



**HAL**  
open science

## The evolution of saponite: An experimental study based on crystal chemistry and crystal growth

Chaoqun Zhang, Hongping He, Sabine Petit, Fabien Baron, Q I Tao, Brian Gregoire, Jianxi Zhu, Yiping Yang, Shichao Ji, And Shangying Li

► **To cite this version:**

Chaoqun Zhang, Hongping He, Sabine Petit, Fabien Baron, Q I Tao, et al.. The evolution of saponite: An experimental study based on crystal chemistry and crystal growth. *The American Mineralogist*, 2020, 10.2138/am-2021-7625 . hal-03006209

**HAL Id: hal-03006209**

**<https://hal.science/hal-03006209v1>**

Submitted on 15 Nov 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Revision 1

### The evolution of saponite: An experimental study based on crystal chemistry and crystal growth

CHAOQUN ZHANG<sup>1,2,3</sup>, HONGPING HE<sup>1,3,\*</sup>, SABINE PETIT<sup>2,\*</sup>, FABIEN BARON<sup>2</sup>,  
QI TAO<sup>1</sup>, BRIAN GREGOIRE<sup>2</sup>, JIANXI ZHU<sup>1,3</sup>, YIPING YANG<sup>1,3</sup>, SHICHAO JI<sup>1,3</sup>,  
AND SHANGYING LI<sup>1,3</sup>

<sup>1</sup> CAS Key Laboratory of Mineralogy and Metallogeny/Guangdong Provincial Key  
Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry,  
Chinese Academy of Sciences, Guangzhou 510640, China

<sup>2</sup> Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), UMR 7285 CNRS,  
Université de Poitiers, F-86073 Poitiers Cedex 9, France

<sup>3</sup> University of Chinese Academy of Sciences, Beijing 100049, China

### Corresponding Authors

Prof. Hongping He

Present address:

Guangzhou Institute of Geochemistry, Chinese Academy of Sciences,  
Guangzhou 510640, China.

\*E-mail: [hehp@gig.ac.cn](mailto:hehp@gig.ac.cn)

19

Prof. Sabine PETIT

Present address:

UMR 7285 CNRS, Université de Poitiers, F-86073 Poitiers Cedex 9, France.

23 \*E-mail: [sabine.petit@univ-poitiers.fr](mailto:sabine.petit@univ-poitiers.fr)

24

## ABSTRACT

25 Element incorporation and partitioning during the evolution of clay minerals have  
26 significant implications for element cycling in geochemical processes. The main aim of  
27 this experimental study is to expand our understanding of element redistribution and  
28 crystal growth during smectite evolution under different physicochemical conditions. The  
29 precursors (i.e., pure Mg- and Ni-saponite) were separately prepared by hydrothermal  
30 syntheses at the same set of temperatures (i.e., RT, 50, 150, 180, 200, and 220 °C) for one  
31 day. Then the starting materials were obtained from the mechanical mixtures of the  
32 identical molar weight of Mg- and Ni-smectite precursors prepared at the same  
33 temperature. Subsequently, Series I samples were obtained by hydrothermally treating  
34 different starting materials at 220 °C for two weeks while Series II samples were  
35 hydrothermally synthesized under various temperatures (220, 300, 400, and 500 °C) for  
36 one week by using the starting materials prepared at 220 °C. Both the precursors and the  
37 resultant saponites were characterized by XRD, FTIR, TEM, and STEM. The FTIR  
38 spectra of the precursors only exhibit the  $\nu\text{Mg}_3\text{OH}$  and  $\nu\text{Ni}_3\text{OH}$  bands, corresponding to  
39 Mg-saponite and Ni-saponite, respectively. However, the occurrence of  $\nu\text{Mg}_2\text{NiOH}$  and  
40  $\nu\text{Ni}_2\text{MgOH}$  bands in the resultant saponite indicates the dissolution of the corresponding  
41 Mg- and Ni-saponite precursors and recrystallization of Mg-Ni mixed saponite. The  
42 dissolution extents of Mg- and Ni-saponite precursors, which affect the degrees of  
43 random distribution of octahedral Ni and Mg in resultant Mg,Ni-saponite, are  
44 significantly controlled by the temperature gap ( $\Delta T$ ) between the precursors prepared and  
45 the resultant Mg,Ni-saponite obtained. In general, a larger  $\Delta T$  leads to a higher  
46 dissolution extent of saponite precursors and a higher degree of random distribution of

47 octahedral Ni and Mg cations in the resultant Mg,Ni-saponite. Thus, the distribution  
48 mode of octahedral cations in saponite, which is not only relevant to a given  
49 hydrothermal temperature but also dependent on  $\Delta T$  for final products, cannot be used as  
50 a geothermometer. TEM and STEM observations provide visual evidence that the  
51 particles of saponite coarsen when  $\Delta T$  is higher than zero. Both the crystal-chemistry and  
52 morphological features during saponite evolution suggest that saponite particles coarsen  
53 mainly via partial/complete dissolution of precursors followed by recrystallization and  
54 growth of Mg,Ni-saponite, in which crystal growth by layer attachment cannot be  
55 excluded. This study presents an experimental model to evaluate the evolution of clay  
56 minerals by crystal-chemistry and crystal growth and offers a better understanding of the  
57 contributions of clay mineral evolution to the element cycling.

58 **Keywords:** smectite, crystal growth, crystal chemistry, cation distribution, clay evolution

59

60

61

62

63

64

65

66

67

68

## INTRODUCTION

69 Smectites, which are ubiquitous on Earth's surface, have received particular  
70 attention because of their geochemical significance and wide applications in industry  
71 (Brigatti et al., 2013). At and near the surface of the Earth, smectites can survive over a  
72 wide range of temperature, pressure, and solution concentration conditions (Tardy et al.,  
73 1987). They can form via weathering as well as diagenesis and hydrothermal alteration of  
74 volcanic glass and other rocks (Eberl, 1984; Merriman, 2005; Voigt et al., 2020). These  
75 formation pathways usually involve a crucial process, element incorporation and  
76 partitioning during smectite growth (Christidis and Huff, 2009; Hazen et al., 2013). Thus,  
77 smectite is not only a reactive template but also a metastable component that will  
78 transform into other minerals in nature. Their evolution is of great importance in  
79 understanding geochemical behaviors of elements and related mineralization in  
80 hypergenic processes, as well as inferring paleo-environment changes in the Earth's  
81 history (Galán and Ferrell, 2013).

82 Weathering usually yields non-crystalline or nanoparticle smectites, which tend to  
83 grow into larger smectite particles when exposed to diagenetic-hydrothermal  
84 environments or buried in sedimentary environments. These processes result in variations  
85 in crystal-chemistry and morphology of smectite, due to physicochemical condition  
86 changes that frequently occur in natural systems (Eberl, 1984; Merriman, 2005; Galán  
87 and Ferrell, 2013). Previous studies have reported that smectites evolve from poorly  
88 crystalline precursors in various environments (Zhou and Fyfe, 1989; Banfield and  
89 Eqqleton, 1990; Kawano and Tomita, 1992; Christidis, 2001; Christidis and Huff, 2009;  
90 Baldermann et al., 2015; Cuadros et al., 2017; Zhang et al., 2020), which is important for

91 the geochemical budget for the elements such as Si, Al, Fe, and Mg. However, literature  
92 dedicated to such evolution mainly focused on the alterations of primary minerals into  
93 smectites instead of the evolution of smectites themselves. So far, very limited studies  
94 have been devoted to the cognition of smectite self-evolution (Christidis, 2001;  
95 Baldermann et al., 2015; Zhang et al., 2020). Christidis (2001) attempted to develop the  
96 growth patterns of natural smectite via morphological analyses. Baldermann et al. (2015)  
97 have reported on the evolution of particle size and crystal chemistry of synthetic Fe/Mg-  
98 saponite. Recently, we highlighted the growth kinetics of smectite by investigating cation  
99 distribution and morphology evolution (Zhang et al., 2020). These studies have greatly  
100 enhanced our understanding of smectite evolution, but many questions remain  
101 unanswered. One of these questions is how the cation distribution and morphology of  
102 smectites evolve under different physicochemical conditions.

103 In view of uncontrollable compositions of natural smectites and mature researches  
104 about smectite synthesis (Kloprogge et al., 1999; Zhang et al., 2010; Petit et al., 2017),  
105 we chose synthetic smectites as the research objects and focused on their crystal  
106 chemistry and morphology under different physicochemical conditions to answer the  
107 question mentioned above. Saponite is easy-synthesized tri-octahedral smectite, with  
108 ideal structural formula  $\text{Na}_x[\text{Si}_{4-x}\text{Al}_x][\text{M}_3]\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , where M corresponds to  
109 divalent cations; x is the fraction of aluminum present in the tetrahedral sheet (generally  
110  $0.3 \leq x \leq 0.6$ ); Na is the interlayer cation compensating the tetrahedral charge; and n is the  
111 number of interlayer water molecules (Brigatti et al., 2013). In the octahedral sheet, each  
112 OH group is linked to three neighboring M atoms, which allows systematically  
113 investigating the octahedral cations distribution in clay minerals via recording the

114 stretching vibration of structural OH (Petit and Madejová, 2013). Hence, the synthesis of  
115 saponite is advantageous to investigate smectite evolution, notably during the early-stage  
116 growth, which is scarcely observed in nature. Based on our previous study about  
117 morphology and crystal-chemistry of saponite with the change of hydrothermal time  
118 (Zhang et al., 2020), we further expand on the evolution trend of saponite by using the  
119 parameters of crystal-chemistry and crystal growth of saponite with the change of  
120 hydrothermal temperature in present study. The Mg- and Ni- saponite system was chosen  
121 as the study of object because they can be easily synthesized. Meanwhile, Mg-saponite  
122 and Ni-saponite have very similar structure due to the similar radii of  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$   
123 whereas the different atomic mass of Mg and Ni are meaningful to perform crystal-  
124 chemistry analysis. Two series of saponites were hydrothermally synthesized. Series I  
125 was obtained by hydrothermal treating different starting materials previously formed at  
126 various temperatures (RT, 50, 150, 180, 200, and 220 °C) at 220 °C for two weeks.  
127 Whereas the Series II was obtained by hydrothermal treating the same starting material  
128 synthesized at 220 °C for one week at various temperatures (220, 300, 400, and 500 °C).  
129 The crystal-chemistry, including chemical composition and ions distribution, was  
130 characterized by Fourier Transform Infrared (FTIR), X-ray energy-dispersive  
131 spectroscopy (EDS), and High-angle annular dark-field scanning transmission electron  
132 microscopy (HAADF-STEM). The morphology related to the crystal growth was  
133 investigated by transmission electron microscopy (TEM).

## 134 **MATERIALS AND METHODS**

### 135 **Synthesis of Mg- and Ni-saponite precursors**

136 Mg- and Ni-saponite precursors were prepared using the method described by He  
137 et al. (2014). The co-precipitated gel with a theoretical molar ratio of Si:Al:Mg =  
138 3.7:0.3:3 was obtained by mixing solutions of  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  
139  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Then, the gel was collected by filtration and gently washed with deionized  
140 water to remove the excess of salt. The wet gel was transferred to a  
141 polytetrafluoroethylene-lined autoclave, and 30 ml of deionized water was added into the  
142 autoclave. The resultant mixture was hydrothermally treated at different temperatures  
143 (RT, 50, 150, 180, 200, and 220 °C) for one day under equilibrium vapor pressure. The  
144 hydrothermal products, named as pMgx (x= gel, 50, 150, 180, 200, and 220), were  
145 obtained after filtration and dried at 45°C. Ni-saponite precursors were prepared by using  
146 the same method as above-mentioned with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  added instead of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .  
147 The resultant products were named as pNix (x= gel, 50, 150, 180, 200, and 220). The  
148 chemical formulae for Mg-saponite and Ni-saponite precursors can be expressed as  
149  $(\text{Si}_{3.7}\text{Al}_{0.3})^{\text{IV}}(\text{Mg}_3)^{\text{VI}}\text{O}_{10}(\text{OH})_2 \cdot 0.3\text{Na}^+$  and  $(\text{Si}_{3.7}\text{Al}_{0.3})^{\text{IV}}(\text{Ni}_3)^{\text{VI}}\text{O}_{10}(\text{OH})_2 \cdot 0.3\text{Na}^+$ ,  
150 respectively, based on their chemical compositions (He et al., 2014).

### 151 **Synthesis of Mg,Ni-saponite**

152 In the syntheses of Mg,Ni-saponite samples, the starting material was prepared by  
153 mixing an identical molar weight of Mg- and Ni-saponite precursors synthesized at the  
154 same temperature (e.g., pMg150 and pNi150). The detailed experimental procedure is as  
155 follows: the mixture of 0.11g Mg-saponite precursor (pMgx) and 0.14 g Ni-saponite  
156 precursor (pNix) was added to 30 ml of deionized water at room temperature and kept  
157 continuous stirring for one day for complete dispersion. By using the same method, a set  
158 of mixtures were prepared, i.e., the mixtures of pMg-gel and pNi-gel, pMg50 and pNi50,

159 pMg150 and pNi150, pMg180 and pNi180, pMg200 and pNi200, and pMg220 and  
160 pNi220. These mixtures were used as the starting materials for further syntheses of  
161 Mg,Ni-saponite under different hydrothermal conditions.

162 **Syntheses of Series I samples.** Every mixture was transferred to a  
163 polytetrafluoroethylene-lined autoclave and treated at 220 °C for two weeks (Table 1).  
164 The products were washed by deionized water, collected by filtration, and dried at 45 °C.  
165 The obtained samples were named as T-220, where T stands for the temperature in  
166 precursor preparation. For example, sample 150-220 means that the saponite was  
167 synthesized at 220 °C, using the Mg- and Ni-saponite precursors that were prepared at  
168 150 °C as starting materials.

169 **Syntheses of Series II samples.** Four identical mixtures of pMg220 and pNi220  
170 were prepared as the above-mentioned method. Each mixture containing 30 ml of  
171 deionized water was transferred to a 56 ml volume gold tube, sealed by using high-  
172 temperature flame. Then, these sealed gold tubes were put into the high-temperature  
173 heating jackets that were pre-set at different temperatures (220, 300, 400, and 500 °C)  
174 and were heated for one week. The obtained products were washed by filtration, dried at  
175 45 °C, and named as 220-T (T stands for the hydrothermal temperature of the product).

