Investigation of dioctahedral smectite hydration properties by modeling of X-ray diffraction profiles: Influence of layer charge and charge location

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19   **ABSTRACT**

20

21   Hydration of the <1 µm size fraction of a high-charge montmorillonite (Clay

22   Minerals Society Source Clay SAz-1), and of low- and high-charge beidellites (Source Clays

23   SbId-1 and SbCa-1, respectively) was studied by modeling of X-ray diffraction patterns

24   recorded under controlled relative humidity (RH) for Sr- and/or Ca-saturated specimens. The

25   influence of layer charge and charge location on smectite hydration was studied. Distribution

26   of layers with different hydration states (dehydrated – 0W, monohydrated – 1W, bi-hydrated

27   – 2W, or tri-hydrated – 3W) within smectite crystals often leads to two distinct contributions

28   to the X-ray diffraction pattern, each contribution having different layer types randomly

29   interstratified.   Structure   models   are   more   heterogeneous   for   beidellite   than   for

30   montmorillonite. For beidellite, two distinct populations of particles with different coherent

31   scattering domain sizes account for the heterogeneity. Increased hydration heterogeneity in

32   beidellite originates also from the presence of 0W (non-expandable) and of 1W layers under

33   high relative humidity (RH) conditions. Similarly, after ethylene-glycol (EG) solvation, some

34   beidellite layers incorporate only one plane of EG molecules whereas homogeneous swelling

35   was observed for montmorillonite with the systematic presence of two planes of EG

36   molecules.

37   For montmorillonite and beidellite, the increase of layer charge shifts the 2W-to-1W

38   and the 1W-to-0W transitions towards lower RH values. For all samples, layer thickness of

39   0W, 1W, and 2W layer types was similar to that determined for low-charge SWy-1

40   montmorillonite (Source Clay SWy-1), and no change of layer thickness was observed as a

41   function of the amount or of the location of layer charge. Layer thickness however increased

42   with increasing RH conditions.

INTRODUCTION

44

45   Bentonite, a rock containing mostly smectite, is a promising buffer material for

46   engineered barriers for nuclear waste disposal. This potential results from its mechanical self-

47   healing ability, its low hydraulic conductivity, and its high sorption capacity. This

48   combination is expected to prevent or delay possible radionuclide migration. However, the

49   properties of smectite can be altered by storage-induced conditions such as the thermal pulse

50   resulting from the waste package. By analogy with burial diagenesis of clayey sediments

51   (Weaver 1960; Hower and Mowatt 1966; Burst 1969; Shutov et al. 1969; Perry and Hower

52   1972; Hower et al. 1976; among many others), smectite is expected to transform to illite by

53   way of intermediate interstratified structures with increasing temperature. This transition was

54   originally conceived as following smectite dehydration (Burst 1969; Shutov et al. 1969; Perry

55   and Hower 1972). More recently, structural changes affecting smectite during the early stages

56   of transformation have been shown to impact essentially the location and amount of layer

57   charge (Sato et al. 1996; Drits et al. 1997; Beaufort et al. 2001), the initial smectite being a

58   low-charge montmorillonite with dominant octahedral charge. Sato et al. (1996) proposed that

59   beidellite-like layers (with dominant tetrahedral charge) initially form from montmorillonite

60   in addition to an increase in layer charge. Then, these beidellite-like layers transform to illite.

61   This proposal is supported by hydrothermal alteration experiments conducted at moderate

62   temperatures (<200°C, see Beaufort et al. 2001) leading to beidellitic layers from alteration of

63   montmorillonite.

64   Modification of layer charge and charge location can possibly affect smectite

65   hydration ability. Crystalline swelling of 2:1 phyllosilicates is controlled indeed by the

66   balance between repulsive forces between adjacent 2:1 layers and attractive forces between

67   hydrated interlayer cations and the negatively charged surface of 2:1 layers (Norrish 1954;

68 Van Olphen 1965; Kittrick 1969a, 1969b; Laird 1996, 1999). Thus crystalline swelling is

69 characterized by the amount of layer charge and its location (octahedral vs. tetrahedral).

70 Different hydration states may correspond to 0, 1, 2 or 3 "planes" of H_2O molecules in

71 smectite interlayers. Intercalation of H_2O planes produces a stepwise hydration depending on

72 RH, easily detected by X-ray diffraction (XRD) by an increase in basal spacing

73 (Nagelschmidt 1936; Bradley et al. 1937; Mooney et al. 1952; Méring and Glaeser 1954;

74 Norrish 1954; Walker 1956; among others).

75   From these considerations, an increase in layer charge increases attractive forces

76 between the hydrated interlayer cation and the 2:1 layers, thus decreasing interlayer thickness.

77 Charge location may affect smectite hydration from the charge under-saturation of oxygen

78 atoms defining the basal surfaces of 2:1 layers. In montmorillonite-like layers, the charge

79 under-saturation resulting from R^{2+}-for-R^{3+} substitutions in the octahedral sheet is distributed

80 among a large number of basal oxygen atoms which are thus weakly under-saturated. In

81 contrast, when Al^{3+}-for-Si^{4+} substitutions occur in tetrahedral sites the charge deficit is

82 distributed by the three nearest neighbor basal oxygen atoms. These oxygen atoms are

83 strongly under-saturated and produce strong attractive interactions with interlayer cations.

84 This strong local under-saturation is sometimes assumed to decrease layer hydration (e.g.,

85 Laird 1996, 1999). However, experimental results are not consistent with this expected

86 influence of the size and location of layer charge on hydration behavior. For example, Sato et

87 al. (1992) reported similar d(001) values for smectite with different layer-charge locations,

88 and smaller d(001) values were not observed for smectite with higher layer charge.

89 Furthermore, Chiou and Rutherford (1997) and Michot et al. (2005) reported an increase in

90 H_2O content with increasing layer charge. Similar results were obtained by Laird (1999) who

91 attributed the increased hydration to H_2O adsorption on external surfaces of the crystallites.

92   This article complements Ferrage et al. (2005b), in which the hydration of low-

93   charge montmorillonite was studied, and investigates the effect of the size and location of

94   layer charge on smectite hydration. The hydration of three reference smectites, including

95   high-charge montmorillonite, and low- and high-charge beidellites, is considered as a function

96   of relative humidity after saturation by Ca^{2+} and Sr^{2+}.

97

98   **MATERIAL AND METHODS**

99

100   **Sample preparation**

101

102   Smectites used here are montmorillonite and beidellite samples from the Source Clay

103   Repository of The Clay Minerals Society. The high-charge montmorillonite (SAz-1) has a

104   structural formula of: $[(Al_{2.80}\ Fe^{3+}_{0.20}\ Mg_{1.00})(Si_{7.86}\ Al_{0.14})O_{20}(OH)_4]\ M^+_{1.14}$ (Jaynes and

105   Bigham 1987). Compared to SWy-1 montmorillonite studied by Ferrage et al. (2005b), SAz-1

106   has more Mg^{2+}-for-Al^{3+} octahedral substitutions and limited tetrahedral substitution.

107   Low-charge SbId-1 beidellite (Glen Silver Pit, DeLamare Mine, Idaho) has a

108   structural formula of: $[(Al_{3.77}\ Fe^{3+}_{0.11}\ Mg_{0.21})(Si_{7.27}\ Al_{0.73})O_{20}(OH)_4]\ M^+_{0.67}$ (Post et al. 1997).

109   High-charge SbCa-1 beidellite contains more Al^{3+}-for-Si^{4+} tetrahedral substitutions with a

110   structural formula: $[(Al_{3.82}\ Fe^{3+}_{0.18}\ Mg_{0.06})(Si_{6.80}\ Al_{1.20})O_{20}(OH)_4]\ M^+_{1.07}$.

111   For all samples, size fractionation to $< 1\ \mu m$ was obtained by centrifugation. Then,

112   ion exchange was achieved with $1\ mol.L^{-1}$ aqueous solutions of $CaCl_2$, for SAz-1 only, and

113   $SrCl_2$, with three steps of saturation followed by three washing steps, as described by Ferrage

114   et al. (2005b). Resulting samples are hereafter referred to as Ca- and Sr-SAz-1, Sr-SbId-1 and

115   Sr-SbCa-1.

116

X-ray diffraction and fitting strategy

XRD patterns were recorded from oriented preparations of the air-dried homoionic samples. Full-width at half-maximum intensity (FWHM) of the 001 reflection and 00l reflection irrationality (ξ parameter) were measured to qualitatively estimate hydration heterogeneity (see Ferrage et al. 2005b). The ξ parameter is calculated as the standard deviation of the $l \times d(00l)$ values (in Å) for all measurable 00l reflections over the 2-50°2θ angular range, although some of these reflections may correspond to various interstratified structures. These values are listed in Table 1.

Models combine the XRD modeling algorithm of Drits and coworkers (Sakharov and Drits 1973; Drits and Sakharov 1976; Drits et al. 1997; Sakharov et al. 1999) with a trial-and-error approach to quantify hydration heterogeneity. The calculation of the XRD profile includes the mean number of layers (N) in the coherent scattering domains (CSDs), the absorption coefficient (μ^*), and the preferred orientation of the sample (σ^*). The z coordinates of dehydrated (0W), monohydrated (1W), and bi-hydrated (2W) layers, and crystal strains (σ_z) described by Ferrage et al. (2005b) were used. H_2O molecules were distributed in 2W smectite as a unique plane of H_2O molecules on each side of the central interlayer mid-plane, at ~1.20 Å along the **c*** axis. The number of interlayer H_2O molecules in hydrated layers was considered a variable parameter.

The fitting strategy developed by Ferrage et al. (2005b) was used to model XRD patterns. A main structure, periodic along the **c*** axis where possible, was used to reproduce the experimental XRD pattern. If required, additional contributions to the diffracted intensity were introduced. These additional contributions are related to random interstratifications of two or three layer types (0W, 1W, 2W layers), which are hereafter referred to as heterogeneous structures as compared to the main structure. Because RH values were < 80%,

142   tri-hydrated layers (3W layers at 18.0-18.5 Å) were not observed, as transition from 2W-to-

143   3W smectite occurs for RH values of > 90% for Ca-exchanged smectites (Watanabe and Sato

144   1988). Up to four structures (periodic and/or interstratified) were used for very heterogeneous

145   samples but these contributions are not necessarily related to distinct populations of crystals.

