Electronic Supplementary Information to:

Nanoscopic feldspar islands on K-feldspar microcline (001)

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1. SAMPLE CHARACTERISATION

1.1 Batches and Analysed Samples

In this and previous studies,[1,2] we analysed microcline samples (SurfaceNet, Germany) from a batch of opaque single crystals with a white, sometimes slightly beige colour. All crystals from this batch, referred to as batch A, were cut from the same original crystal, and most of the samples already show visible cracks parallel to the (001) plane (red arrow in Figure S1 (a)). Moreover, in one of the previous studies,[1] we also used samples from another batch of (semi)transparent and colourless microcline single crystals (batch B). These samples were also acquired from SurfaceNet (Germany). Photographs of representative samples from both batches are shown in Figure S1. In this study, only samples form batch A were analysed.

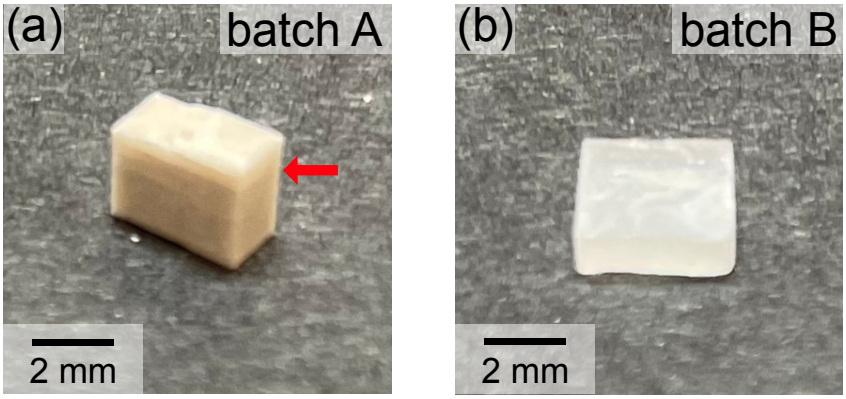

Figure S1: Photographs of representative samples from batches A (a) and B (b). Shown are samples Mi-UHV-5 for batch A (a) and Mi-Ia for batch B (b). The height of one of the internal cracks in batch A is highlighted with a red arrow.

In total, we have characterised the surfaces of six samples – five from batch A and one from batch B. Some of the samples were cleaved several times or we characterised both sides after cleavage. In total, we have looked at the structure of nine cleaved surfaces. Four of these surfaces on two different samples showed the islands discussed in the main text, and the islands were exclusively observed on samples from batch A. A summary of all samples, their preparation and whether they showed islands is given in Table S1.

Table S1: Listing of microcline (001) samples analysed in this study and previous studies from our group. Given are the sample name, batch, preparation method and whether we observed islands on the sample surface. For samples used in previous studies, the reference is given.

Sample	Batch	Preparation	Islands?	Reference
Mi-UHV-1	A	Cleaved in UHV and used for TPD experiments, annealed at 700 K for 6.5 h in UHV after TPD	No	Ref. [2]
Mi-UHV-3	A	Cleaved in UHV and used for TPD experiments	No	Ref. [2]
Mi-UHV-4	A	Cleaved under ambient conditions and annealed at 449 K, 549 K and 649 K for 20 h each (ambient pressure)	No	This study and XRD in Ref. [1] (offcut taken before annealing)
Mi-UHV-5	A	Cleaved and annealed at 450 K for 20 h in UHV	Yes	This study and atomic resolution in Ref. [1]
Mi-UHV-6	A	Cleaved under ambient conditions, investigated both sides of cleavage plane	Yes	This study
Mi-I	B	Cleaved under ambient conditions (cleaved twice)	No	Atomic resolution in Ref. [1]

1.2 Optical Microscopy

Optical microscopy images were taken on the (001) surface of microcline samples from batch A. The sample shown Figure S2 was cleaved under ambient conditions, but the surfaces of UHV cleaved samples show the same characteristics. Both sides of the sample were inspected with an optical microscope (DCM8, Leica, Germany) using confocal imaging. To produce an image showing the entire surface (Figure S2 (a) and (d)), six individual images at 10x magnification were stitched together. Details of the surface were inspected at 50x (Figure S2 (b) and (e)) and 150x (Figure S2 (c) and (f)) magnification. The overview images in Figure S1 (a) and (d) show several large cracks and edges clearly originating from the cleavage. As expected, the shapes of the large step edges on the upper and lower cleavage plane clearly correlate with each other. However, there are also some features that seem to only appear on one of the cleavage planes. Moreover, the surfaces show some lighter spots that almost appear white on the image. In these areas, we also observe interference patterns and sometimes colours

originating from thin microcline slates created by multiple cleavage. 50x magnification images (Figure S2 (b) and (e)) show smaller step edges, cracks and pores. Some of the darker areas might also be mineral inclusions, but we cannot determine this for certain with our instrument. Even more details of the surface features can be seen in the 150x magnification images Figure S2 (c) and (f).

