1   **REVISION 1**

2   **Chlorite topography and dissolution of the interlayer studied with**

3   **Atomic Force Microscopy.**

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13   **Abstract**

14   Chlorite has a structure composed of a combination of two distinct layers, the tetrahedral-

15   octahedral-tetrahedral (TOT) and the interlayer (i.e. the octahedral layer between TOT layers).

16   In this study, the morphology and dissolution of chlorite in pure water has been visualized

17   using Atomic Force Microscopy. Upon cleavage, the TOT layer shows atomically flat

18   terraces and steps, while the interlayer presents strips and voids. In pure water, dissolution

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19   channels and equilateral, mono-oriented triangular etch pits form in the interlayer and lead to

20   progressively increased solubilisation. Dissolution channels are proposed to originate from

21   structural defects, while a conceptual model is discussed to explain the presence of triangular

22   etch pits. In this model, their formation is driven by the different reactivity of the two

23   octahedral configurations along the etch pits. It is not currently known which of these is the

24   most stable configuration, however we propose arguments that point towards a specific

25   orientation. The conceptual model is supported by experimental data and is potentially

26   applicable to all mineral structures constituted by continuous octahedral layers.

27

28   1. Introduction

29   Chlorite, a mineral common in sedimentary and metamorphic rocks (Hamer et al. 2003) as

30   well in soils (Glowa et al. 2003), is a 2:1:1 phyllosilicate that consists of alternating 2:1

31   layers and octahedral interlayer sheets, Fig. 1, with a unit cell c-dimension of 14 Å (Bailey

32   1988). The 2:1 layer is named the TOT layer for its tetrahedral-octahedral-tetrahedral

33   structure; it is also referred to as the talc-like layer because of its structural similarity with the

34   talc mineral. This layer presents an excess of negative charge: unlike other 2:1 phyllosilicates

35   in which the negative charge is neutralized by positive cations, in chlorite the same function

36   is accomplished by a positively-charged hydroxyl interlayer (Bailey 1988), also referred to as

37   the brucite-like layer.

38   Atomic Force Microscopy (AFM) (Binnig et al. 1986) has been used extensively to probe

39   phyllosilicate nano-structure and weathering, as it has the advantage of being able to image

40   and follow alteration of mineral topography in real-time under ambient and elevated

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41   temperature/pressure conditions (e.g. Aldushin et al. 2006; Sánchez-Pastor et al. 2010;

42   Kuwahara 2001; Bickmore et al. 2001). While bulk dissolution studies provide information

43   on reaction rates and products, visualizing the three-dimensional topography at the nanoscale

44   AFM can add important, complementary knowledge such as: the role of surface

45   heterogeneity, the mechanisms of surface complexation and dissolution, and the detection of

46   secondary phase formation (Maurice et al. 1996).

47   In this regard, chlorite represents an interesting substrate for AFM studies due to its

48   composite TOT plus interlayer structure, which presents different surface topographies and

49   dissolution processes of the two layers. As already shown by Antognozzi et al. (2006) and

50   Valdrè et al. (2009), the two layers can be easily recognized with AFM due to their different

51   thickness (10 Å in the TOT and 4 Å in the interlayer, Fig. 1) and their different surface

52   potentials (TOT is negatively charged and the interlayer is positively charged). The latter

53   property is revealed by the AFM cantilever oscillation phase signal in "Tapping" mode,

54   which is sensitive to material composition and properties (Schmitz et al. 1997). In this mode,

55   the oscillations of the tip are affected by differences in the surface potential of the two

56   chlorite layers and lead to a phase lag.

57   The only AFM study on chlorite dissolution that exists to date has shown that the interlayer

58   dissolves faster than the TOT component, and these conclusions were based on visual

59   observations of grain edge retreat (Brandt et al. 2003). The reason for this different reactivity

60   lies in the different structures of the two layers: the TOT layer is similar in structure to

61   common 2:1 phyllosilicates, such as muscovite and talc, which have dissolution rates of order

62   10^{-13} mol m^{-2} s^{-1} at near neutral pH (White and Brantley 1995). In contrast, the interlayer has

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63   a structure similar to the brucite mineral, which has a dissolution rate about 7 orders of

64   magnitude faster than the 2:1 phyllosilicates (White and Brantley 1995).

65   The analysis of 2:1 phyllosilicates dissolution by means of AFM is non-trivial due to their

66   resistance to dissolution; a pre-treatment of the surfaces and extreme weathering conditions,

67   uncommon in soils and rocks, is sometimes required to observe weathering in the time-frame

68   of a typical AFM experiment (Bickmore et al. 2001; Rufe and Hochella 1999). Brandt et al.

69   (2003) pre-conditioned the chlorite grains at pH 2 for several months before the AFM

70   analysis took place; chlorite grains were also obtained through mechanical grinding, which

71   introduced cracks and other surface defects. Although the TOT and interlayer edge retreats

72   were successfully observed, these pre-treatments precluded the evaluation of chlorite

73   structural alterations from its pristine state. Unlike TOT-structured minerals, brucite can be

74   easily studied with AFM in mild weathering conditions because of its higher dissolution rate,

75   as in Kudoh et al. (2006). In their study, brucite formed mono-oriented triangular etch pits

76   while dissolving, a phenomenon attributed to the three-fold axis of symmetry normal to the

77   (001) surface.

78   In this study, our aim is to further characterize chlorite structure and dissolution in the near-

79   pristine state by AFM imaging of surfaces of the mineral in pure water at near-neutral pH;

80   and by examining its reactivity with a special focus on the interlayer component, the most

81   prone to dissolution in mild conditions.

