Structure of the 001 talc surface as seen by atomic force microscopy: Comparison with X-ray and electron diffraction results

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1 **Structure of the {001} talc surface as seen by atomic force**

2 **microscopy: Comparison with X-ray and electron diffraction**

3 **results**

4

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25

26   **Abstract**

27

28   In this study the surface structure of a centimetre sized crystal of talc from the

29   Trimouns deposit (Ariège, France) was imaged by atomic force microscopy. The direct image

30   shows detailed characteristics of clay tetrahedral surfaces. The unit-cell dimensions obtained

31   using atomic force microscopy ($a_{or} = 5.47\pm0.28$ and $b_{or} = 9.48\pm0.28$ Å) are found to be

32   slightly higher, with an increased uncertainty, than those obtained using X-ray diffraction

33   ($a_{or} = 5.288\pm0.007$ and $b_{or} = 9.159\pm0.010$ Å) and selected-area electron diffraction

34   ($a_{or} = 5.32\pm0.03$ and $b_{or} = 9.22\pm0.05$ Å). Talc has a quasi-ideal surface, clean of strong

35   structural distortion as compared to most of other clay minerals and unlikely surface

36   relaxation. The observation on the obtained image of apparent cell dimension enlargement is

37   then more likely attributed to instrumental artefacts, also responsible for scattered values of

38   unit-cell parameters rather than related to any surface structural features.

39

40   Key-words : talc, atomic-force microscopy, surface structure, X-ray diffraction, selected-area

41   electron diffraction.

42

43   **1. Introduction**

44

45   Because of its beneficial properties to manufactured products, talc is widely used in

46   paper coating, paint, ceramics, and polymer industries. In the automotive industry, talc is

47   added to polymers to stabilize and harden automobile spare parts such as fenders, dashboards,

48   steering wheels, etc. However, because different talc varieties can exhibit a wide range of

49   physical and chemical properties it is necessary to optimize the use of these different types of

50   talc for specific industrial applications. In particular, it is necessary to take into account the

51   surface structure of talc which, for example, may or may not allow the epitaxial growth of

52   polymers (Ferrage et al., 2002).

53   Over the last decade, the availability of atomic force microscopes (AFM) has provided

54   new insights into mineral reactivity by providing images of crystal growth or dissolution at

55   the micro-to-nanometer scale (Hillner *et al.*, 1992a and b; Kuwahara *et al.*, 1998, 2001;

56   Bosbach *et al.*, 2000; Lindgren, 2000; Bickmore *et al.*, 2001; Brandt *et al.*, 2003; Tournassat

57   *et al.*, 2003; Aldushin *et al.*, 2004; Yokoyama *et al.*, 2005). AFM has also allowed the direct

58   visualization of the outer surfaces of minerals by imaging either groups of atoms at the

59   molecular scale (Drake *et al.*, 1989; Weisenhorn *et al.*, 1990; Hartman *et al.*, 1990; Johnson *et*

60   *al.*, 1991; Drake & Hellmann 1991; Wicks *et al.*, 1992, 1993, 1998; Vrdoljak *et al.*, 1994;

61   Kuwahara, 1999, 2001) or individual atoms (Lindgreen *et al.*, 1991; Wicks *et al.*, 1992;

62   Vrdoljak *et al.*, 1994; Sokolov *et al.*, 1997, 1999). Because of their perfect cleavage along the

63   {001} plane, which produces extremely flat external surfaces, phyllosilicates are especially

64   well-suited for an AFM study.

65   The structure of talc differs from that of mica, chlorite or lizardite which were

66   previously imaged by AFM (Hartman *et al.*, 1990; Wicks *et al.*, 1992, 1993, 1998; Vrdoljak

67   *et al.*, 1994; Kuwahara, 1999, 2001; Lindgreen *et al.*, 1991). Talc structure presents two

68   similar external tetrahedral faces which is suitable for microscopic observations. In addition,

69   the excess of octahedral charges is compensated for by deficiency in tetrahedral charges

70   (Martin *et al.*, 1999), and the 2:1 sheet remains neutral, the interlayer of talc being thus devoid

71   of cations. Finally, the weak substitution in talc layers induce moderate structural distortions

72   such as tilts or tetrahedral rotations.

73   In this article we report the first atomic force microscope images of the surface of a

74   talc sample composed of very well-stacked layers from the Trimouns deposit (Ariège,

75   France). Images of the talc surface obtained from traditional AFM in repulsive mode are

76   compared with data in the literature and structural parameters of the bulk structure obtained

77   from X-ray diffraction (XRD) and selected-area electron diffraction (SAED).

78

79

80   **2. Background**

81

82   *2.1. Geological setting and sampling*

83   Talc (2:1 layer silicate) has a composition close to that of the [$Mg_3Si_4O_{10}(OH)_2$] end-

84   member but with minor amounts of Fe, Al and F, and traces of Mn, Ti, Cr, Ni, Na and K

85   (Heller-Kallai & Rozenson, 1981; Noack *et al.*, 1986; Abercrombie *et al.*, 1987; Aramu *et al.*,

86   1989; Coey *et al.*, 1991; de Parseval *et al.*, 1991, 1993; Martin *et al.*, 1996, 1999). The sample

87   comes from the Trimouns talc and chlorite deposit, located in the French Pyrenees, ~100 km

88   south of Toulouse, at an altitude of 1,700 m. The origin of talc is well–established and is the

89   result of the hydrothermal alteration of wallrock in a zone of intense shearing between the

90   Saint Barthélémy dome and the low-grade Paleozoic metamorphic cover (Fortuné *et al.*, 1980;

91   Moine *et al.*, 1982, 1989; de Parseval *et al.*, 1993). Dolostones of the Paleozoic cover were

92   transformed to talc, whereas the more siliceous and aluminous rocks (micaschists and granitic

93   pegmatites) evolved to a chlorite-dominant ore characterized by well-defined metasomatic

94   zones. The sampled talc of centimetric flakes that is commonly referred to as "talc flower"

95   when mined, was formed within geodes in the dolomite hanging wall of the ore body and is

96   associated with REE-minerals (de Parseval *et al.*, 1997).