## 176 **Analysis methods**

177 **X-ray diffraction.** Powder X-ray diffraction (XRD) patterns were obtained on a  
178 Bruker D8 advance diffractometer (CuK $\alpha$  radiation, 40 kV and 40 mA) over the range of  
179 2-65° (2 $\theta$ ) with 0.025° (2 $\theta$ ) step size and 0.6 s per step, while the patterns of the oriented  
180 samples and glycolated samples were collected over the range of 2-15° (2 $\theta$ ). The  
181 randomly oriented samples were prepared by pressing saponite powder inside a cavity up

182 to the reference level of the sample holders. The oriented samples were prepared by  
183 carefully pipetting the clay suspension onto a glass slide and allowing it to dry at ambient  
184 temperature. Glycolated samples were prepared by treating the oriented samples in a  
185 glass desiccator with ethylene glycol at 20 °C for 24 h.

186 **FTIR spectra.** Fourier Transform Infrared (FTIR) spectroscopy is available to  
187 study the growth process of saponite by a crystal-chemistry approach. Because OH  
188 vibrations are affected by octahedral cations to which the OH group is coordinated, the  
189 structural OH stretching vibration ( $\nu$ OH) bands allow probing the octahedral environment  
190 (Petit and Madejová, 2013). Thus, the  $\nu$ OH bands in the middle infrared (MIR) region  
191 can be used to determine the crystal-chemistry associated with the evolution process of  
192 saponite. In this study, a Magna-IR 6700 Nicolet spectrometer was used for MIR spectra  
193 over the range 400-4000  $\text{cm}^{-1}$ , with an EverGlo source, a CsI beam splitter, a DTGS-CsI  
194 detector and a resolution of 4  $\text{cm}^{-1}$  with co-additions of 100 scans. MIR spectra were  
195 obtained in transmission through KBr pellets, prepared with 1 mg of sample and 150 mg  
196 of KBr salt. The mixture was pressed for 5 min at 8 kbar and dried overnight in an oven  
197 at 150 °C. Spectral manipulations were performed using the OMNIC software package.  
198 To determine the octahedral cation distribution in the synthesized saponites,  
199 decomposition and curve-fitting have been used to obtain the integrated intensities (S) of  
200 the different OH-stretching bands. The S of the bands is proportional to the concentration  
201 of absorbing centers of the given OH types, assuming that the absorption coefficients are  
202 constant for all metal OH stretching vibration bands (e.g., Slonimskaya et al., 1986; Petit  
203 et al., 2004; Madejová et al., 2017). The decomposition of the spectral envelop into bands  
204 was undertaken by the Peakfit software package, using four Gauss–Lorentz cross-product

205 functions corresponding to the four possible environments associated with structural OH  
206 stretching vibrations ( $\text{Mg}_3\text{OH}$ ,  $\text{Mg}_2\text{NiOH}$ ,  $\text{MgNi}_2\text{OH}$ , and  $\text{Ni}_3\text{OH}$ ). The experimental  
207 spectra were iteratively fitted by fixing the four central positions of four frequencies of  
208 structural OH stretching vibrations until the squared correlation coefficients  $r^2 \geq 0.995$ .  
209 Then, the band positions and area were extracted. The degree of random distribution of  
210 octahedral cations in octahedral sheet of the synthesized saponites ( $R_{(\text{IR})}$ ) was measured  
211 by the ratio of the S of the bands that involve neighboring Mg and Ni cations to the total  
212 S of the structural OH stretching vibrations, i.e.,  $R_{(\text{IR})} = (S_{\nu\text{Mg}_2\text{NiOH}} + S_{\nu\text{Ni}_2\text{MgOH}}) /$   
213  $(S_{\nu\text{Mg}_3\text{OH}} + S_{\nu\text{Mg}_2\text{NiOH}} + S_{\nu\text{Ni}_2\text{MgOH}} + S_{\nu\text{Ni}_3\text{OH}})$ . When the same number of Mg  
214 and Ni randomly distributes in three vacancies around structural OH, the corresponding  
215 theoretical ratio is 0.125 for  $\text{Mg}_3\text{OH}$  and 0.125 for  $\text{Ni}_3\text{OH}$ , 0.375 for  $\text{Mg}_2\text{NiOH}$  and 0.375  
216 for  $\text{Ni}_2\text{MgOH}$ ; thus  $R_{(\text{theory})}$  equals 0.75 (Zhang et al., 2020). Correspondingly, the  
217 dissolution extent (i.e., the dissolution ratio of precursors) can be estimated by  
218  $R_{(\text{IR})}/R_{(\text{theory})}$ .

219 **STEM-EDS.** High-angle annular dark-field scanning transmission electron  
220 microscopy (HAADF-STEM) observations were performed to investigate the  
221 morphology in the *ab* direction of the saponite particles. 1 mg sample was soaked into 10  
222 ml deionized water with slightly stirring for one week to obtain a dilute colloidal  
223 suspension. Specimens were prepared by dispersing the colloidal suspension in 40 ml  
224 ethanol and ultrasonically treating for 30 min. A drop of the resultant suspension was  
225 placed on a porous carbon film supported by a copper grid, then the water and ethanol  
226 were evaporated. STEM images were obtained using a FEI Talos F200S high-resolution  
227 transmission electron microscope (HRTEM) operated at 200 kV. For the HRTEM

228 investigation of the particle size and the lattice fringe along the [001] direction, oriented  
229 samples were embedded in epoxy resin for the preparation of ultrathin sections.  
230 Subsequently, ultrathin sections (~50 nm) were obtained using an ultramicrotome (Leica  
231 EM UC7) with a diamond knife and transferred onto holey carbon-coated TEM copper  
232 grids. HRTEM images and X-ray energy-dispersive spectroscopy (EDS) were carried out  
233 using a FEI Talos F200S high-resolution transmission electron microscope equipped with  
234 Super-X X-ray spectroscopy and operated at 200 kV. The beam diameter for EDS  
235 analyses is about 5 nm. The relative contents of Mg and Ni were collected from ultrathin-  
236 section samples by STEM-EDS as follows: the contents of Mg and Ni at different  
237 positions within one particle was measured, plotting the corresponding Mg/(Mg + Ni)  
238 value on the graph to obtain a variation trend. Then variation trends of Mg/(Mg + Ni) of  
239 numerous randomly selected particles from one sample were summarized into one graph.

## 240 **RESULTS**

### 241 **Mg- and Ni-saponite precursors**

242 Powder XRD patterns of the Mg- and Ni-saponite precursors display  
243 characteristic reflections of trioctahedral smectites with the (001) reflection at ~1.25 nm,  
244 the (06,33) at 0.153 nm and asymmetric (*hk*) bands (Fig. 1) (Brindley, 1966; Borchardt,  
245 1989). The reflections of the saponite precursors became narrow and symmetric with the  
246 increase of hydrothermal temperatures. For the precursors synthesized below 50 °C,  
247 unrecognized reflections suggest that the products are non-crystalline. For the products  
248 synthesized between 50 and 180 °C, weak and broad reflections of (02,11), (13,20), and  
249 (06,33) were recorded, whereas the (001) basal reflection was still not well recognized.  
250 This suggests the formation of TOT layers of saponite but poor layer stacking along the *c*

251 direction. However, when the hydrothermal temperature increased to 200 °C, both  
252 distinct (001) reflection and the reflections related to *ab* planes were exhibited, indicating  
253 the formation of well-crystallized saponite. Both the evolutions of Mg- and Ni-saponite  
254 precursors are similar, consistent with those reported in the literature (Decarreau et al.,  
255 2008; Petit et al., 2008; He et al., 2014).

256 The FTIR spectra of the synthetic precursors are also similar to those reported in  
257 the literature for Ni- and Mg-saponites (Zhang et al., 2020). The band at 3678 cm<sup>-1</sup> in all  
258 Mg-saponite precursors (Fig. 2a) and 3629 cm<sup>-1</sup> in all Ni-saponite precursors (Fig. 2b) are  
259 assigned to the stretching vibrations of Mg<sub>3</sub>OH ( $\nu$ Mg<sub>3</sub>OH) and Ni<sub>3</sub>OH ( $\nu$ Ni<sub>3</sub>OH),  
260 respectively. Both the bands tend to become narrower and more intense with the increase  
261 of hydrothermal temperature. Concomitantly, the broad band (centered at ~ 3420 cm<sup>-1</sup>),  
262 corresponding to the OH stretching vibration of water molecules, decreases (Fig. 2). The  
263 evolution of the width and the intensity of the structural OH vibrations with the  
264 hydrothermal treatment temperature suggests that a high temperature favours the  
265 crystallization of saponite precursors, consistent with the XRD results. Note that the Al  
266 occupancy in the synthetic saponites has been delicately studied in a previous paper (He  
267 et al., 2014). The results indicate that Al prefers to occupy tetrahedral sites rather than  
268 octahedral sites, and little Al occurs in the octahedral sheets of saponite precursors.

### 269 **Mg,Ni-saponites in Series I**

270 The XRD patterns of the oriented samples display the characteristic reflections of  
271 saponites with a basal spacing at ~ 1.24 nm, which shifts to 1.72 nm after exposure to  
272 ethylene glycol (Fig. 3a) (Suquet et al., 1981; Borchardt, 1989). The ethylene glycolated  
273 samples exhibit rational *00l* reflections, representative of the periodic structure of

274 saponite without any interstratified talc-like layers. The intensity of the basal reflections  
275 of samples gel-220, 50-220, and 150-220 is higher than that of samples 180-220, 200-220,  
276 and 220-220, suggesting the layer stacking in the former (i.e., samples gel-220, 50-220,  
277 and 150-220) is more ordered than that in the latter (i.e., samples 180-220, 200-220, and  
278 220-220).

279 In clay minerals, the OH stretching vibrations are closely associated with the  
280 octahedral cations that are coordinated to the hydroxyl groups. For the Mg,Ni-saponite  
281 synthesized in the present study, up to four OH stretching vibrations with different  
282 wavenumbers (i.e., 3675, 3663, 3648, and 3628  $\text{cm}^{-1}$ ) can be distinguished, depending on  
283 the distribution of  $\text{Mg}^{2+}$  and  $\text{Ni}^{2+}$  in octahedral sites. These vibrations correspond to the  
284 four possible combinations of the two different cations distributed in the three octahedral  
285 sites within one structural unit, i.e.,  $\text{Mg}_3\text{OH}$ ,  $\text{Mg}_2\text{NiOH}$ ,  $\text{MgNi}_2\text{OH}$ , and  $\text{Ni}_3\text{OH}$  (Zhang et  
286 al., 2020). In the FTIR spectrum of sample 220-220 of which the temperatures for the  
287 precursors' syntheses and subsequent hydrothermal treatment are the same (i.e., the  
288 temperature gap,  $\Delta T$ , is zero), only two prominent vibrations are recorded at 3675 and  
289 3628  $\text{cm}^{-1}$ , attributed to  $\nu\text{Mg}_3\text{OH}$  and  $\nu\text{Ni}_3\text{OH}$ , respectively (Fig. 4a). However, with an  
290 increase of the temperature gap ( $\Delta T$ ) from sample 200-220 to gel-220, four OH stretching  
291 vibrations at 3675, 3663, 3648, and 3628  $\text{cm}^{-1}$  were displayed with a prominent intensity  
292 decrease of  $\nu\text{Mg}_3\text{OH}$  and  $\nu\text{Ni}_3\text{OH}$  and a simultaneous intensity increase of  $\nu\text{Mg}_2\text{NiOH}$   
293 and  $\nu\text{MgNi}_2\text{OH}$ . For samples 50-220 and gel-220, the band intensities of  $\nu\text{Mg}_2\text{NiOH}$  and  
294  $\nu\text{MgNi}_2\text{OH}$  are much stronger than those of  $\nu\text{Mg}_3\text{OH}$  and  $\nu\text{Ni}_3\text{OH}$ .

295 HRTEM images of ultrathin sections of both the precursors and the corresponding  
296 synthetic Mg,Ni-saponites provide information about particle size and layer stacking

297 (dis)order of saponite (Fig. 5). The precursors prepared at different temperatures display a  
298 prominent variation in particle size. For pMg50 and pNi50 precursors, no well-ordered  
299 layer stacking was observed, which is consistent with the unresolved (001) reflections in  
300 their XRD patterns (Fig. 5a and b). For the precursors synthesized at higher temperatures  
301 (e.g., 150 and 180 °C), the layer structure is recognizable. For example, in the case of the  
302 precursors synthesized at 150 °C (Fig. 5d and e), the lengths of particles along the *a*- or *b*-  
303 axis are approximately 5 - 30 nm, while the heights along *c*-axis is about 1 - 6 nm (i.e., 1  
304 - 4 layers). The few numbers of stacking layers and widespread monolayers of such  
305 precursors may lead to the absence of (001) reflections in their XRD patterns. The  
306 height/length refer mainly to the size of bundles of saponite particles rather than truly the  
307 size of individual particles because the dispersion of the samples was not complete. With  
308 the rise of hydrothermal temperature, both the height and length of precursor particles  
309 increase (Fig. 5g and h). Note that, after hydrothermally treated at 220 °C for all the  
310 precursors prepared at a low temperature (e.g., gel-220, 150-220 and 180-220), lattice-  
311 fringe images show that the resultant Mg,Ni-saponites consist of bulk crystals with 5 - 15  
312 layers along the *c*-axis and 40 - 150 nm in length (Fig. 4c, f and i). The crystal size of the  
313 resultant saponite is much larger than that of their corresponding precursors, which  
314 indicates crystal growth taking place during the hydrothermal treatment.

