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1            CHARACTERIZATION OF IRON-RICH PHYLLOSILICATES FORMED AT  
2                                DIFFERENT Fe/Si RATIOS

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12    **Abstract**–The formation of 2:1 and 1:1 phyllosilicates in Fe–Si–O–H systems occurs in  
13    various geological and engineering settings; however, the identification and characterization  
14    of these minerals is very challenging due to a limited amount that is accessible, the very small  
15    particle size, and often very high heterogeneity of these samples. To overcome these  
16    drawbacks, the synthesis of iron-rich phyllosilicates was attempted in this study with an initial  
17    Fe/Si molar ratio ranging from 0.50 to 2.33. The synthesis was performed at 150°C under  
18    hydrothermal conditions during 7 days. Synthesis products were characterized by X-ray  
19    diffraction and fluorescence, by infrared, Raman, and Mössbauer spectroscopies, and  
20    transmission electron microscopy. Results revealed that the stability field of the 2:1 clay  
21    mineral was wider than that of the 1:1 clay mineral. The 2:1 clay mineral was less sensitive to  
22    redox conditions compared to the 1:1 clay mineral. In addition, a heterogeneity of formed  
23    phases (iron oxides, nontronite, cronstedtite, or greenalite) was identified.

24    **Keywords**–Berthierine, Cronstedtite, Greenalite, Nontronite, Serpentine, Synthesis

25

27 The formation of phyllosilicates in the Fe–Si–O–H system has been reported in various  
28 geological and engineering settings: on meteorites (Elmaleh et al., 2015; Lauretta et al., 2000;  
29 Muller et al., 1979; Zolensky et al., 1993; Zolotov, 2014), on Mars (Bishop et al., 2008;  
30 Ehlmann et al., 2011), in deep-sea sediments (Badaut et al., 1985, 1992; Baldermann et al.,  
31 2015; Marcus & Lam, 2014), in iron-banded formations (Eugster & Chou, 1973; Grubb, 1971),  
32 in ore deposits (Inoué & Kogure, 2016; Rasmussen et al., 1998; Rivas-Sanchez et al., 2006), at  
33 iron-clay (Lanson et al., 2012; Le Pape et al., 2015; Pignatelli et al., 2014) and steel-glass  
34 interfaces (Carriere et al., 2017, 2021; Schlegel et al., 2016), and as a scale deposit in brine-  
35 handling equipment (Manceau et al., 1995). Thermodynamic modeling for some of these  
36 settings has been performed with the intention of estimating the physicochemical conditions  
37 which led to the formation of these minerals in the past (Chevrier et al., 2007; Fritz & Toth,  
38 1997; Zolotov, 2014), or of estimating the evolution of physicochemical conditions for a given  
39 mineralogical composition with time (Ngo et al., 2015; Wilson et al., 2015).

40 The incorporation of iron-rich phyllosilicates in such models is challenging for several reasons.  
41 First, for some settings such as iron–glass interfaces, the identification of newly-formed  
42 minerals is rather arduous due to their very small particle size. The thickness of the alteration  
43 layer between iron and glass is in the range of 1  $\mu\text{m}$  (Carriere et al., 2017, 2021; Schlegel et al.,  
44 2016). Second, the information regarding experimentally measured thermodynamic properties  
45 of iron-rich minerals is very limited. Such data are available only for nontronite (Gailhanou et  
46 al., 2013) and greenalite (Tosca et al., 2016). Last, the minerals such as cronstedtite, hisingerite,  
47 berthierine, brindleyite, minnesotaite, and saponite are not widely abundant and not readily  
48 accessible for experiments. Given the lack of accessible material for experiments, an alternative  
49 approach is to infer the physicochemical properties by estimating the thermodynamic constants  
50 using various methods such as the summation of the properties of respective oxides (Tardy &  
51 Garrels, 1974) or the decomposition into polyhedral units (Blanc et al., 2015). However, these  
52 approaches do not take into account such aspects as polytypism or cation substitution. The study  
53 of Pignatelli et al. (2014) discussed the mismatch between geochemical modelling results and  
54 experimental observations for  $T < 50^\circ\text{C}$ , and attributed the discrepancy to the presence of  
55 different cronstedtite polytypes. Shulte & Shock (2004) considered the difference of stability  
56 between greenalite and cronstedtite. The presence of ferric iron in tetrahedral coordination in  
57 cronstedtite might be the reason for the smaller stability field for cronstedtite (up to  $100^\circ\text{C}$ )  
58 compared to the one of greenalite (up to  $150^\circ\text{C}$ ).

59 Indeed, the characterization of mineral composition of the different settings often reveal the  
60 coexistence of several phyllosilicates (Badaut et al., 1992; Ehlmann et al., 2011; Elmaleh et al.,  
61 2015; Evans et al., 2017; Lanson et al., 2012; Lauretta et al., 2000; Le Pape et al., 2015; Marcus  
62 & Lam, 2014; Pignatelli et al., 2014; Tutolo et al., 2019). Furthermore, for the same type of  
63 phyllosilicate mineral, the basic structure can be heterogeneous in terms of different types of  
64 layers (Chukhrov et al., 1979; Inoué & Kogure, 2016; Suquet et al., 1987), iron distribution  
65 between octahedral and tetrahedral sheets (Gates et al., 2002; Stucki, 2013), as well as the  
66 distribution of iron within the octahedral sheet (Vantelon et al., 2003). Thus, Chukhrov et al.  
67 (1979) reported ferric pyrophyllite exposed to glycol and ethylene glycol having different types  
68 of layers (swelling vs non-swelling) suggesting a heterogeneous structure. Similarly, Suquet et  
69 al. (1987) studied nontronite swelling and observed a continuous evolution of layer-to-layer  
70 distance as a function of relative humidity with no clearly distinguishable steps. Step-like  
71 behavior is characteristic of crystalline, homogeneous phyllosilicates suggesting that the  
72 studied nontronite samples might have a rather complex structure. A detailed study of chlorite  
73 with HRTEM by Inoué & Kogure (2016) also revealed a complex stacking structure of two  
74 different types of layers: berthierine and chlorite. In another study, Gates et al. (2002) explored  
75 the coordination of iron (tetrahedral vs octahedral) in various natural nontronite samples and  
76 reported different distributions between tetrahedral and octahedral iron in various samples.  
77 Finally, Vantelon et al. (2003) studied the distribution of iron in the octahedral sheet of different  
78 dioctahedral smectites and found three distinct groups: the first with an ordered distribution,  
79 the second with a random distribution, and the third group had clusters of iron.