97

98   *2.2. Crystallographic data*

99   Talc is a 2:1 phyllosilicate structure (Fig. 1a) with two Si tetrahedral sheets (forming

100   an array of hexagonal rings of SiO_4 tetrahedra – Fig. 1b) each linked through the apical

101 oxygen to either, and leading to the presence in between of a sheet of octahedrally

102 coordinated Mg^{2+} cations. Early structural characterizations of talc have described its

103 structure as monoclinic (*C-1* space group – Gruner, 1934), but later publications have

104 described it as triclinic (*C-1* space group - Rayner & Brown, 1973) or as pseudomonoclinic

105 (*Cc*) but using a *P-1* space group (Perdikatsis & Burzlaff, 1981). In comparison to aluminous

106 phyllosilicates the misfit in lateral dimensions between tetrahedral and octahedral sheets is

107 smaller, leading to a better accommodation of the two sheets. As a result, the tetrahedral

108 rotation angle is diminished from ~13-14° for muscovite to ~3-4° for talc (Radoslovitch,

109 1961, 1962). The tetrahedral tilt angle out of the basal oxygen plane is very weak, giving an

110 essentially flat {001} surface. The moderate tetrahedral rotations induce a reduction of the

111 SiO_4 ring symmetry from hexagonal into ditrigonal (Fig. 1b).

112

113 **3. Experimental Methods**

114

115 *3.1. Chemical analyses*

116   The chemical composition of the talc sample used in this study was determined using a

117 Cameca SX50 electron microprobe. The sample was included in a resin and polished to obtain

118 perfect flat section. Operating conditions were 15 kV and 10 nA with beam size set to

119 3×3 μm. Standards used for calibration were: wollastonite for Si, corundum for Al, periclase

120 for Mg, haematite for Fe, pyrophanite for Mn and topaze for F.

121

122 *3.2. X-ray diffraction*

123   To obtain information on the crystallographic parameters, particularly in the ab plane,

124 XRD data was collected on a randomly oriented sample. The centimetric talc flakes were

125 ground to a fine powder in an agate mortar. XRD data was collected with a Bruker D5000

126 diffractometer equipped with a Kevex Si(Li) solid-state detector and CuKα radiation.

127 Intensities were recorded at a 0.02°2θ interval, from 2 to 90°, using a 50 sec counting time per

128 step. Accuracy on 2θ positions was better than 0.001°. A rotating sample holder was used to

129 minimize the effect of preferential orientation. The openings of the divergence slit, the two

130 Soller slits, the antiscatter slit, and the resolution slit were 0.5°, 2.3°, 2.3°, 0.5° and 0.06°,

131 respectively. Cell parameters were refined using U-Fit 1.3 software assuming a *P-1* space

132 group (Perdikatsis & Burzlaff, 1981).

133

134 *3.3. ^{57}Fe Mössbauer spectroscopy*

135   A ^{57}Fe Mössbauer absorption spectrum of the talc was collected over the range ±4

136 mm.s^{-1} with a 512 channels analyzer. The Mössbauer spectrometer is composed of a compact

137 detector γ-system for high-counting rates and of a conventional constant-acceleration

138 Mössbauer device (WISSEL). A ^{57}Co (in Rh) source with nominal activity of 50 mCi was

139 used. Talc flakes were finely ground under acetone (to minimize possible oxidation of Fe) and

140 the resulting powder was placed in a plexiglas sample holder. The spectrum was recorded

141 using a Canberra multichannel analyzer at 80°K to benefit from the second-order Doppler

142 effect. The isomer shift was recorded with respect to α-Fe metal. As recommended by

143 Rancourt *et al.* (1992), the absorbtion thickness of the talc sample was calculated to minimize

144 the width of the absorption lines using data from the phlogopite-annite series as phlogopite

145 has a similar Fe-content to that of talc so as. The values are around 200 mg of mineral per

146 cm^2. Lorentzian lines shapes were assumed for decomposition, based on least-squares fitting

147 procedures. The χ^2 and misfit values were used to estimate the goodness of fit.

148

149 *3.4. Selected-area electron diffraction*

150   The electron diffraction study was performed on a Philips 420 transmission electron

151   microscope (TEM) equipped with a tungsten filament and operated at 120kV. Talc flakes

152   were gently crushing in distilled water and dispersed onto a 3mm holey carbon-coated Cu-

153   mesh TEM grid. Selected-area electron diffraction (SAED) patterns were recorded after

154   orienting talc single crystals along the [001] zone axis using a double-tilt sample holder. The

155   camera constant of the talc SAED patterns was calibrated using a gold reference sample with

156   the crystals oriented along [100]. SAED patterns were recorded under the same parallel beam

157   illumination conditions for both gold and talc samples. The error on the camera constant was

158   estimated to be ~0.7%. Distances between diffraction spots were measured on the negatives

159   using a precision measurement table.

160

161   *3.5. Atomic force microscopy*

162   The talc surface was investigated by atomic force microscopy (AFM) using a

163   Nanoscope II AFM from Digital Instruments. The talc sample was scanned in air using the

164   repulsive contact mode with constant deflection. The D-head piezoelectric scanner was

165   calibrated using HOP graphite and mica. The pyramidal shaped Si_3N_4 cantilevers from Digital

166   Instrument with 200 μm wide legs and a spring constant of 0.12 N.m^{-1} were used. The talc

167   sample was cleaved along {001} plane surface prior to observation using adhesive tape.

168   Observations were performed using a vibration isolated platform and the thermal drift was

169   minimized by waiting for the AFM to equilibrate with ambient temperature. Contact forces,

170   scan speeds and scan directions were adjusted to optimize the resolution.

171

172   **4. Results**

173

174   *4.1. Mössbauer spectroscopy*

175   Table 1 lists the iron site-occupancies of the talc spectrum fitting, taking into account

176   the quadrupole splitting distributions (Rancourt, 1994). The spectrum of the talc sample

177   obtained at 80°K (Fig. 2a) is similar to talc spectra reported by Martin *et al.* (1999). It shows a

178   difference in intensity between the two absorption bands, and a significant shoulder on the

179   side of the -0.5 mm.s^{-1} peak. A good fit to the experimental data was obtained with four

180   Lorentzian doublets (Fig. 2b – Table 1). The first two, both with a large quadrupole splitting,

181   are due to Fe^{2+} in octahedral sites. The third doublet with a small quadrupole splitting and a

182   low isomer shift is located within the first absorption band and attributed to Fe^{3+} in the

183   tetrahedral site (Dyar & Burns, 1986; Rancourt *et al.*, 1992; Rancourt, 1993; Martin *et al.*,

184   1999). The last doublet corresponds to Fe^{3+} in octahedral sites (Blaauw *et al.*, 1980; Dyar &

185   Burns, 1986; Rancourt *et al.*, 1992; Dyar, 1993; Rancourt, 1993; Martin *et al.*, 1999).

186   According to this decomposition, Fe^{3+} cations are thus present in both octahedral and

187   tetrahedral sites. However, Fe^{2+} is the dominant iron species (81%), thus indicating reducing

188   conditions during the formation of talc.