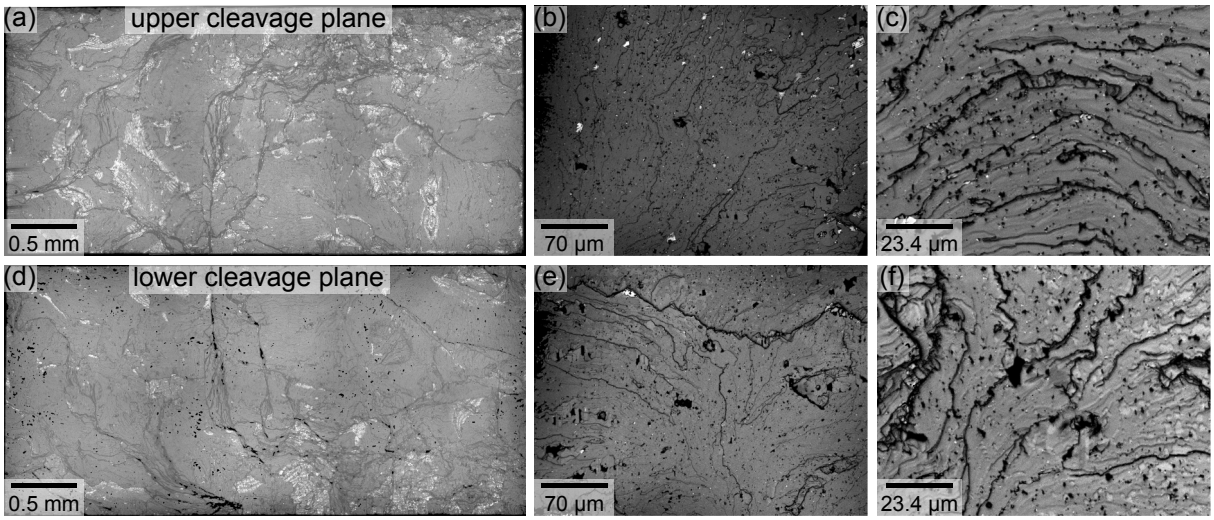

Figure S2: Optical microscopy images taken on the upper (a-c) and lower (d-f) cleavage planes of microcline sample Mi-UHV-6. The images in (a) and (d) show stitching images of the complete cleavage plane. Images are representative for all investigated samples of batch A.

1.3 Scanning Electron Microscopy

Representative SEM and EDX images of the upper and lower cleavage plane of one microcline sample (Mi–UHV–6) are presented in Figure S3. The investigated surfaces exhibit several micrometre wide pores and step edges of different height. The EDX images show a clear separation of K- and Na-rich domains resulting in the known perthitic structure.[3] The atomic concentrations of each element deviated from the expected value (cf. Table S2). Oxygen is overrepresented while the other elements are underrepresented. This composition indicates the existence of pores or cavities inside the feldspar sample, which are filled with water. This finding agrees with previous experiments showing an increase of the partial pressure of water while cleaving feldspar samples in UHV.[2] Samples with a low electrical conductivity like feldspar show surface charging artefacts in SEM measurements (here the black wavy lines). To improve the quality of the picture it is possible to prepare a surface sputter coating with gold or palladium to get the surface conductive, but this treatment will waste our sample for later

experiments, so we abstain from this. Due to the charging issue, longer measurements, which would be needed to rule out small amounts of carbon contaminants, were not possible.