146   To minimize the number of adjustable parameters, layers of same hydration state present in

147   different structures were assumed to have identical properties. Thus, for a given sample, each

148   layer type (0W, 1W or 2W layers) was assigned a chemical composition (number of interlayer

149   H_2O molecules and cations, and chemical composition of the 2:1 layer), layer thickness, and

150   atomic coordinates for each component. Similarly, a unique value of σ^* and σ_z parameters

151   was assigned for each RH value. Each parameter was allowed to vary with RH. For beidellite,

152   models consider either (1) a unique CSD size for all interstratified structures at a given RH, or

153   (2) the physical mixture of two or more interstratified structures with different CSD sizes (see

154   below).

155   Hereafter, indices "00*l*" and "001, 002, …" are used to identify experimental

156   diffraction maxima, although these maxima correspond to interstratified and not to periodic

157   structures.

158

159   **RESULTS**

160

161   **Qualitative description of experimental patterns**

162

163   **Ca- and Sr-saturated montmorillonite SAz-1**. At 0% RH, Ca-SAz-1 (Fig. 1a)

164   exhibits a 001 reflection at ~11.65 Å, a position intermediate between 0W and 1W smectite,

165   indicating hydration heterogeneity. Accordingly, the 001 reflection is broad (FWHM = 1.05°,

166   Table 1) and a large value of ξ parameter was obtained (0.56 Å, Table 1). In contrast, the

167 pattern of Sr-SAz-1 recorded at 0% RH (Fig. 1b) is typical of 1W smectite (001 at ~12.10 Å)

168 with a low value of ξ (0.04 Å), but note the high FWHM of the 001 reflection (0.88°). At 20%

169 RH, the d(001) value of Sr-SAz-1 at ~13.1 Å is intermediate between 2W and 1W smectites.

170 Experimental diffraction maxima are poorly defined, and peaks at ~6.1 Å (002 reflection of

171 1W smectite), and at ~5.1 Å (003 reflection of 2W smectite) are observed (Fig. 1b). For this

172 sample, high values are obtained for ξ and FWHM of the 001 reflection (1.20 Å and 1.66°,

173 respectively). In contrast, Ca-SAz-1 exhibits a 001 reflection at ~14.9 Å and well-defined

174 diffraction maxima of 2W smectite. Over the 35-80% RH range, XRD patterns for Ca- and

175 Sr-SAz-1 are similar, and correspond to dominant 2W smectite (Ca: d(001) = 15.1-15.6 Å; Sr:

176 d(001) = 15.2-15.9 Å – Table 1). Note that the 002 reflection is poorly defined whatever the

177 RH (Figs. 1a, 1b).

178   **Sr-saturated beidellite (SbId-1 and SbCa-1)**. XRD patterns of both beidellites

179 samples include reflections at ~7.2 and ~3.6 Å (K on Figs. 1c, 1d), produced by a minor

180 contribution from kaolinite-group minerals. At 0% RH, Sr-SbId-1 displays poorly defined

181 diffraction maxima with a 001 reflection at ~11.10 Å and large values of FWHM and ξ (1.28°

182 and 0.76 Å, respectively, Fig. 1c, Table 1). In contrast, Sr-SbCa-1 shows well-defined

183 diffraction maxima corresponding to 1W smectite (d(001) ~12.0 Å) and low values for

184 FWHM of the 001 reflection and ξ (0.75° and 0.04 Å, respectively). At 20% RH, d(001)

185 values at ~12.3-12.4 Å for both samples indicate a 1W smectite, along with low values for

186 FWHM and ξ. At ambient RH, the d(001) values near 14.9 Å for Sr-SbId-1 and near 15.2 Å

187 for Sr-SbCa-1 indicate dominant 2W smectite with well-defined diffraction maxima.

188 However, both XRD patterns present a high-angle shoulder of the 001 reflection and a peak at

189 ~6.1 Å corresponding to 1W smectite (Figs. 1c, 1d), which increases ξ. From 40 to 80% RH,

190 the peak at ~6.1 Å is absent and the high-angle shoulder of the 001 reflection decreases with

191 increasing RH (Figs. 1c, 1d). The d(001) values are similar for the two samples throughout

192   this RH range and low values of FWHM and ξ systematically indicate the dominance of 2W

193   smectite. As for SAz-1, the 002 reflection of 2W smectite is poorly defined.

194   Note also the peaks at ~25 Å and ~22 Å for samples recorded over the 35-80% RH

195   and 0-20% RH range, respectively. These peaks may be attributed to an ordered interstratified

196   structure consisting of 2W and 0W and of 1W and 0W smectite, respectively (Figs. 1c, 1d).

197   For Sr-SbCa-1, these reflections are similar to those reported by Chipera and Bish (2001).

198

199   **Modeling of X-ray diffraction profiles**

200

201   Structure models providing optimum fits shown in Figure 1 are described

202   schematically (relative proportion and composition of each structure) in Figure 2 as a function

203   of RH. Structural parameters are listed in Table 2.

204   **Ca- and Sr-SAz-1 montmorillonite**. XRD patterns for Ca-SAz-1 and Sr-SAz-1 over

205   the 0-80% RH range were fitted assuming two structures (Figs. 1a, 1b, 2a, 2b). Over the 20-

206   80% RH range for Ca-SAz-1 and the 35-80% RH range for Sr-SAz-1, the model consists of a

207   main structure dominated by 2W smectite and of a second, heterogeneous, structure

208   containing 0W, 1W, and 2W layers (Figs. 2a, 2b). 2W layers are systematically prevailing in

209   the heterogeneous structure except for Sr-SAz-1 at 35% RH where 2W and 1W smectite are

210   present in equal amounts (Figs. 2a, 2b). Relative abundance of the heterogeneous structure

211   decreases with increasing RH. The proportion of 1W and 0W layers in the dominantly 2W

212   structure decreases also with increasing RH. Both trends account for the sharpening and the

213   increased intensity of the reflection at ~7.75 Å with increasing RH (Figs. 1a, 1b). At 20% RH,

214   two contributions were used to fit the pattern of Sr-SAz-1, a near-periodic 1W smectite, and a

215   heterogeneous structure containing 0W, 1W, and 2W layers. 1W and 2W layers prevail in the

216   latter structure which accounts for the reflection at ~5.1 Å. The different compositions of the

217   two structures produce the broadening of the 001 reflection observed at this RH (1.66°, Table

218   1). At 0% RH, patterns of Ca-SAz-1 and Sr-SAz-1 were fitted assuming a main structure

219   dominated by 1W smectite and a more heterogeneous structure dominated by 0W layers

220   (Figs. 2a, 2b). The irrationality of 00l reflections for Ca-SAz-1 ($\xi = 0.56$ Å) is produced by

221   the high amount of 0W layers in the main structure, in which 1W layers prevail, and by the

222   strong contribution of the most heterogeneous structure.

223   With increasing RH, the layer thickness of 1W and 2W layers increases for both

224   samples to accommodate the larger numbers of interlayer H_2O molecules (Table 2), as

225   reported by Ferrage et al. (2005b) for low-charge montmorillonite. Among other parameters,

226   σ^* was found nearly constant (6.7-7.5°) for all XRD patterns except for 0% RH, whereas N

227   and σ_z are steadily decreasing and increasing, respectively, with increasing RH.

228   **Sr-SbId-1 and Sr-SbCa-1 beidellite**. In the optimum structure model determined

229   for Sr-SbId-1 and Sr-SbCa-1, interstratified structures can have different N values. In this

230   case, the evolution of beidellite hydration results from the hydration properties of two particle

231   populations with distinct N values. However, to minimize the number of adjustable

232   parameters other parameters (layer chemical composition, layer thickness, σ^*, σ_z, e.g.) are

233   identical for all layer types, whatever the interstratified structure (Table 2).

234   At 60% and 80% RH, one particle population contains essentially 2W layers and

235   accounts for the main features of the experimental patterns (Figs. 2c, 2d, 3). The second

236   population is a very heterogeneous structure of small CSD size (3.5 layers, Table 2, Figs. 2c,

237   2d, 3), which produces the asymmetry of the 001 reflection at high angles and of the 005

238   reflection at low angles (Fig. 3). At 40% RH, a second interstratified structure with dominant

239   2W layers coexisting with 1W layers occurs with a large CSD size (30 and 40% of 1W layers

240   for Sr-SbId-1 and Sr-SbCa-1, respectively, Figs. 2c, 2d). Structure models determined at 35%

241   RH include four structures, one structure having a low CSD size (Figs. 2c, 2d). Finally, two

242   structures were considered to reproduce patterns recorded at 20% and 0% RH. The first

243   structure, with a large CSD size, is dominated by 1W smectite and accounts for the shape of

244   the 001 reflection and for the position of other maxima. For Sr-SbId-1 at 0% RH, this

245   structure incorporates significant proportions of 0W layers. The second structure, whose

246   content does not depend on RH, has smaller CSD size and contains 1W and 0W layers, the

247   proportion of 0W layers increasing with decreasing RH (Figs. 2c, 2d).

248   For both Sr-SbId-1 and Sr-SbCa-1 the amount of kaolinite-group minerals did not

249   vary (~16% and ~10% for Sr-SbId-1 and Sr-SbCa-1, respectively, Figs. 2c, 2d). As observed

250   for montmorillonite (this study and Ferrage et al. 2005b), layer thickness of 1W and 2W

251   layers increased with increasing RH for Sr-SbId-1 (11.95-12.70 Å and 15.12-15.65 Å,

252   respectively) and for Sr-SbCa-1 (11.98-12.70 Å and 15.10-15.60 Å, respectively). Among

253   other parameters, σ^* is nearly constant (7.0-8.0° and 4.8-5.5° for Sr-SbId-1 and Sr-SbCa-1,

254   respectively). With increasing RH, σ_z increases whereas N decreases, except at 0% RH for Sr-

255   SbId-1.

256   For beidellite, the low intensity reflection at ~25 Å over the 35-80% RH range may

257   correspond to an ordered (Reichweit parameter R = 1 with maximum possible degree of

258   order, R1-MPDO, see Drits and Tchoubar 1990) interstratified structure containing similar

259   proportions of 0W and 2W layers (Figs. 1c, 1d, 5). Similarly, the reflection at ~22 Å observed

260   over the 0-20% RH range may correspond to a R1-MPDO structure containing 1W and 0W

261   layers in similar proportions. These features are discussed below.

