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**Intercalation of ethylene glycol in smectites:
Several molecular simulation models verified by X-ray diffraction data**

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KEY WORDS: Ethylene glycol, Smectite, Molecular dynamics, X-ray diffraction

ABSTRACT

Organo-clays represent a special challenge for molecular simulations, because they require accurate representation of the clay part and the organic/aqueous part of the model system and an accurate representation of their interactions. Due to a broad diversity of available force field models, it is an important question which sets of parameters will best suit the molecular modeling of the organo-intercalated smectites. To address this question, we use the structure of ethylene glycol (EG)-smectite complex as a testing model, because the intercalation of EG in smectites provides a stable interlayer complex with relatively constant basal spacing.

Three smectite samples with substantially different layer charge and charge localization were selected for X-ray diffraction (XRD) measurements. Their molecular models were built and molecular dynamics simulations were performed using various

26 combinations of the organic force fields (CGenFF, GAFF, CVFF and OPLS-aa) with ClayFF
27 and INTERFACE force fields used to describe smectites. The simulations covered a range of
28 different EG and water contents in the selected smectites. For every structure, the density
29 distribution of interlayer species along the direction perpendicular to the layer plane was
30 calculated and then used to optimize the X-ray diffraction patterns for these simulated models.

31 A comparison of these results with experimental XRD patterns shows very large
32 discrepancies in the obtained structures and basal spacings for different layer charges as well
33 as for different force fields and their combinations. The most important factor affecting the
34 accuracy of the calculated diffractograms is found to be the selection of the clay mineral force
35 field parameters. The second important conclusion is that a slight modification of the basal
36 oxygen parameters for non-electrostatic interactions (increase of their effective atomic
37 diameters) may be a simple and straightforward way to greatly improve the agreement of the
38 modeled diffractograms with experiments, especially for high-charge smectites. Generally,
39 among the organic force fields the least accurate results are obtained with CGenFF. For
40 unmodified ClayFF, its combination with GAFF gives the best results, while the two other
41 sets (OPLS-aa and CVFF) give the best results in combination with ClayFFmod. The
42 INTERFACE and INTERFACEmod force fields are found to be producing much better
43 results for low-charge montmorillonite than for high-charge smectites.

44

45

46 INTRODUCTION

47 Recent growing interest in organo-clay nanocomposites is clearly reflected in the
48 development of computational molecular modeling approaches to quantitative understanding
49 of the structural and dynamic behavior of such systems (e.g. Zeng *et al.*, 2003; Suter and
50 Coveney, 2009; Suter *et al.*, 2011, 2015; Greathouse *et al.*, 2014; Heinz and Ramezani-
51 Dakhel, 2016). Apart from the atomistic structural data necessary to construct the molecular
52 models, the most fundamental information required to perform such simulations is contained
53 in the sets of parameters describing interatomic interactions in the modeled systems, often
54 collectively called the *force fields*. The fact that in the literature there are currently several
55 widely used and well tested classical force fields available for molecular modeling of clays
56 and related inorganic materials (e.g. Heinz *et al.*, 2005) and even a larger number of various
57 force fields for molecular simulations of organic and bio-organic molecules (e.g. Guvench
58 and MacKerell, 2008), often leaves unanswered the important question of finding an optimal
59 combination of the force field parameters for accurate molecular modeling of both the organic
60 and inorganic parts of the composite systems. Indeed, estimating the actual predictive
61 capabilities of such simulations is a highly non-trivial task. In order to quantitatively address
62 this issue one needs a testing model which should be known to provide a stable interlayer
63 complex, and should be supported by sufficient amount of reliable experimental data for
64 comparisons with the simulated results. For these reasons, complexes of smectites with
65 ethylene glycol (EG)-water mixtures were selected for the present study.

66 Intercalation of EG in hydrated divalent ion-smectites is known to provide a structure
67 with relatively constant basal spacing (e.g. Mosser-Ruck *et al.*, 2005). During this process,
68 EG molecules penetrate into the interlayer spaces of the swelling clays, leading to the
69 formation of a two-layer structure ($d \sim 17 \text{ \AA}$). For the purpose of X-ray diffraction data
70 interpretation, a simplified model of this complex has been proposed by Reynolds (1965).

71 Further studies have shown that the basal spacing is larger for clay minerals with lower layer
72 charge, but it also depends on the localization of the charge, the type of the exchangeable
73 cations, the particle size and the relative humidity (Harward and Brindley, 1965; Brindley,
74 1966; Harward *et al.*, 1969; Środoń, 1980; Sato *et al.*, 1992). If the charge is located in the
75 tetrahedral sheet then the values of basal spacing are lower than those observed when the
76 charge is located in the octahedral sheet (Sato *et al.*, 1992). Later studies have shown that
77 smectites may form a one-layer EG complex instead of the two-layer complex at very low
78 relative humidities (Eberl *et al.*, 1987), or with K^+ as the exchange cation even at intermediate
79 humidities (Eberl *et al.*, 1986). The experimental observations were to some extent explained
80 with the help of molecular simulations, e.g. the preference of formation of bilayer structure
81 and the preferred number of water molecules in the structure for the Ca^{2+} form (Szczerba *et*
82 *al.*, 2014). Several methods of clay glycolation with specific technicalities are possible and
83 Mosser-Ruck *et al.* (2005) have demonstrated certain differences and inconsistencies between
84 them. The formation of monolayer or bilayer complexes was found to be dependent on the
85 type of the interlayer cation and the concentration of EG in the close vicinity around smectite
86 (the glycolation protocol). There is also a gradual loss of EG from the complex with smectite
87 because of the equilibration between the complex and the surrounding environment.
88 Therefore, X-ray measurements on such samples should be performed relatively quickly,
89 within a few hours after glycolation. The dynamics of EG intercalation into smectites was
90 studied by Svensson and Hansen (2010) using synchrotron X-ray diffraction techniques. This
91 study showed that EG molecules replace H_2O in the interlayer, however, still leaving
92 significant amounts of water in the structure.

93 The present study was undertaken in order to investigate the effects of different
94 combinations of force field parameters on the accuracy of two-EG layer structure

95 representation. For this purpose inorganic (clay) and organic (EG) force field parameters need
96 to be coupled in one simulation.

97 For clay minerals there exist several force field parameterizations that were used for
98 molecular simulations of these structures over the past three decades. These parameters can be
99 preliminarily divided into two groups: the ones that rely on the assumption of a rigid clay
100 framework and the ones allowing partial or full flexibility of the structure. Historically, the
101 parametrizations of the first kind were developed earlier (e.g. Skipper *et al.*, 1991; Smith,
102 1998). They are, however, inherently limited and can lead to incorrect representation of the
103 processes of adsorption, surface hydration, hydrogen bonding, diffusion rates etc. (e.g. Cygan
104 *et al.*, 2009). The flexible force field parameterizations are currently much wider represented
105 (e.g. Hill and Sauer, 1995; Teppen *et al.*, 1997; Sato *et al.*, 2001; Manevitch and Ruthledge,
106 2004, Cygan *et al.*, 2004; Heinz *et al.*, 2005). It was shown, however, that only the
107 parametrizations of Heinz *et al.* (2005) and ClayFF (Cygan *et al.*, 2004) give cleavage
108 energies that reasonably correspond to the experimental values (Heinz *et al.*, 2005).
109 Therefore, only these force fields were tested in this study. Additionally, Ferrage *et al.* (2011)
110 have shown that a better description of the hydrated interlayer structure with the ClayFF force
111 field can be achieved if the Lennard-Jones parameters of clay surface oxygens are increased
112 by ~7%.

113 The interatomic interaction parameters for EG can be selected from a wide range of
114 different organic force fields. Usually, these force fields are parameterized to optimize the
115 description of certain specific sets of organic molecules. For example, CHARMM was
116 constructed to model proteins (MacKerrel *et al.*, 1998), AMBER – to model peptides, proteins
117 and nucleic acids (Cornell *et al.*, 1995), OPLS-aa for simulations of liquid hydrocarbons
118 (Jorgensen *et al.*, 1996) and CVFF for amino acids, hydrocarbons, and many other organic
119 molecules (Dauber-Osguthorpe *et al.*, 1988). More recent parameterizations which belong to a

120 certain earlier family but were later re-optimized for a larger set of organic molecules include
121 CHARMM-related CGenFF (general force field for drug-like molecules; Vanommeslaeghe *et al.*,
122 2009) and AMBER-related GAFF (general AMBER force field; Wang *et al.*, 2004). For
123 the purpose of this study the parametrization of a given family that was best optimized for
124 small organic molecules, such as EG, was taken into account.