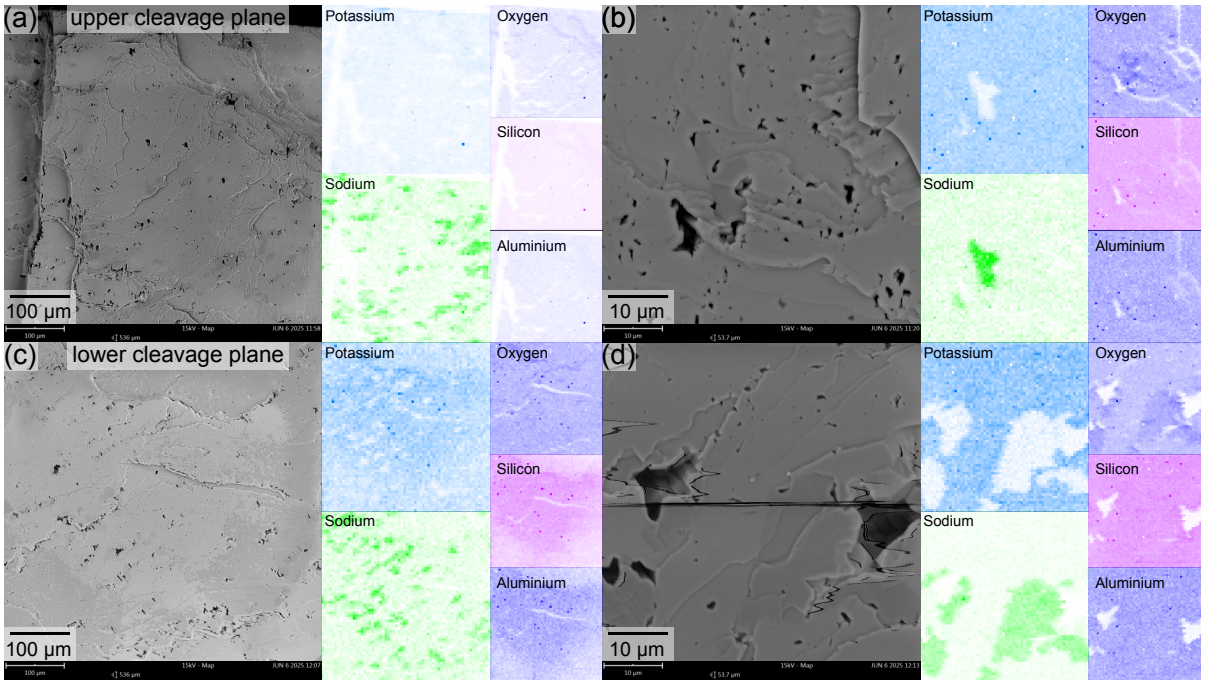

Figure S3: Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis images taken on the upper (a+b) and lower (c+d) cleavage planes of microcline sample Mi-UHV-6. The images were measured with 15 kV acceleration voltage in a high vacuum (pressure around 10^{-6} mbar).

Table S2: Elemental composition derived from the SEM-EDX images in Figure S3, average and expected composition.

element	upper cleavage plane		lower cleavage plane		average	expected for $XAlSi_3O_8$ (X = Na,K)
	S3 (a)	S3 (b)	S3 (c)	S3 (d)		
O	73.8 %	69.4 %	78.5 %	74.4 %	(74.0 ± 3.8) %	61.5 %
Si	14.9 %	17.8 %	12.3 %	13.9 %	(14.7 ± 2.3) %	23.1 %
Al	6.2 %	7.1 %	5.4 %	6.0 %	(6.2 ± 0.7) %	7.7 %
K	3.2 %	5.1 %	2.0 %	3.4 %	(3.4 ± 1.2) %	
Na	1.9 %	0.7 %	1.8 %	2.3 %	(1.7 ± 0.7) %	
K + Na	5.1 %	5.8 %	3.8 %	5.7 %	(5.1 ± 0.9) %	7.7 %

2. ADDITIONAL UHV AFM DATA

Figure S4 shows all AFM channels recorded for the overview image displayed in Figure 1 (a) of the main text. Neither of the channels shows a difference in the contrast between the terraces and islands.