315 A summarization of the Mg/(Mg + Ni) ratios at different positions within a  
316 sample can provide evidence for the statistical distribution of Mg and Ni cations. In such  
317 cases, the more the number of points measured, the more reliable the statistical  
318 information of cation distribution will be. Figure 6 shows our STEM-EDS analyses that  
319 were conducted on a randomly selected particle in the ultrathin section of sample gel-220

320 (Fig. 6a) and the Mg/(Mg+Ni) ratios obtained from different positions (Fig. 6b). Our  
321 measurements show that, in general, the Mg/(Mg+Ni) ratios obtained from different  
322 points of one sample were located within a certain value. For instance, the Mg/(Mg+Ni)  
323 ratios of sample gel-220 were located around 0.5 (Fig. 6), suggesting a random  
324 distribution of both Mg and Ni within the saponite. In the same way, a ratio of 1 for  
325 Mg/(Mg+Ni) means that all the octahedral sites in the measured saponite are occupied by  
326 Mg (i.e., Mg-saponite) while a ratio of 0 reflects that all the octahedral sites are occupied  
327 by Ni (i.e., Ni-saponite). Figure 7 exhibits a summary of the Mg/(Mg+Ni) ratios for  
328 saponites prepared from different precursors. For sample gel-220 that was synthesized at  
329 220 °C by using Mg- and Ni-bearing gel, the Mg/(Mg+Ni) ratios well locate around 0.5  
330 (Fig. 7a), indicating that both Mg and Ni are randomly distributed within the saponite. In  
331 the case of sample 150-220 (Fig. 7b), the Mg/(Mg + Ni) ratios slightly deviate from 0.5  
332 but lower than 0.75, implying that the distribution of most Ni and Mg cations is random  
333 but small clusters of Mg- and Ni- saponite may occur in the sample. Note that Figure 7c  
334 displays the (Mg/Mg+Ni) ratios measured on fifteen randomly selected particles in  
335 sample 180-220, and for each particle, at least five points were measured along layer  
336 direction. For this sample, the Mg/(Mg+Ni) ratios obviously deviate from the value of 0.5  
337 and shift to 0 or 1 (Fig. 7c). Such Mg/(Mg+Ni) ratios suggest that domains of Mg- and  
338 Ni-saponite occur in the resultant saponite.

### 339 **Mg,Ni-saponites in Series II**

340 XRD patterns of the resultant saponites in Series II display characteristic (001)  
341 reflections at 1.20 nm, which shifts to ~1.72 nm upon ethylene glycolation (Fig. 3b). For  
342 the oriented samples, the width of the basal reflections tends to decrease with the increase

343 of the synthesis temperature. For the case of sample 220-500, broad and weak reflections  
344 with a d-value of 2.58 nm and 3.07 nm occur before and after ethylene glycolation (Fig.  
345 3b), respectively. The difference between these two values is  $\sim 0.5$  nm, close to the  
346 difference between 1.20 nm and 1.72 nm, presumably due to the occurrence of  
347 interstratified non-swelling layers (Whitney, 1983). In the present experimental system,  
348 the non-swelling layers are probably low-charged saponite which has a talc-like  
349 behaviour favored by the low pre-setted charge of saponite (0.3 per half unit cell)  
350 (Christidis and Mitsis, 2006; Petit et al., 2008; Fonteneau et al., 2020).

351 The FTIR spectrum of sample 220-220 (Fig. 4b) only displays the  $\nu\text{Mg}_3\text{OH}$  and  
352  $\nu\text{Ni}_3\text{OH}$  vibrations at  $3675$  and  $3628\text{ cm}^{-1}$ , respectively. From sample 220-300 to 220-500,  
353 with an increase of  $\Delta T$ , the intensity and resolution of  $\nu\text{Mg}_2\text{NiOH}$  and  $\nu\text{MgNi}_2\text{OH}$   
354 dramatically increase, and those of  $\nu\text{Mg}_3\text{OH}$  and  $\nu\text{Ni}_3\text{OH}$  decrease concomitantly (Fig.  
355 4b). In the case of 220-500, the intensities of  $\nu\text{Mg}_2\text{NiOH}$  and  $\nu\text{MgNi}_2\text{OH}$  are much  
356 stronger than those of  $\nu\text{Mg}_3\text{OH}$  and  $\nu\text{Ni}_3\text{OH}$ , indicating a more random distribution of  
357 octahedral Mg and Ni.

358 HAADF-STEM images of the samples in Series II display prominent  
359 morphological evolution with increasing  $\Delta T$  (Fig. 8). Some big particles with a size of  
360  $\sim 100$  nm and small shapeless particles are observed in sample 220-220 (Fig. 8a) and 220-  
361 300 (Fig. 8b). The particle size in sample 220-300 seems more uniform than that in  
362 sample 220-220. As the hydrothermal temperature increases, the particle size  
363 dramatically increases. In sample 220-400, the size of most particles reaches 200 nm in-  
364 plane, and there are less small particles overlying in comparison to samples 220-220 and  
365 220-300 (Fig. 8c). For sample 220-500, most particles approach 400 nm in size, and

366 particles less than 50 nm are scarcely observed (Fig. 8d). In the samples 220-400 and  
367 220-500, euhedral elongated particles occur with high frequency (Fig. 8c and d). Note  
368 that the HAADF-STEM images of saponite layers in sample 220-400 show the evidence  
369 of micro-phase segregation, with a typical surrounding structure (Fig. 9a) and irregular  
370 patchworks of micro-regions (Fig. 9b). In addition, HRTEM images of ultrathin sections  
371 of the samples in Series II also provide supplementary information about particle size, as  
372 well as dis(order) of layer stacking (Fig. 10). With the increase of hydrothermal  
373 temperature (from sample 220-220 to 220-500), saponite layers along *a*- or *b*-axis extend  
374 and the order of layer stacking along *c*-axis increases. For example, in sample 220-220,  
375 lattice fringe images show most of particles have a length of 50-150 nm and height of 3-  
376 10 layers (Fig. 10a), similar to other samples synthesized at 220 °C (e.g., gel-220, 150-  
377 220, and 180-220), while for sample 220-500, particles more than 250 nm in length and  
378 6-15 layers in height were observed (Fig. 10d). Such results indicate the prominent  
379 increase of particle size with hydrothermal temperature increasing.

## 380 DISCUSSION

### 381 Crystal-chemistry features of saponite

382 As shown by FTIR spectra (Fig. 4), the occurrence of  $\nu\text{Mg}_2\text{NiOH}$  and  $\nu\text{MgNi}_2\text{OH}$   
383 suggests the distribution of Mg and Ni in neighboring octahedral sites in the synthetic  
384 saponites, implying dissolution of Mg- and Ni-saponite precursors and recrystallization of  
385 Mg-Ni mixed saponite (Zhang et al., 2020). Both the distribution feature of Mg and Ni  
386 cations in the Mg,Ni-saponite (i.e., mixing degree of Mg and Ni in octahedral sites) and  
387 the dissolution of Mg- and Ni-saponite precursors can be revealed by  $R_{(\text{IR})}$  that is usually  
388 obtained via decomposition of the structural OH stretching vibrations in FTIR spectra

389 (Zhang et al., 2020). Figure 11 is an example (sample 220-400) for the spectral  
390 deconvolution, and the corresponding  $R_{(IR)}$  value (0.44) and estimated dissolution extent  
391 (0.59) were obtained by using the method described in Materials and Methods. The  
392 calculated  $R_{(IR)}$  values for all the synthetic saponites and dissolution extent indexes of the  
393 corresponding precursors were summarized in Table 2.

394 For the synthetic saponites in Series I, the  $R_{(IR)}$  values increase with an increase in  
395  $\Delta T$ , i.e., from  $\sim 0.00$  for sample 220-220 to 0.63 for sample gel-220. A maximum of  $R_{(IR)}$   
396 value, 0.63, was obtained from the sample gel-220, while that of sample 50-220 is 0.60.  
397 The  $R_{(IR)}$  values of samples gel-220 and 50-220 are close to the theoretical one (0.75) for  
398 saponite in which the distribution of Mg and Ni is totally random. The above-mentioned  
399 deviations are probably due to the inevitable imprecision of the decomposition (Zhang et  
400 al., 2020). Meanwhile, the residual interlayer water may also generate a small band in the  
401 region of structural-OH stretching vibration in FTIR spectra of smectite (Johnston, 2017).  
402 Thus, it can be inferred that the cation distribution in samples gel-220 and 50-220 is  
403 highly random, resulted from the almost complete dissolution of saponite precursors and  
404 subsequent recrystallization taking place during the hydrothermal processes. Our  
405 calculations show that more than 80% of precursors were dissolved, followed by the  
406 recrystallization of Mg,Ni-saponite in samples gel-220 and 50-220 (Table 2). With a  
407 decrease of  $\Delta T$ , the  $R_{(IR)}$  value decreases prominently (Table 2) and that of the sample  
408 220-220 almost reaches zero. The low  $R_{(IR)}$  values suggest the occurrence of clusters of  
409 octahedral Mg and Ni (i.e., Mg- and Ni-domains/layers), instead of a totally random  
410 distribution. The occurrence of Mg- and Ni-domains/layers should be attributed to the  
411 low dissolution extent of Mg- and Ni-saponite precursors.

412           Such variations in the distribution of Mg and Ni are also found in the saponites in  
413 Series II. For example, the  $R_{(IR)}$  of sample 220-500 is 0.58, corresponding to a random  
414 distribution of Mg and Ni in the Mg,Ni-saponite. This should be attributed to a high  
415 precursors' dissolution extent that is about 0.77 (Table 2). For samples 220-300 and 220-  
416 400, partial dissolution of precursors took place during the hydrothermal processes,  
417 resulting in a prominent decrease of  $R_{(IR)}$ . This reflects that the distribution of cations in  
418 octahedral sites is less random in comparison to sample 220-500.

419           Thus, a statistic distribution of cations in the resultant saponites is provided by  
420 FTIR spectra. The STEM-EDS analyses provide local information about the cation  
421 distribution (Figs. 6 and 7). For example, as shown in Figure 6, the ratios of Mg/Mg+Ni  
422 in different locations are fixed at ca. 0.5, showing a relatively homogenous distribution of  
423 Mg and Ni within saponite layers/particles. Similar cation distribution is further  
424 evidenced by STEM-EDS analyses on a large number of randomly selected particles  
425 within the same sample, corresponding to an almost complete dissolution of precursors.  
426 The plot for Mg/Mg+Ni ratios of sample 180-220 seems more 'scattered' with more  
427 points approaching to 1 or 0 in comparison to those of samples gel-220 and 150-220 (Fig.  
428 7a and b). This suggests that the distribution of Mg and Ni in sample 180-220 is not as  
429 homogeneous as that in samples gel-220 and 150-220. The Mg/Mg+Ni value of 1  
430 represent the occurrence of Mg-rich locations while the ratio of 0 correspond to Ni-rich  
431 locations within layers/particles. Mg- or Ni-rich locations in the resultant saponite, are  
432 possibly due to the undissolved Mg- or Ni-saponite precursor units, respectively.

433           HAADF-STEM images of the resultant saponites give further evidence for  
434 segregations of Mg and Ni cations within one single layer. In the case of 220-400, a

435 typical surrounding structure within one layer (Fig. 9a) and some layers from the stitched  
436 micro-regions (Fig. 9b) are observed. Theoretically, the brighter regions could contain  
437 more Ni than the darker ones. According to the FTIR results, the high dissolution extent  
438 (0.59) in this sample indicates most of its precursor dissolve. The micro-regions with  
439 mixed Mg and Ni (i.e., Mg-Ni mixed saponite) from dissolution-recrystallization are  
440 overwhelming, and the relatively small regions could be undissolved precursor units  
441 (Mg-saponite or Ni-saponite). Thus, the lighter rim and the darker inner region  
442 correspond to Mg-Ni mixed saponite and Mg-saponite, respectively (Fig. 9a). Meanwhile,  
443 residual Ni-saponite units attach along the rim of Mg-Ni mixed saponite (Fig. 9b). Here is  
444 the most visible evidence for the heterogeneous distribution of Mg and Ni within one  
445 layer, resulted from the partial dissolution of precursors and recrystallization and growth  
446 of Mg,Ni-saponite. Importantly, such heterogeneity within nano-scale layers offers visual  
447 interpretations for the results from FTIR spectra and EDS results.

#### 448 **Crystal growth processes**

449 The morphological evolution of saponites from Series I (Fig. 5) and Series II  
450 (Figs. 8 and 10) indicates that the crystal particles of saponites coarsen as long as the  
451 hydrothermal temperatures of samples are higher than that of their precursors. In general,  
452 the saponite particles from a higher temperature have a larger size compared to those  
453 from a lower temperature. In addition, the shapes of crystal size distributions (CSDs) of  
454 clay minerals (e.g., smectite, illite/smectite, and illite) are approximately lognormal, and  
455 the overall increase of crystal size can result in a right shift of CSD (Eberl et al., 1990;  
456 Eberl et al., 1998; Zhang et al., 2020). Hence, we assume the ideal CSDs of saponites  
457 synthesized at different temperatures (Fig. 12), in which the dissolution extents are

458 derived from the  $R_{(IR)}$  (Table 2) and the critical size is based on the theory of crystal  
459 growth (i.e., the hydrothermal system with a higher temperature requiring a larger critical  
460 size of particles). When the precursors exposed to a given physicochemical condition, the  
461 particles smaller than the critical size would tend to dissolve to decrease the Gibbs free  
462 energy of the system (e.g., Kelton, 1991). As shown in Figure 12, for the specific  
463 condition of 220 °C, the assumed critical size of saponites is c220. The precursors  
464 synthesized at 50 °C completely dissolve when they are hydrothermally treated at 220 °C,  
465 suggesting that the particle size of the precursors prepared at 50 °C is smaller than c220.  
466 For Series I samples, with the increase of hydrothermal temperature of precursors, the  
467 dissolution extents decreases. This indicates that the precursors synthesized at a higher  
468 temperature have a lower percentage of particles smaller than the critical size (c220),  
469 leading to a lower dissolution (Fig. 12). In Series II, all the samples are synthesized from  
470 the same precursors (i.e., a mixture of pMg220 and pNi220) with identical CSD  
471 (CSD220). Thus, from sample 220-220 to 220-500, the rise of dissolution extents (i.e.,  
472 ~0.00 to 0.77) is related to the subsequent hydrothermal temperatures. The subsequent  
473 hydrothermal system with a higher temperature demands a larger critical size of saponites.  
474 Thus, with an increase of subsequent temperature, the precursors with CSD220 have a  
475 higher percentage of particles smaller than the critical size of the corresponding  
476 hydrothermal system. As a result, the higher the subsequent temperature is, the more the  
477 precursors with CSD220 dissolve (Fig. 12). Meanwhile, the undissolved particles can  
478 grow into stable phases with a larger size and a chemical composition different from that  
479 of the initial phase (Steefel and Van Cappellen, 1990).