80 The examples reported above illustrate the complexity of phyllosilicates at different levels:  
81 different mineral phases, different types of layers within one mineral, and different distributions  
82 of iron between and within sheets composing the layers. How can one address this complexity  
83 and obtain enough relevant material for experiments for the measurements of physicochemical  
84 properties of iron-rich phyllosilicates? A solution to this issue is to synthesize such materials in  
85 laboratory conditions. Moreover, the conditions of such a synthesis should be as close as  
86 possible to the studied system. This would enable the necessary quantities of phyllosilicates for  
87 detailed characterization of their properties and further experiments to be obtained.

88 The formation of phyllosilicates in the Fe–Si–O–H system has been reported previously under  
89 reducing (Farmer et al., 1991; Flaschen & Osborn, 1957; Francisco et al., 2020; Harder, 1976;  
90 Hinz et al., 2021; Mizutani et al., 1991; Pignatelli et al., 2020; Tosca et al., 2016) and oxidizing  
91 (Baron et al., 2016; Decarreau et al., 1987; Decarreau et al., 2008; Roy & Roy, 1954) conditions

92 at neutral to basic pH and at different temperatures (from 23 to 470°C) and synthesis durations  
93 (4 days to 3 months). In the experiments with Fe/Si initial molar ratio 0.75 or lower, the  
94 formation of nontronites was independent of the atmospheric conditions. The composition of  
95 the precipitated solid with respect to Fe/Si molar ratio is always higher than the initial Fe/Si  
96 molar ratio. The study of Baron et al. (2016) showed that this ratio depended on the pH of the  
97 solution, which in turn determined the speciation of Si in the solution. For the initial Fe/Si molar  
98 ratio higher than 0.75, the formation of 1:1 phyllosilicates was reported except in the study of  
99 Mizutani et al. (1991), where they observed the formation of 2:1 phyllosilicate at initial Fe/Si  
100 = 1.50. Thus, the predominance of one or the other kind of phyllosilicate depends not only on  
101 the physicochemical conditions (i.e. thermodynamics) but also on the respective formation  
102 kinetics, influenced by the temperature (activation energy). This conclusion is in agreement  
103 with the conclusions reached in a previous study (Boumaiza et al., 2020), in which the kinetics  
104 of 2:1 clay mineral formation was faster than for 1:1 clay mineral formation. Thus, the  
105 experiment at higher temperature would have faster kinetics and favor the formation of 2:1  
106 phyllosilicates. Indeed, the experiment of Mizutani et al. (1991) was performed at 150°C. In  
107 comparison, the experiment of Tosca et al. (2016) performed at room temperature reported the  
108 precipitation of greenalite (1:1 phyllosilicate) at initial Fe/Si = 0.8.

109 These previous results show that the initial Fe/Si molar ratio influences the type of phyllosilicate  
110 formed. Therefore, the aim of the current study was to investigate the effect of a wider range of  
111 Fe/Si molar ratio (0.50 to 2.33) on the formation of phyllosilicates. The synthesis of the products  
112 was performed at hydrothermal conditions in order to maximize the yield and crystallinity of  
113 the products (Decarreau et al., 2008).

## 114 EXPERIMENTAL

### 115 *Synthesis of Materials*

116 Iron(II) sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , purity of 99.5%; Sigma Aldrich, India) was dissolved in 70 mL  
117 of deionized water (18.2 M $\Omega$ ·cm), then 0.041 g (0.5 wt.%) of sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ,  
118 purity of 85%; Alfa Aesar, Kandel, Germany) was added to the solution to limit  $\text{Fe}^{2+}$  oxidation.  
119 Next, a certain amount of sodium orthosilicate ( $\text{Na}_4\text{SiO}_4$ ; Alfa Aesar, Karlsruhe, Germany) was  
120 added to the Fe(II) solution; the quantities of Fe(II) sulfate and sodium orthosilicate were  
121 calculated assuming a theoretical yield of 2 g of phyllosilicate with initial Fe/Si molar ratios  
122 ( $(\text{Fe/Si})_{\text{ini}}$ ) ranging from 0.50 to 2.33 (Table 1). The amount of reactants used in the synthesis  
123 for each sample is reported in Supplementary Information Table S1. The suspension was

124 homogenized for 2 h by stirring at 200 rpm. The pH was then measured in an aliquot withdrawn  
 125 from this initial suspension ( $\text{pH}_{\text{ini}}$ ) and then again in an aliquot of the supernatant withdrawn  
 126 after the synthesis ( $\text{pH}_{\text{f}}$ ) using a combination pH electrode (HANNA Instruments, Nusfalau,  
 127 Romania) that was calibrated at 20°C before the measurements using two pH buffer solutions  
 128 ( $\text{pH} = 7.00$  and  $\text{pH} = 10.00$ ). Preliminary tests with standard solutions revealed that the probe  
 129 gave accurate measurements until  $\text{pH} = 13.60$ . The redox potential was measured after 2 h of  
 130 stirring ( $\text{Eh}_{\text{ini}}$ ) in an aliquot withdrawn from the suspension and in the aliquot of the supernatant  
 131 after the synthesis ( $\text{Eh}_{\text{f}}$ ) using a combination redox electrode (HANNA Instruments, Nusfalau,  
 132 Romania). The redox probe was calibrated with a standard solution of +200.00 mV (ORP buffer  
 133 solution, Hach, Loveland, USA) before the measurements. The reported values were  
 134 recalculated with respect to potential of the standard hydrogen electrode.