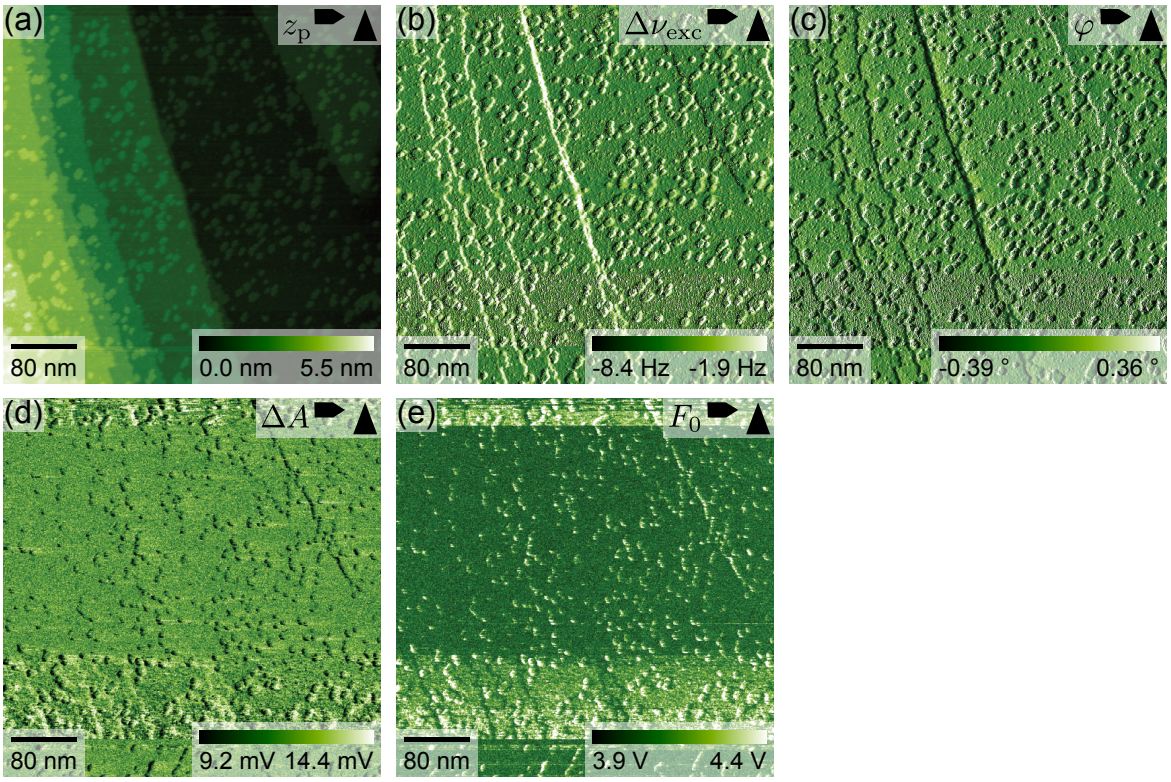

Figure S4: AFM image of the microcline (001) cleavage plane taken under UHV conditions. Shown are the z-piezo displacement (a), excitation frequency shift (b), phase shift (c), excitation amplitude change (d) and excitation force amplitude (e).

Two additional representations of the detail image in Figure 1 (c) of the main text are given in Figure S5 (a) and (b). These images have a different colour scale highlighting either the internal structure of the terrace or islands. From these images it becomes even more clear that both terrace and islands exhibit the same structure and that the observed protrusions are observed on both terraces and islands. All additional AFM channels are displayed in Figure S5 (c) to (f). The excitation frequency shift (c) and phase (d) also nicely show the island structure and protrusions, while the oscillation amplitude (e) and excitation force amplitude (f) show no noticeable contrast. 2D Fourier transform and 2D autocorrelation images in Figure S5 (g) and (h) show that the images exhibit no periodicity, that is, the placement of protrusions follows no periodic structure.