125 Even a more diverse set of force field parameterizations for water molecules are
126 available in the literature (e.g. Wallqvist and Mountain, 1999; Guillot, 2002; Kalinichev,
127 2001). In this study only the SPC (simple point charge) model of Berendsen *et al.* (1981) is
128 considered because it is known to perform well in combination with ClayFF, gives relatively
129 good solution structure for smectite interfaces and interlayers (e.g. Heinz *et al.*, 2005; Morrow
130 *et al.*, 2013; Ngouana-Wakou and Kalinichev, 2014; Greathouse *et al.*, 2015) and is also
131 consistent with the CVFF and INTERFACE parametrizations. Theoretically, the application of
132 different force field parametrizations for H₂O molecules can affect the simulation results for
133 hydrated clays. **The work of Ferrage *et al.* (2011) has shown, however, that using the SPC
134 model is sensible in terms of the agreement of MD simulation results with X-ray diffraction
135 data.**

136 Hybrid organo-clay materials is a rapidly growing area of molecular simulation studies
137 that requires a reliable coupling of different force field parameters. Very often ClayFF is used
138 together with CVFF (e.g. Kumar *et al.*, 2006; Liu *et al.*, 2007; Suter and Coveney, 2009;
139 Kalinichev *et al.*, 2010). There are also examples of successful use of ClayFF in combination
140 with OPLS-aa (e.g. Schampera *et al.*, 2015), CHARMM (e.g. Duque-Redondo *et al.*, 2014)
141 and AMBER (e.g. Wang *et al.*, 2014; Swadling *et al.*, 2010). INTERFACE force field (Heinz
142 *et al.*, 2013) is also recently developed to be used in the studies of interactions of organic
143 molecules with minerals, including smectite clays, together with CVFF, PCFF and
144 COMPASS organic parameterizations. There are also other examples of combinations of

145 older clay mineral force field parameters with different organic force fields: e.g. Tambach *et*
146 *al.* (2006) used force field of Skipper *et al.* (1995) together with OPLS-ua (Jorgensen *et al.*,
147 1986). Not all of these earlier force field combinations were extensively tested before they we
148 used in this area of very active current research.

149 At the same time, the structures obtained from molecular simulations using different
150 force field parameters can be validated by their comparison with available X-ray diffraction
151 data. This methodology has been widely used for hydrated clay minerals (e.g. Ferrage *et al.*,
152 2011). Even though only the atomic density distribution of the interlayer species along a
153 direction perpendicular to the layering plane can be considered for turbostratic smectites, it is
154 still a very powerful methodology. It was used in the present study for the purpose of finding
155 the optimal set of force field parameters for organic molecules interacting with smectites.

156

157 **METHODOLOGY**

158

159 *Smectite samples used in the study*

160 Three smectite samples from the collection of the Source Clays Repository of The Clay
161 Minerals Society were studied. They have crystal structures with notably different layer
162 charge and charge localization: low charge montmorillonite (SWy-1), high charge
163 montmorillonite (SAz-1), and high charge beidellite (SbCa-1). Some of their characteristics
164 are summarized in Table 1.

165

166 === Table 1 ===

167

168 The particle size fractions were separated to avoid contamination with phases other than
169 smectite. All samples were studied in Ca²⁺ form that was prepared via dialysis.

170 The samples were sedimented from aqueous solution on a glass slide. Then all slides
171 were glycolated with the following procedure: each air-dried sample from RH around 50%
172 was put into a closed plastic box (15×15×3 cm) that was placed in a vessel with EG solution
173 poured at the bottom. The sample within the box was heated at 60 °C for 10 h in an oven.

174

175 ***XRD patterns registration***

176 To minimize EG loss from the prepared EG-smectite complexes the XRD patterns for
177 all samples were measured directly after glycolation and in EG-saturated atmosphere. The X-
178 ray diffraction data were collected in the range from 2° to 60° 2 θ using a *Thermo ARL* XRD
179 system, CuK α radiation, and a Peltier-cooled solid-state detector. The tube current and voltage
180 were 45 mA and 35 kV, respectively. The following slit sizes from tube to detector were used:
181 0.9 mm (0.645°), 1.3° Soller, 1.05 mm, sample, 1.0 mm, 1.3° Soller, 0.3 mm. The step size
182 was 0.05° and the counting time was 20 s per step.

183

184 ***Molecular dynamics simulations***

185 The simulated structural models of smectites were based on the pyrophyllite
186 crystallographic data (Lee and Guggenheim, 1981), with several isomorphous substitutions
187 introduced at particular atomic sites to mimic the experimentally studied smectite samples.
188 All three structures were built by substituting a relevant number of Al atoms with Mg and Si
189 with Al in the octahedral and tetrahedral sheets of the clay structure, respectively. The Mg/Al
190 ordering in the octahedral sheets was introduced following the work of Ortega-Castro *et al.*
191 (2010), *i.e.* maximizing the distance between Mg atoms. The Al/Si ordering in the tetrahedral
192 sheet was random but obeying the Löwenstein rule, *i.e.* excluding Al-O-Al linkages. The
193 simulation supercell was 8×4×2 unit cells in the *a*, *b*, and *c* crystallographic directions,

194 respectively ($\sim 41.6 \text{ \AA} \times 36.1 \text{ \AA} \times Z \text{ \AA}$; the value of Z varied depending on the amount of EG
195 and H_2O in the interlayer space and the force field used).

196 The total energy of a molecular model is usually described by a sum of Coulombic
197 (electrostatic) interactions, short-range non-electrostatic interactions (sometimes referred to as
198 the Van der Waals terms), and bonded (intramolecular) interactions:

$$199 \quad E_{Total} = E_{Coul} + E_{VDW} + E_{Bonded} \quad (1)$$

200 The bonded terms are especially important for organic molecules and typically include the
201 bond stretching, angle bending energy terms, various torsional terms, etc. The electrostatic
202 energy is represented by Coulomb's law:

$$203 \quad E_{Coul} = \frac{e^2}{4\pi\epsilon_0} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}}, \quad (2)$$

204 where r_{ij} is the separation distance between the charged atoms i and j , e is the charge of the
205 electron, ϵ_0 is the dielectric permittivity of vacuum ($8.85419 \times 10^{-12} \text{ F/m}$), and the partial
206 charges q_i and q_j are usually derived from quantum mechanics calculations and assigned by
207 the specific force field model. The Van der Waals energy term is usually represented by the
208 conventional Lennard-Jones (12-6) function, and includes the short-range repulsion associated
209 with the increase in energy as two atoms closely approach each other and the attractive
210 dispersion energy:

$$211 \quad E_{VDW} = \sum_{i \neq j} D_{o,ij} \left[\left(\frac{R_{o,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{o,ij}}{r_{ij}} \right)^6 \right]. \quad (3)$$

212 $D_{o,ij}$ and $R_{o,ij}$ are empirical parameters specific to a particular force field model. The
213 interaction parameters between the unlike atoms are usually calculated according to the so-
214 called Lorentz-Berthelot mixing rules (e.g. Allen and Tildesley, 1987): arithmetic mean for
215 the distance parameter, R_o , and the geometric mean for the energy parameter, D_o :

$$216 \quad R_{o,ij} = \frac{1}{2} (R_{o,i} + R_{o,j}) \quad (4)$$

217
$$D_{o,ij} = \sqrt{D_{o,i}D_{o,j}}$$
 (5)

218 The Coulombic and VDW interactions are excluded for proximate intramolecular (bonded)
219 interactions (i.e., 1-2 and 1-3 atom position exclusions) when large organic molecules are
220 modeled.

221 In our case, the interatomic interactions involving smectite structures were described
222 with the ClayFF (Cygan *et al.*, 2004) and the INTERFACE (Heinz *et al.*, 2005) force fields.
223 GAFF, OPLS-aa, CGenFF, and CVFF organic force fields were used for EG, while the SPC
224 model was assumed for water molecules (Berendsen *et al.*, 1981). The INTERFACE force
225 field was only coupled with the CVFF organic force field because of the consistency of its 1-
226 4-scaling factors (value of 1.0). CGenFF assumes no scaling, while OPLS-aa uses a scaling
227 factor of 0.5, and GAFF uses 0.5 for the non-bonded non-electrostatic part of the interaction
228 and 0.8333 for the electrostatic interactions. ClayFF has no restrictions on the organic force
229 field that it can be coupled with, because no 1-4 pairs are present in this parametrization.
230 Additionally, in the original clay mineral force fields, the Lennard-Jones parameters for basal
231 oxygens, O_b, were modified as suggested by Ferrage *et al.* (2011) (ClayFFmod and
232 INTERFACEmod). The LJ parameters of tetrahedral Si and Al atoms were, respectively, also
233 modified in these models to maintain the same Si-O_b and Al-O_b distances as in the original
234 force fields (see Szczerba *et al.*, 2016 and supplementary materials for a more detailed
235 discussion). Ewald summation was applied to calculate the long range corrections to the
236 Coulombic interactions (e.g., Allen and Tildesley, 1987) and the cut-off distance was set to
237 8.5 Å.

238 A set of different EG compositions around those of Reynolds (1965) – 1.7 EG per half
239 unit cell (phuc) – was covered by the simulations to obtain the basal spacing closest to the
240 experimentally observable. A constant number of interlayer water molecules – 0.8 H₂O phuc
241 – was assumed. Additionally, for the set of parameters that gave the best results in previous

242 calculations, the EG content was set to vary from 1.4 to 2.0 with a step of 0.2 phuc, while the
243 water content also varied between 0.0 and 1.2 H₂O phuc with a step of 0.3 phuc.