480 Saponite growth mechanisms can be determined by its morphological evolution  
481 and crystal-chemistry features. For the samples synthesized through a complete  
482 dissolution of precursors and recrystallization (e.g., gel-220, 50-220, 220-500), the  
483 continuous dissolution of precursors and growth of Mg,Ni-saponite occur during the  
484 hydrothermal treatment, in which the species for saponite growth is provided by the  
485 dissolution of precursors. However, it is very hard to define the specific growth patterns  
486 in such processes due to the lack of kinetic data. Note that the occurrence of non-  
487 expandable layers in the case of 220-500 may be due to the super-high temperature (500  
488 °C) of the hydrothermal system (Whitney, 1983). For other samples (e.g., 150-220, 180-  
489 220, 200-220, 220-300, and 220-400), their corresponding precursors partially dissolve,  
490 depending on  $\Delta T$ . Thus, the species for saponite growth include the dissolved precursors  
491 (i.e., simple chemical species or ions) and residual precursors (i.e., solid saponite  
492 nanoparticles). Correspondingly, the growth mechanisms may involve the traditional  
493 nucleation-growth pathway and particle attachment. Such an assumption is supported by  
494 the previous study about the growth kinetics of saponite (Zhang et al., 2020) and the  
495 HAADF-STEM observations in the present study.

496 The kinetic growth process demonstrated that the saponite layers grow with the  
497 dissolution of small-size saponite layers (Zhang et al., 2020). The growth rate of Mg,Ni-  
498 saponite could be limited by the concentration of growth species on the edges of particles.  
499 In such systems, surface free energy tends toward a minimum by the dissolution of small  
500 layers and the growth of large layers as the matter is transferred from the former to the  
501 latter through the solution. As a result, the small particles gradually disappear, and the  
502 mean crystallite size increases (Lifshitz and Slyozov, 1961; Wagner, 1961). In addition to

503 the traditional growth pattern, i.e., the dissolution of small layers and the growth of large  
504 layers, the attachment of saponite nanoparticles was also involved in the growth pathway  
505 to reduce the free energy of the system based on numerous studies about other minerals  
506 (De Yoreo et al., 2015). Several clues support the existence of nanoparticle attachment  
507 during the kinetic growth process. For example, in sample 150-220, the rate of  $R_{(IR)}$   
508 slightly rises, but the mean particle size dramatically increases from 3 to 14 days,  
509 suggesting saponite growth accompanied by particle attachment (Zhang et al., 2020).  
510 Another very important feature, micro-phase segregation, was found in the resultant  
511 saponite (Fig. 9), which confirms the simultaneous occurrence of dissolution-  
512 recrystallization pathway and crystallization of particle attachment. Sample 220-400 is a  
513 typical example with a dissolution extent of its precursors of 0.59 (Table 2), implying that  
514 the dissolution-recrystallization pathway should be the dominant growth mechanism.  
515 These micro-phase distributions within one layer indicate the co-existence of Mg-, Ni-  
516 and Mg-Ni mixed domains, probably resulting from layer attachment. Thus, for all  
517 saponites synthesized through partial dissolution and recrystallization of precursors, their  
518 growth processes may accompany with layer attachment.

### 519 **Evolutionary features of saponite and controlling factors**

520 The changes in temperature will significantly affect the solubility of saponite, pH  
521 and chemistry of solution, which could lead to the evolutions of compositions and  
522 morphology of saponite. In nature, smectites are stable or metastable over geological time  
523 in an unchanged environment but will be destabilized due to the changes in  
524 physicochemical conditions (e.g., chemistry, temperature, pressure, etc.). Changes  
525 running into smectite's environment would bring about the compositional variability and

526 crystal growth of smectite. Records of these changes could provide a useful framework  
527 for interpreting the geochemistry and long-term stability of clay minerals (Tardy et al.,  
528 1987). Present experiments were conducted in a sealed hydrothermal system at different  
529 temperatures. Dissolution and recrystallization are the principal driving forces for all re-  
530 equilibration reactions in the presence of a fluid phase (Putnis, 2009). Thus, when the  
531 saponite precursors that form at a lower temperature are exposed to a higher temperature  
532 fluid, solid-solution reactions tend to take place to reduce the free energy of the whole  
533 system. The neoformed saponite particles are the products of re-equilibration reactions of  
534 the hydrothermal system.

535 In addition to the change of physicochemical conditions, the presence of kinetic  
536 factors (e.g., reaction time, size driven force) may contribute to the smectite evolution.  
537  $R_{(IR)}$  in Series I and II have been expressed in terms of the variations of temperature and  
538 pressure of hydrothermal systems (Table 2, Fig. 13). Interestingly,  $R_{(IR)}$  is probably not  
539 only affected by the changes in physicochemical conditions. For instance, sample 220-  
540 300 ( $\Delta T=80$  °C) necessitates much higher activation energy than sample 150-220 ( $\Delta T=70$   
541 °C) during the hydrothermal processes. In contrast, the former case has a lower  $R_{(IR)}$  (0.24)  
542 than that (0.55) of the latter. In comparison to the samples in Series II, the samples in  
543 Series I have a smaller particle size of starting materials and longer reaction time so that  
544 the kinetic factors contribute more to the dissolution degree. As nano-scale minerals, the  
545 particle size is a key point in determining the energetics and stability of smectite. The  
546 smaller particles with higher surface energy correspond to a higher reactivity and lower  
547 stability as observed for other nano-scale minerals like Fe(III)-[oxi(hydr)] oxide minerals  
548 (Anschutz and Penn, 2005; Madden and Hochella 2005; Hochella et al., 2008; Navrotsky

549 et al., 2008). Therefore, the size driving force may induce the evolution of smectite, even  
550 if there is no change of physicochemical conditions.

## 551 **IMPLICATIONS**

552 Our study indicates that the distribution mode of octahedral cations in saponite is  
553 not only relevant to a given hydrothermal temperature but also dependent on  $\Delta T$  for final  
554 products. In nature, large Ni clusters were systematically observed in natural (Ni-Mg)-  
555 phyllosilicates formed at a low temperature in lateritic weathering profiles (Gérard and  
556 Herbillon, 1983; Manceau and Calas, 1985; Decarreau et al., 1987). During the synthesis  
557 of clay minerals, when the temperature of synthesis decreases, a tendency to clustering  
558 was also observed and specially marked for Ni atoms (Decarreau et al., 1992). These  
559 previous results indicated that segregation is frequently observed in clay minerals formed  
560 at low temperatures, thereby the distribution type could be temperature-dependent.  
561 However, our experiments give information that the element distributions within clay  
562 minerals are also related to the synthesis temperature gap between starting materials and  
563 resultant products. Larger Mg- or Ni- clusters can form when the respective synthesis  
564 temperatures of the starting materials and the resultant products are close (i.e., low  $\Delta T$ ).  
565 Thus, the clustering is not only related to given temperature conditions but also to the  
566 characteristics of the starting materials in terms of crystallinity and particle size.  
567 Consequently, the distribution mode of octahedral cations in saponite can not be used as a  
568 geothermometer. Such results also indicate the various isomorphous substitutions or solid  
569 solutions in natural clay minerals are probably related to the properties of raw materials.

570 Weathering may yield clay minerals with poor crystalline and small particles,  
571 which could transport into sedimentary environments (Wilson and Jones, 1983; Galán

572 and Ferrell, 2013). Clay minerals deposited in a sedimentary environment (e.g.,  
573 subsiding basin) are buried, heated, and eventually enter diagenetic-hydrothermal  
574 environments (Eberl, 1984; Merriman, 2005). As the environment changes, the most  
575 important reactions are phase transformation and crystal growth, accompanied by cation  
576 redistribution. Crystal-chemistry and crystal growth could be used to predict the  
577 environmental transition and element migration. The experimental system used here was  
578 very simple compared to natural systems that are far much complex. However, it was  
579 possible to describe smectite evolution by element redistribution and growth. In nature,  
580 such evolutions of clay minerals are difficult to capture in the early geological stage.  
581 Similar experiments with more complexities could offer potentials to predict the mineral  
582 geochemistry and better understand and parametrize natural processes.

583

#### ACKNOWLEDGMENT

584 The authors acknowledge A. Decarreau for the discussions that enriched this paper. The  
585 financial supports of National Natural Science Foundation of China (Grant Nos.  
586 41921003, 41530313, 41772039), National Science Fund for Distinguished Young  
587 Scholars of China (Grant No.41825003), Key Research Program of Frontier Sciences,  
588 CAS (Grant No. QYZDJ-SSW-DQC023), the European Union (ERDF), "Région  
589 Nouvelle Aquitaine," French « Ministère de l'Enseignement Supérieur et de la  
590 Recherche », and China Scholarship Council are much appreciated.

591

#### REFERENCES

592 Anschutz, A.J., and Penn, R.L. (2005) Reduction of crystalline iron (III) oxyhydroxides using  
593 hydroquinone: Influence of phase and particle size. *Geochemical Transactions*, 6(3), 60.

- 594 Baldermann, A., Warr, L.N., Letofskypapst, I., and Mavromatis, V. (2015) Substantial iron sequestration  
595 during green-clay authigenesis in modern deep-sea sediments. *Nature Geoscience*, 8(11), 885-889.
- 596 Banfield, J.F., and Eggleton, R.A. (1990) Analytical transmission electron microscope studies of  
597 plagioclase, muscovite, and K-feldspar weathering. *Clays and Clay Minerals*, 38(1), 77-89.
- 598 Brigatti, M.F., Galan, E., and Theng, B.K.G. (2006) Chapter 2 - Structures and Mineralogy of Clay  
599 Minerals. In F. Bergaya, B.K.G. Theng, and G. Lagaly, Eds. *Developments in Clay Science*, 1, p.  
600 19-86. Elsevier.
- 601 Brindley, G. (1966) Ethylene glycol and glycerol complexes of smectites and vermiculites. *Clay Minerals*,  
602 6(4), 237-259.
- 603 Borchardt, G. (1989) Chapter 14 - Smectites. In J.B. Dixon and S.B. Weed, Eds. *Minerals in soil*  
604 environments, 1, p. 675-727. Wiley.
- 605 Cuadros, J., Andrade, G.R.P., Ferreira, T.O., Partiti, C.S.D.M., Cohen, R., and Vidaltorradó, P. (2017) The  
606 mangrove reactor: fast clay transformation and potassium sink. *Applied Clay Science*, 140, 50-58.
- 607 Christidis, G.E. (2001) Formation and growth of smectites in bentonites: a case study from Kimolos Island,  
608 Aegean, Greece. *Clays and Clay Minerals*, 49(3), 204-215.
- 609 Christidis, G.E., and Huff, W.D. (2009) Geological aspects and genesis of bentonites. *Elements*, 5(2), 93-  
610 98.
- 611 Christidis, G.E., and Mitsis, I. (2006) A new Ni-rich stevensite from the ophiolite complex of Othrys,  
612 Central Greece. *Clays and Clay Minerals*, 54(6), 653-666.
- 613 De Yoreo, J.J., Gilbert, P.U., Sommerdijk, N.A., Penn, R.L., Whitlam, S., Joester, D., Zhang, H., Rimer,  
614 J.D., Navrotsky, A., and Banfield, J.F. (2015) Crystallization by particle attachment in synthetic,  
615 biogenic, and geologic environments. *Science*, 349(6247), aaa6760.
- 616 Decarreau, A., Colin, F., Herbillon, A., Manceau, A., Nahon, D., Paquet, H., Trauth-Badaud, D., and  
617 Trescases, J. (1987) Domain segregation in Ni-Fe-Mg-smectites. *Clays and Clay Minerals*, 35(1),  
618 1-10.
- 619 Decarreau, A., Grauby, O., and Petit, S. (1992) The actual distribution of octahedral cations in 2: 1 clay  
620 minerals: results from clay synthesis. *Applied Clay Science*, 7(1-3), 147-167.

- 621 Decarreau, A., Petit, S., Martin, F., Farges, F., Vieillard, P., and Joussein, E. (2008) Hydrothermal  
622 synthesis, between 75 and 150 °C, of high-charge, ferric nontronites. *Clays and Clay Minerals*,  
623 56(3), 322-337.
- 624 Eberl, D. (1984) Clay mineral formation and transformation in rocks and soils. *Philosophical Transactions*  
625 of the Royal Society of London. Series A, Mathematical and Physical Sciences, 311(1517), 241-  
626 257.
- 627 Eberl, D., Drits, V., and Środoń, J. (1998) Deducing growth mechanisms for minerals from the shapes of  
628 crystal size distributions. *American journal of Science*, 298(6), 499-533.
- 629 Eberl, D., Środoń, J., Kralik, M., Taylor, B.E., and Peterman, Z.E. (1990) Ostwald ripening of clays and  
630 metamorphic minerals. *Science*, 248(4954), 474-477.
- 631 Fonteneau, L., Caner, L., Petit, S., Juillot, F., Ploquin, F., and Fritsch, E. (2020) Swelling capacity of mixed  
632 talc-like/stevensite layers in white/green clay infillings ('deweylite/'garnierite') from serpentine  
633 veins of faulted peridotites, New Caledonia. *American Mineralogist*, in press.
- 634 Galán, E., and Ferrell, R.E. (2013) Chapter 3 - Genesis of Clay Minerals. In F. Bergaya, and G. Lagaly,  
635 Eds. *Developments in Clay Science*, 5, p. 83-126. Elsevier.
- 636 Gérard, P., and Herbillon, A. (1983) Infrared studies of Ni-bearing clay minerals of the kerolite-pimelite  
637 series. *Clays and Clay Minerals*, 31(2), 143-151.
- 638 Hazen, R.M., Sverjensky, D.A., Azzolini, D., Bish, D.L., Elmore, S.C., Hinnov, L., and Milliken, R.E.  
639 (2013) Clay mineral evolution. *American Mineralogist*, 98(11-12), 2007-2029.
- 640 He, H., Li, T., Tao, Q., Chen, T., Zhang, D., Zhu, J., Yuan, P., and Zhu, R. (2014) Aluminum ion  
641 occupancy in the structure of synthetic saponites: Effect on crystallinity. *American Mineralogist*,  
642 99(1), 109-116.
- 643 Hochella, M.F., Lower, S.K., Maurice, P.A., Penn, R.L., Sahai, N., Sparks, D.L., and Twining, B.S. (2008)  
644 Nanominerals, mineral nanoparticles, and earth systems. *Science*, 319(5870), 1631-1635.
- 645 Johnston, C.T. (2017) Chapter 9 - Infrared Studies of Clay Mineral-Water Interactions. In W.P. Gates, J.T.  
646 Klopogge, J. Madejová, and F. Bergaya, Eds. *Developments in Clay Science*, 8, p. 288-309.  
647 Elsevier.