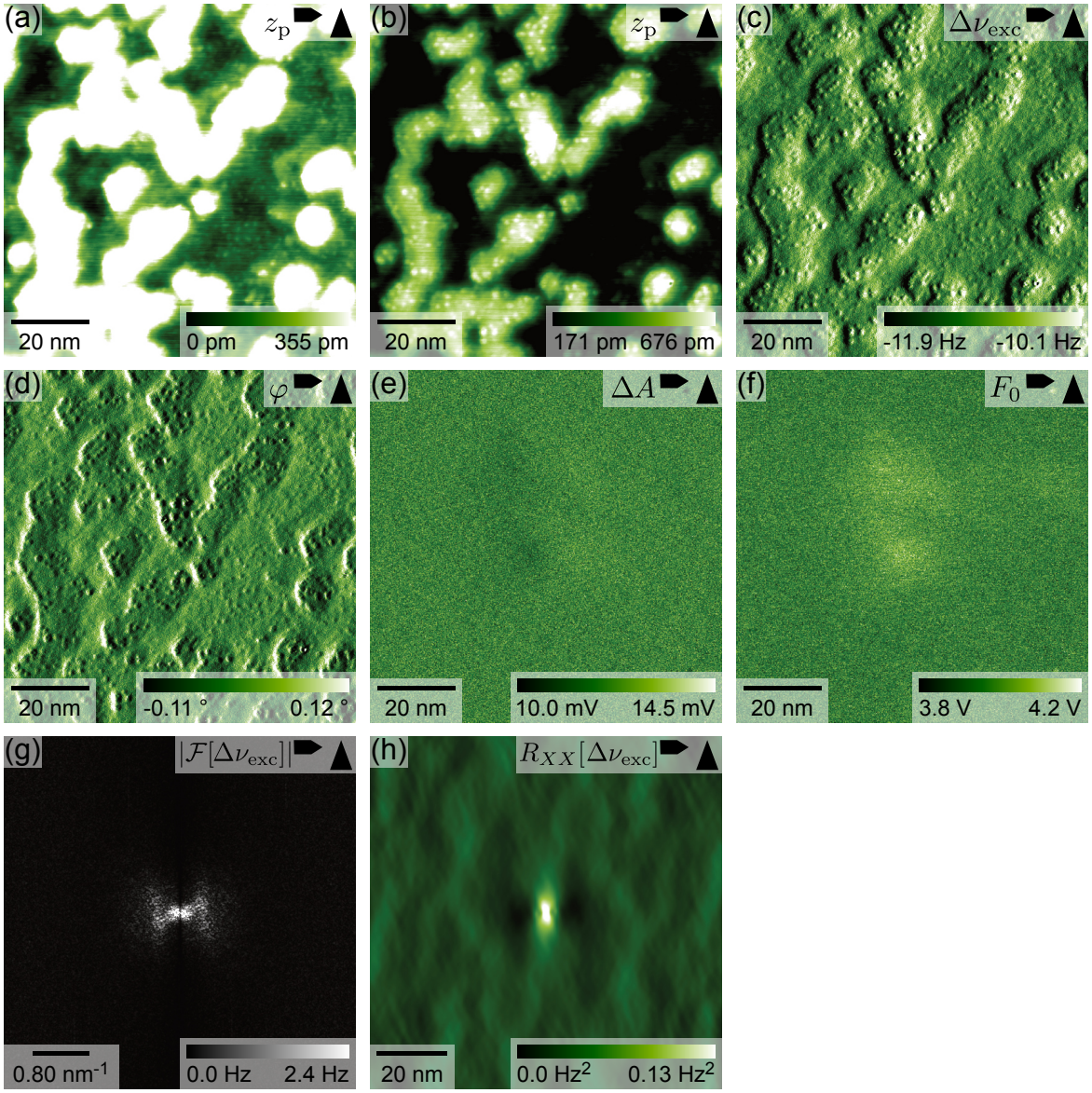

Figure S5: Detail image of the islands observed on microcline (001). Subfigures (a) and (b) show the same z-piezo displacement image given in the Fig. 1(c) but with different colour scales highlighting features on the terrace (a) and islands (b), respectively. Moreover, the corresponding excitation frequency shift (c), phase shift (d), amplitude change (e) and excitation force amplitude (f) images are shown. The 2D Fourier transform and 2D autocorrelation of the image in (c) are given in (g) and (h), respectively. Neither the Fourier transform, nor autocorrelation give any indication for a periodic structure in the image.

Moreover, we show a high-resolution image with atomic resolution on both the terrace and an island in Figure S6. This image again shows that terraces and islands share the same unit cell and atomic contrast further confirming our conclusion that the observed islands are an intrinsic part of the structure of our microcline sample.