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83   **2. Materials and Methods**

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84 **2.1 Preparation of the chlorite flakes**. The empirical formula of the chlorite sample was

85 determined with Electron Probe Micro Analysis (EPMA), and recorded as: $(Mg_{4.90}\ Fe_{0.31}$

86 $Ti_{0.001}\ Mn_{0.005}\ Al_{0.74})\ (Si_{3.34},\ Al_{0.66})\ O_{10}\ (OH)_8$. Mineral flakes, with thicknesses of less than 1

87 mm and areas around 1 cm^2, were attached to PTFE disks with a few drops of EPO-TEK

88 302-3M (Epoxy Technology, Billerica, MA 01821, U.S.A), a two-component epoxy highly

89 resistant to water, solvents and acids. After the epoxy resin was cured, samples were cleaved

90 by removing the external mineral (001) surface with adhesive tape (Scotch-brand, 3M) gently

91 adhered to the (001) surface.

92 **2.2 AFM imaging.** A Bruker Multimode AFM (Bruker, Santa Barbara, CA, USA) was used,

93 equipped with a J scanner, a NanoScope IIIA controller and an Extender Module. The

94 adopted cantilevers were V-shaped (Bruker, Santa Barbara, CA, USA), with a nominal

95 resonance frequency of 56 kHz and a nominal spring constant of 0.24 N m^{-1}. Chlorite

96 imaging and dissolution studies were undertaken in a batch system under 18.2 MΩ-cm ultra-

97 pure water (Fluka, UK) using a Veeco fluid cell and at a scan rate of 1 Hz. Observations were

98 carried out in Tapping Mode (TM), except where specified. Two different AFM signals were

99 recorded, the height and the phase lag signal. The first was used to visualize the topography

100 of the chlorite surface, while the second to distinguish the TOT layer and the interlayer. In

101 this work images constituted by the phase lag signals are labelled as "Phase image". Off-line

102 processing consisted of low-order flattening, plane fitting and image analysis subroutines of

103 the Nanoscope 5.30r1 software suite (Bruker, Santa Barbara, CA, USA) and WSxM 5.0

104 (Horcas et al. 2007).

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105 **2.3 Dissolution Kinetics**. The formula from Rufe and Hochella (1999) was adopted to

106 calculate the dissolution kinetics: rate = $(\Delta V/V_m)/(SAt)$ (1), where ΔV is the dissolved mineral

107 volume between two consecutive AFM images, V_m is the molar volume of the mineral, SA is

108 the total mineral area considered and t is the time. The volume of the etch pits was obtained

109 by multiplying interlayer thickness, 0.4 nm, with the etch pits perimeter. The latter has been

110 measured using the software ImageJ (Abramoff et al. 2004), with five independent

111 measurements for each etch pit considered. To our knowledge, no value for the interlayer V_m

112 has been reported in the scientific literature, therefore it has been approximated as brucite,

113 V_m= 24.54 cm^3/mol (Rothbaue et al. 1967). Step retreat rate has been evaluated using the

114 formula $S = 3\sqrt{3}x^2$, where S is the area of an equilateral triangle and x is the distance between

115 the center of the triangle and its side. By plotting the x as a function of time is then possible

116 to obtain the step retreat rate for each etch pit.

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118 **3. Results**

119 **3.1 Chlorite topography imaged with AFM**. After cleavage, chlorite displays surfaces with

120 terraces and steps (Fig. 2a). The presence of only one z-level of AFM tapping mode phase

121 signal data (Fig. 2b) indicates that only one component is exposed, either the interlayer or the

122 TOT layer. To identify which layer, an area is repetitively scanned for one hour in contact

123 mode at tip-substrate forces stronger than those normally used for non-invasive imaging. This

124 process results in the creation of pits which revealed the internal structure of the chlorite (Fig.

125 2c). Here the exposed layer is about 1 nm thick (line profile), hence this is the TOT layer;

126 while the second layer, of approximate thickness of 0.4 nm, is the interlayer.

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127   Chlorite can also present a discontinuous layer with an irregular appearance and

128   characteristically constituted by strips and surface gaps when cleaved (Fig. 3), the latter often

129   with a directionally-oriented triangular shape, as shown in Fig. 3c. Following the convention

130   of Valdrè et al. (2009), these gaps observed upon cleavage will be referred as "voids". The

131   layer thickness of about 4 Å (line profile) indicates that the discontinuous layer is the

132   interlayer; while the different phase signal of the underlying layer (Fig. 3b) confirms this is

133   the TOT layer, as expected.

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135   **3.2 Dissolution of the interlayer in pure water.** Fig. 4a shows an interlayer area after 2

136   hours immersion in pure water, Fig. 4b shows the same area imaged after a further 2 hours:

137   comparing these images, it is evident that a dissolution reaction is affecting the interlayer.

138   The interlayer dissolves via two main pathways: formation of dissolution channels (Figs. 4b,c)

139   and formation and expansion of mono-oriented equilateral triangular etch pits (Figs.4c-e).

140   This process lasts for about 3.5 hours and leads to the complete dissolution of the interlayer,

141   thus exposing the underlying TOT layer, which is not affected by the solution (Figs. 4a-c).

142   The pH of the dissolution solution was approximately 6 and the morphologies are consistent

143   with what has been observed in brucite (Kudoh et al. 2006). Here identical triangular etch

144   pits formed only at neutral or mildly acidic pHs, whereas irregular step retreat has been

145   observed at lower pH (Jordan and Rammensee 1996; Kudoh et al. 2006).

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147   The dissolution kinetics was calculated on 5 consecutive AFM images (in the same scan

148   direction) of an area of 0.2 μm^2 containing 9 expanding etch pits and captured about halfway

149   of the 3.5 hours-long interlayer dissolution. The dissolution rate was 6.03×10^{-10} mol m^{-2} s^{-1},

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150   calculated using equation (1) and represented by the gradient of the regression line of Fig. 5a.

151   Here the moles of dissolved interlayer per square metre are plotted as a function of the time.

152   Interlayer step retreat rate was calculated for individual etch pit as described in Materials and

153   Methods (section 2.3), with three examples shown in Fig. 5b. The average value obtained

154   from all nine etch pits is 0.0071 ± 0.0020 nm/s.