244 For all models, structural optimizations (total energy minimizations) were performed
245 first, followed by *NPT*-ensemble MD simulations at 1 bar under evolving temperature using a
246 Langevin dynamics algorithm to control the temperature and a Langevin piston to control the
247 pressure. The time step to integrate the equations of atomic motion was set to 1 fs and the
248 dynamic trajectories of all atoms and system properties were recorded every 1 ps. For the first
249 0.5 ns the temperature was set to 398 K. Then the temperature dropped to 298 K and the
250 simulation continued for 1 ns. From the last 0.5 ns the equilibrium system properties were
251 recorded for further analysis. To exclude any undesirable displacement of the center of mass
252 of the simulated model, in all simulations one atom of the octahedral sheet was fixed at its
253 initial position, but its interactions with all neighboring atoms were still fully accounted for.
254 All MD simulations were performed using the LAMMPS computer program (Plimpton, 1995;
255 <http://lammps.sandia.gov>).

256

257 *Parametrization of EG molecules with organic force fields*

258 CGenFF parameters were automatically assigned with the help of the on-line tool
259 (cgenff.paramchem.org) using the NAMD convention, which was modified to make it
260 consistent with the LAMMPS format. GAFF parametrization was performed using the
261 *moltemplate* program (moltemplate.org) with charges automatically assigned using the
262 program *TPACM4* available at www.scfbio-iitd.res.in/software/drugdesign/charge.jsp
263 (Mukherjee *et al.*, 2011). CVFF parameters were automatically assigned within this force
264 field's implementation in the LAMMPS program. Partial atomic charges were calculated
265 based on the bond increments from the file containing CVFF parameters. OPLS-aa parameters
266 were also automatically assigned using the *moltemplate* program. Tcl scripts executed in the

267 VMD molecular visualization program (Humphrey *et al.*, 1996) were used to generate all
268 input files for LAMMPS simulations.

269

270 *Calculation of the simulated XRD patterns*

271 For every simulated structure, the atomic density distributions of the interlayer species
272 as well as electron density profiles along the direction perpendicular to the layering were
273 calculated. Then all the distributions were symmetrized with respect to the interlayer center
274 and used as an input for calculations of the X-ray diffraction patterns using the Sybilla code
275 (Chevron proprietary). The values of T_{mean} , d -spacing, σ^* and Δ - d -spacing were optimized
276 automatically. The range of $2\theta < 4.5^\circ$ was excluded from the optimization because in this
277 range the effect of super-crystallites becomes important, which is not taken into account by
278 the code. The amount of Fe in the octahedral sheet was taken directly from the Table 1 and
279 was not optimized.

280 T_{mean} is the average thickness calculated for a lognormal distribution of crystallite
281 thicknesses. A variation of this value affects mainly the broadening of the 00l peaks. The d -
282 spacing represents the layer-to-layer distance of smectite structures and principally affects
283 only the positions of 00l maxima. The parameter of σ^* is a standard deviation of the Gaussian
284 orientation function of crystallites (Reynolds, 1986). The Δ - d -spacing describes fluctuations
285 of the layer-to-layer distance. The variations of σ^* and Δ - d -spacing parameters affect the
286 relative XRD intensities by a factor that is quite complex to express analytically, but is known
287 to be monotonic function of 2θ . Generally, it can be concluded that the largest modification of
288 the relative intensities of 00l reflections is influenced by the structure of interlayer species,
289 which depends on the force-fields used. This is also because all the parameters were
290 optimized to reproduce very similar values for a certain studied smectite.

291

292 RESULTS AND DISCUSSION

293

294 *Comparison of organic force fields for EG*

295 In order to compare the performance of organic force fields in reproducing bulk liquid
296 EG properties, the density of a box consisting of 230 EG molecules as well as the angular
297 distributions of the torsional O-C-C-O potential energy terms were calculated. Table 2
298 compares the calculated liquid densities with the experimental data. The closest agreement is
299 achieved by the GAFF parameterization, while all other force fields result in densities
300 noticeably lower (OPLS-aa and CGenFF) or higher (CVFF) than the experimental value.

301

302 === Table 2 ===

303

304 The torsional O-C-C-O angle potential energy distributions were compared to a
305 reference obtained from DFT calculations performed under the B3LYP/DGDZVP level of
306 theory using Gaussian Inc. software package (Frisch *et al.*, 2004). In these calculations, all
307 distances and angles were optimized for a certain O-C-C-O angle. The results (Figure 1)
308 demonstrate that the CVFF and OPLS-aa force field parameterizations are the closest to the
309 reference quantum chemical calculation. In the case of GAFF parameterization, the *gauche*
310 conformation is predicted to be too stable relatively to the *trans* one. On the other hand, the
311 stability of the *trans* conformation is overestimated in the CGenFF parameterization. All these
312 differences are important for the proper modeling of EG conformations in smectite
313 interlayers.

314

315 === Figure 1 ===

316

317 *Comparison of intercalate structures with 1.7 EG and 0.8 H₂O phuc*

318 The observed differences between the organic force fields, described in the previous
319 section, should have an effect on the simulated interlayer structure and resulting X-ray
320 diffraction patterns. To study this, the intercalate structure with EG and water content
321 corresponding to that of Reynolds (1965) (1.7 EG and 0.8 H₂O phuc) was calculated first. An
322 example for SWy-1 is shown in Figure 2 (the results for two other smectites are provided in
323 the supplementary materials).

324

325 === Figure 2 ===

326

327 The structures obtained using the INTERFACE and INTERFACEmod force fields are
328 substantially different than those resulting from the application of the ClayFF and ClayFFmod
329 – i.e., oxygen atoms of EG molecules have much higher tendency to be located closer to the
330 surface than their carbon atoms. In the case of the latter force fields, the positions of the
331 closest to the surface carbon and oxygen atoms do not significantly differ. A similar effect is
332 also observed for water molecules: they are located closer to the clay surface for the
333 INTERFACE- than for the ClayFF-based models.

334 Different organic force fields have also substantial effect on the resulting averaged
335 structures of the intercalate. The effect of different EG liquid density is reflected in the
336 differences in the basal spacings – the lower the density, the higher the basal spacing. There is
337 no obvious relation between the observed relative stabilities of the trans-gauche conformers
338 (Figure 1) and the obtained interlayer structures. The position of carbon atoms is relatively
339 similar for all the organic force fields tested, while there are substantial differences in the
340 positions of the oxygen atoms of EG. These differences, however, do not affect substantially
341 the calculated electron density profiles (Figure 3 and supplementary materials).

342 The modification of the Lennard-Jones parameters for the basal oxygens of smectites
343 leads to a very slight modification of the basal spacing. However, it affects the interlayer
344 structure in such a way that organic and H₂O molecules are located at somewhat larger
345 distances from the clay surface than in the original ClayFF models (Figure 2). The same
346 tendency was observed by Ferrage *et al.* (2011). These changes, in turn, affect the calculated
347 electron density profiles (Figure 3).

348

349 === Figure 3 ===

350

351 *Comparison of intercalate structures with 0.8 H₂O phuc and basal spacing close to*
352 *experimental*

353 Based on the structure proposed by Reynolds (1965) and on the previous MD
354 simulation studies of EG-smectite structure (Szczerba *et al.*, 2014), the content of water is
355 estimated to be around 0.8 - 1.0 molecules phuc. This value was therefore assumed as a
356 constant and chosen to be equal 0.8 phuc in the present simulations. The EG content was
357 adjusted to achieve the basal spacing close to the experimental value. This is an obvious
358 approximation due to the fact that the content of water in the structure will be related to the
359 actual relative humidity and the time between the sample glycolation and XRD measurement
360 and the conditions of the XRD profile registration. The content of water and EG is also
361 dependent on the glycolation procedure (Mosser-Ruck *et al.*, 2005). Without this
362 approximation, however, the number of necessary calculations would increase dramatically,
363 but without affecting the main conclusions too much.

364 The results of the calculations for SWy-1 are presented in Figure 4 (the results for two
365 other smectites are presented in the supplementary materials). The effect of the variation in
366 the EG content on the structures is not very strong (in comparison to Figure 2), and the main

367 factors affecting the distribution of atoms in the interlayer space are the organic force field as
368 well as the clay mineral force field.

369

370 === Figure 4 ===

371

372 *Comparison of the calculated X-ray diffractograms*

373 In order to evaluate and further quantify the differences due to the application of
374 different organic force fields in the molecular modeling studies of organic-smectite
375 interactions, all the above calculated distributions were incorporated into the Sybilla code to
376 calculate X-ray diffractograms for the simulated structures. Thus calculated diffractograms
377 with optimized values of T_{mean} , d -spacing, σ^* , and Δ - d -spacing were then compared with
378 experimental ones (Figures 5 - 7). The results show quite significant discrepancies in the
379 obtained XRD patterns for different layer charges as well as for different combinations of
380 force fields. Because XRD is only sensitive to the distribution of electrons (the simulated
381 electron density profiles are shown in Figure 3), different electron density profiles may results
382 in different calculated XRD patterns, especially in the distribution of relative 00l intensities.

383 For low-charge montmorillonite (SWy-1; charge 0.27 phuc) the calculated results
384 agree well with experiment for all clay mineral force fields, and only relatively small
385 differences between the organic force fields used are noticeable. The modification of the
386 Lennard-Jones parameters for the basal oxygens leads to some increase of intensities of the
387 002 and 003 peaks and to a small decrease of intensities of the 004, 005 and 006 peaks.