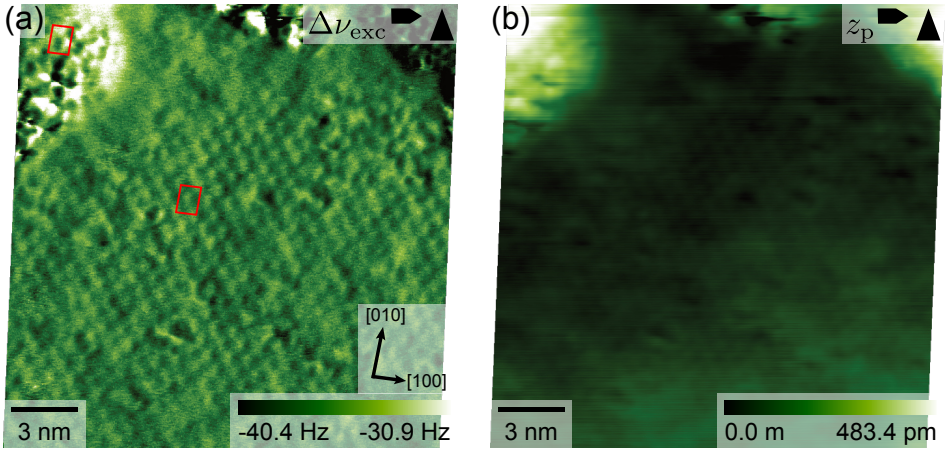

Figure S6: High-resolution AFM images taken on microcline (001) under UHV conditions. (a) Excitation frequency shift AFM image showing atomic resolution on the terrace and the island in the top left corner. Both, terrace and island exhibit the same contrast. (b) z-piezo displacement image corresponding to (a). All images are calibrated and corrected for linear drift. The unit cells and directions were derived from the 2D Fourier transforms.

3. ANNEALING EXPERIMENTS UNDER ENVIRONMENTAL CONDITIONS

Figure S7 (a) shows a 1.0 x 1.0 µm^2 AFM image at the microcline-water interface of a freshly prepared microcline (001) surface. The microcline crystal is from the same batch as the crystal that exhibits the islands shown in Figure 1 (a) of the main text. Flat terraces are seen, separated by step edges. No islands are observed. After this initial measurement, the water was removed, the microcline crystal was taken out of the PEEK sample holder and placed in a porcelain crucible in an oven (Nabertherm P330, Germany). After annealing at 449 K and ambient pressure for 20 h, the crystal was clamped again in the PEEK sample holder and a fresh drop of water was placed on it. For the following AFM experiments, a position close to the initial position was chosen by eye. This procedure was repeated twice at higher annealing temperatures (549 K and 649 K) for the same microcline crystal. Figure S7 (b) – (d) shows 1.0 x 1.0 µm^2 AFM images of the interface between the annealed microcline (001) surface and water. In agreement with the freshly prepared surface, exclusively flat terraces separated by step edges of various heights are observed. The appearance of the terraces and the number of step edges differ from image to image; however, this difference is more likely due to differences in positioning than to changes in surface topology. As these AFM images show, we could not induce island formation by annealing the microcline crystal up to 649 K for 20 h at ambient pressure.

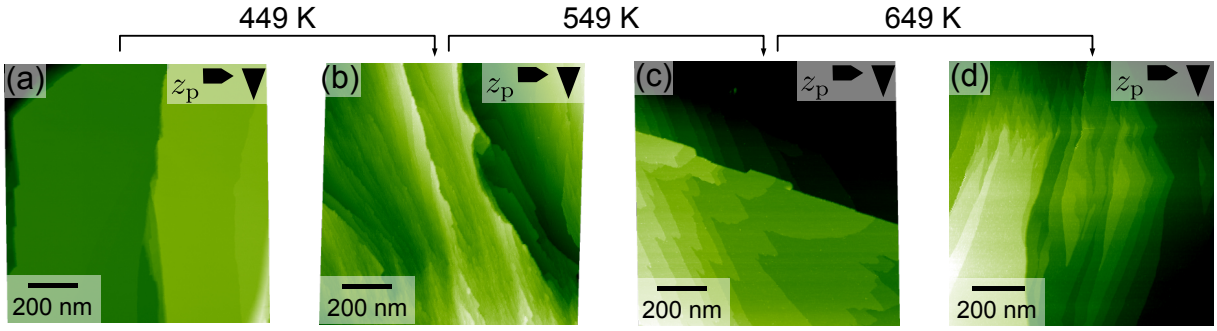

Figure S7: Impact of annealing on the surface structure of microcline (001). Shown are AFM images taken at the microcline (001)-water interface directly after cleavage (a) and after consecutive annealing for 20 h each at 449 K (b), 549 K (c) and 649 K (d), respectively.