135 **Table 1.** Initial Fe/Si molar ratios and solution characteristics before and after the synthesis.  
 136 ( $\text{Fe/Si}_{\text{solid}}$ ) molar ratio after the synthesis was calculated using XRF results

Before synthesis			After synthesis		
$(\text{Fe/Si})_{\text{ini}}$ molar	$\text{pH}_{\text{ini}}$	$\text{Eh}_{\text{ini}}$ (mV/SHE)	$(\text{Fe/Si})_{\text{solid}}$ molar	$\text{pH}_{\text{f}}$	$\text{Eh}_{\text{f}}$ (mV/SHE)
2.33	7.36	-481	5.40	4.73	355
1.50	12.64	-375	2.99	12.81	36
1.00	13.22	-576	1.47	13.41	24
0.75	13.33	-592	1.41	13.41	155
0.50	13.60	-624	1.46	13.61	80

137  
 138 The synthesis was performed in 150 mL Teflon-lined stainless-steel mineralization bombs  
 139 (Ref.: 2148.6000, Top Industry®, Vaux-le-Pénil, France) at 150°C for 7 days, the pressure  
 140 corresponded to the saturation pressure at 150°C. After 7 days, the autoclaves were removed  
 141 from the oven and left to cool down. The samples were removed from the autoclaves and  
 142 washed with deionized water 3 times by centrifugation at 10,000 rpm (12,860×g) for 10 min.

### 143 *Characterization Methods*

144 *Powder X-ray diffraction.* Data were collected with a powder diffractometer D8 ADVANCE  
 145 A25 from Bruker (Karlsruhe, Germany) in Bragg-Brentano reflexion geometry  $\theta$ - $\theta$   
 146 (goniometer radius 280 mm). This diffractometer was equipped with the LynxEye XE-T high  
 147 resolution energy dispersive 1-D detector ( $\text{CuK}\alpha_{1,2}$ ), leading to ultra-fast X-ray diffraction

148 measurements. A motorized anti-scatter screen was used for effective suppression of instrument  
149 background, most importantly air-scatter at low angles. Optical components were limited to  
150 two Soller slits ( $2.5^\circ$ ) for primary and secondary optics, and motorized divergence slits.  
151 Conditions for data collection were the following: angular area  $3\text{--}70^\circ 2\theta$ , step size  $0.017^\circ 2\theta$ ,  
152 time per step 1.8 s (total time per step was 345 s), variable divergence slits mode (irradiated  
153 sample length 15 mm), total time for acquisition 2 h. During data collection, powder samples  
154 were rotated at 5 rpm. All the data were converted and presented into fixed divergence slits  
155 mode.

156 After the identification of phyllosilicates by powder X-ray diffraction, three samples with  
157  $(\text{Fe}/\text{Si})_{\text{ini}} = 1.00, 0.75, \text{ and } 0.50$  containing 2:1 phyllosilicates were saturated with  $\text{Ca}^{2+}$  using  
158 1 M  $\text{CaCl}_2$  ( $\geq 99.0\%$ , Sigma Aldrich, Steinheim, Germany) solution (Bergaya & Lagaly, 2013)  
159 to limit a possible impact of relative humidity conditions during the characterization. After  
160 washing, the samples were dried at  $40^\circ\text{C}$ , ground by hand in a mortar, and stored in glass vials  
161 at room conditions. To differentiate between chlorite and swelling 2:1 phyllosilicates, these  
162 three samples were exchanged with 1 M  $\text{CH}_3\text{COONH}_4$  ( $>98\%$ , Emsure, Darmstadt, Germany)  
163 for 24 h.

164 *X-ray diffraction of oriented preparations.* To discriminate between swelling/non-swelling  
165 phyllosilicates, orientated preparations were made by dispersing synthesis products in  $\sim 1$  mL  
166 distilled water. Oriented preparations allow enhancement of  $00l$  reflections characteristic for  
167 layered minerals. Saturation with ethylene glycol was performed by exposing oriented slides to  
168 an ethylene glycol saturated atmosphere in a desiccator for 2 days. Samples were recorded  
169 immediately after the removal from the desiccator from  $2$  to  $15^\circ 2\theta$  angular range on an X'Pert  
170 Pro from PANalytical (Almelo, The Netherlands) equipped with an X'Celerator real-time  
171 multiple strip detector operating with an angular aperture of  $2.12^\circ 2\theta$  using  $\text{CuK}\alpha$  radiation with  
172 a wavelength of  $0.15418$  nm. Diffractograms were recorded at room temperature with a step  
173 size of  $0.017^\circ 2\theta$  and a scan time of 4 s per step (total time per step was 220 s). The divergence  
174 slit, the anti-scatter slit, and the two Soller slits were  $0.0625^\circ$ ,  $0.125^\circ$ , and  $2.3^\circ$ , respectively.  
175 To ensure that the sample did not evolve during the recording, the diffraction pattern was  
176 recorded twice for some samples. As no change was observed between the two recordings, it  
177 was concluded that during the recording time the sample remained stable.

178 *X-ray fluorescence.* The Fe/Si ratio in synthesis products was determined by X-Ray  
179 fluorescence with a PANalytical (Almelo, The Netherlands) Zetium spectrometer. Dry samples  
180 of 200 mg were pressed into 13 mm diameter pellets by applying a pressure of 4 T for 5 min.

181 *Infrared spectroscopy.* The FTIR spectra were recorded using a Bruker Equinox 55 FTIR  
182 spectrometer (Karlsruhe, Germany) equipped with a DTGS detector in transmission mode. The  
183 spectra were recorded in the mid-infrared region (MIR) from 4000 to 400  $\text{cm}^{-1}$  with a resolution  
184 of 4  $\text{cm}^{-1}$ . Samples were prepared in the form of KBr pellets obtained by mixing 1 mg of sample  
185 with 100 mg of KBr, pressed, and dried at 120°C.

