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#### The growth process of saponite: A study based on particle size distributions and

morphological evolution

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# 28 Abstract

29 Smectite growth is of great importance for the geochemistry of clay minerals 30 on the Earth's surface and their applications in industries. However, the growth 31 process and mechanism controlling the physicochemical properties of smectite are 32 still poorly understood. Through an effective integration of particle size distributions 33 (PSDs) and morphology of particles, this study has enhanced the understanding of 34 smectite growth by investigating the growth processes of a synthetic tri-octahedral 35 smectite (saponite). The starting materials were equimolar Mg-saponite and Ni-36 saponite that had been hydrothermally synthesised at 220°C. Two Mg-Ni-saponite 37 samples were obtained through further hydrothermal treatment of the starting 38 materials at 400 and 500°C. A systematic measurement of the size in the *ab*-plane of 39 numerous saponite particles was performed to obtain their PSDs. The parameters a 40 and  $\beta^2$ , derived from PSDs and the morphology of saponite, indicate that saponites 41 grow mainly via surface-controlled growth and likely via supply-controlled growth in 42 open systems. Particle attachment via the edge surfaces of saponite is an 43 accompanying growth mechanism, and talc-like layers favour the "three-dimensional 44 growth". In addition, the heterogeneous tetrahedral Al distribution of saponite could 45 lead to the formation of elongated laths.

46 Keywords: Crystal growth; particle size distribution (PSD); saponite; particle47 attachment; smectite morphology

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# 52 1. Introduction

53 The smectite group of clay minerals, composed of a central octahedral sheet 54 and two tetrahedral sheets, has attracted particular attention due to their geochemical 55 significance (Eberl, 1984; Tardy et al., 1987; Sposito et al., 1999; Merriman et al., 56 2005; Christidis and Huff, 2009; Voigt et al., 2020) and wide applications (Odom, 1984; Murray, 1991; Bergaya and Lagaly, 2013). Its formation processes, including 57 58 phase transformation and crystal growth, not only affect its applications in industries 59 but also respond to the physicochemical environment where it formed. The alteration 60 of other minerals into smectite has been extensively studied (e.g., Badaut, et al., 1983; 61 Banfield et al., 1994; Cuadros et al., 2012; Tao et al., 2019). However, only a few 62 studies on smectite growth have been made available thus far, owing to the limitations 63 of its special properties (e.g., complex compositions, hydrated layers, and small 64 particle size) (Christidis 2001; Decarreau et al., 2014; Zhang et al., 2020; Besselink et 65 al., 2020).

66 The particle size distribution (PSD) of a mineral has a distinctive shape related 67 to its growth history. It is possible to describe the mineral growth processes based on 68 their measured PSDs (Wagner, 1961; Baronnet, 1982). Eberl et al. (1998) simulated 69 PSDs of different crystal growth patterns in closed and open systems. An open system is defined as a system in which matter is supplied to the growing crystals by a source 70 71 other than the growing phase; whereas a closed system is defined as a system where a 72 single phase is involved, and the less stable crystals dissolve to supply materials for 73 the growth of other crystals. Eberl et al. (1998) defined surface-controlled growth in 74 open systems when crystals grow with an essentially unlimited supply of nutrients, 75 and the dissolution rate of the "source" is not the limiting factor. Supply-controlled 76 growth in open systems refers to the rate of crystal growth, which is controlled by the

rate of nutrients. Ostwald ripening in closed systems is a recrystallisation process in a
closed system that is characterized by the simultaneous dissolution and growth of a
mineral in a single medium (Wagner et al., 1961). In such a system, large particles
grow at the expense of dissolving small particles, resulting in the minimization of
surface free energy (Lifshitz and Slyozov, 1961).

82 Środoń et al. (2000) measured PSDs of natural illite and illite-smectite using 83 transmission electron microscopy (TEM) and concluded that illite grew through 84 surface-controlled growth in open systems. Christidis (2001) also applied the PSD 85 model of Eberl et al. (1998) to the investigation of the growth mechanisms of smectite 86 in a natural system. Their results indicated that smectite experiences supply-controlled 87 growth in an open system and random ripening in a closed system. Zhang et al. (2020) 88 studied the growth process of synthetic saponite by combining PSDs of particle 89 measurements obtained from scanning transmission electron microscopy (STEM) 90 images, argon adsorption, and crystal chemistry. Obtained results implied that 91 saponite growth proceeds via a lateral extension of layers by surface-controlled 92 growth in an open system.