4. ISLANDS ON AIR-CLEAVED SAMPLES

After performing the UHV and in-liquid AFM experiments discussed in the main text, sample Mi-UHV-5 was cleaved a second time under ambient conditions approximately 1 mm below the first cleavage plane. This second cleavage created a new surface, which has not previously been in direct contact with the UHV and potential contaminations in the UHV setup. The new cleavage plane showed islands in three different positions shown in Figure S8 (a) to (c). Figure S8 (d) shows a cutout from the image in (a) to highlight that the islands show the same characteristics as discussed in the main text. The islands have a height of around 0.6 nm (consistent with the atomic step height on microcline) and the same contrast as the terrace. These images also confirm that the island density can be widely different even on the same cleavage plane as can be easily seen when comparing Figure S8 (a) to (c). On a fourth position (Figure S8 (e)), the surface shows either islands with a rather low density or small particles originating from the cleavage. Since some of these features are significantly higher than the islands (up to around 2 nm), we conclude that this area does not exhibit islands. As discussed in the main text, the islands likely formed in preexisting cracks through previous weathering. Hence, we expected that our samples should also exhibit areas without islands.

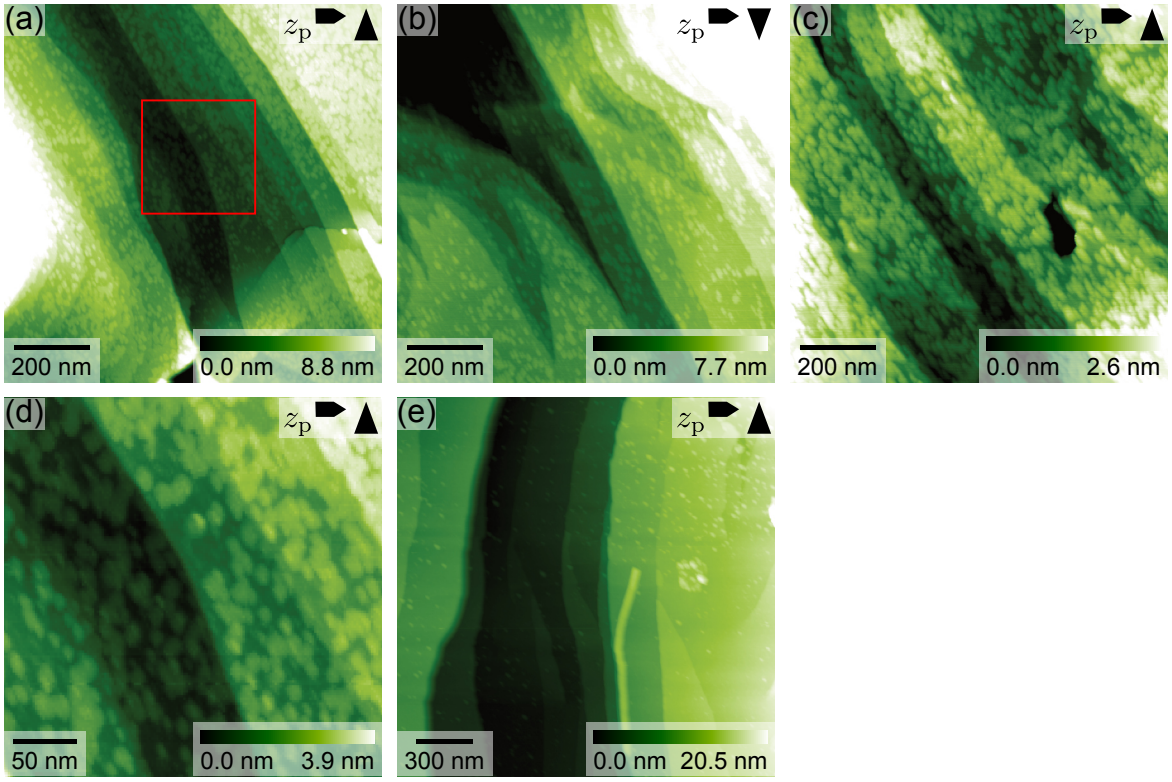

Figure S8: AFM overview images measured at the microcline (001)-water interface of sample Mi-UHV-5 after a second cleavage under ambient conditions. Shown are images taken at four macroscopically different positions (a) – (c) and (e). In panel (d) a cutout of the area marked with a red rectangle in (a) is presented to make the surface details easier to see.