186 *Mössbauer spectroscopy.* Mössbauer spectroscopy was performed at 290, 77, 15, and 4 K with  
187 a constant acceleration device. The Mössbauer spectrometer was equipped with a 512  
188 multichannel analyzer (Halder Electronic GmbH, Seehausen, Germany) and a 50 mCi source of  
189  $^{57}\text{Co}$  in a Rh matrix. Data were obtained from appropriate amounts (10 mg of Fe per  $\text{cm}^2$ ) of  
190 solid samples to get optimal experimental conditions. In order to avoid the condensation of  
191 oxygen and water on the walls of the cryostat, samples were transferred rapidly under an inert  
192 He atmosphere to a cold-head cryostat, equipped with a vibration isolation stand and developed  
193 in the LCPME Laboratory. The recordings at 290, 77, and 15 K were performed on a  
194 spectrometer equipped with the Advanced Research Systems cryostat (model DE-204SF),  
195 while the recordings at 4 K were done on the spectrometer coupled to the Janis Cryostat (model  
196 SHI-850-5). Both cryostats operate in a closed cycle on the principle of the Gifford-Mc Mahon  
197 refrigeration. Mössbauer spectra were collected in transmission mode. The 50 mCi source of  
198  $^{57}\text{Co}$  in a Rh matrix was maintained at room temperature (RT) and mounted at the end of a  
199 Mössbauer velocity transducer. The spectrometer was calibrated with a 25  $\mu\text{m}$  foil of  $\alpha\text{-Fe}$  at  
200 RT. Analysis of the Mössbauer spectra consisted of least-squares fitting of data with a  
201 combination of two-peak quadrupole components (doublets) and, when present, six-peak  
202 magnetic hyperfine components (sextets). The Voigt-based fitting method of Rancourt & Ping  
203 (1991) for quadrupole splitting distribution (QSDs) and magnetic hyperfine fields (HFDs) was  
204 used to fit spectra.

205 *Transmission electron microscopy coupled with energy dispersive X-ray spectroscopy.* For the  
206 observations under transmission electron microscopy (TEM), a few particles of sample were  
207 dispersed in chloroform using ultrasound and deposited on a 300-mesh copper TEM grid.  
208 Images were acquired using an ARM200 field emission transmission electron microscope  
209 (JEOL, Tokyo, Japan) equipped with an ultra-high resolution pole-piece operating at 200 kV.  
210 The TEM images were analyzed using *Digital Micrograph* software. Chemical analysis of  
211 selected zones was performed using energy dispersive X-ray spectroscopy. The reported semi-  
212 quantitative values of the chemical compositions (or ratios) were the mean of 5 measurements.

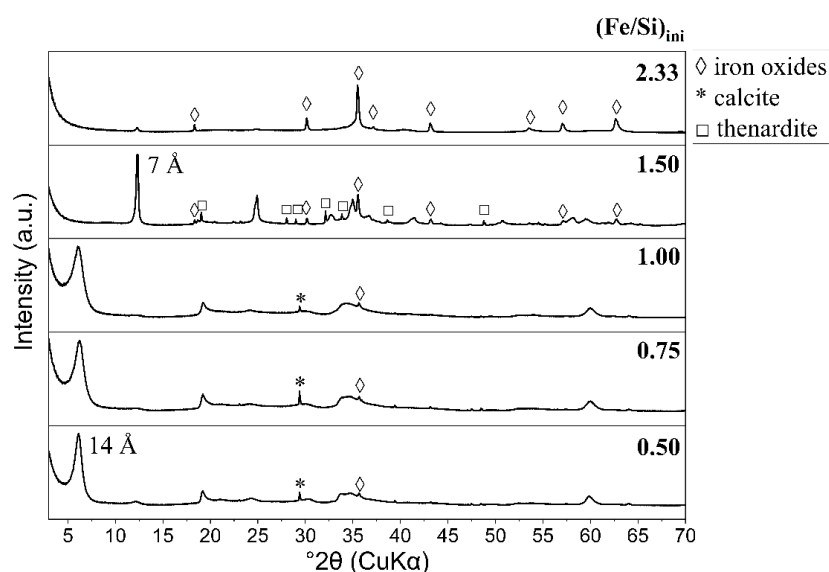


213 *Raman spectroscopy.* Raman spectra were obtained with a Horiba LABRAM 300 confocal-  
214 Raman spectrometer (Lille, France) equipped with a Compass 315M-50 laser (50 mW,  
215 532 nm), diffraction gratings of 600 grooves  $\text{mm}^{-1}$  and a CCD matrix detector. Laser focusing  
216 and sample viewing were performed through an Olympus BX40 microscope fitted with  $\times 50$   
217 objective lens. The spot size was  $\sim 15\text{--}20\ \mu\text{m}$  with a resolution of  $4\ \text{cm}^{-1}$ . Laser power could be  
218 reduced by filters to  $\sim 1, 0.1,$  and  $0.01\ \text{mW}$ .

## 219 RESULTS

### 220 *Mineralogical and Chemical Composition of Synthesis Products*

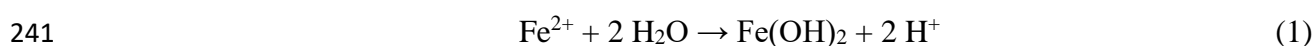
221 Crystalline phase analysis of synthesis products showed that for  $(\text{Fe}/\text{Si})_{\text{ini}} \leq 1.00$ , 2:1  
222 phyllosilicate was formed (Fig. 1). The 2:1 phyllosilicate was identified in XRD by its  
223 characteristic reflections at  $6.26; \sim 19.20\text{--}19.30; \sim 34.00,$  and  $60.06^\circ 2\theta$  (i.e.  $14.11, 4.62\text{--}4.58,$   
224  $2.60,$  and  $1.54\ \text{\AA}$ , respectively) (Brindley & Brown, 1982). Calcite ( $\text{CaCO}_3$ ) was also present  
225 as an impurity. This could be due to the use of dithionite, in which calcite was used as a  
226 stabilizer; or it may have been the result of precipitation of carbonate upon the sample saturation  
227 with calcium during post-synthesis treatment. For  $(\text{Fe}/\text{Si})_{\text{ini}} > 1.00$ , a 1:1 phyllosilicate was  
228 identified (Fig. 1) based on characteristic reflections at  $12.36, 24.91, 35.01, 41.33, 50.84, 58.21,$   
229 and  $59.56^\circ 2\theta$  (i.e.  $7.16, 3.57, 2.56, 2.19, 1.79, 1.59,$  and  $1.55\ \text{\AA}$ , respectively) (Bailey, 1988;  
230 Hybler, 2006). For the sample with  $(\text{Fe}/\text{Si})_{\text{ini}} = 1.50$ , thenardite ( $\text{Na}_2\text{SO}_4$ ) was identified, due to  
231 the use of dithionite and sulfate as anions during the synthesis. For samples with  $(\text{Fe}/\text{Si})_{\text{ini}} =$   
232  $2.33$ , various iron oxide phases were identified.