262   Note that fits of similar quality were obtained for Sr-SbId-1 and Sr-SbCa-1 with

263   structures models in which all contributions contain identical layers and have identical crystal

264   parameters (N, σ^*). However, modeling of XRD patterns obtained after ethylene-glycol (EG)

265   solvation allows rejection of these alternative models (see below).

266　　　　**Modeling of X-ray diffraction profiles after EG solvation**. XRD patterns obtained

267　　after EG solvation of Ca-saturated SWy-1 and SAz-1 and of Sr-saturated SbId-1 and SbCa-1

268　　are compared to calculated profiles in Figure 4 and optimal structural parameters are listed in

269　　Table 3. For montmorillonite, the best model involves a unique structure of 2EG layers (with

270　　two planes of interlayer EG molecules), interstratified with non-expandable (0EG) layers at

271　　1% and 2% in Ca-SWy-1 and Ca-SAz-1, respectively. These contents of collapsed layers are

272　　similar to samples at 80% RH. No 1EG layers were found.

273　　　　　XRD patterns of EG-solvated beidellite were only simulated assuming two

274　　interstratified structures (Table 3). One (with a large CSD size) contains mostly 2EG layers,

275　　and the second is more heterogeneous and contains 15% of 1EG and 15% of 0EG layers.

276　　After EG solvation, the relative abundance of the most heterogeneous structure (with a low

277　　CSD size) is similar to that of the population with a low CSD size in the air-dried state (38%

278　　and 42% for Sr-SbId-1 and Sr-SbCa-1, respectively). This similarity strongly supports the

279　　presence of different particle populations. Combining the two contributions leads to a

280　　2EG:1EG:0EG ratio of 86:7:7 for both Sr-SbId-1 and Sr-SbCa-1.

281

282　　　　　　　　　　　　　　　　DISCUSSION

283

284　　**Structure models**

285

286　　　　**Montmorillonite**. Structure models determined for SAz-1 (this study) and SWy-1

287　　(Ferrage et al. 2005b) are consistent for a given interlayer cation. From ambient to 80% RH

288　　these models include two interstratified structures dominated by 2W layers, one being more

289　　heterogeneous with the presence of the three layer types (0W, 1W and 2W layers – Figs. 2a,

290 2b). Hydration of high-charge SAz-1 montmorillonite is thus homogeneous, with a slight

291 segregation of 2W layers.

292   **Beidellite**. Complex structure models with numerous contributions were required to

293 reproduce experimental XRD patterns for beidellites. At ambient RH, the large high-angle

294 asymmetry of the 001 reflection and reflections from both 1W- and 2W-dominated structures

295 required a greater number of contributions. In addition, structure models include a

296 heterogeneous structure containing high proportions of 0W and 1W layers even at 80% RH.

297 This contribution has a small CSD size (3.5-5.0 layers), and its relative proportion is constant

298 (~40-45% for Sr-SbId-1 and Sr-SbCa-1) through the RH range investigated.

299   The particle population with a large CSD size (population A in Figure 6) exhibits

300 transitions to higher hydration states with increasing RH: from 0W/1W to 1W and further to

301 2W (for Sr-SbId-1) and from 1W to 2W (for Sr-SbCa-1). In both samples, the 1W-2W

302 transition occurs through intermediate 2W/1W interstratified structures. The particle

303 population with a small CSD size (population B in Figure 6) maintains its heterogeneous layer

304 composition throughout the RH range despite the steady increase of the 2W layer proportion,

305 at the expense of 0W layers, with increasing RH.

306   **Impurities in beidellites**. For Sr-SbId-1 and Sr-SbCa-1, low-intensity reflections

307 occur at ~25 Å and ~22 Å (for the 35-80% and 0-20% RH ranges, respectively). The ~25 Å

308 peak possibly corresponds to a R1-MPDO structure containing similar proportions of 0W and

309 2W layers (Figs. 1c, 1d). Similarly, the reflection at ~22 Å possibly corresponds to a R1-

310 MPDO structure containing 1W and 0W layers in similar proportions. The positions of these

311 reflections do not significantly change after EG solvation (Fig. 4). The relative proportion of

312 this structure was determined for Sr-SbId at 80% RH (Fig. 5). For Figure 5a, the optimum

313 model (Fig. 2c) is shown for $2\theta < 5°$. Note that the computed "background" intensity is

314 inconsistent with the measured one. Over this region, a R1-MPDO structure containing 0W

315   and 2W layers exhibits two main reflections at ~25.0 Å and ~12.5 Å, the latter being much

316   weaker. To reproduce the shoulder at ~25 Å, the R1-MPDO structure should contribute ~3%

317   of the total diffracted intensity (Fig. 5b), without affecting the relative proportion of the

318   different layer types. Consequently, the low-angle reflections may be related to impurities.

319   **Origin of hydration heterogeneity in beidellite**. Two populations of particles were

320   found in beidellites (Fig. 6). Hydration of population A, with a large CSD size, is

321   homogeneous with dominant 1W and 2W layer types except for Sr-SbId-1 at 0 and 35% RH

322   and for Sr-SbCa-1 at 35 and 40% RH. In contrast, hydration of population B, with a small

323   CSD size, is heterogeneous over the entire RH range for each beidellite. This observation

324   suggests that layer charge and charge location in population B are likely similar for both

325   samples. In addition, populations A and B probably differ in both samples from the

326   heterogeneity of their layer charge distributions.

327   Because of population B, the number of 0W and 1W layers is relatively high at 80%

328   RH for Sr-SbId-1 (14% and 10%, respectively) and Sr-SbCa-1 (9% and 14%, respectively). In

329   contrast, at this high RH value, Sr-SWy-1 contains 2% of 0W and 1W layers and Sr-SAz-1

330   shows 1% and 4% of 0W and 1W layers, respectively. Hydration heterogeneity persists at

331   high relative humidity only for beidellite. XRD profile modeling of EG-solvated samples

332   confirmed the observed hydration/swelling heterogeneity of beidellite (global 2EG:1EG:0EG

333   ratio of 86:7:7 for both Sr-SbId-1 and Sr-SbCa-1), although EG solvation is known to induce

334   homogeneous configuration of smectite interlayers (2EG layers). Collapsed layers after EG

335   solvation are considered as non-expandable layers. Although the nature of 1EG layers is

336   unknown, they may possess a higher layer charge than smectite (vermiculite-type layers).

337   Note that 0EG and 1EG layers are present mostly in the most heterogeneous structure.

338   Finally, 2EG layers in populations A and B probably have a similar layer charge, which is

339 close to that determined for the whole sample [~0.67 and ~1.07 per $O_{20}(OH)_4$, respectively for

340 SbId-1 and SbCa-1] because of the high proportion of 2EG layers in EG-solvated samples.

341 The near complete swelling of layers following EG solvation is observed for

342 montmorillonite and for population A of beidellite. In contrast, for beidellite increasing layer

343 charge from the mean layer charge may produce vermiculite-like layers, discrete illite layers

344 or irreversibly collapsed K-beidellite layers when potassium is present as assumed for SbId-1

345 (Post et al. 1997). However, heterogeneous structures where layers have different

346 hydration/swelling abilities is not *a priori* characteristic of smectite with layer charge

347 originating in the tetrahedra, although such interstratified structures probably occur more

348 frequently in beidellite compared to montmorillonite. Further study is required to assess the

349 systematic (?) presence of highly heterogeneous structures in natural beidellite.

350

351 **Influence of layer charge and charge location on hydration of 2:1 phyllosilicates**

352 The influence of layer charge on smectite hydration (Fig. 7) was derived from the

353 relative proportions of layer types as a function of RH. For all samples, XRD patterns were

354 recorded from RH = 35 (ambient) to 80% RH in adsorption conditions and then at 20% and

355 0% RH in desorption conditions. Relative proportions of the different layer types were

356 considered for montmorillonite and beidellite along the adsorption (40%, 60% and 80% RH)

357 and desorption (35%, 20% and 0% RH) pathways. See Ferrage et al. (2005b) for data on Ca-

358 and Sr-saturated SWy-1 montmorillonite.

359 **Smectite**. 0W layer content is equal or slightly lower for Ca-SAz-1 compared to Ca-

360 SWy-1 and gradually decreases with increasing RH (Fig. 7a). In adsorption conditions, 2W

361 layers dominate the two samples, 1W layers being more abundant for Ca-SWy-1. At 20% RH

362 along the desorption pathway, Ca-SAz-1 is dominated by 2W layers (~75%) whereas Ca-

363 SWy-1 contains similar amounts of 2W and 1W layers. This difference indicates that the 2W-

364   to-1W transition occurs at lower RH values for Ca-SAz-1 compared to Ca-SWy-1. At 0% RH,

365   the two samples have similar contents of 2W and 1W layers, 0W layers being more abundant

366   in Ca-SAz-1.

367   The proportion of 0W layers is similar in Sr-SAz-1 and Sr-SWy-1 (Fig. 7b) except at

368   0% RH, where Sr-SAz-1 is dominated by 1W layers and Sr-SWy-1 is mostly dehydrated. At

369   20% RH, Sr-SWy-1 and Sr-SAz-1 are dominated by 1W layers, with a greater number of 0W

370   and 2W layers in the latter. At 35% RH, 2W layers prevail in Sr-SAz-1 and Sr-SWy-1 is

371   mostly monohydrated. These observations are similar to those made on Ca-saturated

372   specimens: 2W-to-1W and 1W-to-0W transitions are shifted towards lower RH values with

373   increasing layer charge. Along the adsorption pathway, the number of 2W layers in Sr-SAz-1

374   is similar (at 40 and 80% RH) or slightly lower (at 60% RH) compared to Sr-SWy-1, in

375   contrast to Ca-saturated samples.