5. AFM MEASUREMENTS ON THE UPPER AND LOWER CLEAVAGE PLANE

Furthermore, we investigated whether the other side of the cleavage plane would also exhibit islands or rather depressions/holes as might be expected for cleavage of bulk microstructure. To do so, we cleaved a pristine sample (Mi-UHV-6) under ambient conditions. From the resulting two pieces, one was mounted in a PEEK sample holder (upper cleavage plane), while the other (lower cleavage plane) was glued to a metal sample plate. These experiments were performed under ambient conditions, because our UHV setup does not allow for investigating the second side of the cleavage plane. AFM images taken at the microcline-water interface on the upper and lower cleavage plane are shown in Figure S9 (a) – (c) and (d) – (f), respectively. The images clearly show that both cleavage planes exhibit islands. However, directly after cleavage, the lower cleavage plane exhibited the “scaly” structure shown in Figure S9 (d), which is why we treated the sample for 5 min in an ultrasonic bath. Afterwards, the surface still exhibited some rough areas, but we also observed islands as shown in Figure S9 (e) and (f).

Unfortunately, the contrast here is not as good as in the previous images, because of the remaining rough areas. Still, the images show that the lower cleavage plane also exhibits islands and no depressions or holes.

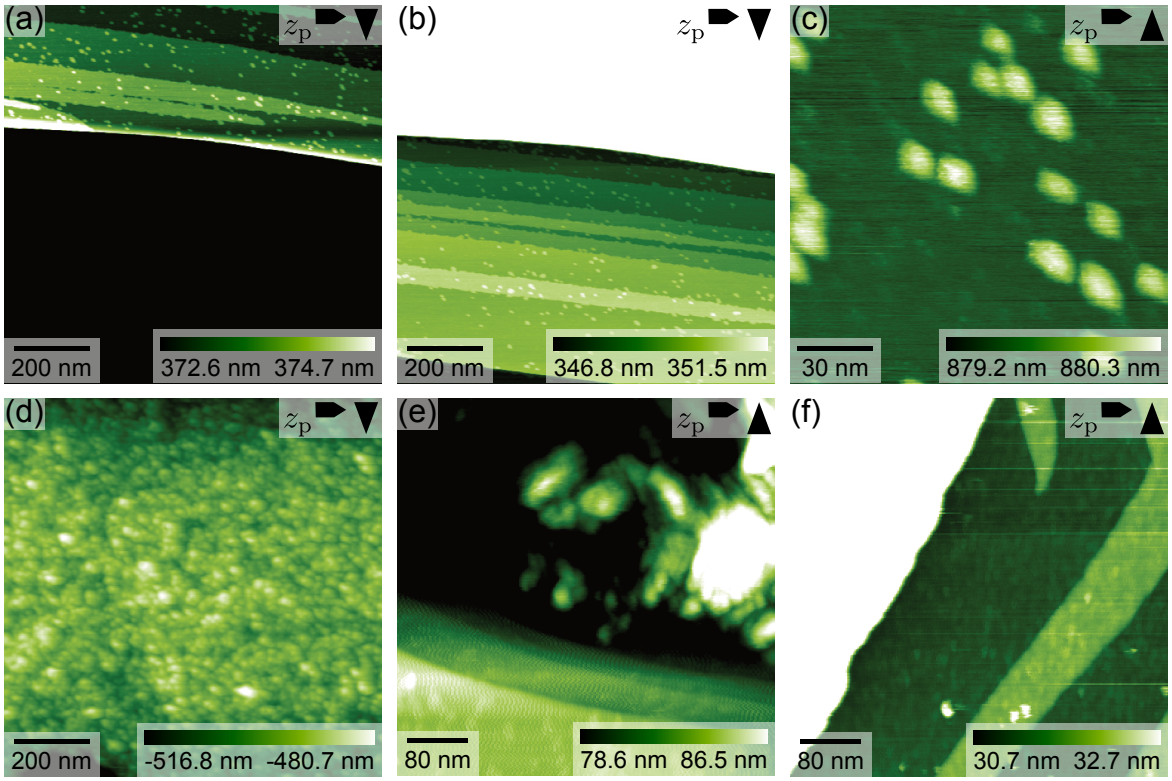

Figure S9: In-liquid AFM images taken at the microcline (001)-water interface on the upper (a) – (c) and lower (d) – (f) cleavage plane of sample Mi-UHV-6. The sample was cleaved in air and the images were taken as fast after cleavage as possible. The upper cleavage plane was imaged first. The lower cleavage plane was sonicated for 5 min in water before images (e) and (f) were measured.

6. REFERENCES

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3. W. A. Deer, R. A. Howie and J. Zussman, *An introduction to the rock-forming minerals*, Mineralogical Society of Great Britain and Ireland, 2013.