189

190   *4.2. Chemical composition*

191   The structural formula of the talc sample was calculated on the basis of eleven

192   oxygens from the average of ten bulk analyses obtained by electron microprobe:

193    $[Mg_{2.890}Fe^{2+}_{0.023}Mn^{2+}_{0.003}Fe^{3+}_{0.002}Al_{0.002}]_{\Sigma2.917}$ $[Si_{4.030}Fe^{3+}_{0.003}Al_{0.001}]_{\Sigma4.034}$ O_{10} $(OH_{1.975}F_{0.025})$

194   µThe distribution of iron between $^{[6]}Fe^{2+}$, $^{[4]}Fe^{3+}$ and $^{[6]}Fe^{3+}$ was deduced from Mössbauer

195   spectroscopy results. Aluminum was split into $^{[4]}Al$ and $^{[6]}Al$ to insure the neutralization of

196   charges in the octahedral and the tetrahedral sheets, leading to the electroneutrality of the

197   layer. The composition of the talc sample is thus very close to that of the representative talc

198   determined by Martin *et al.* (1999) for the Trimouns deposit. Only minor substitutions are

199 present in the octahedral or tetrahedral sites leading to moderate local distortions in the

200 tetrahedral sheet and thus to a nearly flat {001} surface.

201

202 *4.3. X-ray diffraction*

203   The powder diffraction pattern of the ground talc powder is characteristic of pure talc

204 with sharp 00ℓ reflections that form a harmonic series ($d_{001} = \ell \times d_{00\ell}$) thus indicating a well-

205 ordered structure along the **c*** axis without interstratification of chlorite layers (Fig. 3). Traces

206 of quartz and dolomite are also detected. Sample unit-cell parameters were refined in the

207 triclinic system (*P*-1 space group - Perdikatsis & Burzlaff, 1981) from the positions of all

208 measurable reflections between 2 and 90°2θ. Unit-cell parameters from the present study are

209 in agreement with those reported by Perdikatsis & Burzlaff (1981 – Table 2). It is possible to

210 deduce the a_{or} and b_{or} dimensions of the usual C-centered pseudo-orthogonal unit cell from

211 the refined abc unit-cell parameters defined in the triclinic system (Fig. 1b). As the γ angle is

212 close to 120°, a_{or} is similar to *a* and b_{or} can be calculated as $b_{or} = a_{or}\sqrt{3}$ (Table 2).

213

214 *4.4. Selected-area electron diffraction*

215   The SAED pattern of a talc single crystal observed along the [001] zone axis contains

216 very sharp *hk*0 diffraction spots arranged according to a pseudo-hexagonal pattern (Figure 4).

217 In order to determine unit-cell dimensions in the **a*b*** plane, $a_1{}^*$, $a_2{}^*$ and $a_3{}^*$ distances were

218 measured along [100], [010] and [110], respectively, and averaged to a single *a** dimension.

219 Measurements were repeated for twelve crystals perfectly aligned along [001], and all values

220 were then averaged to obtain a single *a** unit-cell dimension in the reciprocal space. However,

221 in order to determine the unit-cell dimension in the **ab** plane in the direct space, it is necessary

222 to take into account the 3D symmetry of the unit-cell:

223         $a = (\sin\alpha \,/\, a^*) \,/\, [1 + 2.\cos\alpha.\cos\beta.\cos\gamma - \cos^2\alpha - \cos^2\beta - \cos^2\gamma]^{-2}$ (1)

224   As talc crystallizes in a triclinic system, unit-cell dimensions in the direct space cannot be

225   simply deduced from the distances measured on the SAED pattern without making some

226   assumptions for the values of α, β and γ angles. Therefore, α, β and γ values from XRD

227   analysis (Table 2) were used in Eq. 1, and the following relationship was then obtained:

228        $a = 1.1545/a^*$ (2)

229   Note that the same relationship can be obtained, without using results from XRD, if one

230   assumes that (i) the γ angle is close to 120°, and that (ii) the α and β angles are between 85

231   and 100° then the approximations $\sin\alpha{\sim}1$ and $\cos^2\alpha{\sim}\cos^2\beta{\sim}\cos\alpha.\cos\beta{\sim}0$ can be used. It

232   follows that from direct measurements of the SAED patterns and from the relation given

233   above (Eq. 2), it is possible to deduce that $a_{or} = a = 5.32(3)$ Å and that $b_{or} = a_{or} \sqrt{3} = 9.22(5)$ Å

234   (Table 2).

235

236   *4.5. Atomic force microscopy*

237

238   *Micro-topography of cleaved surface*

239   A high-resolution image was recorded to observe the talc surface micro-topography

240   ($500{\times}500$ nm^2 – Fig. 5). Talc sample exhibits thick crystals in agreement with the

241   macrocrystalline character of the investigated sample. A perpendicular section of talc

242   topography is shown in Figure 5d and reveals that after cleavage these crystals are several

243   tens of unit layers thick. This sample also has very large domains with flat surfaces which are

244   particularly suitable for AFM imaging. Note the variation in Z direction on these almost flat

245   regions that can be attributed to cantilever vibration which is greater when recording in air

246   condition as contrast to images recorded in liquid (Kuwahara *et al.*, 1998, 2001). These

247   regions were chosen for recording molecular-scale image.

248

Molecular scale

250   The raw image obtained at the molecular scale (5×5 nm^2 - Fig. 6) shows an alignment

251   of triangles on the tetrahedral sheet surface. The of this raw image allows determining the m_i

252   periodicity between adjacent triangles and the n_i periodicities for the second neighbor

253   triangles along the perpendicular direction. Figure 7a shows the two-dimensional (2D) fast

254   Fourier transform (FFT) of the raw image. On this numerical diffraction pattern, spots are

255   distributed according to a pseudo-hexagonal pattern and different orders are visible that

256   indicate a well-defined periodic surface structure. It is then possible to index these spots

257   which correspond to m_i and n_i periodicities along two perpendicular directions in the raw

258   image (Fig. 7b). The regularity of the structure deduced from the sharpness of the diffraction

259   spots on 2D FFT is confirmed by direct periodicity measurements done on the raw image and

260   reported in Figure 8, and leading to mean values of 5.47±0.28 Å and 9.48±0.28 Å for m_i and

261   n_i periodic distances, respectively.