233

234 **Fig. 1.** Powder X-ray diffractograms of synthesis products for  $0.50 \leq (\text{Fe}/\text{Si})_{\text{ini}} \leq 2.33$

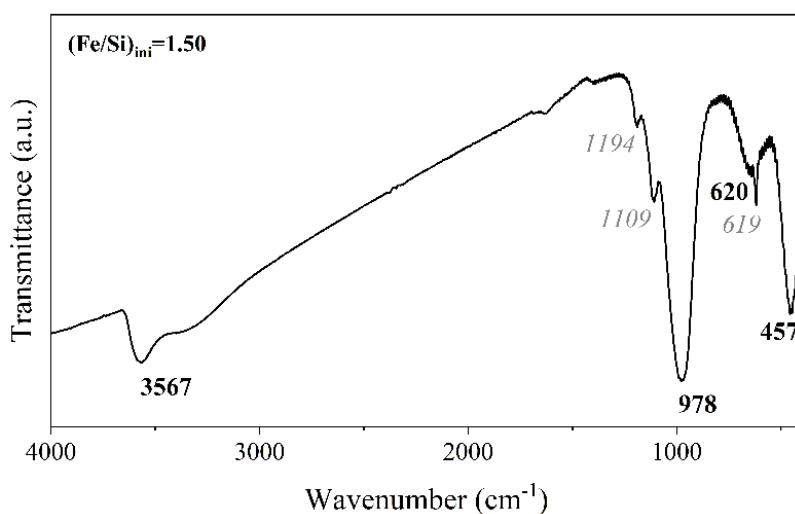
235 Analysis by XRF of synthesis products showed that the (Fe/Si) molar ratio after the synthesis  
236 was higher than the (Fe/Si) molar ratio introduced in the mixture, suggesting only partial iron-  
237 rich phyllosilicate precipitation and the formation of other Fe-bearing phases (Table 1). This is  
238 in agreement with the identified crystalline phases. For the sample with the initial Fe/Si = 2.33,  
239 the pH dropped significantly upon precipitation and after synthesis due to the hydrolysis and  
240 condensation of iron and silicon into various solid phases (Eqs 1 and 2).



243 The solubility of silica is lower in acidic pH compared to basic pH (Iler, 1979). It could thus  
244 explain the absence of phyllosilicates and the presence of various iron oxides identified only by  
245 XRD. Magnetite was identified in the sample with  $(\text{Fe}/\text{Si})_{\text{ini}} = 1.50$  and hematite in samples  
246 with  $(\text{Fe}/\text{Si})_{\text{ini}} \leq 1.00$ . Although the system was in reducing conditions upon precipitation  
247 (negative Eh), after synthesis it clearly became oxidizing (close to zero or positive Eh) (Table  
248 1).

#### 249 *Characterization of 1:1 Phyllosilicate Containing Synthesis Product*

250 The sample with  $(\text{Fe}/\text{Si})_{\text{ini}} = 1.50$  was chosen for a more detailed characterization as it indicated  
251 a superior phyllosilicate phase crystallinity compared to the sample with  $(\text{Fe}/\text{Si})_{\text{ini}} = 2.33$   
252 (Fig. 1). Infrared spectroscopy showed O-H and Si-O bond stretching and bending vibrations  
253 (Fig. 2 and Table 2). Sharp peaks at 1194, 1109, and 619  $\text{cm}^{-1}$  correspond to thenardite, which  
254 was also identified by pXRD (Farmer, 1974). The 620  $\text{cm}^{-1}$  band could be a combination of O-  
255 H deformation and Fe(III)-O<sub>apical</sub> stretching vibrations (Neumann et al., 2011). Previous studies  
256 reported that the presence of Fe(II) in phyllosilicate makes the spectra featureless (Fialips et al.,  
257 2002; Manceau et al., 2000), suggesting that some of the iron might have been incorporated as  
258 Fe(II). It has to be noted that the intensity and position of bands can be affected by sample  
259 orientation, and polytypic sequence. Two low-intensity bands at 1634 and 1400  $\text{cm}^{-1}$   
260 correspond to vibrations of water molecules and carbonate anions, respectively.



261

262

**Fig. 2.** FTIR spectrum of  $(\text{Fe/Si})_{\text{ini}} = 1.50$  synthesis product

263

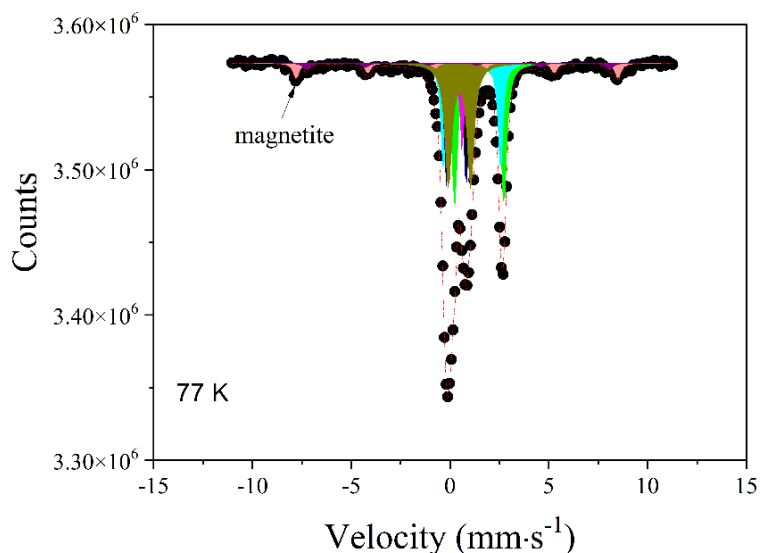
**Table 2.** Identified FTIR bands and corresponding vibration modes for  $(\text{Fe/Si})_{\text{ini}} = 1.50$