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156   **3.3 Round-to-triangular etch pit conversion.** Fig. 6 shows the evolution of a set of five

157   etch pits, recorded within the time interval used for the calculation of the weathering rate

158   (section 3.2), where three of them expand their triangular shape, while two have an initial

159   rounded outline (Fig. 6a). Rounded shape has been observed to appear transiently on about

160   10% of the etch pits in the course of their expanding triangular shape. The expansion process

161   of the larger rounded etch pit in Fig. 6 involves a preferential enlargement along three faces,

162   equally spaced on the perimeter by 120°, which results in its conversion into a triangular etch

163   pit (Figs. 6b,c); a similar process is also present with the smaller rounded etch pit.

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165   **3.4 Conceptual model: the case of rounded etch pits.** Fig. 7 shows a possible model of

166   rounded etch pit evolution. Along the etch pit edges, the octahedra arrange in two

167   configurations easily identifiable as they present either an exposed edge, indicated as "Φ", or

168   an exposed corner, indicated as "Ψ". The present model supposes that these configurations

169   present a different reactivity in water and here we assume that it is the Ψ-octahedron which is

170   less stable (see Discussion). As shown in Fig. 7, during dissolution the preferential removal

171   of Ψ-octahedra eventually leads to the formation of a triangular etch pit, comparable in

172   outline shape to the etch pits observed during interlayer dissolution. Etch pit edges are now

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173 composed of the less-reactive Φ-type octahedra. Both experimentally and in the conceptual

174 model, a preferential dissolution at three equally-spaced areas of the rounded etch pit occurs,

175 where the putative more highly reactive Ψ-octahedra are located. Identical results are

176 obtained when it is assumed that the Φ-octahedra are the less stable.

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178 **3.4 Conceptual model: the case of triangular etch pits**. Only two triangular orientations

179 are possible on an octahedral layer, which are characterized by different octahedral

180 configurations along their respective edges: Φ for orientation A and Ψ for orientation B (Fig.

181 8a). Taking again the Ψ-configuration as the less stable, the selective removal of Ψ-octahedra

182 will convert triangular orientation B to A, Fig. 8b. In contrast the orientation A will continue

183 to grow maintaining this orientation, as removal of Φ-octahedra will expose the same

184 octahedral configuration. According to the model only one triangular orientation is allowed in

185 a dissolving octahedral layer and this is indeed what has been observed experimentally, as

186 shown in Fig. 4e.

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188

189 **4. Discussion**

190 **4.1 Morphology and structure of chlorite imaged with AFM**. Following cleavage, the two

191 chlorite layers display distinct forms of surface morphology: homogeneous surfaces arranged

192 in steps and terraces in the case of the TOT layer (Figs. 2a,b), and surfaces pitted with voids

193 and organized in strips as regards the interlayer component (Fig. 3). The specific pattern of

194 both layers could result from the cleavage process: in fact, upon removal of the exposed

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195   layers with the adhesive tape (see paragraph 2.1), the bonds existing between the stacked

196   layers could lead to the excision of portions of the newly exposed areas. This is particularly

197   relevant for the octahedral interlayer, whose lower tensile strength compared to the TOT

198   tetrahedral layer could lead to the removal of areas in the basal plane, thus determining the

199   observed voids. However, as it was very difficult to test this hypothesis by imaging the

200   removed chlorite layers to look for the torn areas, the possibility that the observed features

201   are pre-existing in the interlayer cannot be ruled out.

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203   The cleavage origin of interlayer features is supported by other studies (Antognozzi et al.

204   2006; Valdrè et al. 2009). According to Valdrè et al. (2009), the formation of specific

205   geometric features in the interlayer after cleavage may be determined by the distribution of

206   either Al^{3+} cations or hydrogen bonds between TOT and interlayer. For example, the highest

207   density of hydrogen bonds occurs along the [100] direction and could be responsible for the

208   interlayer strips along the [100] direction, as these are more strongly bound to the underlying

209   TOT layer. Regarding the triangular voids (Fig. 3c), here we propose that their formation

210   could be linked instead to the intrinsic octahedral structure of the interlayer. As discussed

211   later on, triangular etch pits during interlayer dissolution form because this is the most stable

212   structure the octahedra can assume along the etch pits edge. Therefore it is possible to infer

213   that during the cleavage, interlayer fragments are removed along the edges of the stable

214   triangular orientation which hold the interlayer in place, thus leading to triangular voids.

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216   **4.2 Interlayer dissolution: kinetics.** The R^2 value of 0.997 of the regression line of Fig. 5a

217   shows that the dissolution rate is linear, which indicates that at this stage, i.e. at about

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218   halfway of the 3.5 hours-long interlayer dissolution, the varying saturation state over the

219   course of the experiment is not probably limiting the weathering rate. The latter, 6.03×10^{-10}

220   mol m^{-2} s^{-1}, is about two orders of magnitude lower than the rate calculated for brucite with

221   AFM imaging at pH 5, 1.10×10^{-8} mol m^2 s^{-1} (Kudoh et al. 2006). This is in line with what

222   has been observed by Brandt et al. (2003), which reported a rate two orders of magnitude

223   lower in the interlayer compared to brucite at pH 2. Brandt et al. (2003) attributed this

224   behaviour to the presence of Fe and Al cations in the interlayer, which reduce the weathering

225   rate. A similar result is present when the step retreat rate is considered, with a slower rate for

226   the interlayer (0.0071 ± 0.0020 nm/s) compared to brucite, 0.015 nm/s (Kudoh et al. 2006).

227   Similarly to Kudoh et al. (2006), the step retreat has been calculated from the distance centre-

228   side of ideally perfect equilateral triangular etch pits (see section 2.3). Although the etch pits

229   often deviate from a perfect equilateral shape, taking the average value for all nine

230   considered etch pits represents an acceptable approximation of step retreat rate.

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232   **4.3 Interlayer dissolution: channels.** The presence of dissolution channels in chlorite has

233   been attributed to mineral structural defects (Brandt et al. 2003), and the channels in the

234   interlayer may have a similar origin. For example, the main channel of Fig. 4b initially could

235   have been nucleated following structural defects in the interlayer (its initial formation is

236   indicated by an arrow in Fig. 4a). The dissolution process can progressively affect and

237   weaken the nearby areas, where new channels form (Fig. 4b). These structural defects may be

238   intrinsic to the crystal structure of the mineral flake or could be introduced by the cleaving

239   procedure, as suggested by the occasional absence of interlayer areas in form of strips and

240   voids. Channel edges are often observed parallel to the edges of the etch pits, which can

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241   coalesce with them, as seen in Fig. 4c. Therefore the same mechanism that leads to the

242   formation of triangular etch pits, discussed below, can also be involved in the enlargement of

243   the channels.