262

263   **5. Discussion**

264

265   *5.1 Surface structure of talc*

266   The raw image of talc surface (Fig. 6) is consistent with those found in the wealth of

267   literature devoted to AFM studies of tetrahedral sheet surfaces of phyllosilicates. If some

268   images present an arrangement of hexagonal rings corresponding to the basal oxygen plane of

269   tetrahedral sheet other images, obtained on micas, show a bright spot periodicity of about

270   5.1 - 5.3 Å (which could correspond to the layer unit-cell parameter of most phyllosilicates –

271   Hartman et al., 1990; Lindgreen *et al.*, 1991; Wicks *et al.*, 1992, 1993; Vrdoljak *et al.*, 1994;

272   Kuwahara, 1999, 2001). This periodicity was initially interpreted as the hexagonal array of

273   interlayer cations but Kuwahara (1999) showed that it was possible to obtain both types of

274   image by varying the scan angle on the same sample. In addition, basal oxygen surface often

275   show the alternation of high and low positions for any tetrahedron defining a hexagonal ring.

276   This feature was first interpreted as resulting from the tetrahedral tilt of the basal oxygens but

277   is now commonly considered as a topography artefact induced by the interaction between an

278   asymmetric, double-atom, cantilever tip and the surface atoms (Gould *et al.*, 1989; Vrdoljak

279   *et al.*, 1994; Wicks *et al.*, 1998; Kuwahara, 1999, 2001). According to these studies, triangles

280   on the unfiltered image (Fig. 6) represent a height exaggerated of half of a tetrahedra. Thus,

281   m- and n- periodicities between adjacent triangles correspond to a_{or} and b_{or} unit-cell

282   dimensions of talc. Although the AFM image was recorded in air, the image is most likely of

283   the basal oxygen surface rather than of some adsorbed species on the talc surface. Such

284   adsorption would indeed result in a blurry image with holes and/or aggregation of these

285   molecules. However, because cantilever drift easily removes interlayer cations from the mica

286   surface, in spite of the strong electrostatic binding forces (Kuwahara, 1999, 2001), a similar

287   "cleaning" of adsorbed species from the uncharged talc surface is most likely to occur.

288   The 2D FFT in which pseudo-hexagonal pattern was shown with different orders has

289   indicated a well-defined periodic structure (Fig. 7). Back 2D FFT is commonly applied to

290   remove extraneous signal from images but appears to be a controversial method. The two

291   main criticisms are: i) important features of the raw image are removed and/or features that

292   were not initially present are introduced, and ii) atomic positions are averaged. Wicks *et al.*

293   (1998) discussed thoroughly these potential pitfalls, pointing out that the first point is

294   essentially dependent on the competence of the user who should check carefully the FFT

295   spots. Then, if all the structure information is used in the back 2D FFT operation, only high-

296   frequency noise is removed, and the overall image enhancement does not affect structure

297   details. Wicks *et al.* (1998) also demonstrated that following this image processing, atoms

298   displaced from their ideal positions were not averaged as initially supposed. Figure 9a shows

12

299   the filtered image from the back 2D FFT of areas outlined on the numerical diffraction pattern

300   (Fig. 7a). The filtered image (Fig. 9a) is essentially similar to the raw image (Fig. 6) but

301   shows a spectacular enhancement of structural features, mainly alternate tetrahedra. The

302   individual tetrahedra positions can be drawn to reveal the surface structure of talc (Fig. 9b).

303   Note the presence of a small "hump" in the siloxane cavity. However, because of evident

304   artefacts due in particular to the interaction between the double-atom cantilever tip and the

305   sample, extreme care should be taken in the interpretation of these features in structural terms.

306

307   *5.2 Talc unit-cell parameters*

308   To determine the unit-cell dimension of the talc surface layer, approximately 100

309   measurements in each of the m and n three directions (corresponding to $\mathbf{a_{or}}$ and $\mathbf{b_{or}}$ directions,

310   respectively) were performed on the raw images (Fig. 8). The frequency distribution of m and

311   n indicates a single-mode distribution for each which agrees with published distributions

312   (Vrdoljak *et al.*, 1994; Kuwahara, 1999, 2001).

313   The a_{or} and b_{or} parameters measured on the talc surface by AFM are 5.47±0.28 Å and

314   9.48±0.28 Å, respectively (Table 2). The uncertainty is quite high (~5% and 3% for a_{or} and

315   b_{or}, respectively), but is consistent with other AFM studies on clay minerals (between ~2%

316   and 8%, *e.g.*, Vrdoljak *et al.*, 1994; Kuwahara, 1999, 2001) regardless of the number of

317   measurements performed on a single image and of the number of images processed. The

318   obtained range for a_{or} and b_{or} parameters includes the values expected from the bulk structure

319   determination although the mean values are high. Similar large unit cell parameters have been

320   reported for other phyllosilicates, but the uncertainty systematically includes the ideal unit-

321   cell dimensions (Vrdoljak *et al.* (1994) and Kuwahara (1999) on chlorite and muscovite,

322   respectively). This enlargement of unit-cell parameters was attributed to surface relaxation.

323   However, in contrast to micas or chlorite, no interlayer sheet or cation contributes to

324 interlayer cohesion in talc. As a result, surface relaxation is unlikely for talc and the observed

325 variation in unit-cell dimensions may rather be attributed to instrumental effects as evoked by

326 Vrdoljak *et al.* (1994). Note that improved unit-cell dimensions could be obtained by

327 recording images in liquid environment rather than in air conditions as done in the present

328 study (Kuwahara 1999, 2001; Sokolov *et al.*, 1997, 1999;).

329 Unit-cell dimensions obtained from XRD and SAED are consistent (Table 2) despite

330 difficulties intrinsic to SAED such as the calibration of the camera constant, the alignment of

331 a single crystal along [001] and the inability to precisely determine α, β and γ angles for a

332 triclinic system. Moreover, the uncertainty on the measured values is low for the two methods

333 (~0.1% and 0.6% for XRD and SAED, respectively – Table 2). In contrast, a_{or} and b_{or}

334 parameters measured on the talc surface by AFM are scattered and the resulting uncertainty

335 on the unit-cell parameter is much higher as discussed above. XRD and SAED (providing a

336 good calibration of the camera constant) are more accurate methods to determine unit-cell

337 parameters because of the improved statistics (for XRD) and of the enhanced sensitivity to

338 crystal geometry.