93 Natural smectite has complex compositions, and in particular its early stages 94 of growth cannot be reprised. Thus, a synthetic laboratory approach has been 95 extensively used to investigate the crystal growth of smectite (e.g., Kloprogge et al., 96 1999; Zhang et al., 2010; Petit et al., 2017). It should be noted that a smectite 'crystal' 97 is more comparable to an assemblage of layers than a true crystal (Lagaly and Dékany, 98 2013), and smectite growth essentially consists of a two-dimensional lateral extension 99 of layers (Decarreau et al., 2014; Zhang et al., 2020). Thus, the PSDs obtained by 100 recording the crystal size in the *ab*-plane of particles are useful for studying smectite 101 growth.

In this study, the growth processes of endmember Mg-saponite and Nisaponite synthesised at 220°C, and two Mg–Ni-saponites synthesised at 400 and 500°C, respectively, were investigated through a combination of PSDs and morphologies. The diameters of numerous synthetic saponite particles were measured from STEM images to obtain a series of PSD models. These PSD models were further used to discuss the growth history of saponite.

#### 108 2. Materials and Methods

# 109 2.1. Synthesis of samples

110 The synthesis and characterisation of the saponites used in this study have 111 been described in detail by Zhang et al. (2021). Briefly, Mg-saponite and Ni-saponite 112 precursors were synthesised by the hydrothermal treatment (220°C, 1 d) of a co-113 precipitated gel with a theoretical molar ratio of Si:Al:Mg = 3.7:0.3:3. The Mg-114 saponite and Ni-saponite precursors were named pMg220 and pNi220, respectively. 115 The starting material for Mg–Ni-saponite synthesis was prepared by mixing identical 116 molar weights of pMg220 and pNi220, and named pMg220+pNi220. Two samples 117 were obtained by hydrothermal treatment of the starting material at 400 and 500°C, 118 and were named 220-400 and 220-500, respectively.

# 119 2.2. Characterizations of synthetic saponites

Powder X-ray diffraction (XRD) patterns were obtained using a Bruker D8 advance diffractometer (CuK $\alpha$  radiation, 40 kV and 40 mA) over the range of 2–65° (2 $\theta$ ) with a 0.025° (2 $\theta$ ) step size and 0.6 s per step, while the patterns of the oriented samples and ethylene glycol treated samples were collected over the range of 2–15° (2 $\theta$ ). The randomly oriented samples were prepared by pressing the saponite powder inside a cavity up to the reference level of the sample holders. The oriented samples 126 were prepared by carefully pipetting the clay suspension onto a glass slide and 127 allowing it to dry at ambient temperature. Ethylene glycol treated samples were 128 prepared by treating the oriented samples in a glass desiccator with ethylene glycol at 129 25°C for 24 h.

130 High-angle annular dark-field scanning transmission electron microscopy 131 (HAADF-STEM) observations were performed to investigate the morphology of the 132 saponite particles in the *ab*-plane. A mixture of 1 mg of sample and 10 ml of 133 deionised water was lightly stirred for one week to obtain a diluted colloidal 134 suspension. The specimens were prepared by dispersing the colloidal suspension in 40 135 ml of ethanol and treating them ultrasonically for 30 min. A drop of the resultant 136 suspension was placed on a porous carbon film supported by a copper grid, then water 137 and ethanol were evaporated. STEM images were obtained using an FEI Talos F200S 138 high-resolution transmission electron microscope operated at 200 kV.