Wavenumber ( $\text{cm}^{-1}$ )	Vibration mode
3567	O–H stretching
978	Si–O stretching
620	O–H bending / Fe(III)–O <sub>ap</sub> stretching
457	Si–O bending

264

265 To explore if Fe(II) was present in the sample as suggested by FTIR, further analysis using  
 266 Mössbauer spectroscopy was performed. The Mössbauer spectrum at 77 K was chosen to be  
 267 presented and discussed here, as at this temperature iron oxides can be differentiated from  
 268 phyllosilicates. Often, the recording spectra at 4 K is considered as a true diagnostic for the  
 269 presence of most minerals. However, in the case of polymineralic samples at very low  
 270 temperature, to discern the presence of magnetite and its multiple sextets might be challenging  
 271 due to the overlap of the magnetite sextets with other phases (e.g. spectra at 15 and 4 K in  
 272 Figs S1 and S2 in Supplementary Information). Exploiting the spectrum at 77 K is more  
 273 convincing, even if the magnetically ordered phase was much less abundant than the  
 274 paramagnetic component. The spectrum at room temperature showed just a few traces of the  
 275 magnetically ordered phase in the background noise (Fig. S1 in Supplementary Information).  
 276 This component was more enhanced at 77 K due to the temperature effect. The spectrum of

277 (Fe/Si)<sub>ini</sub> = 1.50 sample obtained at 77 K clearly confirmed the presence of Fe(II) as two  
278 doublets with chemical shift of 1.21 and 1.39 mm/s (Fig. 3 and Table 3) (Murad, 2006).



279

280 **Fig. 3.** Mössbauer spectrum for synthesis product with (Fe/Si)<sub>ini</sub> = 1.50 at 77 K

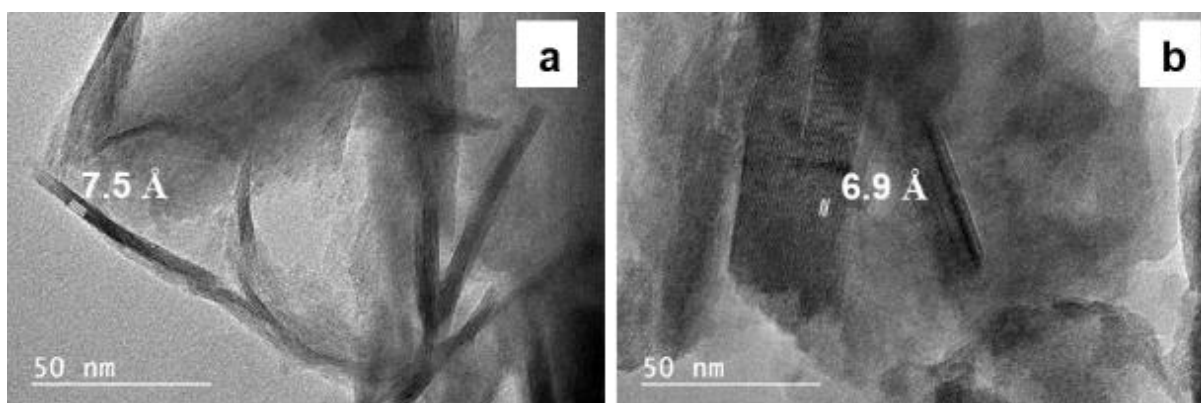
281 In total, five doublets and two sextets were necessary to describe the experimentally obtained  
282 spectra (Table 3). The two sextets corresponded to magnetite (Stucki, 2013), which was  
283 identified also by pXRD. It is generally agreed that below the Verwey temperature the magnetite  
284 spectrum is fitted with 5 sextets (Vandenberghe et al., 2000). In the current case, given the  
285 abundance of the magnetically ordered component, it seemed misleading to fit the spectrum  
286 part corresponding to magnetite with 5 components as indicated in the literature. It seemed  
287 more convincing to fit with only two sextets of most abundant components instead. Three  
288 doublets with center shifts of 0.26, 0.33, and 0.54 mm/s were attributed to Fe(III). Two doublets  
289 with center shifts of 0.33 and 0.26 mm/s corresponded to octahedrally and probably  
290 tetrahedrally coordinated Fe(III) of 1:1 phyllosilicate, respectively (Baron et al., 2017). The  
291 third doublet of Fe(III) with center shift of 0.54 mm/s could be attributed to amorphous or  
292 poorly crystalline iron oxides not revealed by pXRD. Finally, the two doublets with large values  
293 of center shifts of 1.21 and 1.39 mm/s corresponded to Fe(II) of 1:1 phyllosilicate (Chemtob et  
294 al., 2015). Mössbauer spectroscopy revealed the high complexity of the sample having several  
295 mineral phases: phyllosilicates, magnetite, and poorly crystallized iron oxide.

296

297 **Table 3.** Mössbauer parameters for synthesis product with  $(\text{Fe}/\text{Si})_{\text{ini}} = 1.50$  at 77 K, where CS  
 298 is center shift,  $\Delta$  is quadrupole splitting, H is hyperfine field, and R.A. is relative abundance

	CS (mm/s)	$\Delta$ (mm/s)	H (kOe)	R.A. (%)	
Doublet (1)	1.39	2.33		21	Fe(II) in clay mineral
Doublet (2)	1.21	3.05		20	Fe(II) in clay mineral
Doublet (3)	0.33	0.96		16	Fe(III) octahedral clay
Doublet (4)	0.26	0.66		9	Fe(III) tetrahedral clay
Doublet (5)	0.54	0.99		26	Fe(III) poorly cryst. iron oxides
Sextet (6)	0.45	-0.09	505	5	Magnetite
Sextet (7)	0.27	0.13	475	3	Magnetite

299  
 300 Considering the complex mineralogy of the sample, an observation of particles under  
 301 transmission electron microscopy (TEM) was carried out to learn more in detail about the  
 302 structure and chemistry of phyllosilicates only. Observations by TEM revealed the layer  
 303 structure characteristics of 1:1 phyllosilicates with an average layer-to-layer distance of 7 Å  
 304 (Fig. 4). Different thicknessed of particles was observed, ranging from a few layers to several  
 305 tens of layers.