339 Because the sample used in the present study presents a quasi-ideal surface structure

340 with extremely limited tetrahedral tilts/rotations and limited, if any, surface relaxation, the

341 variation in unit-cell dimensions can therefore rather be attributed to instrumental variability

342 (calibration, tip-sample interaction). Extreme care should thus be used when interpreting the

343 changes in unit-cell dimensions in terms of structural features for other clay minerals such as

344 micas, kaolinites and chlorites in which such structural deformations are likely

345

346 **6. Conclusion**

347

348   In relation with the peculiar crystallinity of the studied talc sample from the Trimouns

349   deposit (Ariège, France), it has been possible using atomic force microscopy to obtain a

350   detailed image of the talc surface at the molecular scale. However, in spite of the high-quality

351   image obtained, artefacts that lead to the observation of only one tetrahedron out of two were

352   detected (double-atom cantilever tip interaction). In addition, the very peculiar crystal-

353   chemistry of talc (very limited tetrahedral tilts and tetrahedral rotations, unlikely structure

354   relaxation) has revealed the existence of additional instrumental effects. These effects lead to

355   a slight distortion of the image that make a structural interpretation of these distortions,

356   described in previous studies for other clay minerals (micas, chlorites), ambiguous. Finally

357   the comparison of structure dimensions with data obtained by XRD and SAED shows AFM

358   limitations for unit-cell dimensions determination because of the increased uncertainty and of

359   the possible distortion (enlargement) by instrumental effects.

360

370   **References**

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Tables

Table 1. Mössbauer parameters of talc sample at 80 K. Quadrupole splitting (Δ) and isomer shift (δ) are given in mm.s^{-1}.

Fe^{2+}				Fe^{3+}				Fe^{2+}
$\delta*$	Δ	%	Site	$\delta*$	Δ	%	Site	$(Fe^{2+}+Fe^{3+})$
1.15	2.85			-0.25	0.21	12	[4]	
		81	[6]					81
1.21	2.96			0.07	0.68	7	[6]	

Note: δ values relative to Fe-metal.

Table 2. Comparison of cell parameters. Distances are given in Angstroms and angles in degrees. a_{or} and b_{or} represent dimensions of the equivalent C-centered unit-cell with $\gamma_{or} = 90°$).

	a	b	c	α	β	γ	a_{or}	b_{or}
Perdikatsis & Burzlaff (1981)	5.291(3)	5.290(3)	9.460(5)	98.68(5)	85.27(5)	119.90(5)	5.293(4)	9.168(8)
XRD refinement (this study)	5.294(1)	5.281(1)	9.469(1)	98.71(1)	85.11(1)	119.98(1)	5.288(7)	9.159(10)
Electron diffraction (this study)	5.32(3)	-	-	-	-	-	5.32(3)	9.22(5)
AFM (this study)	-	-	-	-	-	-	5.47(28)	9.48(28)

Note: Unit-cell parameters from Perdikatsis & Burzlaff (1981) are transformed to appear in the *C-1* space group.

515

516

517   **Figure 1.** Talc structure along $c*$ (a) and the tetrahedral surface plane where a and b cell

518   parameters in a quasi-orthogonal system (a_{or}, b_{or}) are indicated (b).

519

520   **Figure 2.** Experimental and fitted Mössbauer spectrum of talc sample at 80 K (a) and

521   different components of the fitted spectrum (b).

522

523   **Figure 3.** X-ray-diffraction pattern of talc sample. Dol. and Qtz. represent dolomite and

524   quartz traces, respectively.

525

526   **Figure 4.** SAED pattern of talc sample recorded along the [001] zone axis.

527

528   **Figure 5.** Micro-topography of talc surface (a) and the same image with isoaltitude curves

529   separated by 70 Å to enhance topography contrasts (b). (c) and (d) represent profiles

530   of cleaved surface morphology.

531

532   **Figure 6.** AFM image of talc surface at molecular scale 5×5 nm^2.

533

534   **Figure 7.** Two-Dimensional Fourier Transform applied to molecular scale AFM image (Fig. 6

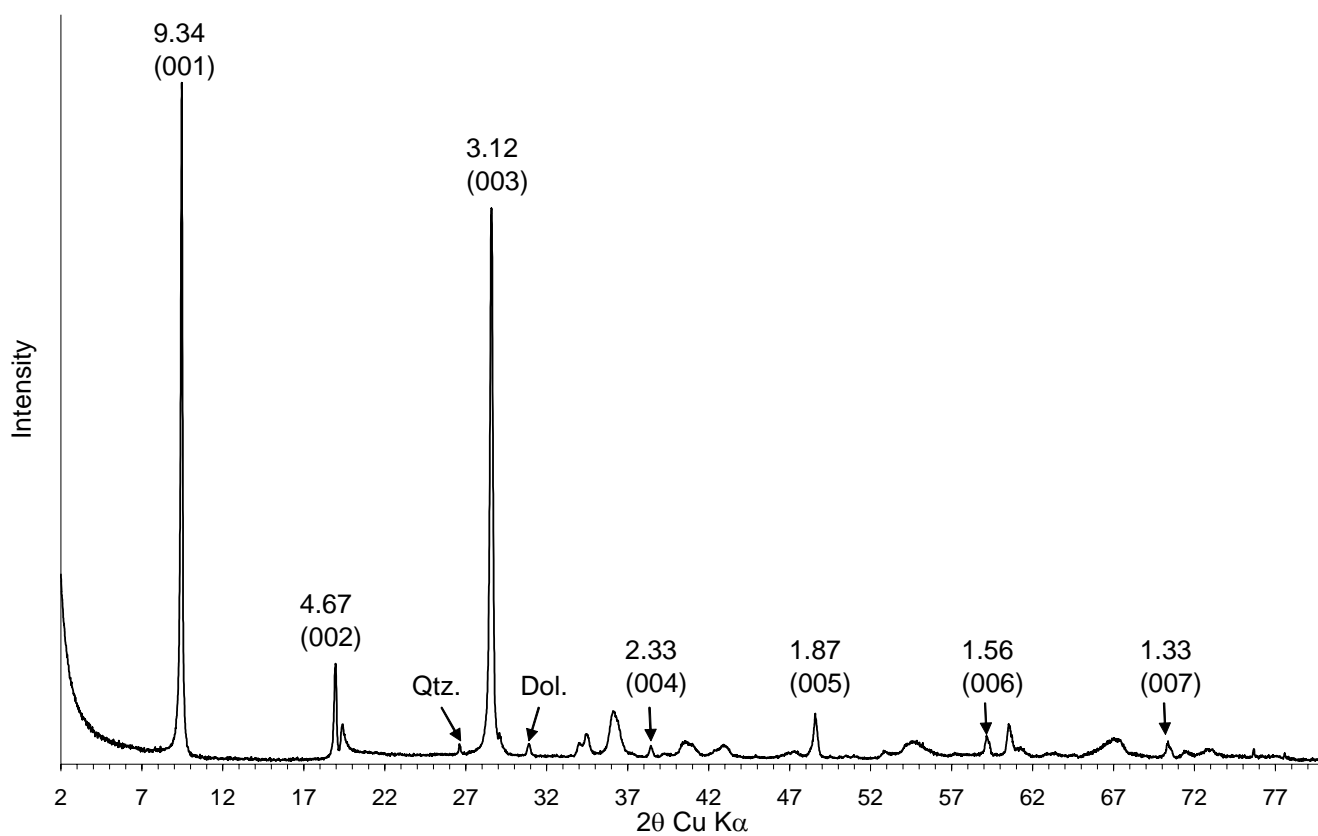535   - a) and indexation of spots in reciprocal space (b).