388 For high-charge montmorillonite (SAz-1; charge 0.54 phuc) and beidellite (SbCa-1;
389 charge 0.50 phuc), the modification of the Lennard-Jones basal oxygens parameters of the
390 ClayFF-based models substantially improves the agreement between the theoretical and
391 experimental diffractograms for all the organic force fields tested. A substantial correction of

392 the 002 and 003 peak intensities towards those of experimental values is observed. A similar
393 modification applied to the INTERFACE-based models leads to only relatively small
394 improvement. This indicates that, although this force field provides a good structure for low-
395 charge montmorillonites, it should be probably modified to describe more accurately the
396 interlayer structure of high-charge smectites.

397 Among the organic force fields, the least accurate results are obtained with CGenFF.
398 This is probably related to its overestimation of the *trans* EG molecular conformation and its
399 poor agreement of the EG liquid density with experiment (Figure 1 and Table 2). Combined
400 with unmodified ClayFF, GAFF gives the best results. The resulting X-ray diffractogram is,
401 however, poor for high charge-beidellite in any combination of organic force field with
402 unmodified clay mineral set of parameters. The two other sets (OPLS-aa and CVFF) give the
403 best results for ClayFFmod. The observed differences can be related to the approximations of
404 the organic, clay mineral and water force fields and possible uncertainties in the number of
405 EG and water molecules in the interlayer estimated from experimental data and assumed in
406 the models.

407

408 === Figure 5 ===

409

410 === Figure 6 ===

411

412 === Figure 7 ===

413

414 ***Comparison of the structures with different water and EG contents***

415 Based on the results presented in the previous section, one of the two best sets of force
416 field combinations (ClayFFmod + CVFF) was used to study the interlayer structures further

417 and to check if the variation of the assumed EG and water content can improve the calculated
 418 X-ray diffractograms. A range of EG compositions was systematically probed between 1.4
 419 and 2.0 phuc with a step of 0.2 phuc, with water contents varying between 0.0 and 1.2 phuc
 420 with a step of 0.3 phuc. The variation of d -spacing depending on the EG and water content
 421 (Figure 8) shows a plateau at around 16.5 – 17.0 Å with some further variation depending on
 422 the layer charge. Based on these plots, several structures were selected (black circles in Figure
 423 8) to calculate average atomic distributions and then to calculate the corresponding X-ray
 424 diffraction patterns for two-layer intercalate structures.

425 The best of the calculated X-ray diffractograms shows only a small improvement
 426 compared to the results shown in figures 5-7 (Figure 9; all results are presented in the
 427 supplementary materials). The discrepancy between the simulated and experimental
 428 diffractograms can, therefore, be primarily attributed to the inaccuracy of the force fields
 429 used. The most important factor is clearly the selection of the clay mineral force field - its
 430 parameters may require additional improvement.

431

432 == Figure 8 ==

433

434 == Figure 9 ==

435

436 **CONCLUSIONS**

437 The main factor affecting the accuracy of the calculated X-ray diffractograms of EG-
 438 water intercalate in smectites is the force field selected to model clay mineral substrate. The
 439 selection of organic force field parameters, although also important, has only a secondary
 440 effect on the results obtained. The best set of parameters for smectite was found to be ClayFF
 441 with modified Lennard-Jones parameters of the basal surface oxygens (ClayFFmod). All

442 tested organic force fields perform relatively well in combination with ClayFFmod and small
443 differences between them depend on the value and location of the smectite charge. Generally,
444 among the organic force fields tested, GAFF, OPLS-aa, and CVFF perform relatively well,
445 while the application of CgenFF leads to the least accurate results.

446 The INTERFACE force field produces relatively good results for low-charge
447 montmorillonite, but it performs less well for high-charge smectites. Unlike for ClayFF,
448 modifications of the Lennard-Jones parameters for INTERFACE do not help much to
449 improve the resulting simulated X-ray diffractograms. The origin of the discrepancy between
450 the simulated and experimental diffractograms is apparently in the overestimation of the
451 interlayer atomic populations close to the clay surface.

452 Further assessment of molecular models could be performed using neutron diffraction.
453 This would, in particular, help in discriminating between models giving relatively similar
454 electron density profiles but contrasting distributions of interlayer hydrogen atoms. Using this
455 approach, positions of water molecules in the interlayer space of smectite complexes with
456 organic molecules can be much more precisely determined.

457

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- 661
662

663

Table 1. Smectites used in the study.

Smectite	Tetrahedral charge	Octahedral charge	Fe in octahedral sheet	Particle size fraction
SWy-1	0.0	0.28	0.20	<0.1 μm
SAz-1	0.0	0.56	0.26	<2.0 μm
SbCa-1	0.50	0.0	0.09	<1.0 μm

664

665

Table 2. Comparison of calculated and experimental liquid EG density values

Organic force field	Density at 20°C (g/cm ³)
OPLS-aa	1.060
GAFF	1.123
CGenFF	1.054
CVFF	1.188
Experimental	1.115^a

666

^a The experimental value of EG density at 20°C is taken from Dow Chemicals (dow.com/ethyleneglycol/about/properties.htm).

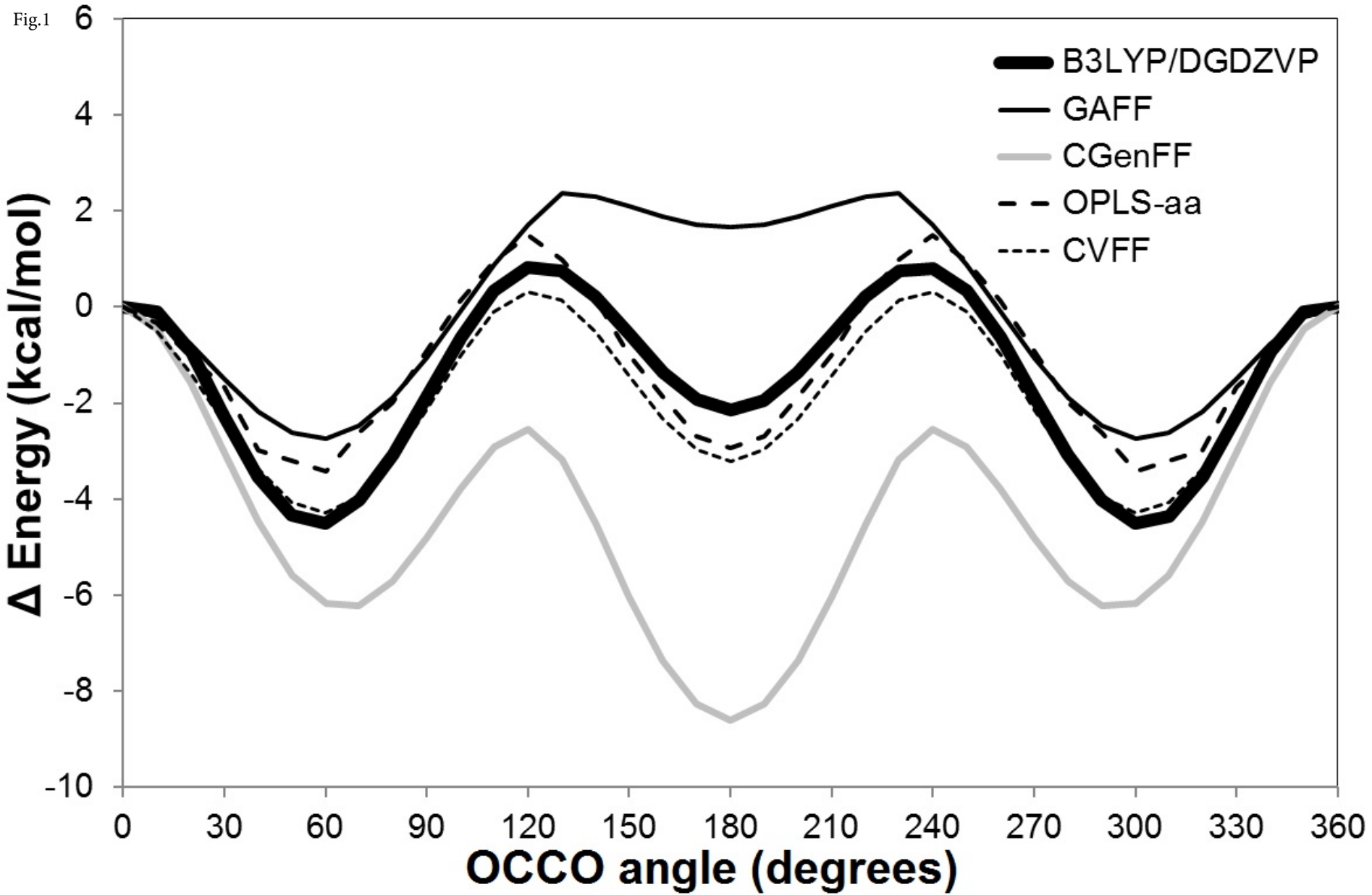
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669