306  
 307 **Fig. 4.** TEM images of synthesis product with  $(\text{Fe}/\text{Si})_{\text{ini}} = 1.50$

308 The chemical analysis revealed two sets of zones (Table 4). One with  $(\text{Fe}/\text{Si})_{\text{EDX}}$  molar ratio of  
 309 2.3 and the second one with  $(\text{Fe}/\text{Si})_{\text{EDX}} = 1.2$ . Both ratios were lower than determined by XRF

310 (Table 1). The results of XRF analysis gave the average composition for the entire synthesis  
 311 product which contained different phases as shown by XRD and Mössbauer spectroscopy.  
 312 However, EDX was performed over a limited zone of particles dispersed on the copper grid  
 313 and, as suggested by observations, related to phyllosilicate particles.

314 **Table 4.** Semi-quantitative chemical analysis of particles of sample  $(\text{Fe}/\text{Si})_{\text{ini}} = 1.50$  by TEM-  
 315 EDX

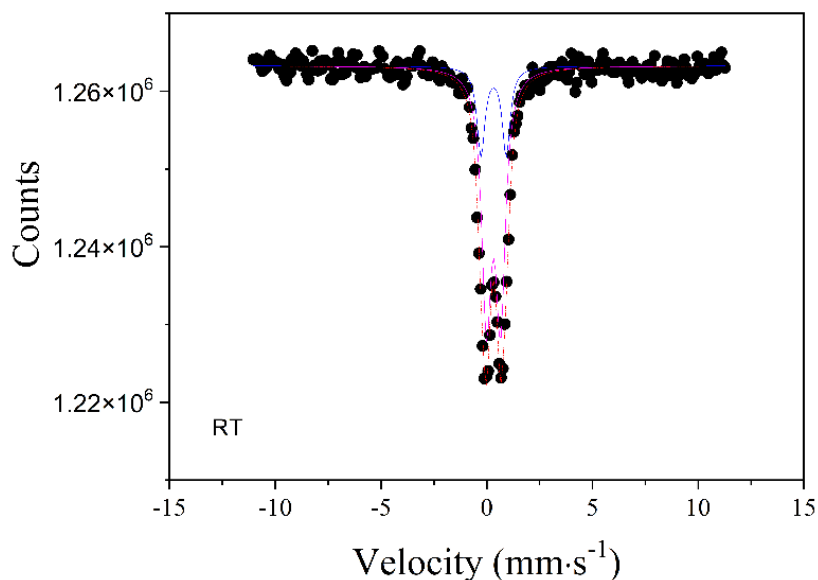
	Set I	Set II
Element mass (%)		
O	40±1	41±1
Na	0.9±0.3	0.9±0.3
Si	10.5±0.5	17±1
Fe	48±2	41±1
Molar ratio		
$(\text{Fe}/\text{Si})_{\text{EDX}}$	2.3±0.2	1.2±0.1

316  
 317 Considering the information gathered from different characterization techniques, it could be  
 318 concluded that the synthetic sample contained 1:1 phyllosilicate with Fe(III) and Fe(II) entities.  
 319 The  $(\text{Fe}/\text{Si})_{\text{EDX}} = 2.3$  was close to the ratio corresponding to the crystal chemistry of  
 320 cronstedtite, where Fe was located in both the octahedral (with presence of ferrous and ferric  
 321 cations) and tetrahedral sheets (containing ferric cations), whereas  $(\text{Fe}/\text{Si})_{\text{EDX}} = 1.2$   
 322 corresponded to greenalite, where Fe is located only in the octahedral sheet (only ferrous  
 323 cations). Such variation of  $(\text{Fe}/\text{Si})$  suggested important heterogeneity in the chemistry of the  
 324 neoformed phyllosilicate phases.

#### 325 *Characterization of 2:1 Phyllosilicate Containing Synthesis Product*

326 Powder XRD of synthesis products with  $(\text{Fe}/\text{Si})_{\text{ini}}$  from 0.50 to 1.00 were very similar and two  
 327 iron-containing crystalline phases were identified: 2:1 phyllosilicate and iron oxide (Fig. 1).  
 328 The analysis of the sample with  $(\text{Fe}/\text{Si})_{\text{ini}} = 0.75$  by Mössbauer spectroscopy at room  
 329 temperature showed the presence of Fe(III) only (Fig. 5). Due to the low signal/noise ratio and

330 the complexity of data, further analysis of Mössbauer spectra obtained at 4 K was not  
 331 performed. The spectrum at room temperature permitted the hypothesis of the presence of Fe(II)  
 332 in the sample to be discarded (Table 5).