536

537   **Figure 8.** Histogram of a_{or} and b_{or} cell parameters from AFM molecular scale image.

538

539   **Figure 9.** Image shown in Fig. 5 after application of back 2D FFT to remove extraneous

540   signal (a). An enlarged view of a image with a redraw of individual tetrahedrons

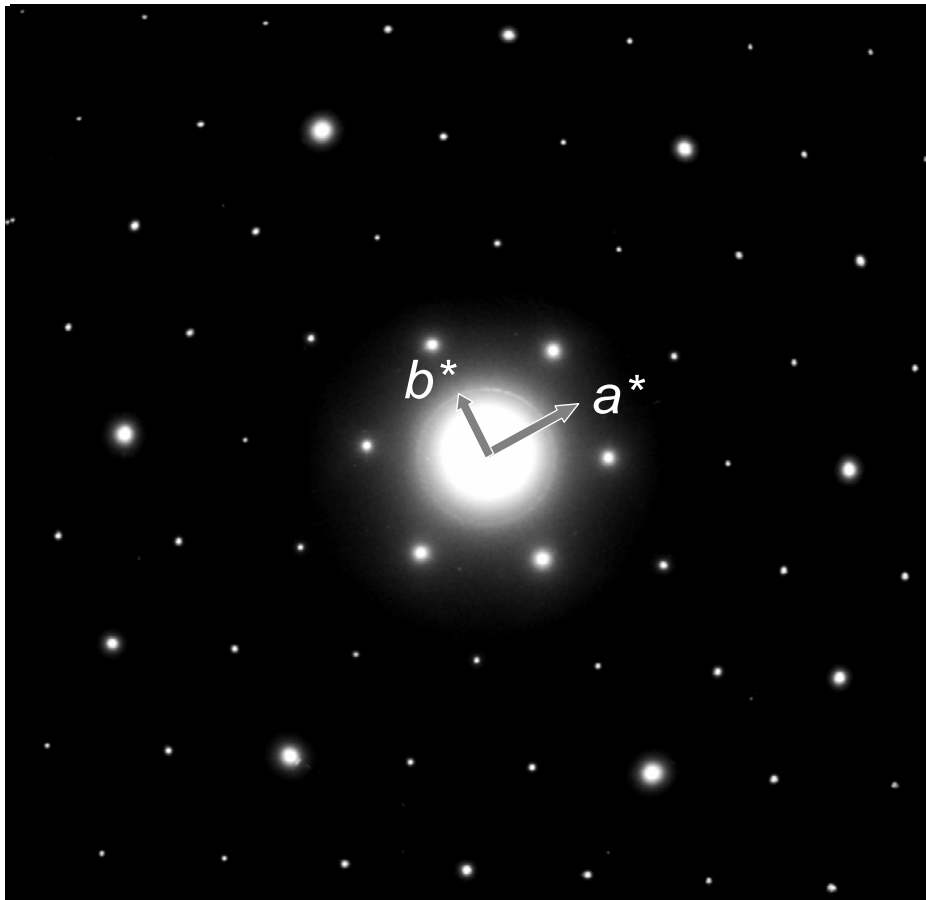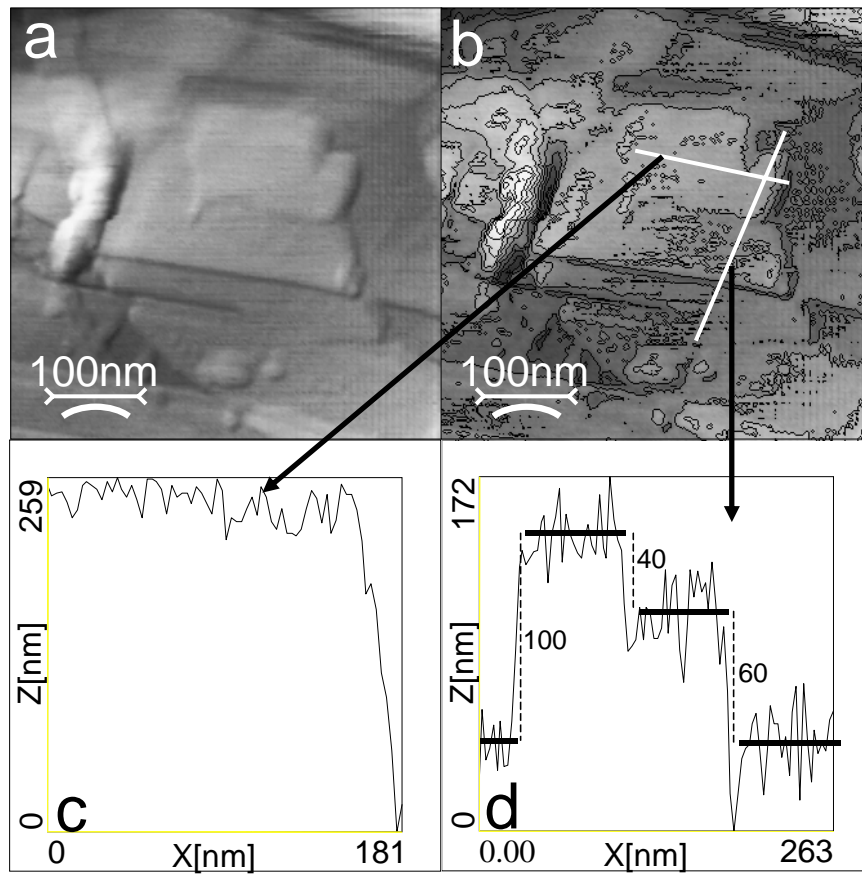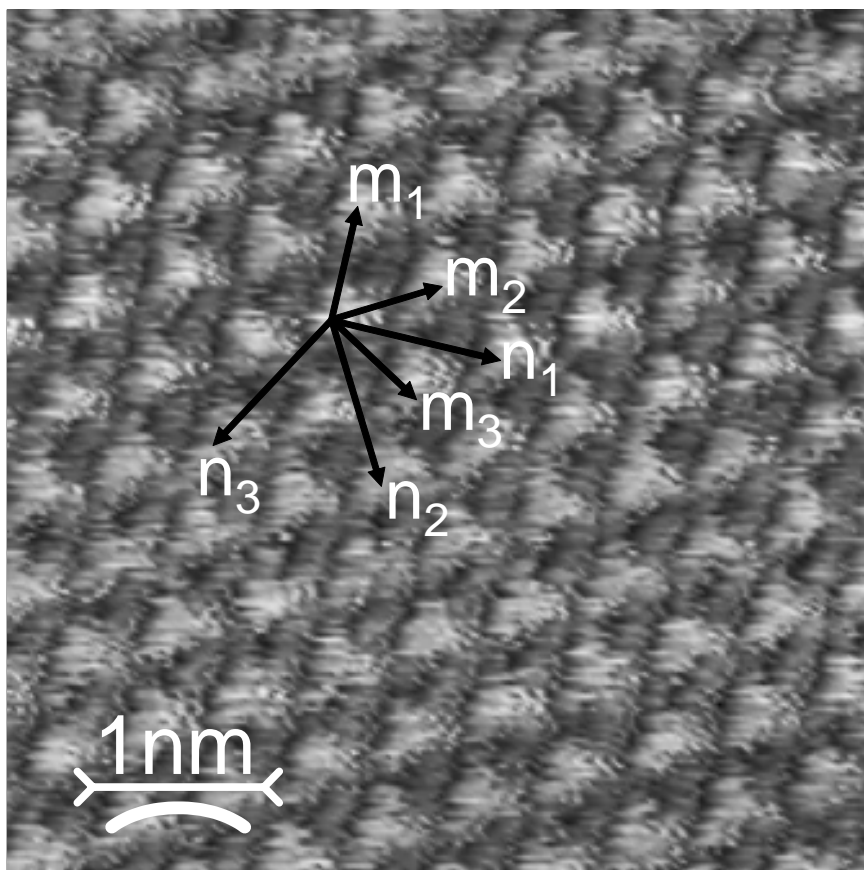541   (theoretical tetrahedral rotation not being taken into account).