- 670 Figure 1. Potential energy scan of the torsional O-C-C-O angle of the EG molecule as reproduced by different
671 organic force fields in comparison with quantum chemical calculations at the B3LYP/DGDZVP level
672 of theory.
673
- 674 Figure 2. Z-density profile distributions for carbon and oxygen of EG, oxygen and hydrogen of water, and Ca²⁺
675 ions for SWy-1 for 1.7 EG and 0.8 H₂O phuc. The resulting basal spacings are also shown.
676
- 677 Figure 3. Electron density profiles obtained from MD simulations (black lines) compared to the profiles
678 suggested by Reynolds (1965) (grey lines) for SWy-1 for 1.7 EG and 0.8 H₂O phuc.
679
- 680 Figure 4. Z-density profile distributions for carbon and oxygen atoms of EG, oxygen and hydrogen atoms of
681 water and Ca²⁺ ions for SWy-1 with 0.8 H₂O phuc and variable EG content for which the basal
682 spacing is close to 16.92 Å. The resulting basal spacings are also shown.
683
- 684 Figure 5. Comparison of **SWy-1** XRD patterns for various force field combinations (red – experimental, black –
685 calculated).
686
- 687 Figure 6. Comparison of **SAz-1** XRD patterns for various force field combinations (red – experimental, black –
688 calculated).
689
- 690 Figure 7. Comparison of **SbCa-1** XRD patterns for various force field combinations (red – experimental, black
691 – calculated).
692
- 693 Figure 8. *d*-spacing dependence on the EG and water content for: a) SWy-1, b) SAz-1, c) SbCa-1 smectites.
694 Small circles mark the structures which were used to calculate X-ray diffraction patterns. Thick black
695 lines correspond to experimental basal spacings.
696
- 697 Figure 9. Comparison of XRD patterns for different smectites selected from the compositions in figure 8, that
698 provide the best agreement between experimental and theoretical diffractograms.
699