- 648 Kawano, M., and Tomita, K. (1992) Formation of allophane and beidellite during hydrothermal alteration  
649 of volcanic glass below 200 oC. *Clays and Clay Minerals*, 40(6), 666-674.
- 650 Kelton, K.F. (1991) Crystal Nucleation in Liquids and Glasses. In H. Ehrenreich, and D. Turnbull, Eds.  
651 *Solid State Physics*, 45, p. 75-177. Academic Press.
- 652 Klopogge, J.T., Komarneni, S., and Amonette, J.E. (1999) Synthesis of smectite clay minerals: a critical  
653 review. *Clays and Clay Minerals*, 47(5), 529-554.
- 654 Lifshitz, I.M., and Slyozov, V.V. (1961) The kinetics of precipitation from supersaturated solid solutions.  
655 *Journal of physics and chemistry of solids*, 19(1-2), 35-50.
- 656 Madden, A.S., and Hochella, M.F. (2005) A test of geochemical reactivity as a function of mineral size:  
657 Manganese oxidation promoted by hematite nanoparticles. *Geochimica et Cosmochimica Acta*,  
658 69(2), 389-398.
- 659 Madejová, J., Gates, W.P., and Petit, S. (2017) Chapter 5 - IR Spectra of Clay Minerals. In W.P. Gates, J.T.  
660 Klopogge, J. Madejová, and F. Bergaya, Eds. *Developments in Clay Science*, 8, p. 107-149.  
661 Elsevier.
- 662 Manceau, A., and Calas, G. (1985) Heterogeneous distribution of nickel in hydrous silicates from New  
663 Caledonia ore deposits. *American Mineralogist*, 70(5-6), 549-558.
- 664 Merriman, R.J. (2005) Clay minerals and sedimentary basin history. *European Journal of Mineralogy*,  
665 17(1), 7-20.
- 666 Navrotsky, A., Mazeina, L., and Majzlan, J. (2008) Size-driven structural and thermodynamic complexity  
667 in iron oxides. *Science*, 319(5870), 1635-1638.
- 668 Petit, S., Baron, F., and Decarreau, A. (2017) Synthesis of nontronite and other Fe-rich smectites: a critical  
669 review. *Clay Minerals*, 52(4), 469-483.
- 670 Petit, S., and Madejová, J. (2013) Chapter 2.7 - Fourier Transform Infrared Spectroscopy. In F. Bergaya,  
671 and G. Lagaly, Eds. *Developments in Clay Science*, 5, p. 213-231. Elsevier.
- 672 Petit, S., Martin, F., Wiewiora, A., De Parseval, P., and Decarreau, A. (2004) Crystal-chemistry of talc: A  
673 near infrared (NIR) spectroscopy study. *American Mineralogist*, 89(2-3), 319-326.
- 674 Petit, S., Righi, D., and Decarreau, A. (2008) Transformation of synthetic Zn-stevensite to Zn-talc induced  
675 by the Hofmann-Klemen effect. *Clays and Clay Minerals*, 56(6), 645-654.

- 676 Putnis, A. (2009) Mineral replacement reactions. *Reviews in mineralogy and geochemistry*, 70(1), 87-124.
- 677 Slonimskaya, M., Besson, G., Dainyak, L., Tchoubar, C., and Drits, V. (1986) Interpretation of the IR  
678 spectra of celadonites and glauconites in the region of OH-stretching frequencies. *Clay Minerals*,  
679 21(3), 377-388.
- 680 Steefel, C.I., and Van Cappellen, P. (1990) A new kinetic approach to modeling water-rock interaction: The  
681 role of nucleation, precursors, and Ostwald ripening. *Geochimica et Cosmochimica Acta*, 54(10),  
682 2657-2677.
- 683 Suquet, H., Malard, C., Copin, E., and Pezerat, H. (1981) Variation du paramètre b et de la distance basale  
684 d 001 dans une série de saponites à charge croissante: I. Etats hydratés. *Clay Minerals*, 16(1), 53-  
685 67.
- 686 Tardy, Y., Duplay, J., and Fritz, B. (1987) Stability fields of smectites and illites as a function of  
687 temperature and chemical composition. Swedish Nuclear Fuel and Waste Management Co, p. 3-8.
- 688 Voigt, M., Pearce, C.R., Fries, D.M., Baldermann, A., and Oelkers, E.H. (2020) Magnesium isotope  
689 fractionation during hydrothermal seawater-basalt interaction. *Geochimica et Cosmochimica Acta*,  
690 272, 21-35.
- 691 Wagner, C. (1961) Theorie der alterung von niederschlägen durch umlösen (Ostwald-reifung). *Zeitschrift*  
692 *für Elektrochemie, Berichte der Bunsengesellschaft für physikalische Chemie*, 65(7-8), 581-591.
- 693 Whitney, G. (1983) Hydrothermal reactivity of saponite. *Clays and Clay Minerals*, 31(1), 1-8.
- 694 Wilson, M., and Jones, D. (1983) Lichen weathering of minerals: implications for pedogenesis. *Geological*  
695 *Society, London, Special Publications*, 11(1), 5-12.
- 696 Zhang, C., Petit, S., He, H., Villiéras, F., Razafitianamaharavo, A., Baron, F., Tao, Q., and Zhu, J. (2020)  
697 Crystal Growth of Smectite: A Study Based on the Change in Crystal Chemistry and Morphology  
698 of Saponites with Synthesis Time. *ACS Earth and Space Chemistry*, 4(1), 14-23.
- 699 Zhang, D., Zhou, C. H., Lin, C. X., Tong, D. S., and Yu, W. H. (2010) Synthesis of clay minerals. *Applied*  
700 *Clay Science*, 50(1), 1-11.
- 701 Zhou, Z., and Fyfe, W. (1989) Palagonitization of basaltic glass from DSDP Site 335, Leg 37; textures,  
702 chemical composition, and mechanism of formation. *American Mineralogist*, 74(9-10), 1045-  
703 1053.

704

705

## FIGURE CAPTIONS

706 **Figure 1.** Powder XRD patterns of Mg-saponite (a) and Ni-saponite (b) precursors

707 synthesized at different temperatures for one day.

708 **Figure 2.** Structural OH stretching vibration region in the FTIR spectra of Mg-saponite (a)

709 and Ni-saponite (b) precursors synthesized at different temperatures for one day.

710 **Figure 3.** XRD patterns of oriented samples (air-dried - red dot; after glycolation - black

711 solid). a, Series I. b, Series II.

712 **Figure 4.** The Structural OH stretching vibration region of the FTIR spectra of synthetic

713 samples. a, Series I. b, Series II.

714 **Figure 5.** HRTEM images of Mg- and Ni-saponite precursors (a, b, d, e, g, h) and the

715 corresponding synthetic Mg,Ni-saponites from Series I (c, f, i).

716 **Figure 6.** The (Mg/Mg+Ni) ratios deduced from STEM-EDS analyses at different

717 positions along a single particle in a ultra-thin section.

718 **Figure 7.** The Mg/(Mg+Ni) ratios for saponites prepared from different precursors. a,

719 gel-220. b, 150-220. c, 180-220. For each sample, the squares with the same color

720 connected by a dotted line correspond to the Mg/(Mg+Ni) ratios at different positions

721 within the same particle.

722 **Figure 8.** STEM images of synthetic saponites in Series II. a, 220-220. b, 220-300. c,

723 220-400. d, 220-500.

724 **Figure 9.** HAADF-STEM images of saponite layers from sample 220-400, the darker  
725 areas could be Mg-rich while the lighter ones could be Ni-rich.

726 **Figure 10.** HRTEM images of synthetic saponites in Series II. a, 220-220. b, 220-300. c,  
727 220-400. d, 220-500.

728 **Figure 11.** Decomposition and fitting of the  $\nu$ OH vibrations in the FTIR spectrum of  
729 sample 200-400.

730 **Figure 12.** The assumed CSDs of synthesized saponite under different physicochemical  
731 conditions. Series I, the red areas are the dissolution extents of precursors synthesized at  
732 different temperature (50, 150, 180, and 220 °C) after subsequent hydrothermal treatment  
733 at 220 °C; Series II, the red area, is the dissolution extents of precursors synthesized at  
734 220 °C after exposing to the different hydrothermal systems (220, 300, 400, and 500 °C).  
735  $c_T$  stands for the required critical size in corresponding physicochemical system, e.g.,  
736  $c_{220}$  is the critical size of saponite in the hydrothermal system at 220 °C.

737 **Figure 13.** Temperature and pressure diagram in closed hydrothermal systems.  
738 Percentages denote the  $R_{(IR)}$  of saponite from one physicochemical condition to another  
739 one. Red, series I. Blue, series II.

740

741

742

743

744

745

## TABLES

746

747 **Table 1.** The synthesis conditions of hydrothermal products at 220, 300, 400 and 500 °C.

	Samples	precursors	Temperature (°C)		Pressure (Mpa)		pH <sub>i</sub>	pH <sub>f</sub>
			precursors	products	precursors	products		
	gel-220	PMg-gel; pNi-gel	RT	220	--	2.5	10.20	9.59
	50-220	pMg50; pNi50	50	200	0.1	2.5	10.16	9.56
Series I	150-220	pMg150; pNi150	150	220	1.0	2.5	10.02	9.57
	180-220	pMg180; pNi180	180	220	1.6	2.5	9.95	10.17
	200-220	pMg200; pNi200	200	220	2.0	2.5	9.54	9.52
	220-220	pMg220; pNi220	220	220	2.5	2.5	8.59	8.98
	220-220	pMg220; pNi220	220	220	2.5	2.5	8.59	8.87
Series II	220-300	pMg220; pNi220	220	300	2.5	7.5	8.59	7.90
	220-400	pMg220; pNi220	220	400	2.5	61.0	8.59	7.86
	220-500	pMg220; pNi220	220	500	2.5	136.0	8.59	7.40

748

749

750

751

752

753

754

755

756

757

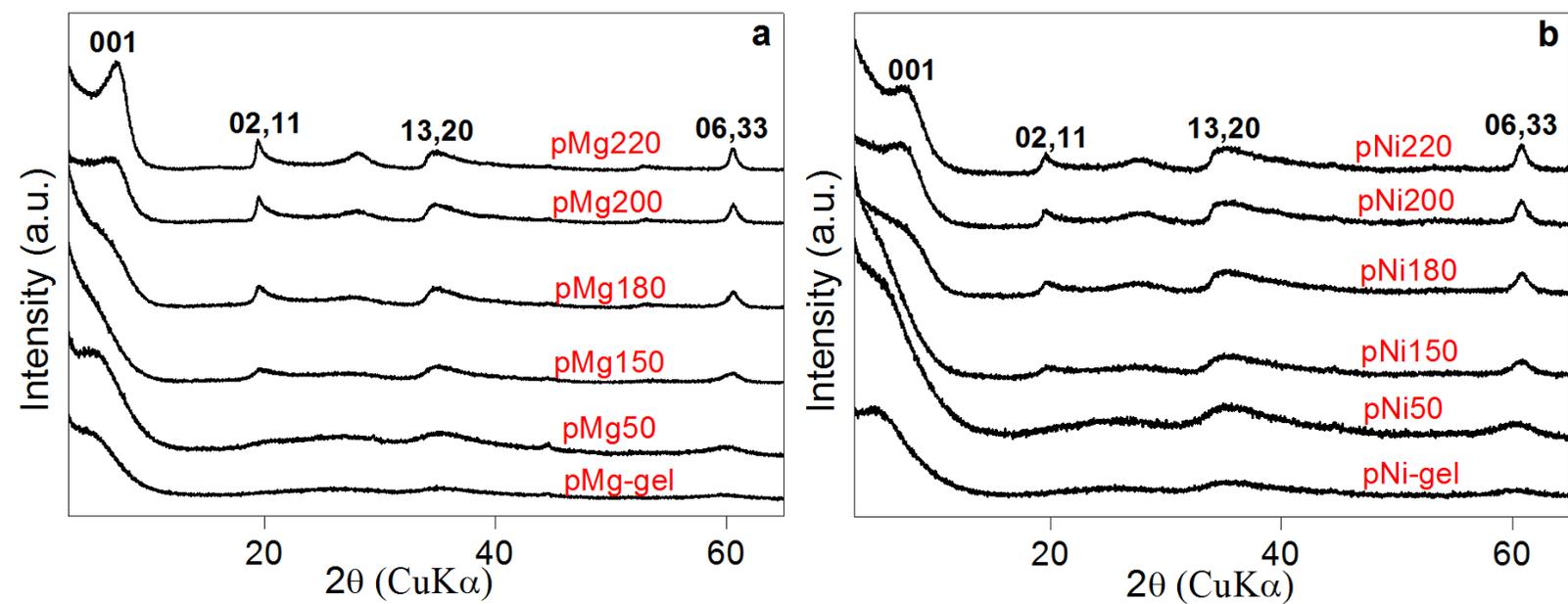
758 **Table 2.**  $R_{(IR)}$  for all synthetic Mg,Ni-saponites and calculated dissolution extents for the  
759 corresponding precursors.