244

245   **4.4 Interlayer dissolution: triangular etch pits.** Triangular etch pits form, expand, and

246   coalesce during dissolution of the chlorite interlayer in pure water (Figs. 4d,e and 6). These

247   etch pits have an apparent equilateral shape and the same crystallographic orientation, Fig. 4e.

248   To explain the presence of these peculiar features a conceptual model has been developed, in

249   which the interlayer was described using the polyhedral representation in CrystalMaker

250   (CrystalMaker Software Limited, Begbroke, UK), Figs. 7 and 8. In the model, whichever

251   etch pit shape is created, along their edges the octahedra assume only two distinct

252   configurations: one with the edge exposed, named here as "Φ", and the other with an exposed

253   corner, "Ψ" (Fig. 7). After proposing that one octahedral configuration is more prone to

254   dissolution than the other, this hypothesis was tested by comparing the shapes of dissolving

255   etch pits in the model with the experimental results. Arbitrarily we considered the Ψ-

256   octahedron less stable than the Φ-octahedron, although identical conclusions are obtained

257   when the reactivity order is inverted. In the case of rounded etch pit evolution, both

258   experimental (Fig. 6) and modeling (Fig. 7) results show that the conversion to the triangular

259   shape happens through selective dissolution along three equally spaced sections of the

260   perimeter of the etch pit. In the model, this conversion is due to the preferential dissolution of

261   the Ψ-octahedra. These observations show that sites along some crystallographic directions

262   dissolve faster than others and that triangular etch pits may be the steady state dissolution

263   feature. Indeed, this is confirmed by the large prevalence of triangular etch pits while the

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264 dissolution reaction was at steady state (Fig. 4e), with only few rounded etch pits which

265 promptly convert in the more stable form (Fig. 6). In addition, while two orientations of

266 equilateral triangular etch pits are possible on an octahedral layer (Fig. 8a), the etch pits

267 observed with AFM have the same crystallographic orientation (Fig. 4e). This can be

268 explained with the conceptual model, in which the triangular orientation with the more

269 reactive exposed octahedra converts to the more stable orientation during dissolution, as

270 illustrated in Fig. 8b. More generally, the preferential dissolution of a specific octahedron

271 (either Ψ- or Φ-) will convert all the possible shapes of etch pits (e.g. squared, rectangular,

272 and so on) to steady state triangular etch pits that contain the more stable octahedral

273 configuration along the edges.

274

275 If the origin of the triangular etch pits is indeed crystallographic in nature, this indicates

276 something about the relative rates of the dissolution reactions that occur on these mineral

277 surfaces. Materials that grow or dissolve by strongly following crystallographic directions

278 suggest that the rate of kink site nucleation (removal of the initial material from an otherwise

279 smooth monomolecular step) is much slower than the rate of kink site propagation (removal

280 of material neighbouring a previously existing kink) and thus limits the rate of dissolution

281 (De Yoreo et al., 2009). Materials that grow and dissolve with extremely rough steps likely

282 contain rates of kink site nucleation and propagation that are similar. This phenomena is most

283 often discussed with respect to calcite (De Yoreo et al., 2009; Stack and Grantham, 2010), but

284 other crystalline materials display steps that vary widely in the roughness of their steps,

285 indicating the density of kinks along the length of the step. The extreme cases are KDP,

286 where nearly every surface unit cell contains a kink, versus crystalline lysosyme, where one

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287   kink is observed every several hundred unit cells (Rashkovich et al., 2006; Rashkovich et al.,

288   2001). From Figs. 4 and 6, the chlorite interlayer appears to react similarly to calcite (Stack

289   and Grantham, 2010; Rashkovich et al., 2006) in that some roughness in the steps is observed

290   but steps still strongly follow crystallographic directions.

291

292   **4.5 Relative stability of triangular etch-pits.** As stated above, there are two possible

293   crystallographic orientations of the etch pits (Fig. 9). It is not possible to determine uniquely

294   which of these is dominant from the AFM images alone due to the rotational symmetry of the

295   crystal. With the exception of the simplest isomorphic materials, this ambiguity is common in

296   minerals. For some systems such as the calcite {1014} surface, steps such as the acute and

297   obtuse are aligned with the macroscopic shape of the crystal and so a unique determination

298   can be made from the orientation of the crystal. Other systems like the barite {001} contain a

299   screw axis so that the molecular orientation of steps is unknown and the system tends to form

300   bilayer steps (Higgins et al., 1998). The difficulty in determining the orientation of a given

301   step on mineral surfaces such as barite and chlorite creates ambiguity in determining precise

302   molecular level mechanisms; we can tell that one orientation reacts at a different rate, but

303   inference must be used to determine their identity. For brucite, Kudoh et al. (2006) proposed

304   that the orientation of the triangular etch pits are consistent with the orientation A of Fig. 9a

305   by determining the relationship between the triangular etch pits and the crystal structure of

306   brucite with Electron Back-Scattered Diffraction (EBSD). Again, due to the center of

307   symmetry, the EBSD cannot distinguish if it is the Ψ- or Φ-octahedra that comprise the etch

308   pit walls. Kudoh et al. (2006) speculated that the orientation A with the Φ-octahedra-

309   terminated steps is more stable because the OH groups not bound to the underlying TOT

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310 layer (OH groups above the plane in Fig. 9a) coordinate with two cations and thus are more

311 stable than the OH groups in the orientation B with Ψ-terminated steps, which coordinate to

312 only one cation (OH groups above the plane in Fig. 9b). The other OH groups present along

313 the edges in both orientations (OH groups below the plane in Figs. 9a,b) are considered less

314 reactive as they are bound to the underlying TOT layer via hydrogen bonds.