Fig.1



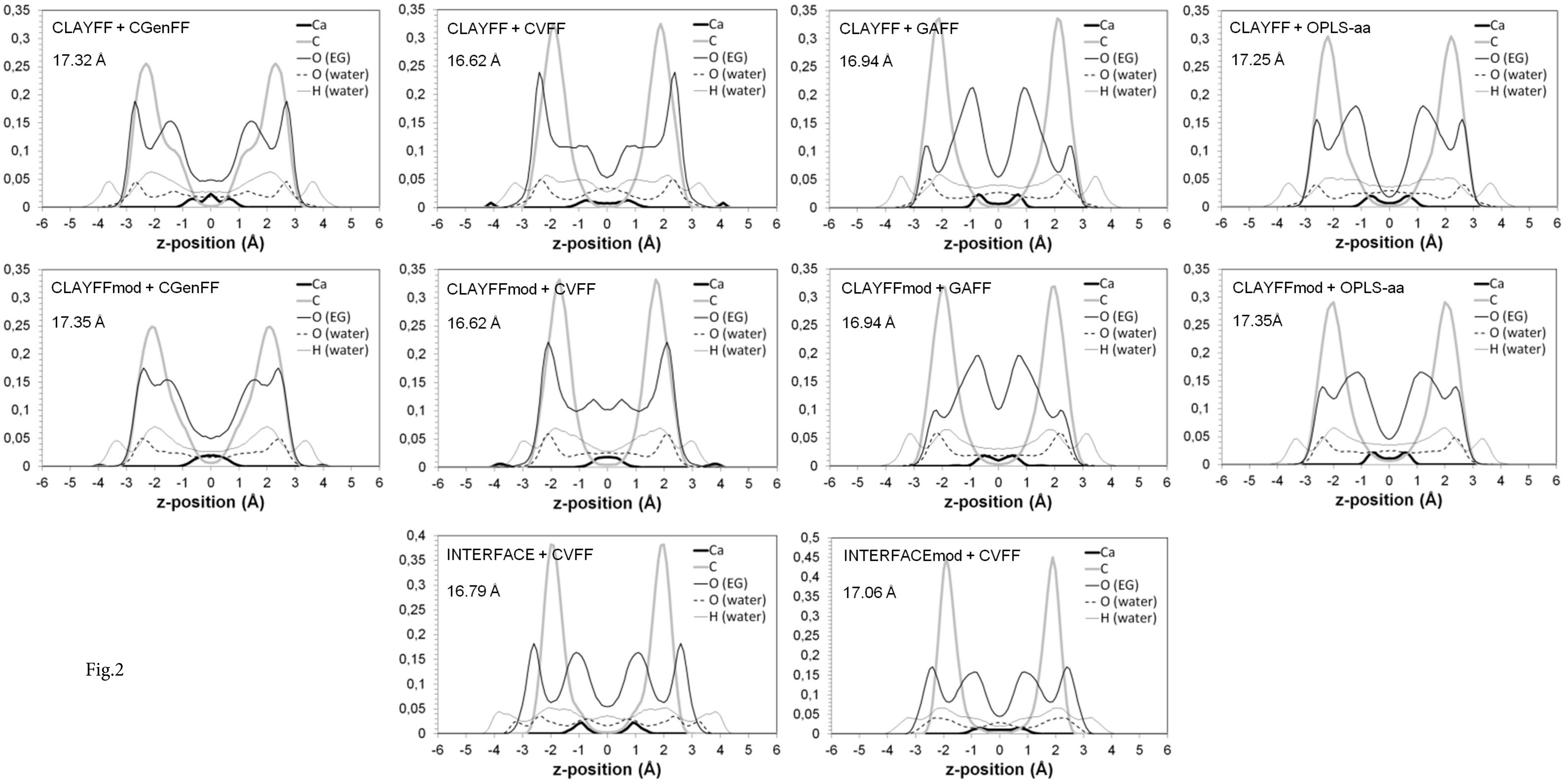


Fig.2

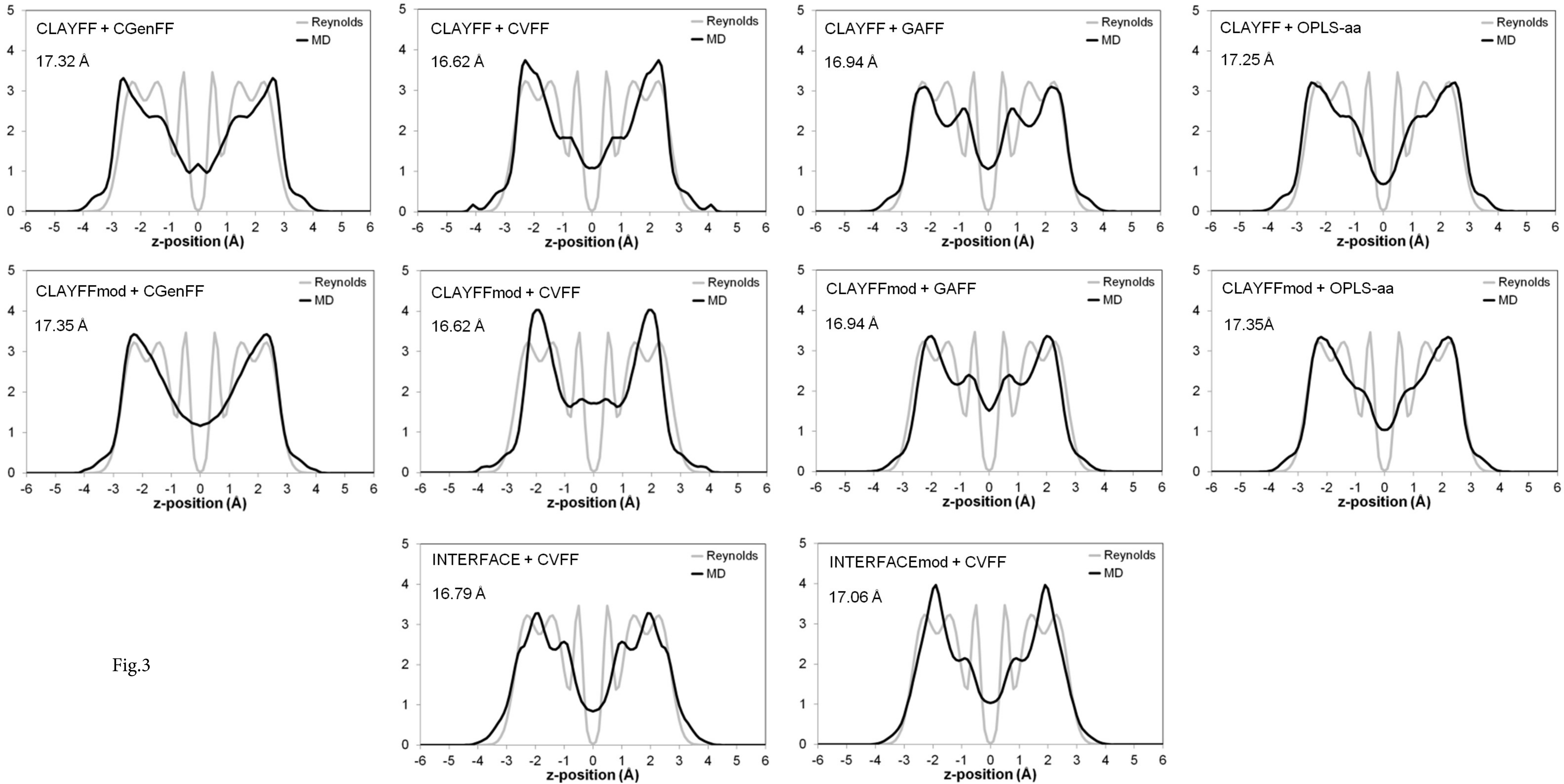


Fig.3

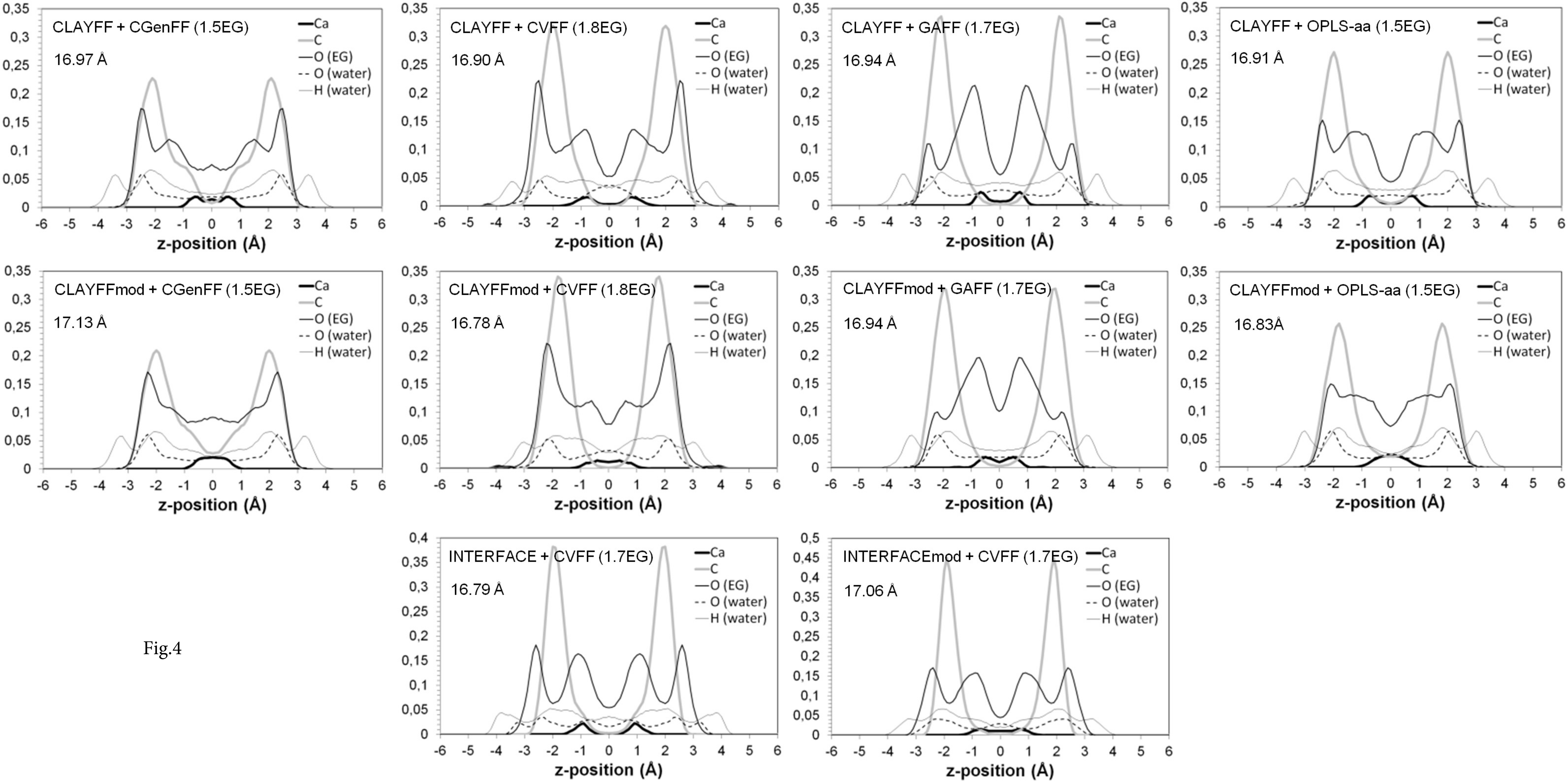
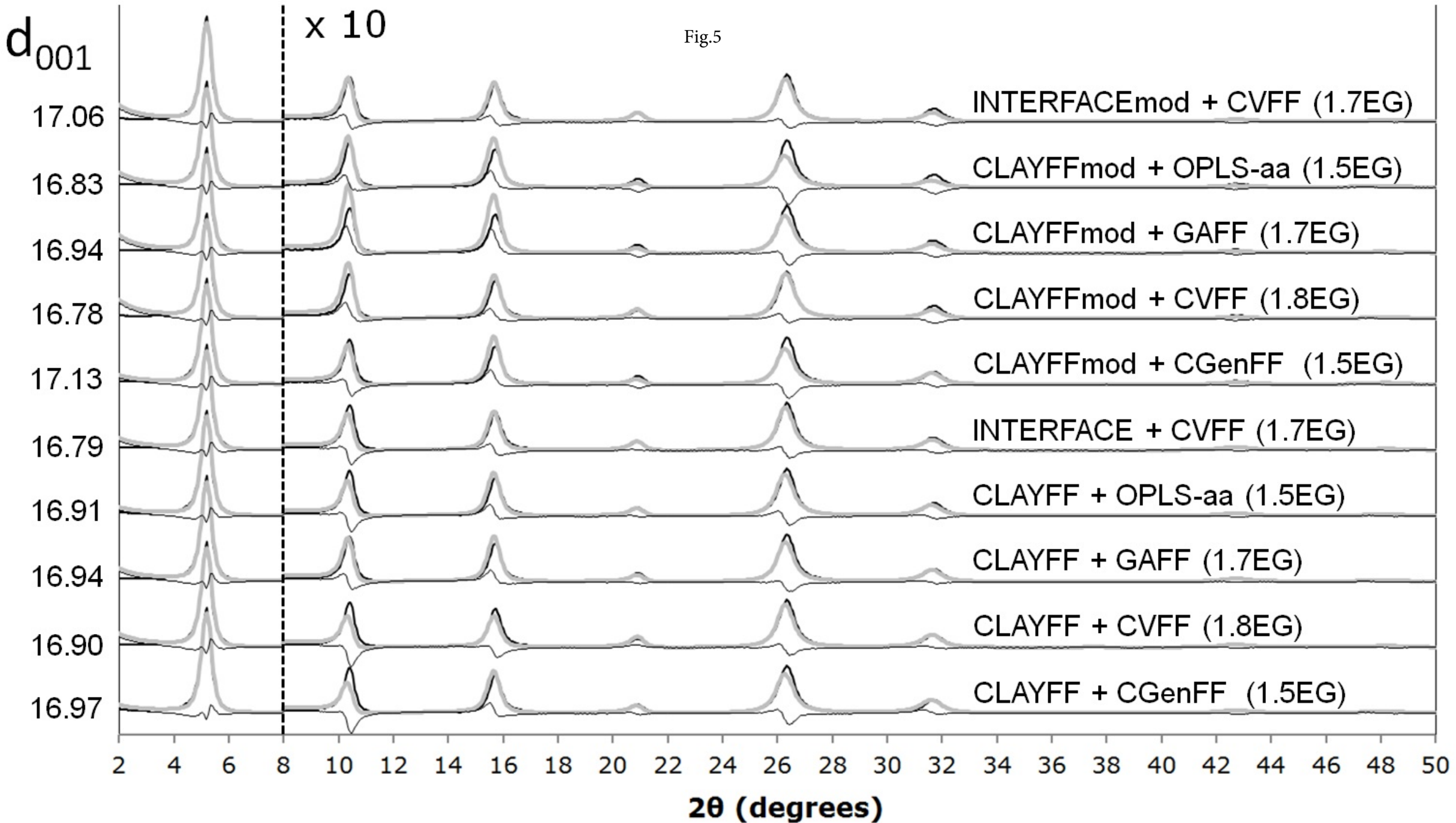