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#### 2.3. Measurement of PSDs

140 The saponite growth studied in this study was based on the two-dimensional 141 extension of the particles in the *ab*-plane. Zhang et al. (2020, 2021) successfully 142 observed well-dispersed particles of synthetic saponite by STEM and measured the 143 size of a series of particles to obtain their PSDs by taking the mean value of length 144 plus width in the *ab*-plane. Because saponite particles are generally irregularly shaped, 145 we have developed a new method to measure the particle size of saponite, which is 146 more accurate than that in Zhang et al. (2020) (Fig. 1). After obtaining well-dispersed 147 saponite particles from STEM images, the area of the *ab*-plane of a particle was 148 calculated using Image-ProPlus 6.0 software package in a manual mode. Then, the 149 obtained area was treated as a circle with a calculable diameter (d) that represents the 150 mean size of the particle. The number of measured saponite particles to obtain PSDs

151 was close to 1500 (1508 for 220-400, 1434 for 220-500, 1325 for pMg220, and 1499 152 for pNi220). The experimental PSD curves were simulated using a log-normal 153 distribution function. Parameter  $\alpha$  describes the mean of natural logarithms of 154 observations *d* (diameter), with  $\alpha = \sum (\ln d) f(d)$ ; while  $\beta^2$  describes the variance of 155 natural logarithms of observations *d*, with  $\beta^2 = \sum [\ln(d) - \alpha]^2 f(d)$ ; where f(d) is the 156 frequency of *d* (Eberl et al., 1998).

- 157 3. Results and discussion
- 158 3.1. Crystal habit

159 Powder XRD patterns of Mg-saponite (pMg220) and Ni-saponite (pNi220) 160 precursors displayed characteristic reflections of tri-octahedral smectite with the (001) 161 reflection at ~1.25 nm, the (06, 33) at 0.153 nm, and asymmetric (hk) reflections (Fig. 162 2), as described by Zhang et al. (2021). Compared with that of pMg220, the broader 163 reflections for pNi220 suggested that the coherent scattering domains in the layer 164 plane, as well as the number of stacked layers, are smaller for Ni-saponite than for 165 Mg-saponite. The XRD patterns of the oriented samples display the characteristic 166 reflections of saponites with a basal spacing d(001) at ~1.2 nm, which shifts to 1.72 167 nm after exposure to ethylene glycol (Fig. 3) (Zhang et al., 2021). For 220-500, 168 reflections at 2.58 nm and 3.07 nm are observed before and after ethylene glycol 169 treatment (Fig. 3), respectively. The difference between these two values is ~0.5 nm, 170 comparable to the difference between 1.20 nm and 1.72 nm, presumably due to the 171 occurrence of interstratified non-swelling layers (Whitney, 1983). The non-swelling 172 layers are likely low-charge talc-like layers according to the low pre-set layer charge of saponite (0.3) (Christidis and Mitsis, 2006; Petit et al., 2008; Fonteneau et al., 173 174 2020).

175 The STEM images provided detailed morphological information on the abplane of the particles of all saponites (Figs. 4-5). The layers of pMg220 were 176 177 generally irregular in shape (Fig. 4a), whereas those of pNi220 exhibited 178 geometrically hexagonal shapes (Fig. 4b). It was noted that some elongated laths and 179 120° angles between lateral faces occur in sample pMg220, which were also observed 180 in Kozákov natural saponite (Suquet et al., 1975). The elongated laths were also 181 observed in nontronite and hectorite, and were identified as elongations along the a-182 axis (Mering and Oberling, 1967). Figure 5 reveals an increase in particle size from 183 the starting materials to obtained samples (220-400 and 220-500), providing evidence 184 of saponite particle growth. At higher temperatures, more euhedral elongated particles 185 were observed.

# 186 3.2. PSDs of Mg-saponite, Ni-saponite, and Mg-Ni saponite

The shape of the PSDs and the reduced PSD profiles of Mg-saponite, Nisaponite, and Mg-Ni saponite were approximately log-normal (Figs. 6-8). The diameters of the pMg220 particles were in the range of 10–450 nm, with most of them fell within the range of 10–200 nm (Fig. 6a). In contrast, the diameter of the pNi220 particles varied from 5 to 250 nm, and most of them were in the range of 5–120 nm (Fig. 6c). The mean particle diameter in pNi220 was 36.7 nm, which was far less than that of pMg220 (87.2 nm) (Table 1).