315

316 Work on the mechanism of oxygen exchange on the alumina ε-keggin polyoxocations has

317 revealed an alternate hypothesis. These molecules are composed of sets of three aluminum

318 octahedra that are bonded in the same arrangements as found in the chlorite interlayer here.

319 In the proposed mechanism for oxygen exchange of the μ_2-oxo species (Rustad et al. 2004), it

320 was found that the bonds to two of the μ_4-oxo groups (i.e., an oxygen shared amongst four

321 cations) lengthen and dissociate simultaneously, additional water molecules adsorb to

322 coordinatively saturate the partially-detached octahedra and a metastable intermediate is

323 formed. Due to their structural similarity, it is reasonable to assume that this reaction pathway

324 is also present in the brucite-like sheets (including the chlorite interlayer here). In minerals

325 the metastable intermediate formation may be a precursor to the dissolution of one of both of

326 the octahedra. This mechanism can help to elucidate the orientation of the etch-pits as well:

327 the key is that the lengthening of the μ_4-oxo bond in the keggin (μ_3-hydroxos here) allows the

328 octahedra to partially detach from the surface. If the Φ-octahedra were to lengthen their bond

329 to the μ_3-hydroxo group, it would not lead to a partial detachment of the octahedra because

330 these are pinned by the hydrogen bonds of their terminal hydroxyls (η-OH) to the TOT layer

331 below (this species is η-H_2O in the ε-keggin). The Ψ-octahedra also each have a μ_2-OH

332 bound to the TOT layer below, but it is speculated that during the formation of a metastable

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333   intermediate, a single species bound to the surface (i.e., the shared μ_3-OH) will more readily

334   act as an axis of rotation, or possibly break its bonds, than the two species bound to the

335   interlayer below in the Φ-octahedra.

336

337   Lastly, the wider rotational axis of the η-OH that are exposed to the solution in the Ψ-

338   octahedra will lead to more facile attack by water to coordinate the cation (see Stack et al.

339   2005 for evidence of this effect on the η-H_2O groups of the ε-keggin). In the Φ-octahedra, the

340   η-H_2O may be pinned to the TOT layer below, and the μ_2-oxo that are exposed to solution

341   may have less flexibility, and hence probability of attack by water. Since the etch-pits do

342   expand over time, it is clear that the Φ-octahedra do have a mechanism for detaching

343   (possibly proton-promoted dissolution at the μ_3-OH due to the pH dependence of etch-pit

344   formation discussed above), but the mechanistic arguments clearly present the hypothesis that

345   the Ψ-octahedra will detach more quickly due to this mechanism. Further modeling and

346   energy calculation studies would be required to test this hypothesis.

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348   **Acknowledgments**

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453

454   **Figures**

455   **Figure 1**. Schematic structure of chlorite. The tetrahedral sheets, light blue in colour, contain

456   Si^{4+} and Al^{3+} cations in the ratio 3:1, and the octahedral sheets, yellow in colour, contain

457   Mg^{2+}, $Fe^{2+/3+}$ and Al^{3+} cations. The interlayer is sandwiched between two TOT layers through

458   hydrogen bonds. The thickness of chlorite unit cell, composed of a TOT layer and the

459   interlayer, is 14 Å (Bailey, 1988), where the TOT has a thickness of 10 Å and the interlayer

460   of 4 Å. Image generated using CrystalMaker® v. 2.3.

21

461

462   **Figure 2.** TOT-exposed chlorite. In some areas the solvent-exposed surface of chlorite (a)

463   displays a single composition as revealed by the presence of only one phase signal level (b).

464   Chlorite etch pits, derived from continuous and invasive scanning of the surface in contact

465   mode, are shown in (c). Within the etch-pit a second underlying layer, partially exposed by

466   the scanning, is visible. The depth of the solvent-exposed layer is 10 Å (line profile) and

467   corresponds to the TOT layer. The depth of the underlying layer is 4 Å and corresponds to the

468   interlayer. Z range: 0-12 nm (a), 0-15º (b), 0-2.6 nm (c).

469

470   **Figure 3.** Interlayer can present strips and areas with voids (a). The identity of the interlayer

471   is confirmed by its thickness (~ 4 Å, line profile) and the difference in the phase signal data

472   from the underlying TOT layer (b). The peaks present in the line profile corresponds to the

473   impurities on the interlayer, shown as rounded white particles in (a). Voids can also have an

474   equilateral triangular shape with the same spatial orientation (asterisks in c). Z range: 0-3 nm

475   (a,c), 0-20° (b).

476

477   **Figure 4.** The interlayer surface dissolves through dissolution channels (b,c) and etch pits

478   (c,d,e). Following two hours in contact with water, the initial formation of the main channel

479   is indicated by an arrow in (a). After further two hours, channels extend in the interlayer

480   surface (b,c). In (c) a higher magnification of a channel segment is displayed, where the

481   asterisk indicates an etch pit that is coalescing with the channel. Channel edges are parallel to

482   etch pits edges, which have a mono-oriented triangular shape (c,d,e). The area in (a) has been

22

483 captured about halfway of the overall dissolution reaction. Some of the expanding etch pits

484 are indicated by numbers in (d) and (e). Z ranges: 0-10 nm (a,b), 0-2 nm (c), 0-5 nm (d,e).

485

486 **Figure 5.** In (a) a dissolving area of 0.2 μm^2, containing nine etch pits, is plotted in function

487 of the time. The standard deviation for each point is indicated by error bars in the plot and

488 their values range between 0.037×10^{-7} mol/m^2 and 0.244×10^{-7} mol/m^2: for their low value,

489 the errors bars are often graphically masked by the respective points. The dissolution rate,

490 obtained from the slope of the regression line, is 6.03 x 10^{-10} mol m^{-2} s^{-1}. The R^2 value of the

491 regression line is 0.997. In (b) the distance between the center of equilateral triangular etch

492 pits and their side is plotted in function of the time. The step retreat for three etch pits is

493 displayed, with step retreat rates of 0.0079 nm/s (squares), 0.0058 nm/s (rhombi) and 0.0060

494 nm/s (triangles).