376   Proportions of layer types are plotted in Figures 7c, 7d as a function of RH for

377   beidellite. Figure 7c describes the overall behavior of the two populations of particles, and the

378   behavior of population A is given in Figure 7d. Note that for population A, the layer charge is

379   likely homogeneous and close to that of the entire sample. Along the adsorption pathway and

380   at 20% RH, hydration of Sr-SbCa-1 and Sr-SbId-1 is similar for the entire sample and for

381   population A crystallites (Figs. 7c, 7d). At 35% RH, Sr-SbCa-1 contains more 2W layers than

382   Sr-SbId-1 indicating that a greater layer charge shifts the 2W-to-1W transition to lower RH

383   values, similar to montmorillonite. At 0% RH, the different composition of the two samples

384   produces a shift of the 1W-to-0W transition to lower RH values with increasing layer charge.

385   Hydration of montmorillonite and beidellite is compared in Figures 7e, 7f for a given

386   layer charge [~0.7 per $O_{20}(OH)_4$ for SWy-1 and SbId-1, and ~1.1 per $O_{20}(OH)_4$ for SAz-1 and

387   SbCa-1]. Hydration of SbCa-1 and SbId-1 may be estimated from their population A. For a

388   similar layer charge, hydration is greater for beidellite than for montmorillonite over 0-80%

389   RH. Additional studies on beidellite with a more homogenous layer charge distribution are

390   required to confirm this observation.

391   **Expandable 2:1 phyllosilicates**. In summary, it appears that a greater layer charge

392   increases the stability of 1W and 2W layers towards lower RH values, at least upon H_2O

393   desorption, for montmorillonite and beidellite. This trend probably occurs owing to the

394   greater number of interlayer cations when increasing layer charge. Whatever the size and

395   location of layer charge, smectite interlayer thickness and the number of interlayer H_2O

396   molecules are about constant for a given interlayer cation and RH value (see below). As the

397   number of interlayer H_2O molecules is systematically higher than necessary to provide

398   octahedral coordination to interlayer cations, the hydration sphere of a given cation is constant

399   for smectite. The amount of H_2O molecules coordinating interlayer cations thus increases at

400   the expense of H_2O molecules not directly bound to these cations when layer charge

401   increases. As the 2W-to-1W transition occurs as interlayer H_2O molecules not coordinated to

402   interlayer cations are still present in 2W smectite (Ferrage et al. 2007) the higher density of

403   hydrated interlayer cations is likely responsible for the observed increased stability of most

404   hydrated layers towards lower RH values when layer charge is increased.

405   Although consistent with the molecular simulations performed by Smith et al.(2004),

406   this increased stability may appear as contradicting the conventional wisdom that high-charge

407   layers are less hydrated than low-charge layers (Laird 1999). The inverse relationship between

408   hydration (as measured from layer basal distance) and layer charge is the foundation to

409   differentiate smectite from vermiculite (Brindley 1980; Calle and Suquet 1988; Suquet and

410   Pezerat 1988). In addition, trioctahedral vermiculite basal distance decreases with increasing

411   layer charge (Calle and Suquet 1988; Suquet and Pezerat 1988), and the stability of less

412   hydrated layers is increased towards higher RH values when layer charge is increased (Suquet

413   and Pezerat 1987). The present results can be reconciled with the hydration behaviors

414   attributed to smectite and vermiculite. In the present study, stability of hydrated smectite

415   layers increases with increasing layer charge and is thus maximum at the upper limit of

416   smectite layer charge [0.5-0.6 net charge per $O_{10}(OH)_2$]. This charge threshold is the lower

417   charge limit for vermiculite, whose hydration differs from that of smectite most likely because

418   of the prevalence of attractive forces between interlayer cations and the 2:1 layer above this

419   threshold. The total number of interlayer H_2O molecules is however slightly higher for

420   vermiculite (6.6-7.6 per $O_{20}(OH)_4$ – Le Renard and Mamy 1971; Calle et al. 1977; Slade et al.

421   1985) than for smectite (5.0-7.0 per $O_{20}(OH)_4$ – This study and Laird 1999; Ferrage et al.

422   2005b). The reduced layer basal distance is thus not due to a reduced hydration of vermiculite

423   compared to smectite but more likely linked to the reorganization of H_2O molecules

424   coordinated to interlayer cations. Consistently, increasing the layer charge favors ordering in

425   the interlayer cation distribution (Drits 1987), and the layer-charge boundary between

426   smectite and vermiculite may correspond to the onset of this ordering. This boundary may

427   also coincide with the formation of a two-dimensional network of H_2O molecules in the

428   interlayer above a certain density of H_2O molecules bound to interlayer cations. This

429   hypothesis is supported by the reduced breadth of the H_2O molecule distributions determined

430   for saponite when layer charge is increased (Ferrage et al. 2005a).

431   In addition, the contrast of layer basal distance observed between dioctahedral

432   smectite (this study) and trioctahedral vermiculite (Suquet and Pezerat 1987; Calle and Suquet

433   1988; Suquet and Pezerat 1988) is possibly enhanced by the ordered distribution of

434   isomorphic substitutions in vermiculite, which probably favors interlayer species ordering.

435   Trioctahedral vermiculites are indeed isostructural to trioctahedral micas from which they

436   differ essentially by the hydrophilic character of their interlayer cations. Layer stacking,

437   which is commonly ordered for trioctahedral vermiculite in contrast to dioctahedral smectite,

438   and more especially to montmorillonite, can also favor ordering of interlayer species and thus

439   enhance the observed contrast of layer basal distance. The influence of charge location

440   (tetrahedral vs. octahedral) is probably minor, at least for dioctahedral smectite, because

441   montmorillonite and beidellite display an equal hydration behavior as a function of layer

442   charge (Fig. 7). Finally, note that 3W layer appears not to follow the same trend, in that their

443   stability is more restricted when layer charge of dioctahedral smectite is increased (Laird et al.

444   1995). However, in this study layer-charge increase may be influenced by the relative

445   proportion of tetrahedral substitutions.

446   **Interlayer thickness (IT)**. The ratio of IT to cation radius is plotted in Figure 8 as a

447   function of RH. Similar values were obtained for all samples, in agreement with Sato et al.

448   (1992) who reported similar d(001)-values for hydrated smectite regardless of the size and

449   location of layer charge. This observation is consistent with the similar H_2O content

450   determined at a given RH for each sample (Table 2) but is counter to the frequently assumed

451   decrease of layer thickness with increasing layer charge (Laird 1996).

452   For Ca-saturated samples, the greater number of 2W layers and the associated

453   increase of H_2O content in SAz-1 compared to SWy-1 (Figs. 7a, 7b) is consistent with the

454   water-adsorption isotherms reported by Chiou and Rutherford (1997) for the same samples.

455   By comparing the water-adsorption isotherms for SAz-1 and SWy-1, these authors showed

456   that the interlayer H_2O uptake increases with the layer charge. Laird (1999) criticized these

457   results as counter to the frequently accepted decrease of hydration ability with an increase in

458   smectite layer charge. However, Laird (1999) reported similar d(001) values for smectites

459   with different charges and attributed the increased number of adsorbed H_2O to the adsorption

460   on clay external surfaces. The results in the present article account only for interlayer H_2O

461   and support the conclusions of Chiou and Rutherford (1997), in agreement with Michot et al.

462   (2005). The water-vapor adsorption isotherms obtained by the latter authors on synthetic

463   saponite showed an increased number of adsorbed H_2O molecules with increasing layer

464   charge over the entire RH range.

465

466   **Dehydrated layer thickness**

467

468   Except for Sr-SbId-1 at 0% RH, the thickness of 0W layers was equal to 10.0 Å for

469   Ca- and Sr-SAz-1 and for Sr-saturated beidellite (Table 2). Similar results were obtained for

470   SWy-1 when saturated with Mg^{2+}, Ca^{2+} and Sr^{2+}, whereas the thickness of 0W layers was

471   lower for samples saturated with monovalent cations at 9.6 Å, 9.6 Å and 10.0 Å for Na^+, Li^+

472   and K^+, respectively (Ferrage et al. 2005b). The latter values are consistent with those

473   expected for dehydrated specimens. Because of the smaller radii of divalent cations, layer

474   thickness values of ~10.0 Å appear high. Ferrage et al. (2005b) observed an increase of σ_z in

475   samples dominated by 2W layers compared to those dominated by 1W layers. This increase

476   was attributed to the greater interlayer thickness, and thus to the weaker electrostatic

477   interactions between the 2:1 layer and interlayer cations in 2W layers. Similar results were

478   obtained for SAz-1 and beidellite samples (Table 2). However, σ_z does not decrease further in

479   0W layers, except for Na-SWy-1 at 0% RH (Ferrage et al. 2005b), probably because of

480   residual H_2O in the "dehydrated" layers. Monovalent interlayer cations ensures a local

481   compensation of under-saturated basal oxygen atoms, whereas charge compensation is more

482   diffuse with long-distance interactions, possibly through H-bonds, for divalent cations. The

483   latter configuration would probably favor the presence of H_2O molecules linked with under-

484   saturated oxygen atoms via H-bonds. The presence of additional H_2O molecules is favored

485   also by the higher ionic potential (valency/ionic radius) of divalent cations. The coulombic

486   radius of a H_2O molecule (r = 1.4-1.5 Å – Williams et al. 1994; Li and Nussinov 1998) is

487   similar to that of a K^+ cation (r = 1.38 Å – Shannon 1976), and their presence may account for

488   the 10.0 Å layer thickness determined here and by Ferrage et al. (2005b) for 0W layers in

489   samples saturated with divalent cations. Residual H_2O molecules would produce an increased

490   σ_z, as observed, because of the different radii of H_2O molecules and interlayer cations. Local

491   charge compensation by monovalent interlayer cations reduces the number of interlayer H_2O

492   molecules, as observed for K- and Na-saturated SWy-1 montmorillonites (Ferrage et al.

493   2005b). For these two samples, the thickness of 0W layers is similar to that expected for

494   totally dehydrated layers at 9.6 Å and 10.0 Å for Na- and K-saturated SWy-1 at 0% RH,

495   respectively (Ferrage et al. 2005b). For Li-saturated SWy-1 montmorillonite, the layer

496   thickness is higher than expected and σ_z is higher at 0% compared to other RH conditions,

497   possibly from the presence of residual H_2O molecules in 0W layers, in agreement with the

498   high affinity of Li^+ for H_2O.