	Samples	$R_{(IR)}$	Dissolution extent	$\Delta T$ (°C)
Series I	Gel-220	0.63	0.84	~200
	50-220	0.60	0.80	170
	150-220	0.55	0.73	70
	180-220	0.30	0.40	40
	200-220	0.17	0.23	20
	220-220	~0.00	~0.00	0
Series II	220-220	~0.00	~0.00	0
	220-300	0.24	0.32	80
	220-400	0.44	0.59	180
	220-500	0.58	0.77	280

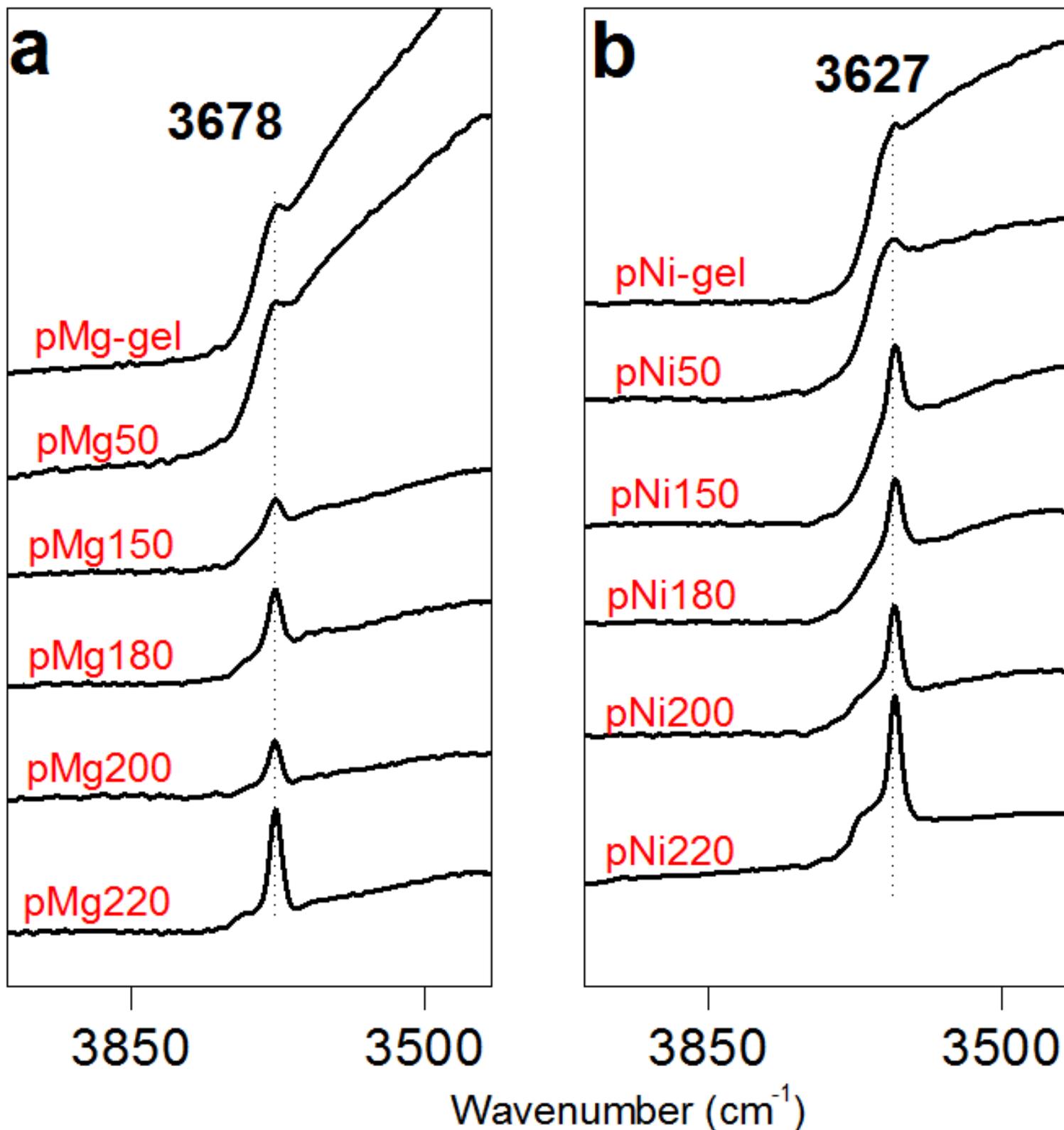
760

761

Figure 1



# Figure 2



# Figure 3

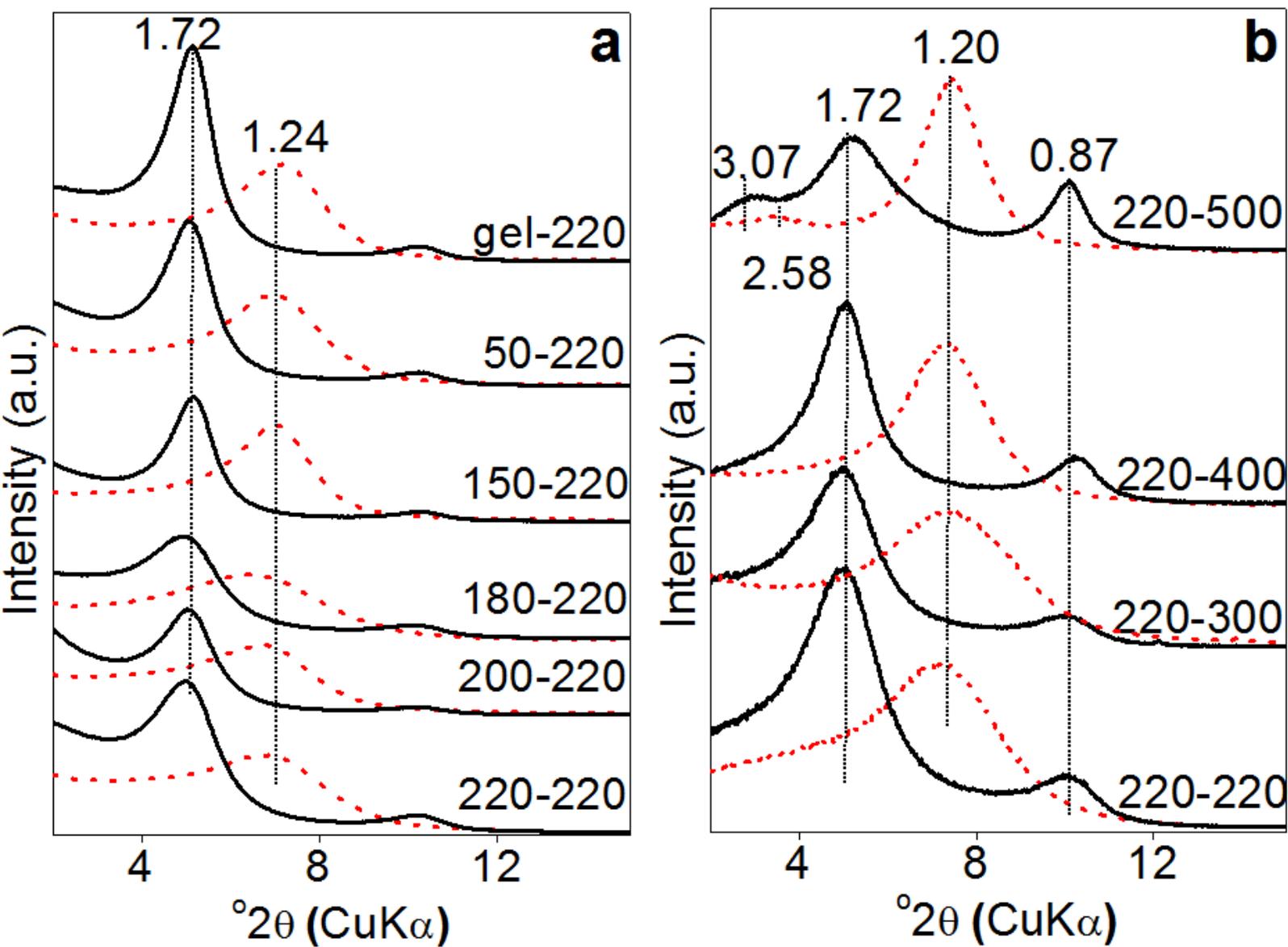
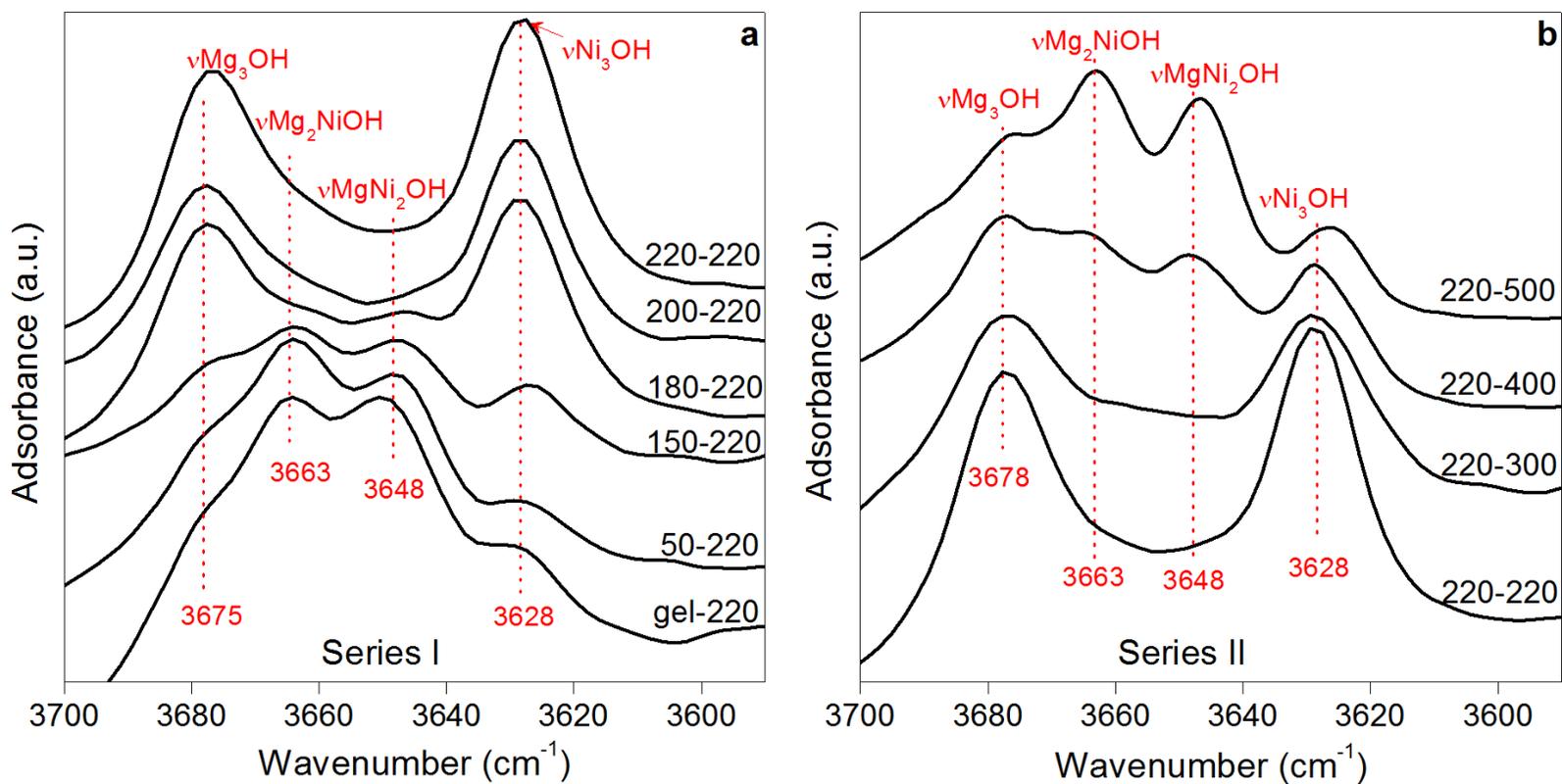