495

496 **Figure 6.** Etch pits evolution in a time interval of 13 min, captured midway of the dissolution

497 process. Three equilateral triangular etch pits are present in (a), which expands and coalesce

498 maintaining the triangular shape (b, c). Two initially rounded shaped etch pits (a) convert to a

499 triangular form (b,c) through a preferential expansion along three equidistant regions,

500 indicated by arrows in (a) and (c). Z range: 0-5 nm (a,b), 0-6 nm (c).

501

502 **Figure 7.** Modeling of the evolution of a rounded etch pit. The edges of the etch pit presents

503 either corner-exposed octahedra (Ψ configuration) or edge-exposed octahedra (Φ

504 configuration) (a). The higher reactivity of the Ψ configuration expose more Φ octahedra (b)

23

505   and eventually leads to the formation of an equilateral triangular etch pit with only Φ

506   octahedra exposed to the solution. Images generated using CrystalMaker® v.2.3.

507

508   **Figure 8.** Relative stability of triangular etch pits on an octahedral layer. (a) Two different

509   orientations (indicated as A and B) can be originated on an octahedral layer, with each one

510   presenting edges with either edge-exposed octahedra (Φ octahedra in orientation A) or

511   corner-exposed octahedra (Ψ octahedra in orientation B). (b) The preferential dissolution of

512   the Ψ octahedra leads to the conversion from orientation B to orientation A, which edges

513   present only Φ octahedra. Broken lines represent the region previously occupied by the

514   removed octahedra. Images generated using CrystalMaker® v. 2.3.

515

516   **Figure 9.** Polyhedral (right) and ball-and-stick (left) representations of the two triangular

517   orientations possible on an octahedral layer. In the ball-and-stick representation, the plane

518   defined by the cation atoms (yellow) is shown in gray. The OH groups (orange) below the

519   plane are darker in colour and are bound to the underlying TOT layer through H-bonds.