499

500   **Limitations for qualitative indicators of smectite hydration heterogeneity**

501

502   For SWy-1, Ferrage et al. (2005b) related smectite-hydration heterogeneity to the

503   qualitative ξ parameter describing the irrationality of 00l reflection positions. Values of ξ

504   were < 0.4 Å when a specific layer type accounted for > 70% of the layer content. However,

505   this relation is mostly due to the specific distribution of the different layer types in SWy-1.

506   The different layer types are indeed randomly distributed in SWy-1, with possibly a slight

507   tendency to segregation. In this case, diffraction features follow Méring's principle (Méring

508   1949) and an increased heterogeneity broadens the 001 reflection and increases the positional

509   irrationality of 00l reflections.

510   The relative proportion of the prevailing layer type is plotted in Figure 9 as a

511   function of ξ for SAz-1, SbId-1 and Sr-SbCa-1. For beidellite, results are given after

512   subtraction of the kaolinite contribution and normalization of the smectite layer abundances to

513   100%. As reported by Ferrage et al. (2005b), for most samples, ξ is > 0.4 Å when the

514   dominant layer type accounts for ~70% or less of the layer content. However, note the

515   "outliers" in Figure 9. For instance, Sr-SbId-1 and Sr-SbCa-1 at 40% RH do not follow the

516   trend and most beidellites have low ξ values relative to their hydration heterogeneity (Figs.

517   2c, 2d, 9). Furthermore, Sr-SbCa-1 at 35% and 40% RH have similar contents of the

518   dominant layer type of 55-59% of 2W layers (Fig. 9) but different ξ of 1.54 Å and 0.05 Å at

519   35% and 40% RH, respectively (Table 1). Similarly, Sr-SAz-1 contains 66 % of 1W layers at

520   20% RH and 69% of 2W layers at 35% RH but has different ξ values of 1.20 Å and 0.12 Å,

521   respectively (Table 1).

522   These discrepancies are related to the inability of qualitative parameters, such as ξ, to

523   describe hydration heterogeneity in complex systems. The ξ parameter depends not only on

524   the proportion of layer types but also on their distribution within crystallites. Similarly, the

525   FWHM of the 001 reflection is influenced by CSD size and hydration heterogeneity. Some

526   discrepancies observed for beidellite are explained from the experimental XRD patterns (Figs.

527   1c, 1d). At 40% RH, the 001 reflection of Sr-SbId-1 and Sr-SbCa-1 exhibits a sharp

528   maximum and a pronounced high-angle shoulder. This shoulder corresponds to a

529   heterogeneous structure with a small CSD size (Figs. 2c, 2d), which does not contribute much

530   intensity to the XRD pattern. In contrast, the essentially 2W structure contributes more to the

531   001 reflection (position and shape) and most of the diffraction features, including ξ. Similarly,

532   the FWHM of the 001 reflection is not influenced by the high-angle shoulders, although they

533   stem from hydration heterogeneity (Figs. 1c, 1d, 2c, 2d).

534   The high value of ξ for Sr-SbCa-1 at 35% RH results mainly from the reflection at

535   ~6.1 Å, which results from an interstratified structure dominated by 1W layers in a sample

536   dominated by 2W layers. However, this structure accounts for 8% of the clay fraction and

537   does not modify significantly the proportion of the different layer types compared to the same

538   sample at 40% RH. The inability of the qualitative parameters, such as ξ, to provide a realistic

539   description of the beidellite hydration is a result of the segregation of the different layer types,

540   leading to the numerous structures involved in the models and their compositions.

541   Finally, Sr-SAz-1 recorded at 20% and 35% RH have nearly equal contents of 1W

542   and 2W layers, respectively, but different ξ values. For each sample, structure models consist

543   of a main interstratified structure, dominated by 1W layers at 20% RH and 2W layers at 35%

544   RH, whereas a minor, more heterogeneous structure contains 1W and 2W layers in nearly

545   equal proportions. The different values of ξ obtained for these two samples (Fig. 9) result

546   from the different structure factors for 1W and 2W layers. The structure factor is larger for

547   2W layers than for 1W layers over the low-angle region, and if they exist equally in an

548   interstratified structure, then related reflections are near the position expected for a periodic

549   2W smectite (e.g., peak at ~5.1 Å for Sr-SAz-1 at 20% RH, see Fig. 1b). The coexistence of a

550   1W/2W interstratified structure with a near periodic 2W smectite does not produce significant

551   peak shift or broadening, and low value of ξ is determined at 35% RH. In contrast, the

552   coexistence of a 1W/2W interstratified structure with a near periodic 1W structure produces a

553   greater ξ value, as measured at 20% RH.

554   The above discussion outlines the limitations of qualitative parameters to describe

555   hydration heterogeneity. These criteria are relevant only when layer types are randomly

556   distributed (Ferrage et al. 2005b). Relevance of the qualitative parameters may be enhanced

557   by careful analysis of position, intensity and profile of basal reflections over the entire 2-

558   50°2θ CuKα angular range. However, quantitative analysis of smectite hydration as obtained

559   from XRD pattern modeling is preferred if the distribution of layer types is to be determined.

560

572   **REFERENCES**

573

574   Beaufort, D., Berger, G., Lacharpagne, J.-C., and Meunier, A. (2001) An experimental

575   alteration of montmorillonite to a di + trioctahedral smectite assemblage at 100 and

576   200°C. Clay Minerals, 36, 211-225.

577   Bradley, W.F., Grim, R.E., and Clark, G.F. (1937) A study of the behavior of montmorillonite

578   upon wetting. Zeitschrift Kristallographie, 97, 216-222.

579   Brindley, G.W. (1980) Order-disorder in clay mineral structures. In G.W. Brindley, and G.

580   Brown, Eds., Crystal Structures of Clay Minerals and their X-ray Identification, p.

581   125-195. Mineralogical Society, London.

582   Burst, J.F. (1969) Diagenesis of Gulf Coast clayey sediments and its possible relation to

583   petroleum migration. American Association of Petroleum Geologists Bulletin, 53, 73-

584   93.

585   Calle, C. de la, Pezerat, H., and Gasperin, M. (1977) Poblèmes d'ordre-désordre dans les

586   vermiculites - Structure du minéral calcique hydraté à deux couches. Journal de

587   physique, 38, C7 128-133.

588   Calle, C. de la and Suquet, H. (1988) Vermiculite. In S.W. Bailey, Ed., Hydrous

589   phyllosilicates (exclusive of micas), 19, p. 455-496. Mineralogical Society of

590   America, Chantilly, Va.

591   Chiou, C.T. and Rutherford, W. (1997) Effects of exchanged cation and layer charge on the

592   sorption of water and egme vapors on montmorillonite clays. Clays & Clay Minerals,

593   45, 867-880.

594   Chipera, S.J. and Bish, D.L. (2001) Baseline studies of the clay minerals society source clays:

595   Powder X-ray diffraction analyses. Clays & Clay Minerals, 49, 398-409.

596   Drits, V.A. (1987) Electron diffraction and high-resolution electron microscopy of mineral

597   structures, 304 p. Springer Verlag, Berlin Heidelberg.

598   Drits, V.A., Lindgreen, H., Sakharov, B.A., and Salyn, A.S. (1997) Sequential structure

599   transformation of illite-smectite-vermiculite during diagenesis of Upper Jurassic

600   shales, North Sea. Clay Minerals, 33, 351-371.

601   Drits, V.A. and Sakharov, B.A. (1976) X-Ray structure analysis of mixed-layer minerals, 256

602   p. Dokl. Akad. Nauk SSSR, Moscow.

603   Drits, V.A. and Tchoubar, C. (1990) X-ray diffraction by disordered lamellar structures:

604   Theory and applications to microdivided silicates and carbons, 371 p. Springer-

605   Verlag, Berlin.

606   Ferrage, E., Kirk, C.A., Cressey, G., and Cuadros, J. (2007) Dehydration of Ca-

607   montmorillonite at the crystal scale. Part 1. Structure evolution. American

608   Mineralogist, in press.

609   Ferrage, E., Lanson, B., Malikova, N., Plançon, A., Sakharov, B.A., and Drits, V.A. (2005a)

610   New insights on the distribution of interlayer water in bi-hydrated smectite from X-ray

611   diffraction profile modeling of 00l reflections. Chemistry of Materials, 17, 3499-3512.

612   Ferrage, E., Lanson, B., Sakharov, B.A., and Drits, V.A. (2005b) Investigation of smectite

613   hydration properties by modeling of X-ray diffraction profiles. Part 1. Montmorillonite

614   hydration properties. American Mineralogist, 90, 1358-1374.

615   Hower, J., Eslinger, E.V., Hower, M.E., and Perry, E.A. (1976) Mechanism of burial

616   metamorphism of argillaceous sediments: 1. Mineralogical and chemical evidence.

617   Geological Society of America Bulletin, 87, 725-737.

618   Hower, J. and Mowatt, T.C. (1966) The mineralogy of illites and mixed-layer

619   illite/montmorillonites. American Mineralogist, 51, 825-854.

620 Jaynes, W.F. and Bigham, J.M. (1987) Charge reduction, octahedral charge, and lithium

621   retention in heated, Li-saturated smectites. Clays & Clay Minerals, 35, 440-448.

622 Kittrick, J.A. (1969a) Interlayer forces in montmorillonite and vermiculite. Soil Science

623   Society of America Journal, 33, 217-222.

624 ———. (1969b) Quantitative evaluation of the strong-force model for expansion and

625   contraction of vermiculite. Soil Science Society of America Journal, 33, 222-225.

626 Laird, D.A. (1996) Model for crystalline swelling of 2:1 phyllosilicates. Clays & Clay

627   Minerals, 44, 553-559.

628 ———. (1999) Layer charge influences on the hydration of expandable 2:1 phyllosilicates.