The PSD of sample 220-400 had a log-normal shape with a range of 10–500 nm (Fig. 7a). Meanwhile, from the starting materials to 220-400, the mean diameter of the particles increases from 58.2 to 79.2 nm (Table 1), which indicates the growth of saponite layers. The PSD of sample 220-500 overall displayed a log-normal shape with several secondary maxima in the range of 30–850 nm (Fig. 8a). From the starting material to 220-500, the mean diameter increased from 58.2 to 156.8 nm (Table 1), 200 suggesting a strong growth of saponite particles. Zhang et al. (2021) provided a 201 comprehensive FTIR analysis on the evolutionary processes of the starting material 202 (pMg220+pNi220) into the samples (220-400 and 220-500). The results indicated that 203 partial dissolution (~0.59) of the starting material and recrystallisation of Mg-Ni-204 saponite occurred in sample 220-400, whereas a total dissolution of the starting 205 material and recrystallisation of Mg-Ni-saponite occurred in sample 220-500. Thus, 206 saponite growth for both samples proceeded via dissolution of the starting material 207 and the recrystallisation of Mg-Ni-saponite.

# 208 3.3. Ripening process

209 Eberl et al. (1998) summarised the crystal growth (ripening) mechanisms 210 based on the dissolution-recrystallisation mechanism. The log-normal shape of PSDs 211 (Figs. 6–8) and the coordinates of  $(\alpha, \beta^2)$  (Fig. 9) can be used to discuss the ripening 212 processes of the saponite (Eberl et al., 1998; Środoń et al., 2000). Generally, a log-213 normal shape may imply that crystal growth follows either Ostwald ripening or random ripening in a closed system, and surface-controlled growth or supply-214 controlled growth in an open system, according to the  $\alpha$  and  $\beta^2$  values (Fig. 9). 215 216 Following the definitions of open or closed systems (see Introduction), the systems 217 discussed in this study are open systems, because the source and the growing crystals 218 are not in the same phase. The source of pMg220 and pNi220 were co-precipitated 219 gels, comprising Mg-saponite and Ni-saponite compositions, respectively; whereas 220 the source of Mg-Ni-saponites (220-400 and 220-500) was the starting material 221 (pMg220+pNi220). Furthermore, the log-normal shape of PSD and reduced PSD 222 profiles for pMg220, pNi220, and 220-400 are heavily skewed to the left (Figs. 6-7), 223 which indicates supply-controlled growth or surface-controlled growth in open 224 systems (Eberl et al., 1998).

The coordinates of  $(\alpha, \beta^2)$  provided more information about the ripening 225 226 processes. For pMg220 and sample 220-400, the coordinates of  $(\alpha, \beta^2)$  (Table 1) in 227 open systems placed them close to the line of surface-controlled growth (Fig. 9). 228 These results are also consistent with the surface-controlled growth of Mg-Ni-229 saponite reported by Zhang et al. (2020). For pMg220, the source refers to the co-230 precipitated gel and the growing crystals of Mg-saponite, whereas for 220-400, the 231 starting material (pMg220+pNi220) is the source and Mg-Ni-saponite form the 232 growing crystals. Surface-controlled growth proceeds through incorporating the 233 species from the dissolution/disarticulation of the source into the growth surface, and 234 the concentration of the species on the growth surface is the same as that in the source 235 (Konak et al., 1974; Eberl et al., 1998). Thus, for pMg220 and 220-400, the 236 dissolution/ disarticulation rate of the source is not the limiting factor (Eberl et al., 237 1998). In such systems, the surface free energy then tends toward a minimum by the 238 dis-articulation/dissolution of the source and growth of the neoformed saponite. As a 239 result, the mean diameter increases (e.g., from 58.2 nm to 79.2 nm in sample 220-400) (Table 1; Fig. 5), and finally, the level of supersaturation in the solution decreases 240 241 (Lifshitz and Slyozov, 1961; Wagner, 1961).

242 For pNi220, the point of  $(\alpha, \beta^2)$  locates on the line of supply-controlled growth 243 in open systems, near the intersection with the line of surface-controlled growth in 244 open systems (Fig. 9). Decarreau (1985) demonstrated that Ni-smectites are generally 245 less soluble than Mg-smectites in a hydrothermal environment. pMg220 and pNi220 246 were synthesised from co-precipitated gels containing "embryos" (germs) of saponite 247 (Zhang et al., 2021). Consequently, Mg-containing gels dissolved more easily than 248 Ni-containing gels. The mean diameter of the pNi220 particles was half that of 249 pMg220 (Table 1), indicating a less efficient crystal growth process for Ni-saponite.