a

b

a_{or}

b_{or}

Ferrage et al., Fig. 01

a

Absorbance

Velocity (mm/s)

b

[6] Fe^{3+}
δ = 0,067 mm/s
Δ = 0,685 mm/s
% = 7

δ = 1.150 mm/s
Δ = 2.852 mm/s
% = 23

[6] Fe^{2+}

[4] Fe^{3+}
δ = -0.255 mm/s
Δ = 0.210 mm/s
% = 12

[6] Fe^{2+}

δ = 1,214 mm/s
Δ = 2.962 mm/s
% = 58

Fitted

Fe^{2+}/(Fe^{2+} + Fe^{3+}) = 81 %

Absorbance

Velocity (mm/s)
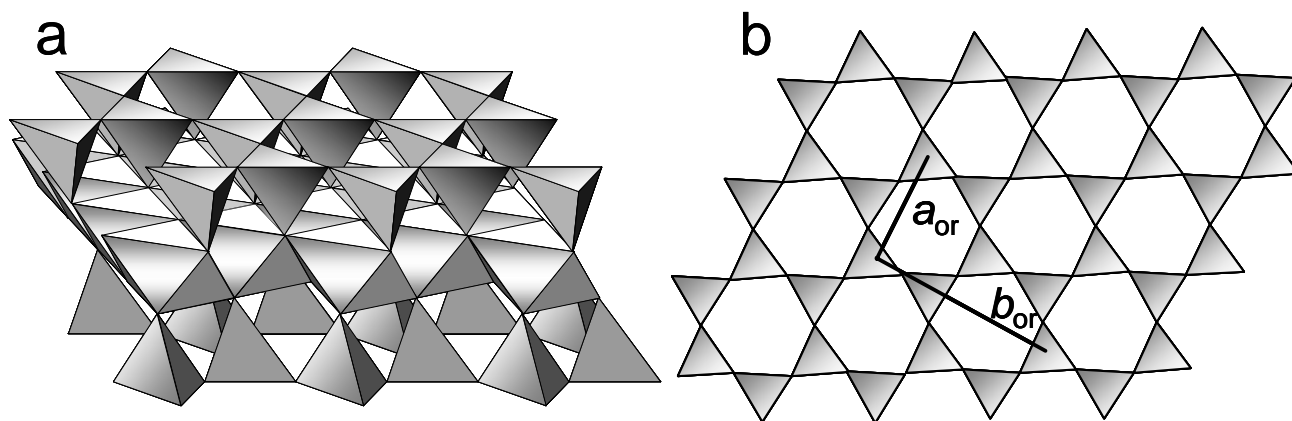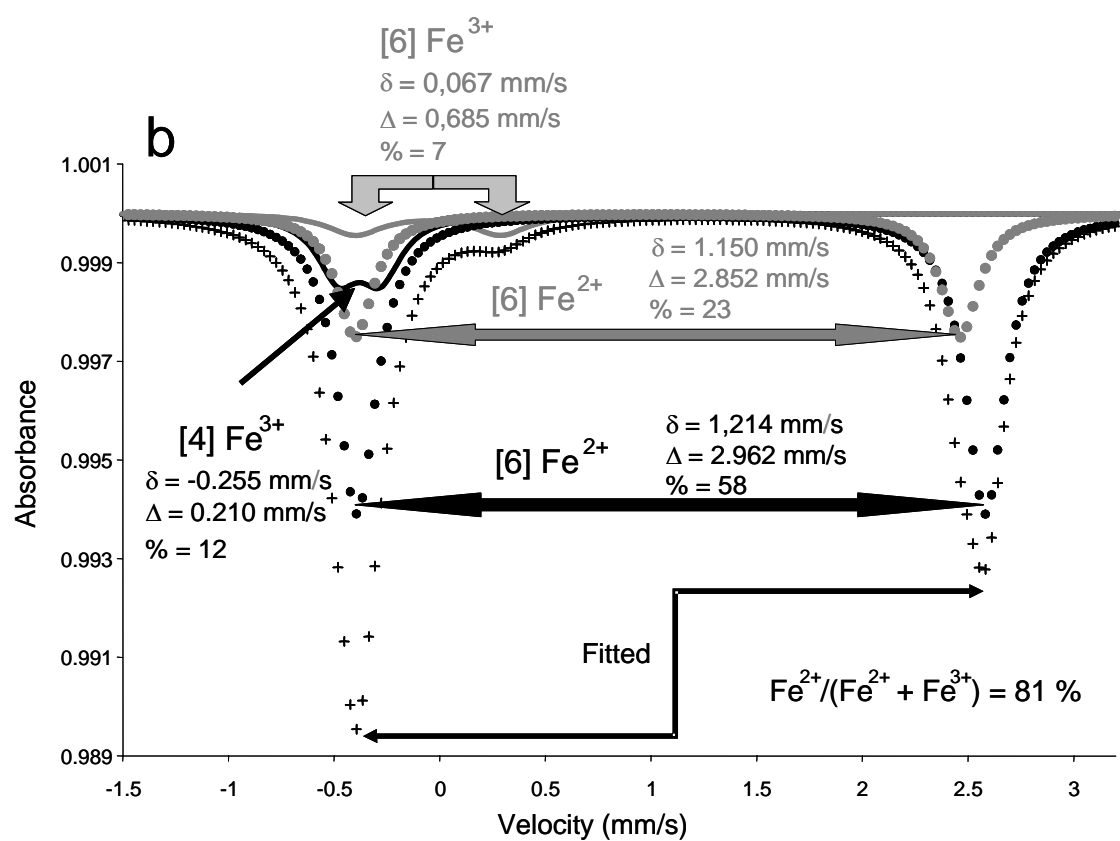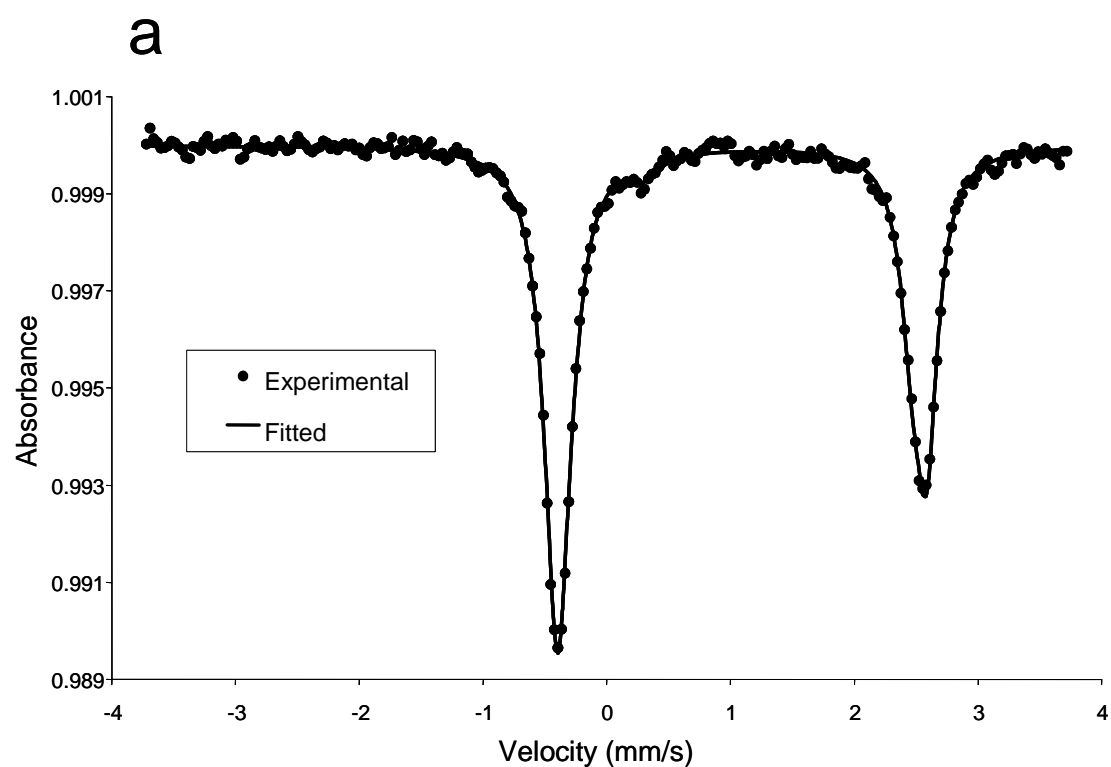
Ferrage et al., Fig. 02