629   Clays & Clay Minerals, 47, 630-636.

630 Laird, D.A., Shang, C., and Thompson, M.L. (1995) Hysteresis in crystalline swelling of

631   smectites. Journal of Colloid and Interface Science, 171, 240-245.

632 Le Renard, J. and Mamy, J. (1971) Etude de la structure des phases hydratées des phlogopites

633   altérées par des projections de fourier monodimensionnelles. Bulletin du Groupe

634   Français des Argiles, 23, 119-127.

635 Li, A.-J. and Nussinov, R. (1998) A set of van der Waals and Coulombic radii of protein

636   atoms for molecular and solvent-accessible surface calculation, packing evaluation,

637   and docking. Proteins: Structure, function, and genetics, 32, 111-127.

638 Méring, J. (1949) L'interférence des rayons-X dans les systèmes à stratification désordonnée.

639   Acta Crystallographica, 2, 371-377.

640 Méring, J. and Glaeser, R. (1954) Sur le rôle de la valence des cations échangeables dans la

641   montmorillonite. Bulletin de la Société Francaise de Minéralogie et Cristallographie,

642   77, 519-530.

643   Michot, L.J., Bihannic, I., Pelletier, M., Rinnert, E., and Robert, J.L. (2005) Hydration and

644   swelling of synthetic Na-saponites: influence of layer charge. American Mineralogist,

645   90, 166-172.

646   Mooney, R.W., Keenan, A.G., and Wood, L.A. (1952) Adsorption of water by

647   montmorillonite. II. Effect of exchangeable ions and lattice swelling as measured by

648   X-ray diffraction. Journal of American Chemical Society, 74, 1371-1374.

649   Nagelschmidt, G. (1936) On the lattice shrinkage and structure of montmorillonite. Zeitschrift

650   Kristallographie, 93, 481-487.

651   Norrish, K. (1954) The swelling of montmorillonite. Discussions of the Faraday society, 18,

652   120-133.

653   Perry, E.A. and Hower, J. (1972) Late-stage dehydration in deeply buried pelitic sediments.

654   American Association of Petroleum Geologists Bulletin, 56, 2013-2021.

655   Post, J.L., Cupp, B.L., and Madsen, F.T. (1997) Beidellite and associated clays from the

656   DeLamar mine and Florida Mountain area, Idaho. Clays & Clay Minerals, 45, 240-

657   250.

658   Sakharov, B.A. and Drits, V.A. (1973) Mixed-layer kaolinte-montmorillonite: a comparison

659   observed and calculated diffraction patterns. Clays & Clay Minerals, 21, 15-17.

660   Sakharov, B.A., Lindgreen, H., Salyn, A., and Drits, V.A. (1999) Determination of illite-

661   smectite structures using multispecimen X-Ray diffraction profile fitting. Clays &

662   Clay Minerals, 47, 555-566.

663   Sato, T., Murakami, T., and Watanabe, T. (1996) Change in layer charge of smectites and

664   smectite layers in illite/smectite during diagenetic alteration. Clays & Clay Minerals,

665   44, 460-469.

666   Sato, T., Watanabe, T., and Otsuka, R. (1992) Effects of layer charge, charge location, and

667   energy change on expansion properties of dioctahedral smectites. Clays & Clay

668   Minerals, 40, 103-113.

669   Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic

670   distances in halides and chalcogenides. Acta Crystallographica, A 32, 751-767.

671   Shutov, V.D., Drits, V.A., and Sakharov, B.A. (1969) On the mechanism of a

672   postsedimentary transformation of montmorillonite into hydromica. In L. Heller, Ed.

673   International Clay Conference, 1, p. 523-531. Israel University Press, Jerusalem,

674   Tokyo, Japan.

675   Slade, P.G., Stone, P.A., and Radoslovitch, E.W. (1985) Interlayer structures of the two-layer

676   hydrates of Na- and Ca-vermiculites. Clays & Clay Minerals, 33, 51-61.

677   Smith, D.E., Wang, Y., and Whitley, H.D. (2004) Molecular simulations of hydration and

678   swelling in clay minerals. Fluid Phase Equilibria, 222-223, 189-194.

679   Suquet, H. and Pezerat, H. (1987) Parameters influencing layer stacking types in saponite and

680   vermiculite: A review. Clays & Clay Minerals, 35, 353-362.

681   ——. (1988) Comments on the classification of trioctahedral 2:1 phyllosilicates. Clays and

682   Clay Minerals, 36, 184-186.

683   Van Olphen, H. (1965) Thermodynamics of interlayer adsorption of water in clays. Journal of

684   Colloid Science, 20, 822-837.

685   Walker, G.F. (1956) The mechanism of dehydration of Mg-vermiculite. Clays & Clay

686   Minerals, 4, 101-115.

687   Watanabe, T. and Sato, T. (1988) Expansion characteristics of montmorillonite and saponite

688   under various relative humidity conditions. Clay Science, 7, 129-138.

689   Weaver, C.E. (1960) Possible uses of clay minerals in search for oil. American Association of

690   Petroleum Geologists Bulletin, 44, 1505-1518.

691   Williams, M.A., Goodfellow, J.M., and Thornnton, J.M. (1994) Buried water and internal

692   cavities in monomeric proteins. Protein Science, 3, 1224-1235.

FIGURE CAPTIONS

694

695   **Figure 1.** Comparison between experimental and calculated XRD patterns as a function of

696   RH. Experimental and calculated optimal XRD patterns are shown as crosses and as

697   solid lines, respectively. **a**) Ca-SAz-1. **b**) Sr-SAz-1. **c**) Sr-SbId-1. **d**) Sr-SbCa-1. For

698   all samples, the gray bar indicates a modified scale factor for the high-angle region.

699

700   **Figure 2.** Structure models obtained from XRD profiles modeling as a function of RH.

701   Relative proportions, expressed in wt%, of the interstratified contributions are plotted

702   on the y-axis whereas their compositions (relative proportions of the different layer

703   types) are plotted on the x-axis. Light gray, dark gray and solid bars represent 0W,

704   1W, and 2W layers, respectively. Open bars with a dashed outline represent a

705   kaolinite contribution.

706

707   **Figure 3.** Illustration of the contributions to the calculated profiles for Sr-SbId-1 at 80% RH.

708   Intensities in the high-angle region (10-50°2θ) are scaled by ×10 compared to the

709   low-angle region (4-10°2θ). Maxima corresponding to kaolinite-group minerals are

710   labeled Kaol.

711

712   **Figure 4.** Comparison between calculated and experimental XRD patterns obtained after

713   ethylene-glycol solvation of the samples. Experimental and calculated optimal XRD

714   patterns are shown as crosses and as solid lines, respectively. For all samples, the

715   gray bar indicates a modified scale factor for the high-angle region.

716

717   **Figure 5.** Contribution of an ordered R1-MPDO (see text for details) interstratified structure

718   to the XRD pattern of Sr-SbId-1 recorded at 80% RH. **a**) Experimental and

719   calculated pattern as in Figure 1c. XRD profile corresponding to the R1-MPDO

720   structure is shown as open circles. **b**) Optimal fit to the experimental data including

721   the contribution of a R1-MPDO structure to the diffracted intensity (see text for

722   details). The gray bar indicates a modified scale factor for the high-angle region.

723

724   **Figure 6.** Evolution of relative abundance of the layer types as function of RH for each

725   population of particles, including all interstratified structures contributing to that

726   population, considered for beidellites. **a**) Sr-SbId-1. **b**) Sr-SbCa-1. Triangles,

727   diamonds, and squares represent 0W, 1W and 2W layers.

728

729   **Figure 7.** Evolution of relative abundance of layer types as a function of RH. **a**) Ca-SAz-1

730   and Ca-SWy-1. **b**) Sr-SAz-1 and Sr-SWy-1. **c**) Sr-SbId-1 and Sr-SbCa-1. **d**)

731   Population A of Sr-SbId-1 and Sr-SbCa-1. **e**) Sr-SAz-1 and population A of Sr-

732   SbCa-1. **f**) Sr-SWy-1 and population A of Sr-SbId-1. Triangles, diamonds, and

733   squares represent 0W, 1W and 2W layers. Data for Ca- and Sr-SWy-1 are those

734   reported by Ferrage et al. (2005b). XRD data collection was perfomed in adsorption

735   conditions at 40, 60, and 80% RH, and in desorption conditions at 0, 20, 35% RH.

736

737   **Figure 8.** Evolution of layer thickness of hydrated layers as a function of RH for all samples

738   including SWy-1 (Ferrage et al. 2005b). Interlayer thickness (IT) is represented by

739   the ratio IT:ionic radius. IT is calculated as the basal distance d(001) minus the

740   thickness of the 2:1 layer (6.54 Å). Linear regression lines are plotted for each cation

741   and include all samples saturated with this cation.

742

743   **Figure 9.** Relative proportion of the major layer type derived from XRD profile modeling as a

744   function of departure from rationality parameter ξ. Values of these two parameters

745   (70% and 0.4 Å, respectively) limiting the "homogeneous" hydration are shown as

746   dotted lines. Open symbols indicate samples with ξ parameters > 0.4 Å.

747

Table 1: Basal-reflection qualitative parameters (position, width and rationality) as a function of relative humidity.

Sample	Ca-Saz-1			Sr-Saz-1		
	d(001)	FWHM	ξ/X_i	*d*(001)	FWHM	ξ/X_i
~0% (vacuum)	11.65	1.05	0.56/4	12.10	0.88	0.04/4
20%	14.88	0.90	0.13/4	13.15	1.66	1.20/4
~35% (room)	15.10	0.83	0.15/4	15.20	0.92	0.12/4
40%	15.28	0.79	0.12/4	15.33	0.86	0.10/4
60%	15.37	0.74	0.10/4	15.59	0.81	0.25/4
80%	15.62	0.77	0.19/4	15.87	0.80	0.26/4

Sample	Sr-SbId-1			Sr-SbCa-1		
	d(001)	FWHM	ξ/X_i	*d*(001)	FWHM	ξ/X_i
~0% (vacuum)	11.10	1.28	0.76/4	11.97	0.75	0.04/4
20%	12.34	0.65	0.04/4	12.36	0.80	0.04/4
~35% (room)	14.90	1.23	1.50/4	15.22	0.95	1.54/3
40%	15.29	0.68	0.06/3	15.29	0.87	0.05/3
60%	15.55	0.63	0.05/3	15.55	0.73	0.02/3
80%	15.73	0.61	0.08/3	15.74	0.72	0.11/3

Notes: Position [*d*(001)] and FWHM of the 001 reflection are given in Å and in °2θ Cu Kα, respectively. The ξ parameter which accounts for the departure from rationality of the 00*l* reflection series is calculated as the standard deviation of the $l \times d(00l)$ values (in Å) for the X_i measurable reflections over the 2-50°2θ Cu Kα angular range.