The low kinetics of pNi220 crystal growth are likely linked to the low solubility of Ni-containing gel, which limits the transformation of the gel into Ni-saponite in the aqueous system and induces a partially supply-controlled growth process.

# 253 3.4. Non-classical crystal growth of saponite

254 The PSD and reduced PSD profile of sample 220-500 displayed a mean log-255 normal shape with several small secondary maxima (Fig. 8). However, the coordinate 256 of  $(\alpha, \beta^2)$  for sample 220-500 is placed neither on the surface-controlled line nor the 257 supply-controlled line, suggesting that this sample may undergo complex ripening 258 processes (Fig. 9). Eberl et al. (1998) proposed that agglomeration growth may occur 259 simultaneously with ripening, leading to multimodal distributions. The STEM 260 observations provided direct evidence for attachments between saponite particles (Fig. 261 10). As shown in Figure 10a, a smaller particle (marked by 1) attaches to a larger 262 particle (marked by 2) by their edge surfaces (marked by red arrows), where the gap 263 (red dotted line) suggests that the fusion between both particles is likely ongoing. The 264 irregularly shaped particle in Figure 10b is composed of at least three sub-particles, that is, the elongated lath (labelled "3") and two irregular particles (labelled "1" and 265 266 "2"). In sample 220-500, several secondary maxima resulted from non-classical 267 crystal growth (i.e., particle attachment) (Wang et al., 2014). Thus, both indeterminate ripening and particle attachment were involved in the formation of Mg-Ni-saponite in 268 269 sample 220-500. Particle attachment was also sporadically observed in the STEM 270 images of sample 220-400 (Fig. S1), where saponite growth proceeded via the fusion 271 of the particle edges (red dotted line). Thus, in sample 220-400, particle attachment 272 occurred simultaneously with surface-controlled ripening but was too imperceptible to 273 be recorded by the PSD model (Fig. 7). For two adjacent particles (Figs. 10 and S1), 274 there is the possibility that one particle is preferentially growing at the expense of the other one, because heterogeneity in composition from one particle to another may
drive such preferential dissolution and growth. Such viewpoint could be confirmed by *in situ* observation during saponite growth processes when the technology is feasible.

278 It was reported that crystal growth by particle attachment occurs widely in 279 geochemical, biological, and synthetic material systems (De Yoreo et al., 2015). 280 However, there is little research on the non-traditional growth of clay minerals. 281 García-romero et al. (2018) used a TEM to locate and identify smectite and kaolinite 282 particles that seemed to originate from non-classical crystal growth. Furthermore, the 283 authors proposed for the first time that growth by particle attachment is present in clay 284 minerals, and such growth patterns are related to the depositional environments. 285 Zhang et al. (2020) found that the size of Mg-Ni-saponite layers significantly 286 increased with a slight increase in the degree of dissolution in its corresponding 287 precursors, and proposed the existence of non-classical growth during the formation 288 of Mg-Ni-saponite in a hydrothermal synthesis system. He et al. (2021) performed 289 TEM on natural biotite, natural muscovite, and synthetic fluorophlogopite. Their 290 results showed that in addition to the traditional crystal growth mechanism, the 291 oriented attachment of particles is common in the growth process of mica. A non-292 classical crystallisation model was proposed for the formation of phyllosilicates at 293 elevated temperatures in magmatic and metamorphic environments, where the 294 oriented attachment of building blocks occurs; frequently along the (001) plane or the [001] direction, or both simultaneously (He et al., 2021). Such a study not only 295 296 showed that non-classical crystal growth patterns are widespread in phyllosilicates, 297 but also extended the observations of particle attachment to magma and high-grade 298 metamorphic processes. In this study, the combination of PSDs and morphology 299 provided evidence that the non-classical growth of clay minerals may exist in hightemperature hydrothermal environments. These results provide important references
for further research on the genesis of complex clay minerals and related geochemical
processes.

303 3.5. Crystal growth process

Meunier (2006) had applied the periodic bond chain (PBC) theory of Hartman (1973) to the crystal growth in clay minerals, which essentially implied a twodimensional extension of clay minerals within the (001) plane. For smectite, it is not clear whether the extensional crystals are composed of stacked multi-layers or a single layer (Meunier, 2006; Decarreau et al., 2014).