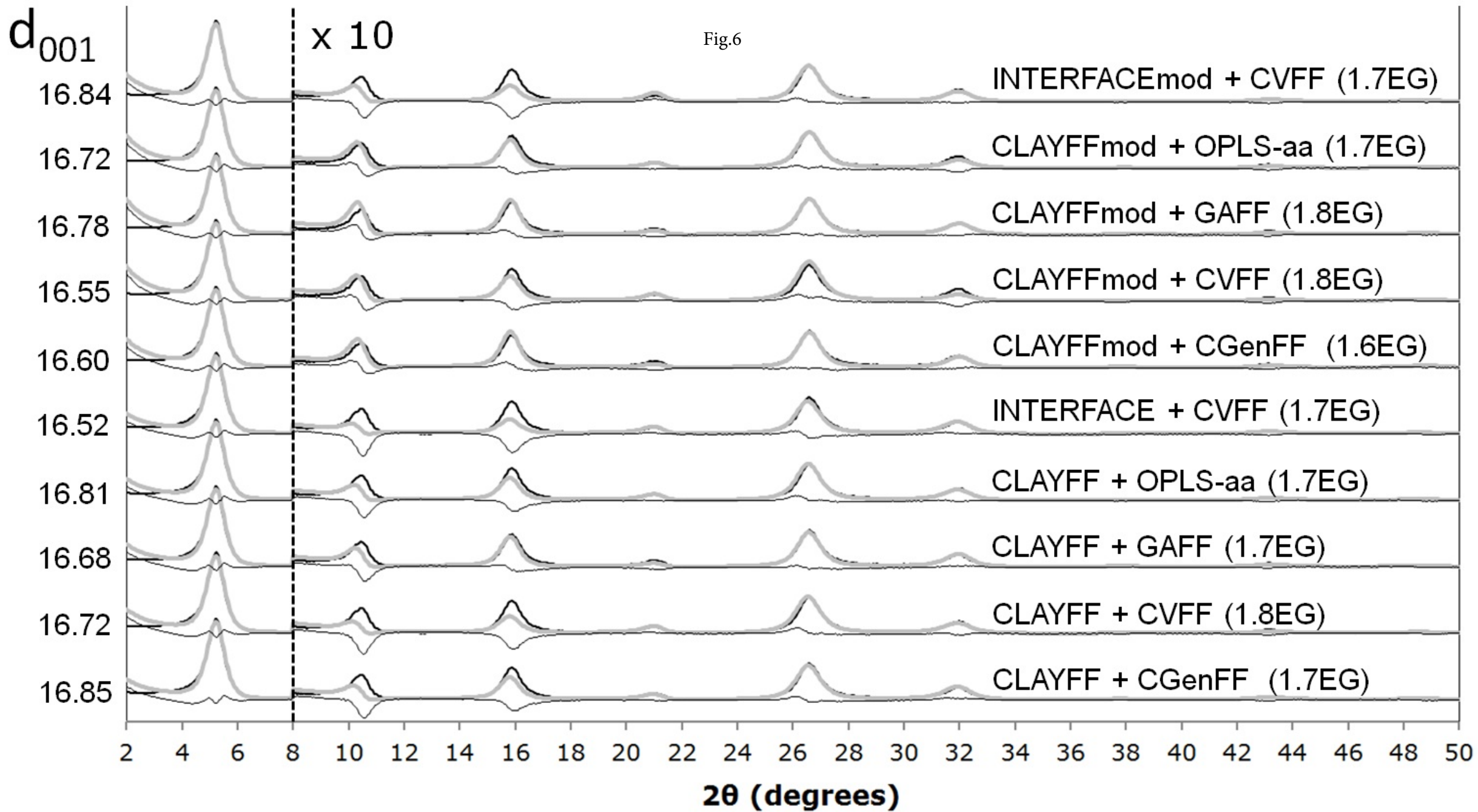
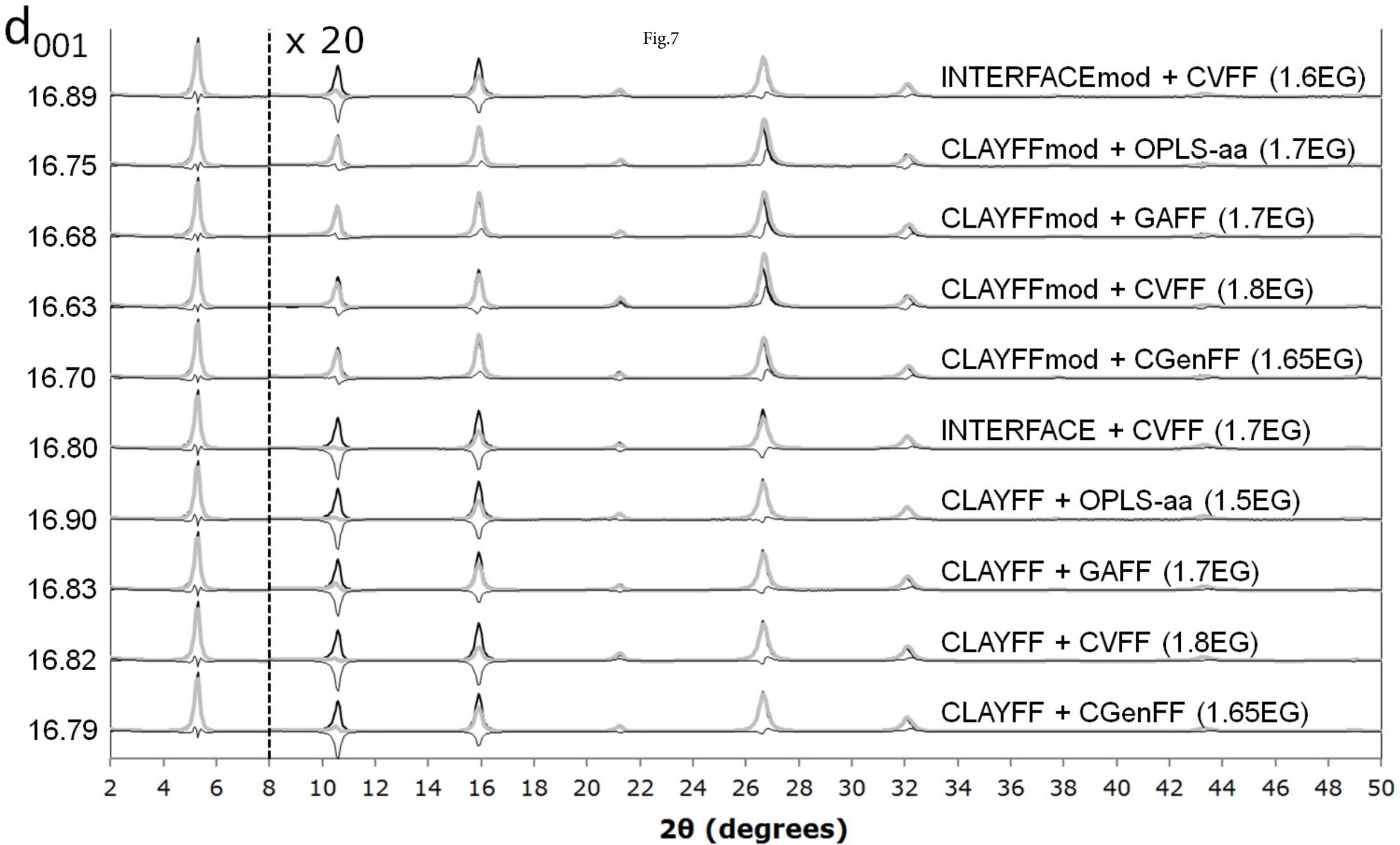
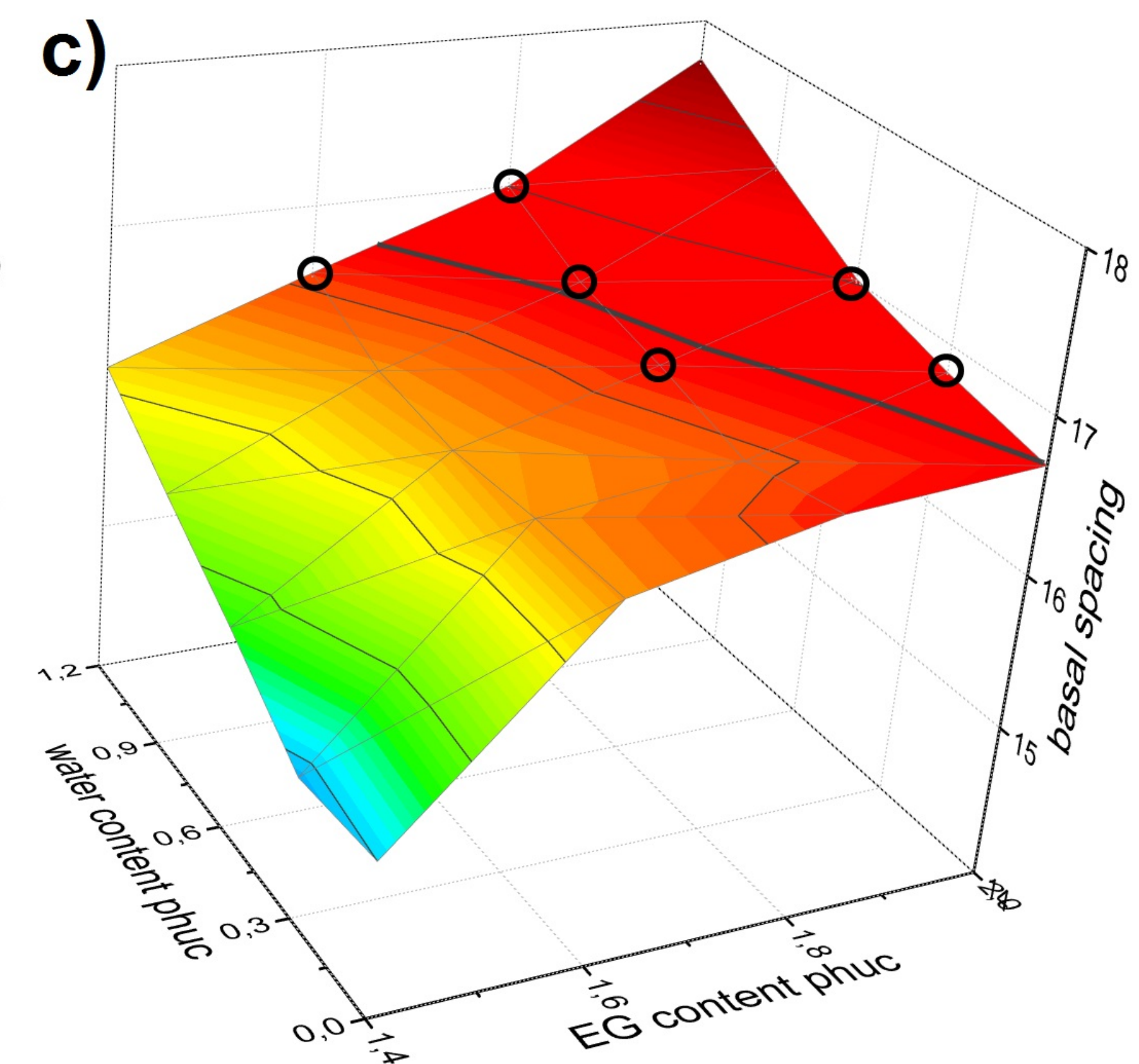
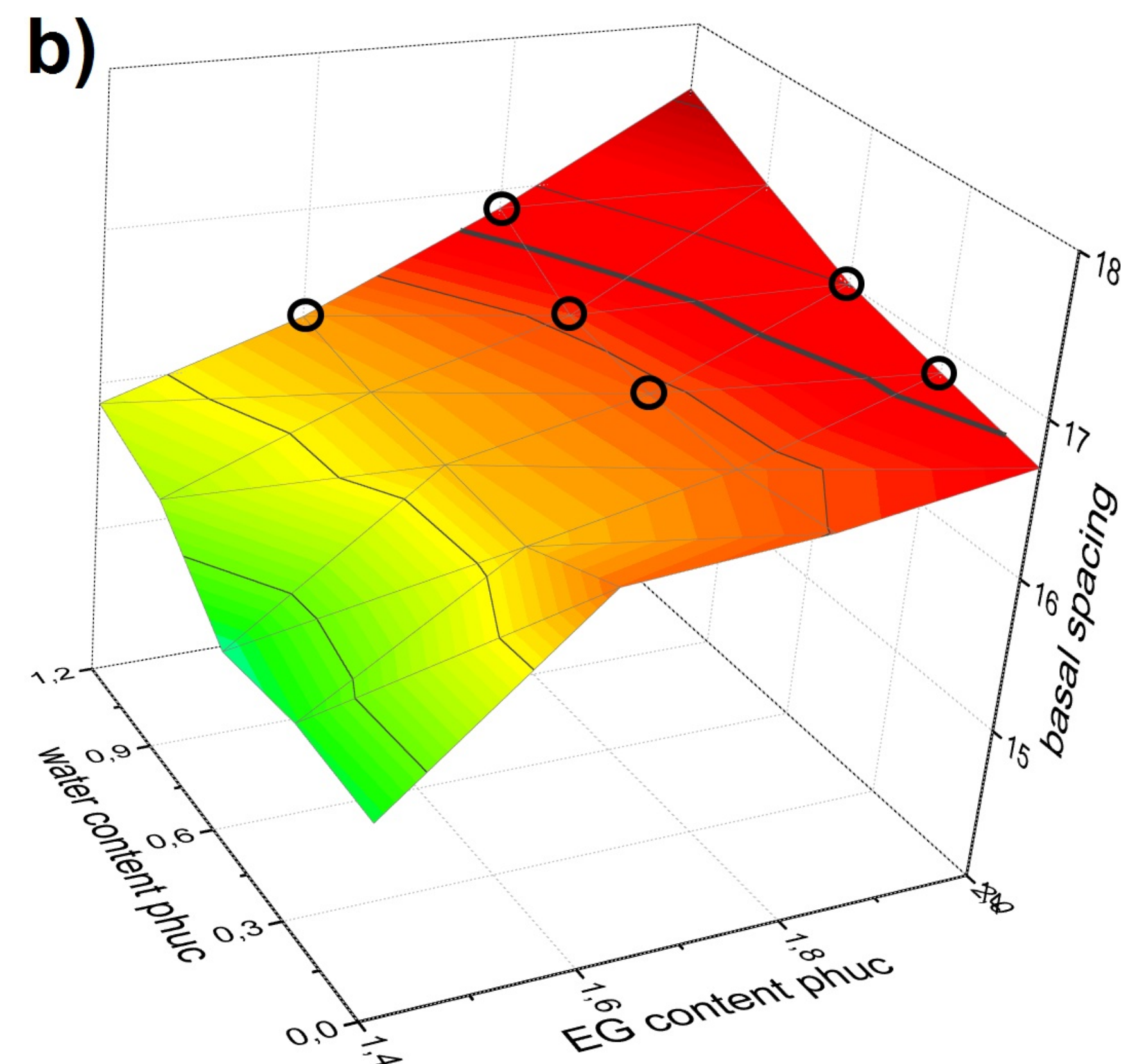
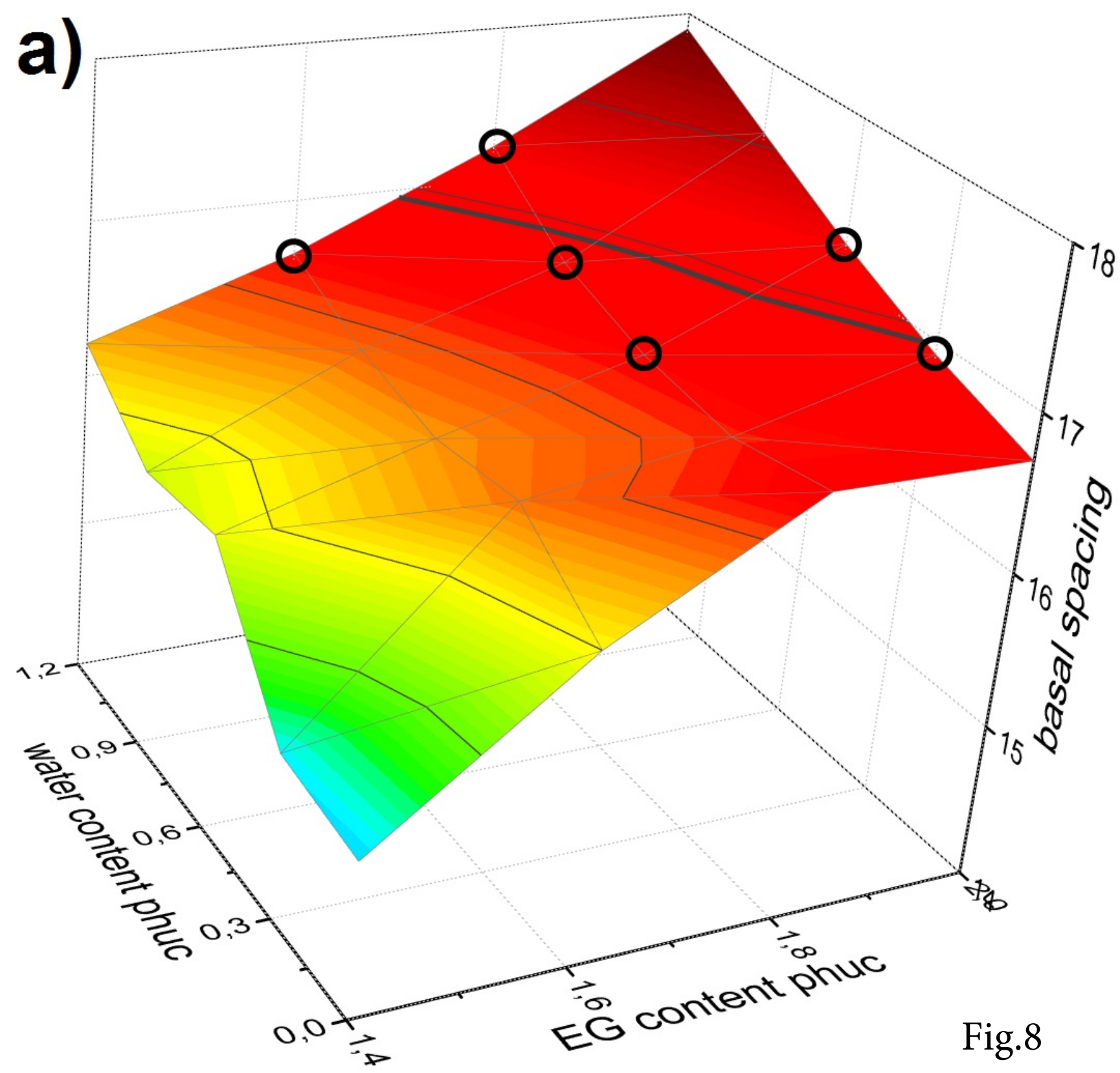


Fig.4









d_{001}

x 20

Fig.9

SbCa-1 (1.6EG + 1.2W)

SAz-1 (1.8EG + 0.6W)

SWy-1 (1.8EG + 1.2W)

2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50

2 θ (degrees)