Figure 4



# Figure 5

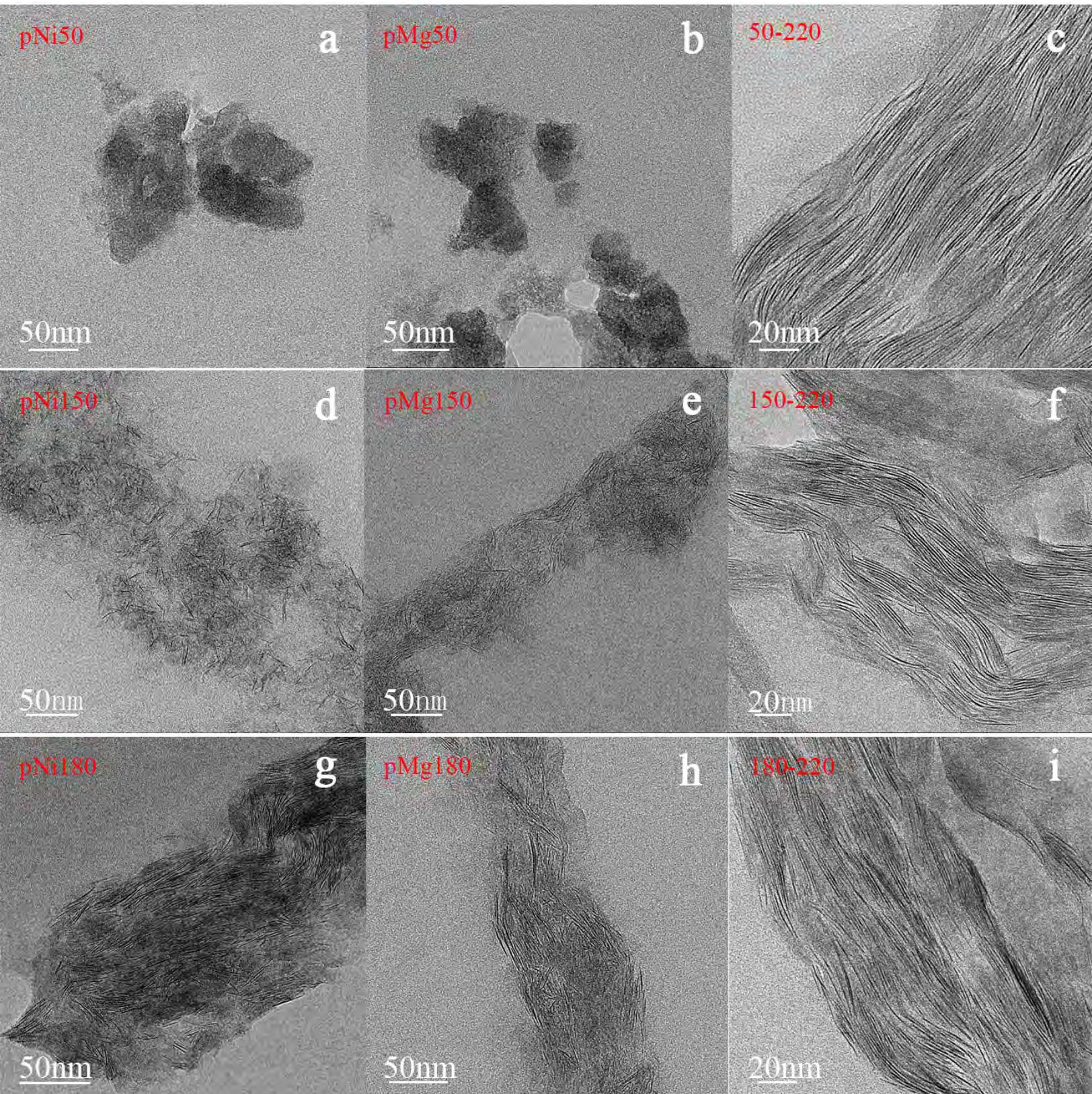
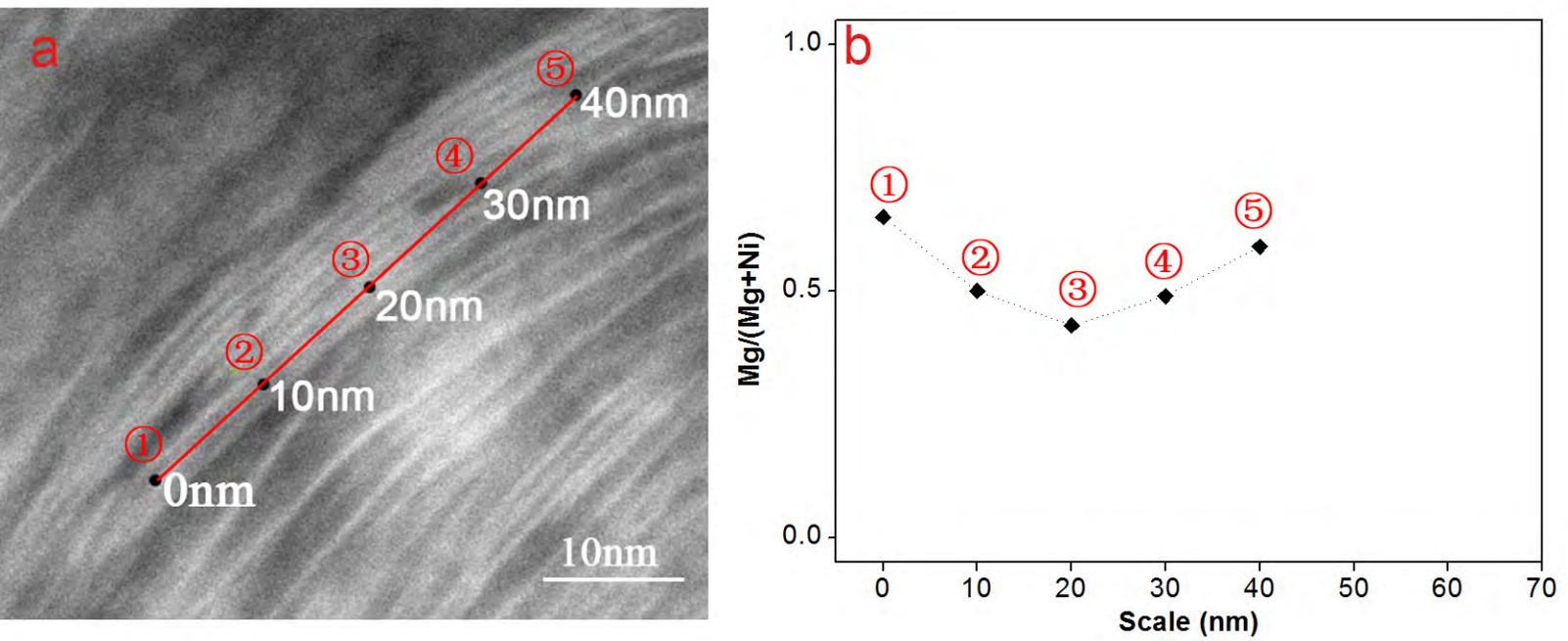
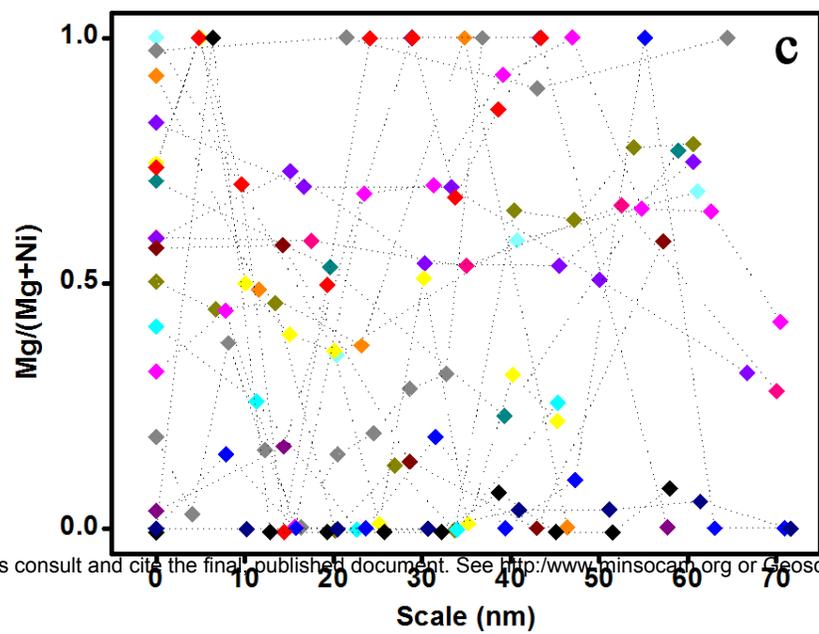
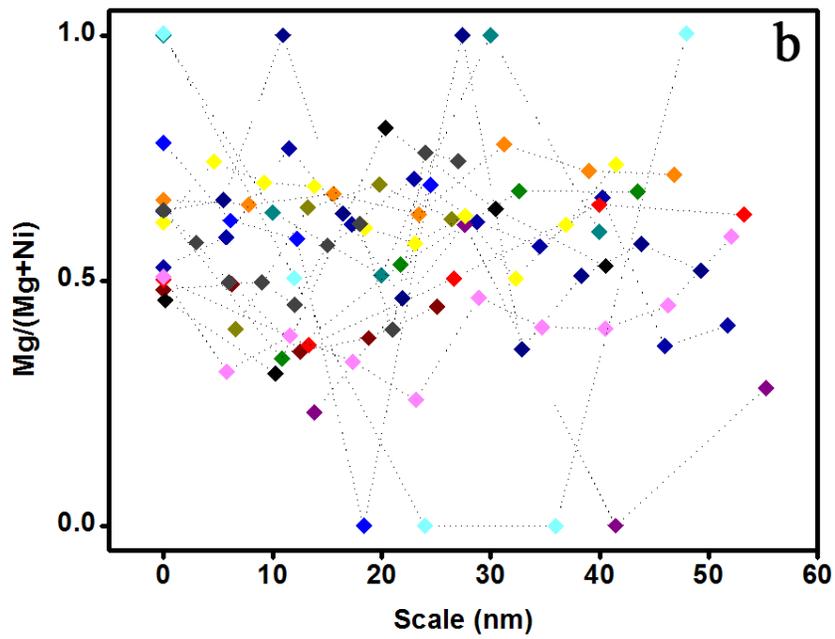
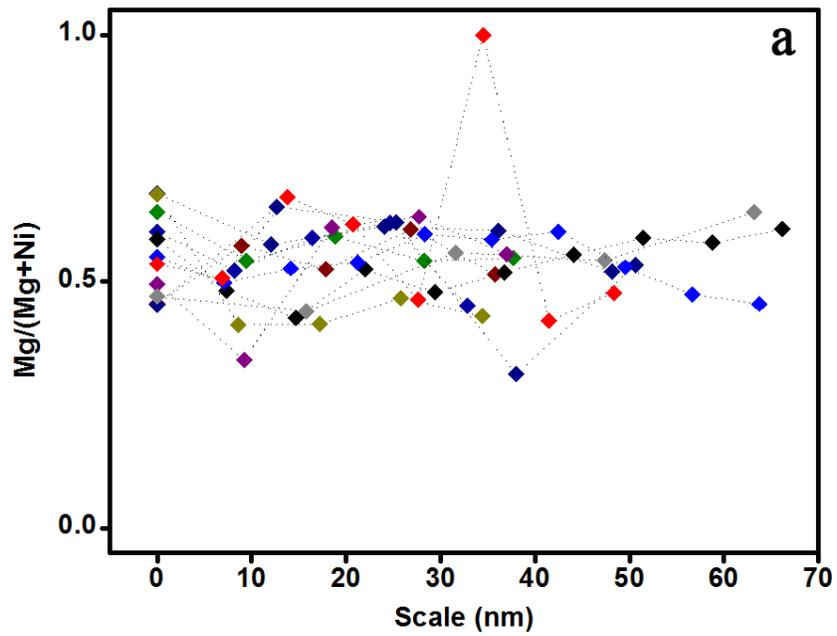