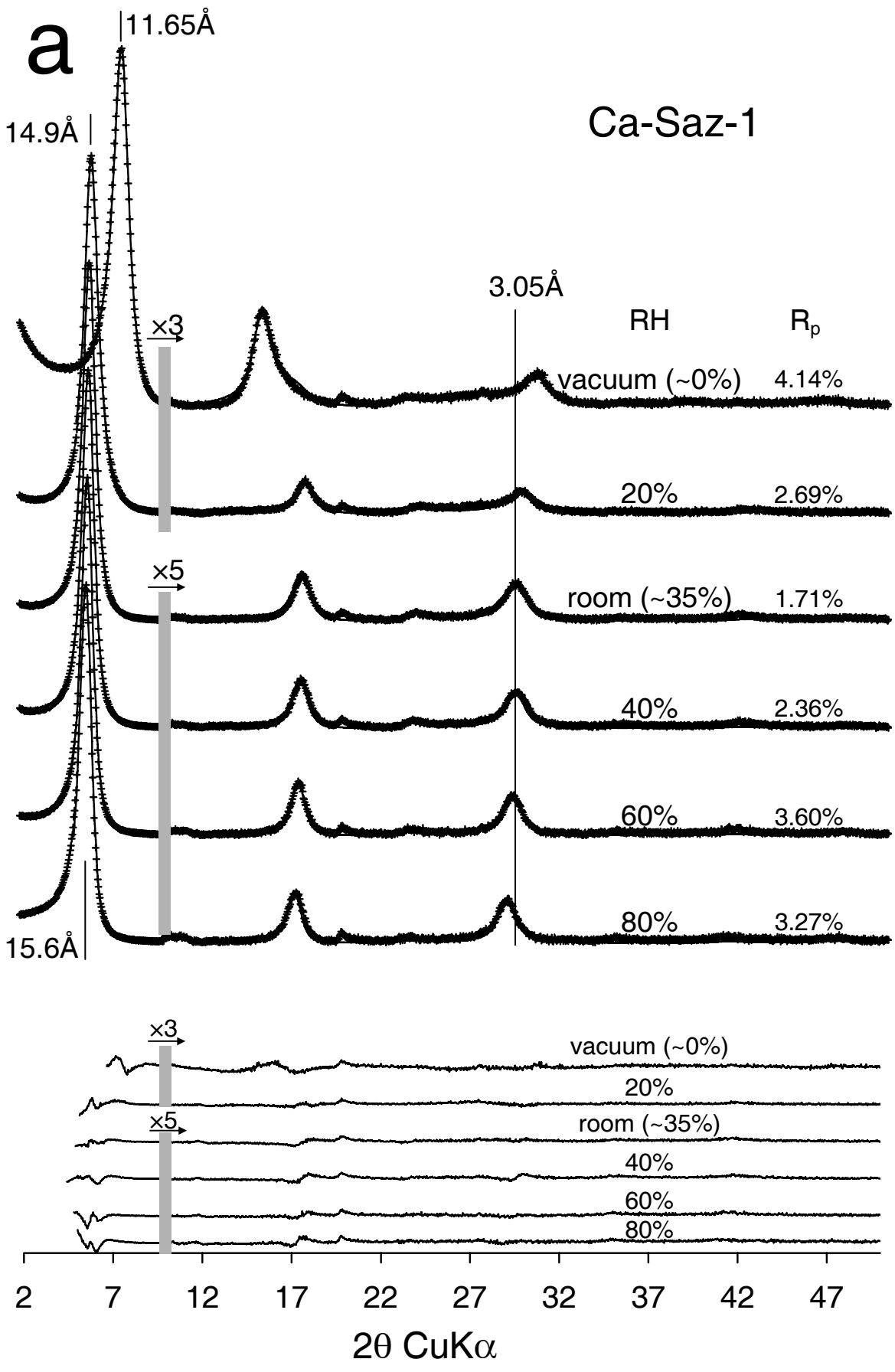**Table 2:** Optimum structural parameters used for the simulation of XRD profiles.

RH	0	20	room	40	60	80
Ca-SAz-1						
L. Tck. 2W	14.30	14.88	15.10	15.16	15.25	15.42
nH_2O	2*3.1	2*3.2	2*3.2	2*3.3	2*3.5	2*3.5
L. Tck. 1W	11.7	12.61	12.70	12.76	12.80	12.85
nH_2O	1.5	2.9	3.2	3.2	3.6	4.0
L. Tck. 0W	10.00	10.00	10.00	10.00	10.00	10.00
N	6.1	5.7	5.3	5.2	5.2	4.7
σ^*	5.0	6.7	7.5	7.5	7.5	7.5
σ_z	0.25	0.35	0.35	0.35	0.35	0.35
Sr-Saz-1						
L. Tck. 2W	-	15.10	15.26	15.30	15.50	15.65
nH_2O	-	2*3.0	2*3.0	2*3.0	2*3.1	2*3.5
L. Tck. 1W	12.03	12.30	12.32	12.32	12.40	12.75
nH_2O	0.3	2.7	3.0	3.0	4.2	4.5
L. Tck. 0W	10.00	10.00	10.00	10.00	10.00	10.00
N	6.3	6.0	5.8	5.8	5.5	4.8
σ^*	5.0	7.0	7.0	7.0	7.0	7.0
σ_z	0.20	0.30	0.40	0.40	0.40	0.40
Sr-SbId-1						
L. Tck. 2W		15.12	15.24	15.30	15.50	15.65
nH_2O	-	2*2.5	2*3.2	2*3.2	2*3.2	2*3.5
L. Tck. 1W	11.95	12.32	12.32	12.32	12.40	12.70
nH_2O	1.0	2.9	3.5	3.5	3.6	4.5
L. Tck. 0W	9.80	10.00	10.00	10.00	10.00	10.00
N	6.5(5.0)	9.0(4.0)	7.2(3.5)	7.2(3.5)	7.0(3.5)	6.5(3.5)
σ^*	8.0	7.0	7.0	7.0	7.0	7.0
σ_z	0.20	0.20	0.25	0.28	0.35	0.30
Sr-SbCa-1						
L. Tck. 2W	-	15.10	15.30	15.30	15.53	15.60
nH_2O	-	2*3.0	2*3.0	2*3.0	2*3.0	2*3.2
L. Tck. 1W	11.98	12.30	12.30	12.35	12.42	12.70
nH_2O	1.5	2.5	3.2	3.0	3.0	4.5
L. Tck. 0W	10.00	10.00	10.00	10.00	10.00	10.00
N	7.6(5.0)	6.5(4.0)	6.5(3.5)	6.5(3.5)	6.3(3.5)	5.7(3.5)
σ^*	4.8	5.2	5.7	5.7	5.7	5.5
σ_z	0.30	0.25	0.30	0.35	0.35	0.35

Notes: Layer thickness (L. Tck.) of 2W, 1W and 0W layers are given in Å. For hydrated layers, the number of interlayer H_2O molecules (nH_2O) is indicated per $O_{20}(OH)_4$. N is the mean number of layers in the coherent scattering domains, orientation parameter (σ^*) and layer thickness variability parameter (σ_z) are given in ° and in Å, respectively. N values in parentheses correspond to the second population of particles (see text for details).
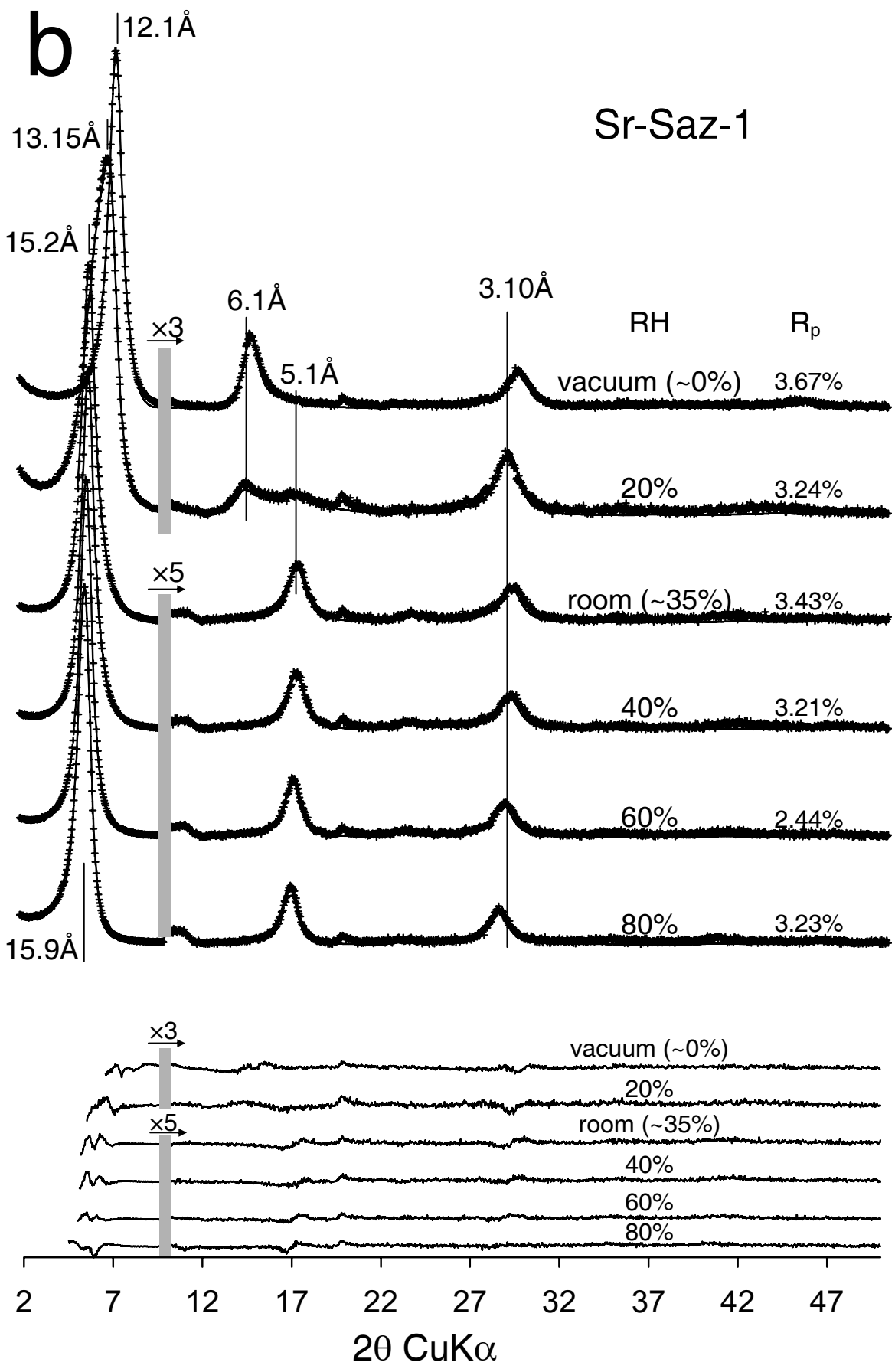
Table 3. Optimum structural parameters used for the simulation of XRD profiles obtained after EG solvation.