520   Examples of η-OH, μ_2-OH and μ_3-OH groups are shown. The Ψ-terminated step (Orientation

521   B) is likely less stable because the mechanism of dissolution is more facile. Images generated
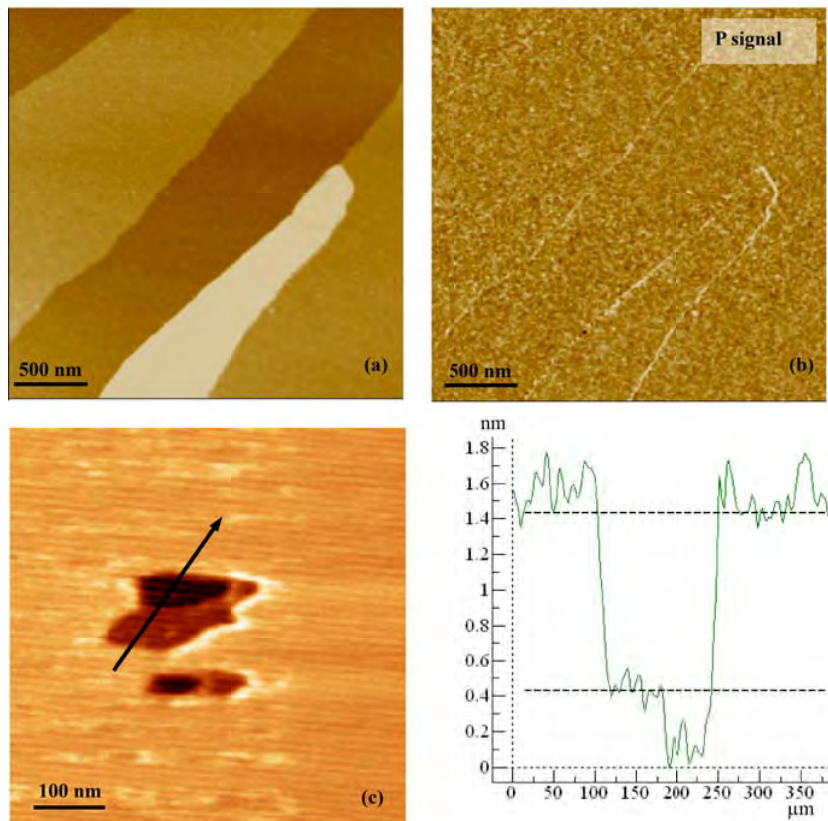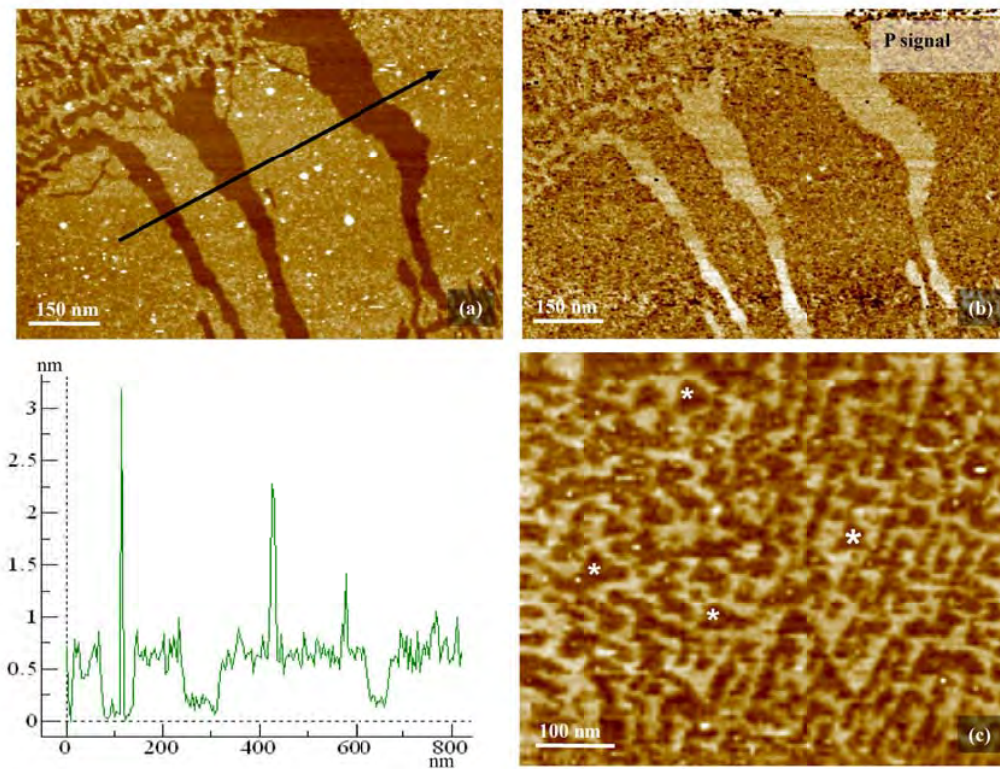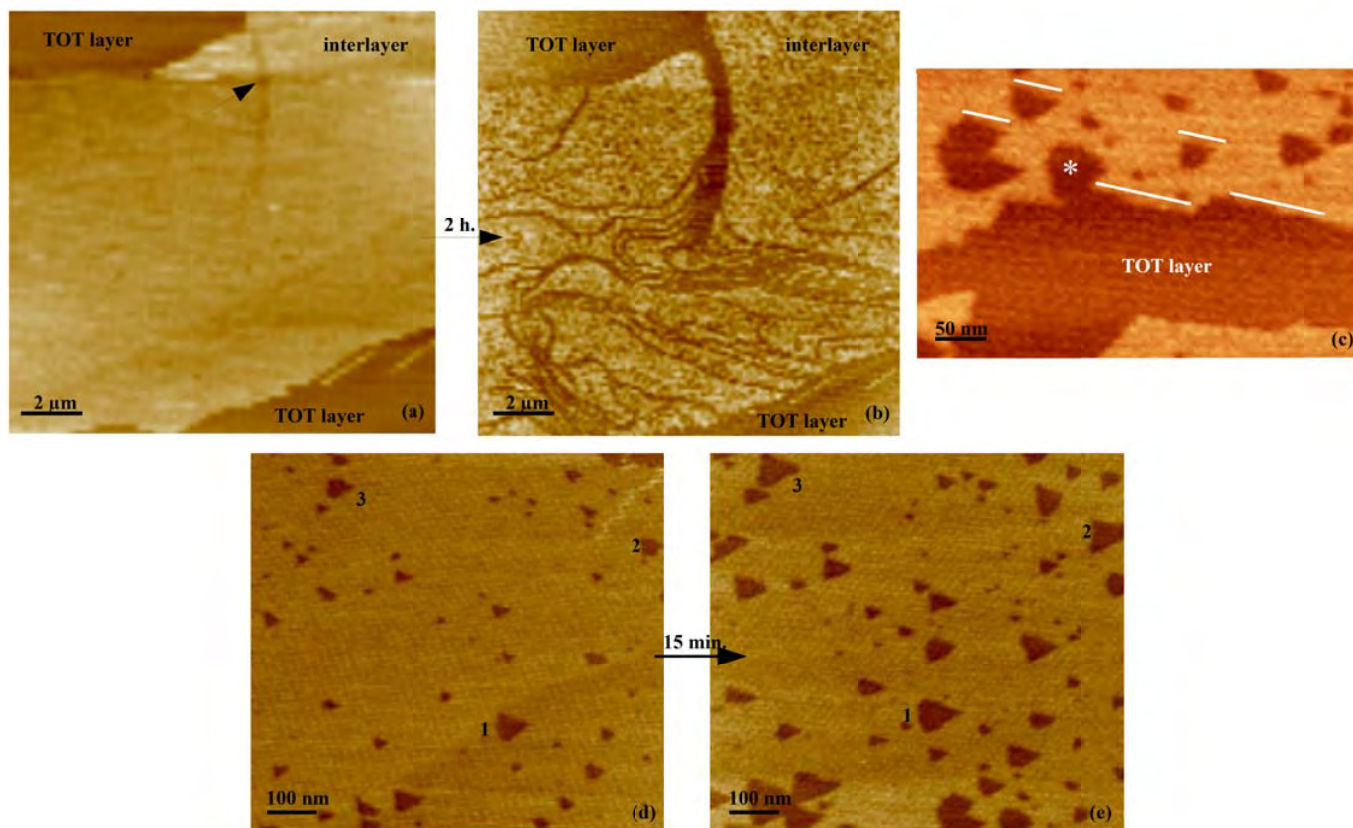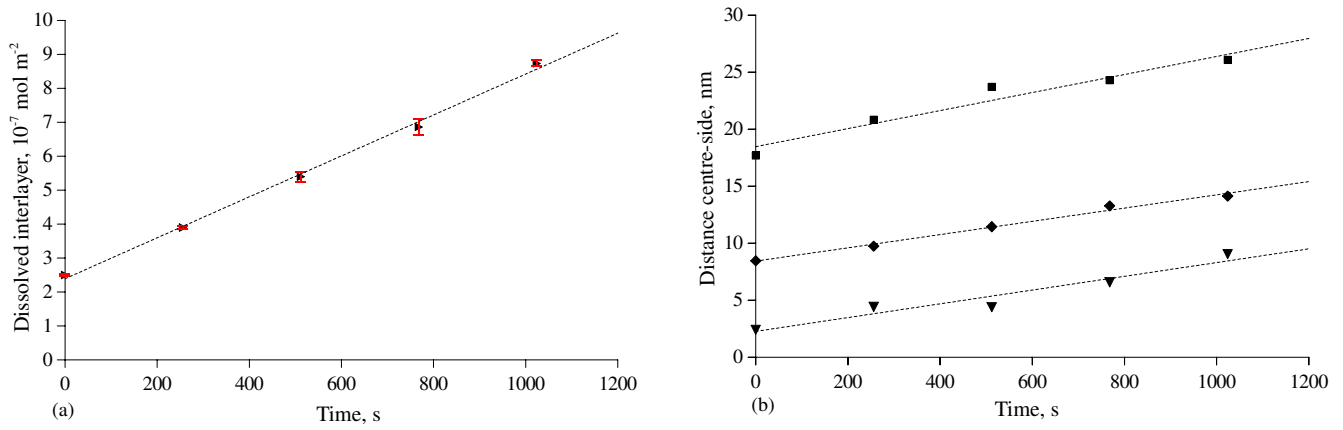
522   using CrystalMaker® v.2.3.