Figure 6





# Figure 8

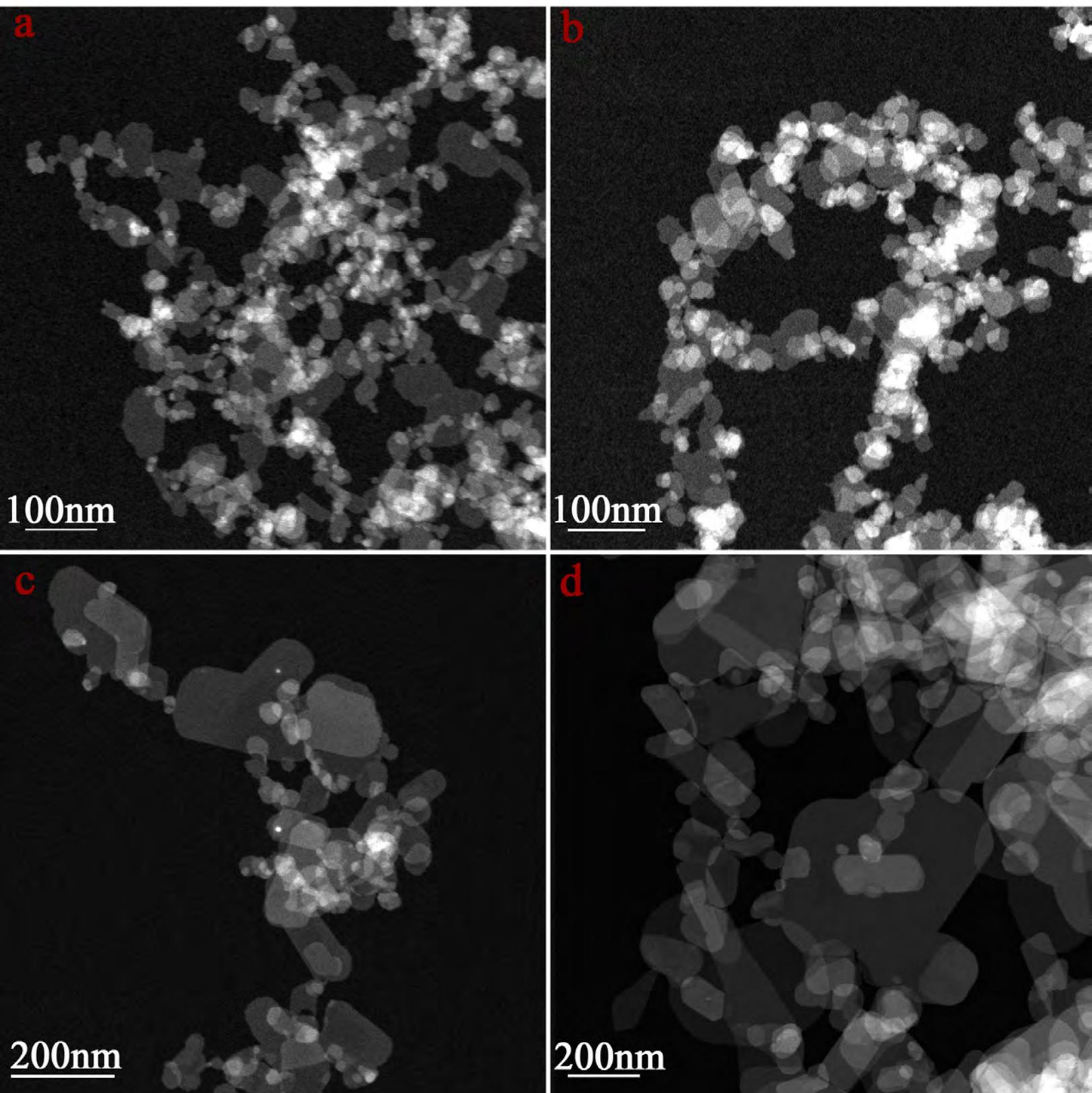
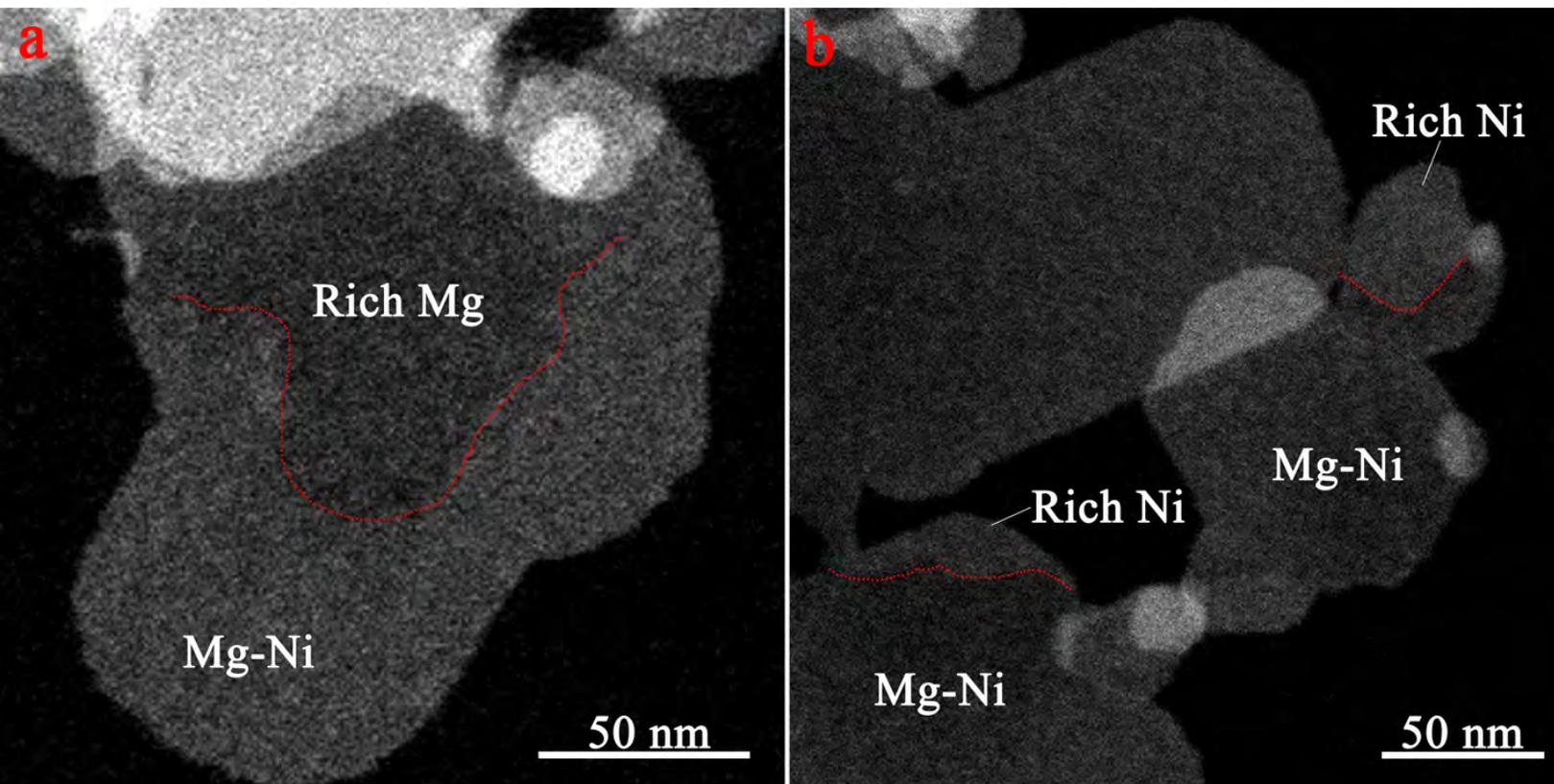
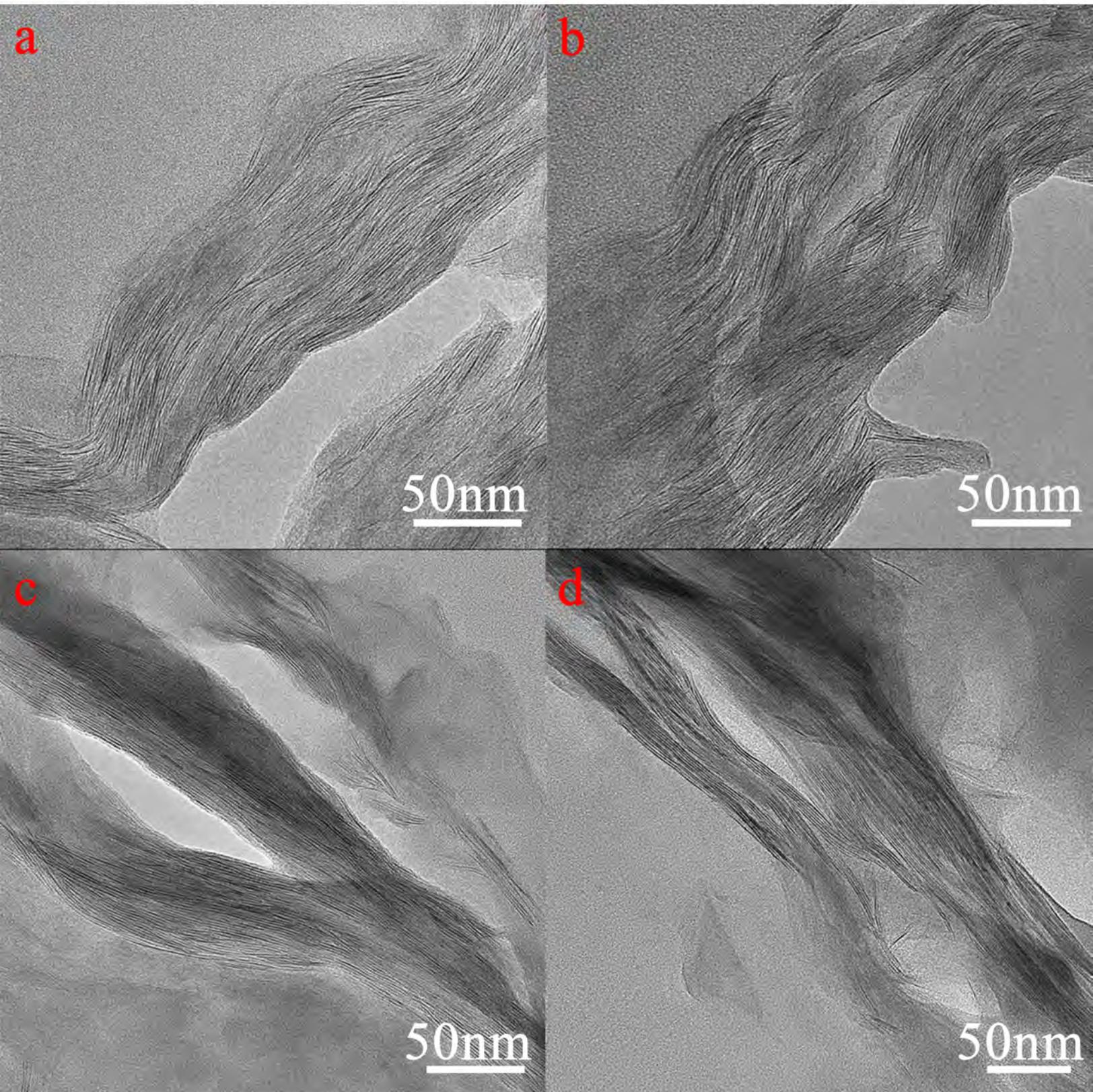


Figure 9



# Figure 10



# Figure 11

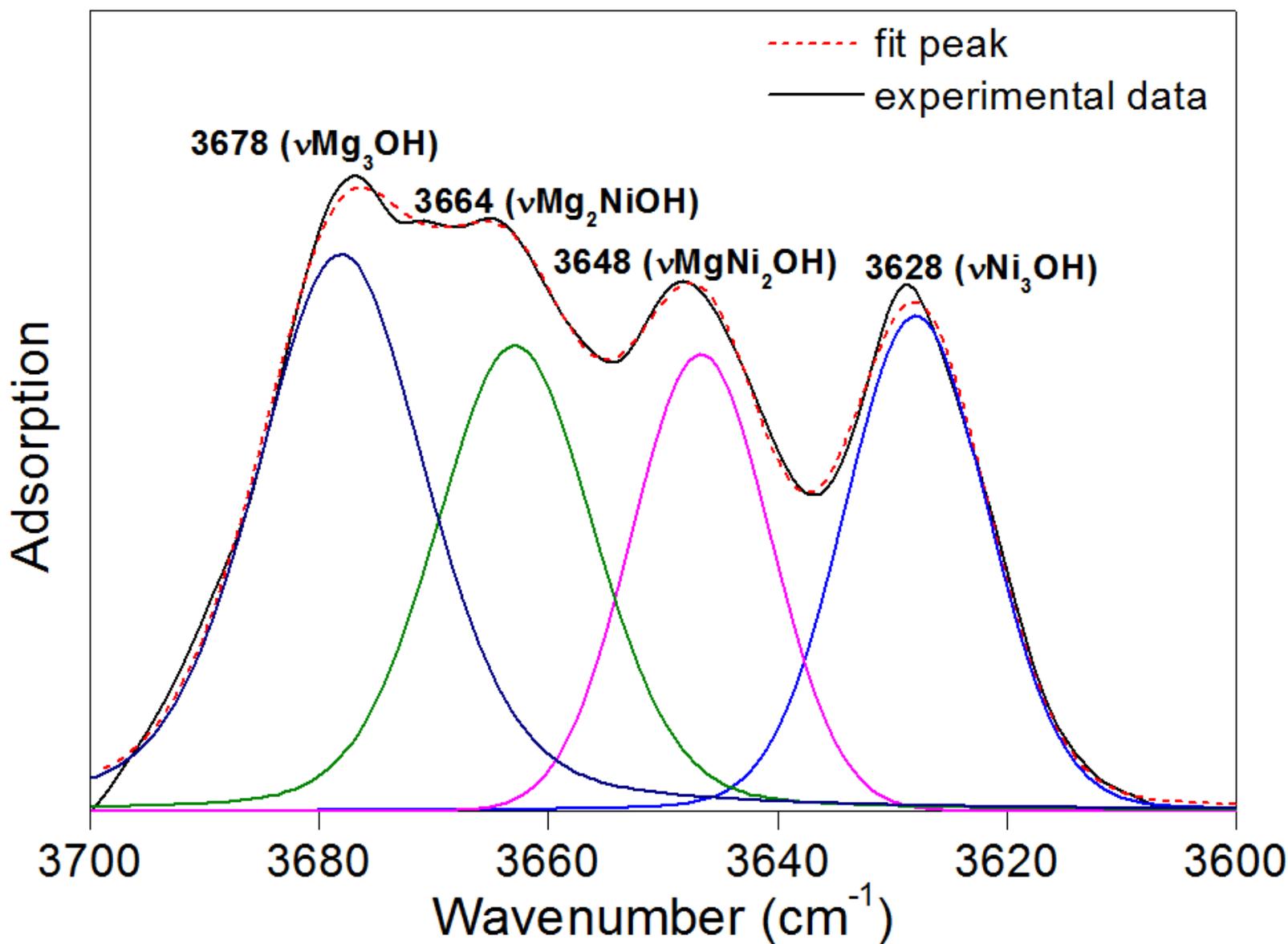
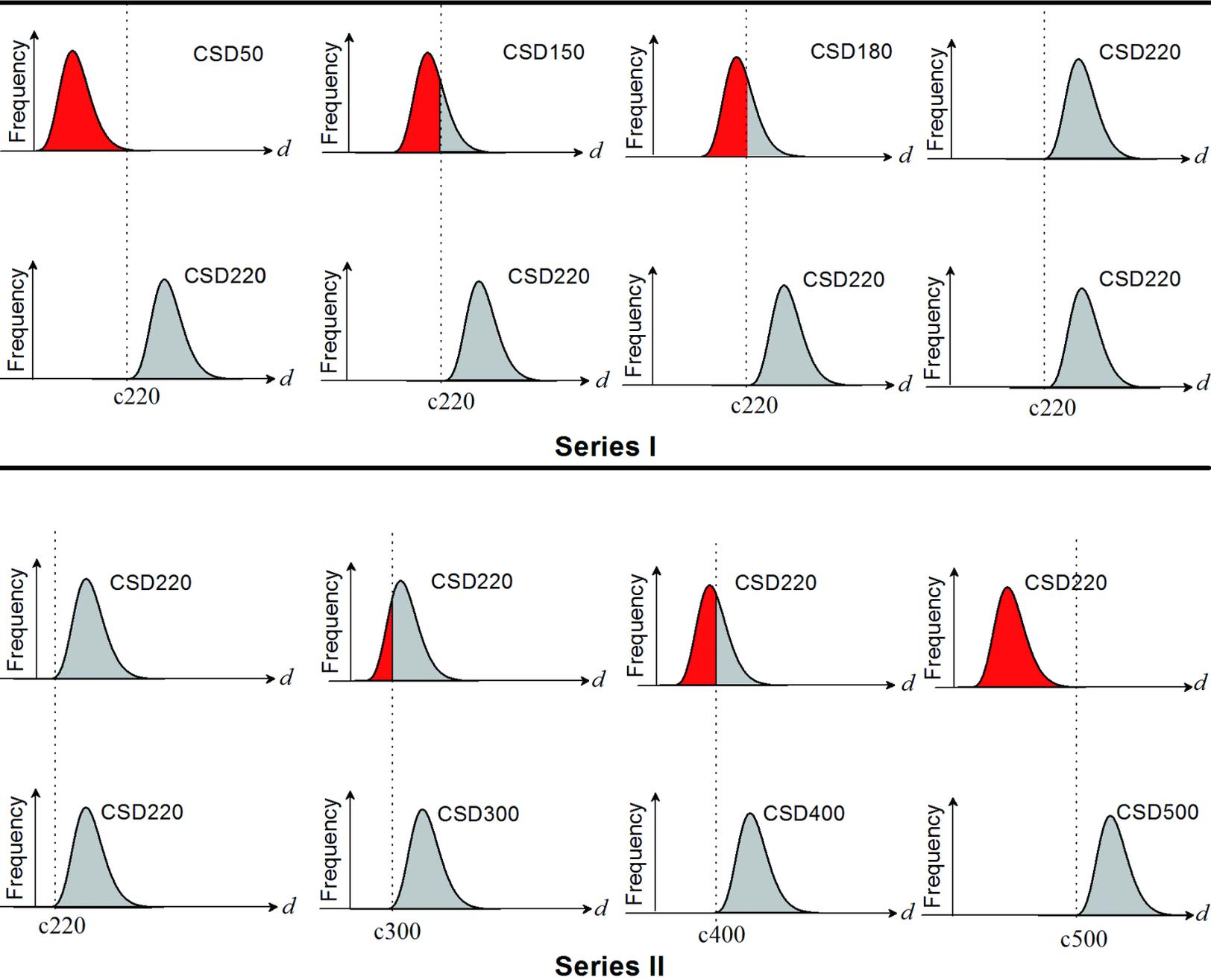


Figure 12



# Figure 13

