations compared to the surface layer of the unreacted sample (yellow: unreacted biotite; orange and blue: data points collected on two reacted biotite samples; T: tetrahedral cations; O: octahedral cations; I: interlayer cations).

Figure S7. Ex-situ AFM deflection images of basal surfaces of biotite altered for 50 days at pH 6.8 and 200 °C. (A) Structurally controlled etch pit (up to ten layers) with constant angles between ~ 130 and 106° . (B) Secondary phases mainly composed of Al and Fe, and some Ti in the centre of the structure.

Figure S8. Time-resolved imaging of the formation of a 1.2 nm coating of on the basal surface of muscovite due to the precipitation of secondary phase(s) after 2h 39 min (A), 3h 39 min (B), 5h 9min (C) and 7h 31min (D) of reaction with a pH 6.8 solution at 100 °C.

Figure S9. Chemical analysis of basal surface of biotite altered for 7 hours and 30 min at pH 6.8 and 120 °C, Spectrum 109 corresponds to a Fe-rich phase, Spectrum 110 is a Si-rich precipitate and Spectrum 111 is a Si-rich edge layer.