24

TOT layer
10 Å

Interlayer
4 Å
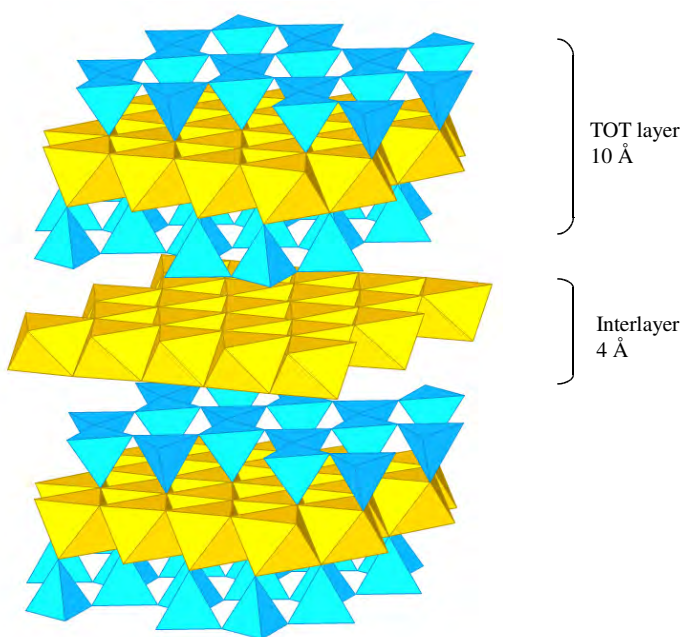
Figure 1.

Figure 2.

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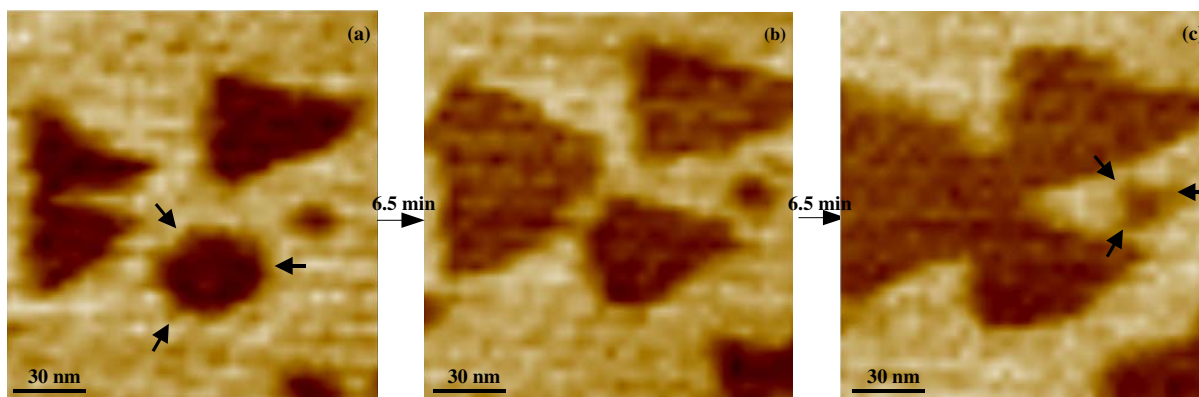
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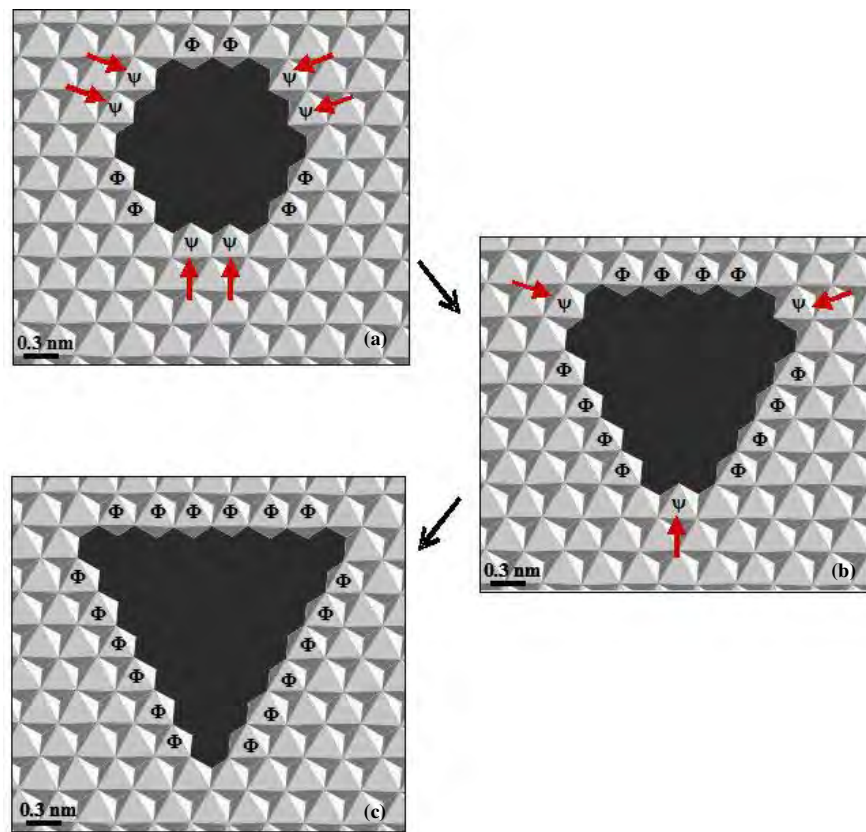
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Figure 8.

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