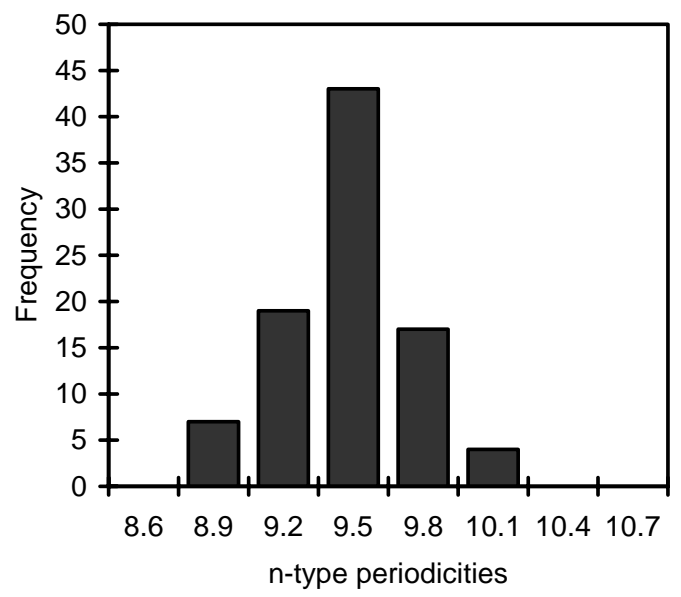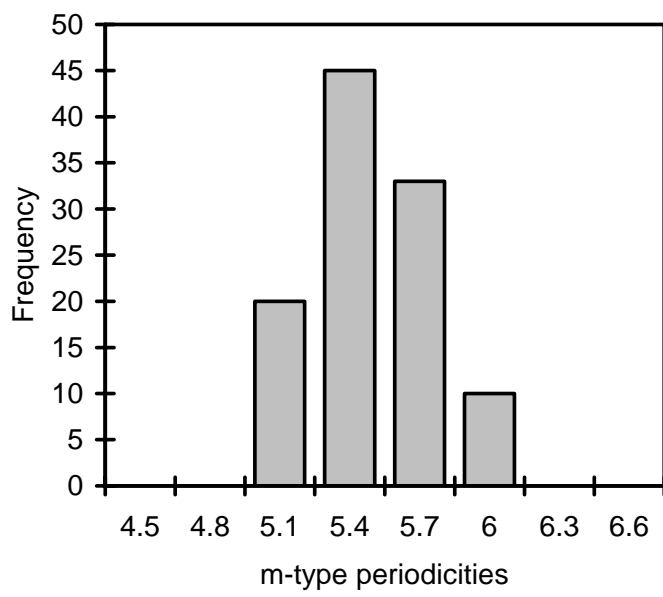Ferrage et al., Fig. 03

Ferrage et al., Fig. 05

1nm

a

b

Ferrage et al., Fig. 07

Ferrage et al., Fig. 08