309 In this study, in the saponite synthesised at 220°C, it appears that the well-310 dispersed particles are single layers (Fig. 4). For saponite, the hydrated interlayer 311 cations could hinder a stack and thus the dominant growth pattern is the two-312 dimensional lateral growth of single layer (or a few layers). These saponite layers 313 stack layer by layer randomly during the process of water loss, leading to 314 heterogeneous saponite particles. In the sample synthesised at 500°C, some observed 315 particles clearly consisted of several stacked layers (Fig. 10), suggesting a different 316 crystal growth process. The XRD patterns of 220-500 indicated the occurrence of 317 talc-like layers (Fig. 3), which have low (no) interlayer charge and easily stack into 318 relatively homogeneous crystals with similar dissolution/growth behaviour. 319 Consequently, 220-500 can grow following, at least partly, a three-dimensional 320 structure, similar to other clay minerals.

The PBCs present in this study were those within the (001) plane, that is, the PBCs of [100], [110], and [ $\overline{1}10$ ]. The growth faces of the crystal were observed lying parallel to one or more continuous PBCs. Al distribution can affect the shape of 324 saponite by controlling the development of PBCs (Meunier, 2006). In this study,
325 saponite with a very low charge (0.3) most likely led to the heterogeneous distribution
326 of tetrahedral Al, which induced defects in the saponite layers. Such defects may
327 hinder the development of PBCs in saponite structures. The occurrence of elongated
328 laths in saponites (pMg220, 220-400, and 220-500) likely suggests that only one PBC
329 is favoured in the saponite structure. For Ni-saponite (pNi220), the small layers with a
330 relatively regular shapes like hexagons may indicate that all PBCs are affected.

#### **331 4.** Conclusions

332 The present study combines the PSD model and STEM observations to 333 investigate the growth processes of synthetic saponite. The results have indicated that 334 saponite particle growth proceeds mainly via surface-controlled growth and possibly 335 via supply-controlled growth in closed systems, based on the shape of the PSDs and the plotted coordinates of  $(\alpha, \beta^2)$  following Eberl et al. (1998)'s model. Particle 336 337 attachment, which leads to a multimodal PSD shape, is probably a corresponding 338 growth mechanism. The heterogeneous Al distribution of the low-charge saponite 339 could lead to the formation of elongated laths, and talc-like layers which favour the 340 "three-dimensional growth" of saponite in high-temperature environments.

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461 Fig. 1. Schematic measurement process of saponite particle size (diameter) in the *ab*-

plane.



468 Fig. 2. Powder XRD patterns of synthetic Mg-saponite (pMg220) and Ni-saponite



(pNi220) precursors.

482 Fig. 4. STEM images of synthetic precursors: (a) Mg-saponite (pMg220), and (b) Ni483 saponite (pNi220).



491 Fig. 5. STEM images of the starting materials (a) (pMg220+pNi220), (b) sample 220-

- 492 400, and (c) sample 220-500.









Fig. 7. PSD (a) and PSD reduced profile (b) of sample 220-400.





Fig. 8. PSD (a) and PSD reduced profile (b) of sample 220-500.





508 Fig. 9. Simple diagram of variations in  $\alpha - \beta^2$  of synthetic Mg-saponite (pMg220), Ni-

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saponite (pNi220), and Mg–Ni-saponite (220-400, and 220-500), plotted on the
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510 diagram of Eberl et al. (1998).

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	a b contraction of the second
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515	Fig. 10. STEM images of characteristic particle attachment in sample 220-500.
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Table 1. Mean diameter in *ab*-plane of particles,  $\alpha$ ,  $\beta^2$  of synthetic saponites.  $\alpha$  and  $\beta^2$ are the mean and variance of the natural logarithms of the observed diameters, respectively.

Samples	Mean diameter	a	ß <sup>2</sup>
	(nm)	u	þ
pMg220	87.2	4.24	0.454
pNi220	36.7	3.40	0.177
pMg220+pNi220	58.2	/	/
220-400	79.2	4.20	0.325
220-500	156.8	4.88	0.312

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