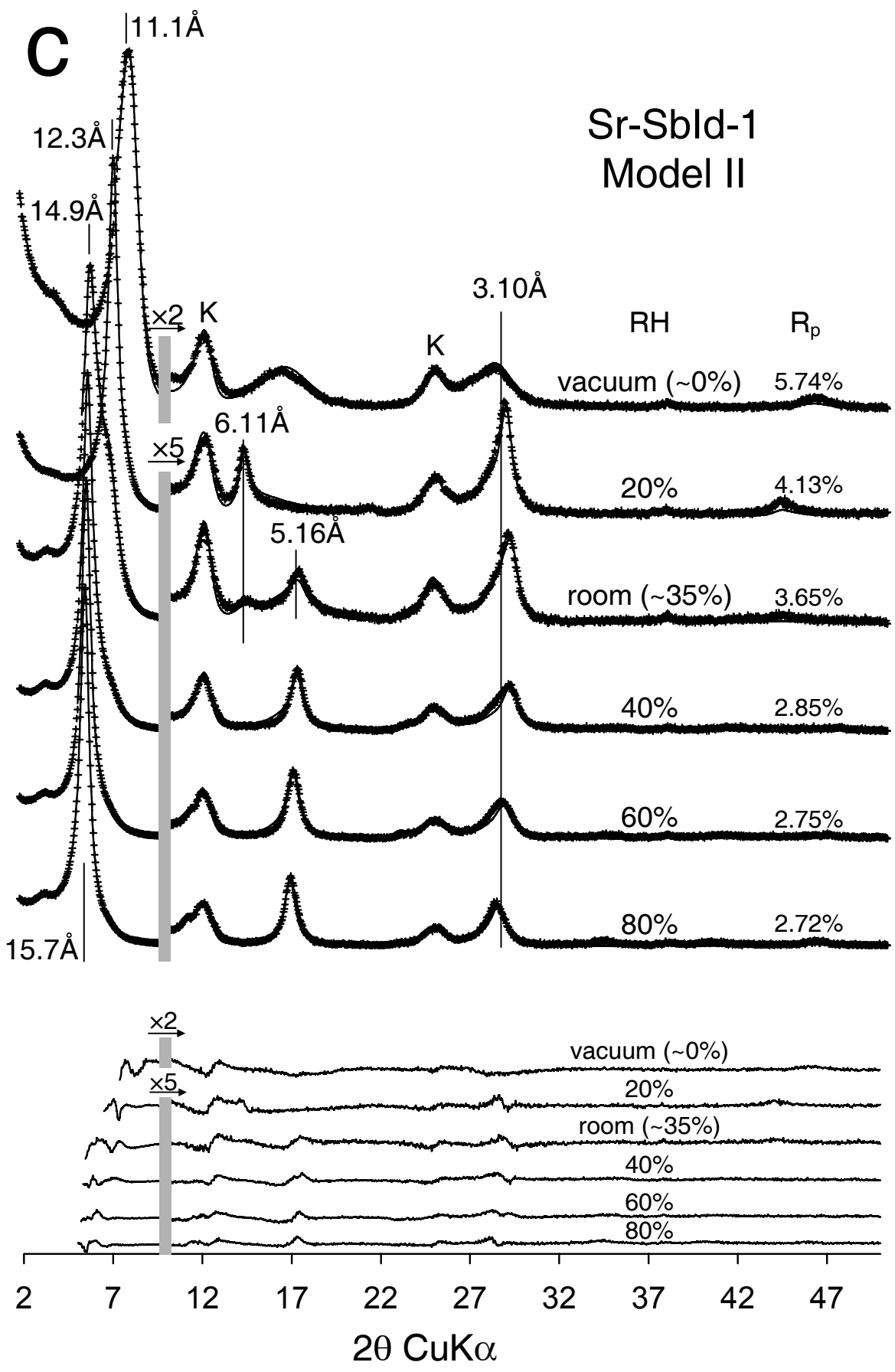| Sample	S cont. (%)	% 2EG	% 1EG	% 0EG	N	L. Tck. 2EG	L. Tck. 1EG	L. Tck. 0EG	σ^*	σ_z
Ca-SWy-1 EG	100	99	0	1	7.0	16.90	-	10.00	8.0	0.27
Ca-SAz-1 EG	100	98	0	2	5.5	16.75	-	10.00	9.0	0.30
Sr-Sbld-1 EG	46	98	0	2	7.2	16.88	12.90	10.00	5.0	0.35
	38	70	15	15	3.8					
Sr-SbCa-1 EG	49	100	0	0	6.8	16.88	12.90	10.00	7.0	0.35
	42	70	15	15	3.8					

Notes: Calculated XRD patterns include the contributions of one or two interstratified structures (S). Layer thickness (L. Tck.) of 2EG, 1EG, and 0EG layers are given in Å. N, σ^*, and σ_z as in Table 2. For beidellites the contribution of kaolinite-group minerals should be added to fit the experimental XRD pattern.

a

14.9Å |

|11.65Å

3.05Å

Ca-Saz-1

RH	R_p
×3	
vacuum (~0%)	4.14%
20%	2.69%
×5	
room (~35%)	1.71%
40%	2.36%
60%	3.60%
80%	3.27%

15.6Å |

×3
vacuum (~0%)
20%
×5
room (~35%)
40%
60%
80%

2   7   12   17   22   27   32   37   42   47

2θ CuKα

Ms#2273R2 Fig.01

b

12.1Å

13.15Å

15.2Å

6.1Å

3.10Å

×3

5.1Å

RH R_p

vacuum (~0%)   3.67%

20%   3.24%

×5

room (~35%)   3.43%

40%   3.21%

60%   2.44%

80%   3.23%

15.9Å

Sr-Saz-1

×3

vacuum (~0%)
20%
×5
room (~35%)
40%
60%
80%

2   7   12   17   22   27   32   37   42   47

2θ CuKα

Ms#2273R2 Fig. 01

C

11.1Å

12.3Å

14.9Å

Sr-SbId-1
Model II

3.10Å

×2 K

×5

6.11Å

5.16Å

15.7Å

	RH	R_p
	vacuum (~0%)	5.74%
	20%	4.13%
	room (~35%)	3.65%
	40%	2.85%
	60%	2.75%
	80%	2.72%

K

K

×2

×5

vacuum (~0%)

20%

room (~35%)

40%

60%

80%

2   7   12   17   22   27   32   37   42   47

2θ CuKα

Ms#2273R2 Fig. 01

d

12.0Å

12.4Å

15.2Å

15.7Å

×5

K

6.11Å

5.16Å

3.10Å

K

Sr-SbCa-1
Model II

RH	R_p
vacuum (~0%)	3.34%
20%	2.93%
room (~35%)	2.12%
40%	2.90%
60%	2.73%
80%	3.57%

×5

vacuum (~0%)
20%
room (~35%)
40%
60%
80%

2   7   12   17   22   27   32   37   42   47

2θ CuKα

Ms#2273R2 Fig. 01

a – Ca-SAz-1

59
41
48
52
73
27
82
18
76
24
96
4

b – Sr-SAz-1

70
30
57
43
61
39
62
38
73
27
93
7

c – Sr-SbId-1 Model II

40
44
16
N=5

42
42
16
N=4

12
12
19
42
15
N=3.5

25
17
42
16
N=3.5

41
43
16
N=3.5

44
40
16
N=3.5

d– Sr-SbCa-1 Model II

46
44
10
N=5

46
44
10
N=4

8
18
20
44
10
N=3.5

24
22
44
10
N=3.5

46
44
10
N=3.5

49
41
10
N=3.5

vacuum (~0%)   20%   room (~35%)   40%   60%   80%

□ 0W   ▨ 1W   ■ 2W   ⌐¬ Kaolinite

Ms#2273R2 Fig.02

2W

N=3.5
50% 2W
20% 1W
30% 0W

Sr-SbId-1
RH=80%
Model II

2θ CuKα

Ms#2273R2 Fig.03

×5

R_p

Ca-SWy-1   4.87%

Ca-SAz-1   4.35%

Sr-SbId-1   4.20%

Sr-SbCa-1   4.22%

×5

2   7   12   17   22   27   32   37   42   47

2θ CuKα

Ms#2273R2 Fig. 04

a

R1 MPDO
50% 2W
50% 0W

Kaol.

Kaol.

b

R1 MPDO
50% 2W
50% 0W

2W

N=3.5
50% 2W
20% 1W
30% 0W

Kaol.

Kaol.

2θ Cu Kα

Ms#2273R2 Fig.05

Ms#2273R2 Fig. 07

Ms#2273R2 Fig. 09