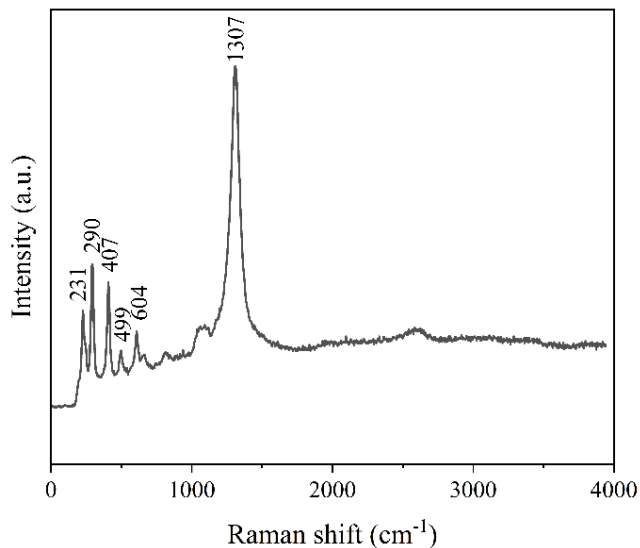
333  
 334 **Fig. 5.** Mössbauer spectrum for synthesis product with  $(\text{Fe}/\text{Si})_{\text{ini}} = 0.75$  at 290 K

335 **Table 5.** Mössbauer parameters for synthesis product with  $(\text{Fe}/\text{Si})_{\text{ini}} = 0.75$  at 290 K , where  
 336 CS is center shift,  $\Delta$  is quadrupole splitting,  $\varepsilon$  quadrupole shift, H is hyperfine field, and R.A.  
 337 is relative abundance

	CS (mm/s)	$\Delta$ or $\varepsilon$ (mm/s)	H (kOe)	R.A. (%)	
Doublet (1)	0.32	1.20		23	Fe(III) poorly cryst. iron oxides
Doublet (2)	0.32	0.67		77	Fe(III) in clay mineral

338 Owing to the complexity of the results from the Mössbauer spectroscopy, Raman spectroscopy  
 339 was performed for this sample to investigate in more detail the possible iron oxides present in  
 340 the sample (Fig. 6). Different powers were applied to examine if iron oxide would oxidize under  
 341 the beam. However, the same spectral pattern was obtained, confirming that no changes  
 342 happened to the sample upon its exposure to the beam. The spectrum obtained corresponded to

343 hematite with characteristic intense bands at 231, 290, 407, 499, 604, and 1316  $\text{cm}^{-1}$  (Hanesch,  
344 2009).



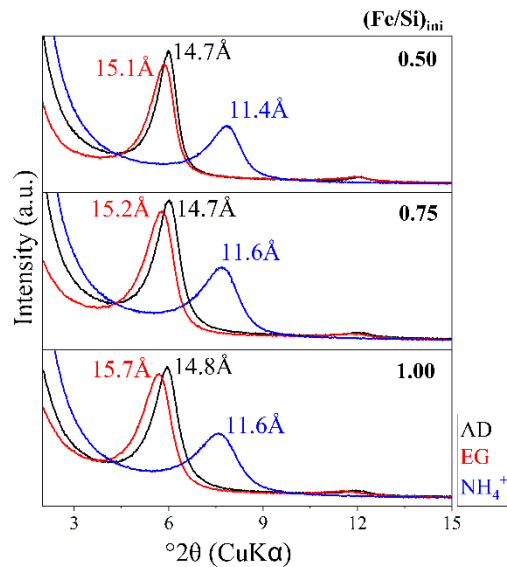
345

346 **Fig. 6.** Raman spectrum for synthesis product with  $(\text{Fe}/\text{Si})_{\text{ini}} = 0.75$

347 In summary, Raman spectroscopy allowed the type of iron (III) oxide to be identified (not  
348 possible by XRD). This information gave a more complete vision of the complexity of the  
349 sample, where hematite was present along with 2:1 Fe(III)-rich phyllosilicate. Further  
350 characterization by XRD (oriented slides), FTIR, and TEM were undertaken to investigate in  
351 more detail the 2:1 phyllosilicate.

352 Regarding the 2:1 phyllosilicate, air-dried oriented preparations (AD) treated with ethylene  
353 glycol (EG) did not exhibit significant swelling, suggesting high-charge smectite or chlorite  
354 (Fig. 7). The exchange with  $\text{NH}_4^+$  allowed the hypothesis of chlorite to be discarded; however,  
355 the asymmetry and broadness of peaks suggested a rather heterogeneous sample in terms of  
356 layer chemistry.

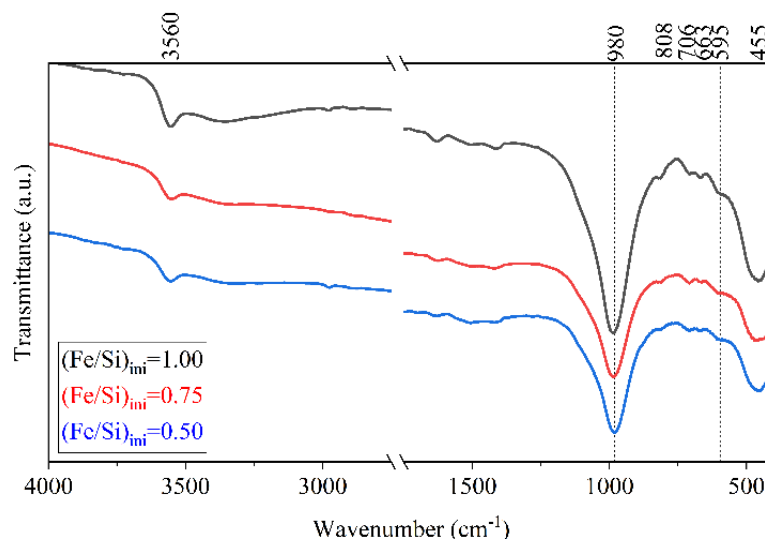




357

358 **Fig. 7.** X-ray diffractograms of oriented preparations for samples with  $(\text{Fe}/\text{Si})_{\text{ini}}$  from 0.50 to  
 359 1.00. AD correspond to air-dried preparation, EG – saturated with ethylene glycol and  $\text{NH}_4^+$  –  
 360 exchanged with  $\text{NH}_4^+$

361 The analysis of FTIR spectra showed characteristic O–H and Si–O vibrations (Fig. 8). The low  
 362 value of Si–O stretching at  $980\text{ cm}^{-1}$  suggested Fe(III) substitution in the tetrahedral sheet  
 363 (Baron et al., 2016). The band of O–H stretching at  $3560\text{ cm}^{-1}$  corresponded to the O–H group  
 364 linked to Fe(III). Other characteristic bands of Fe-rich smectites (nontronites) could also be  
 365 identified according to literature (Table 6) (Neumann et al., 2011).



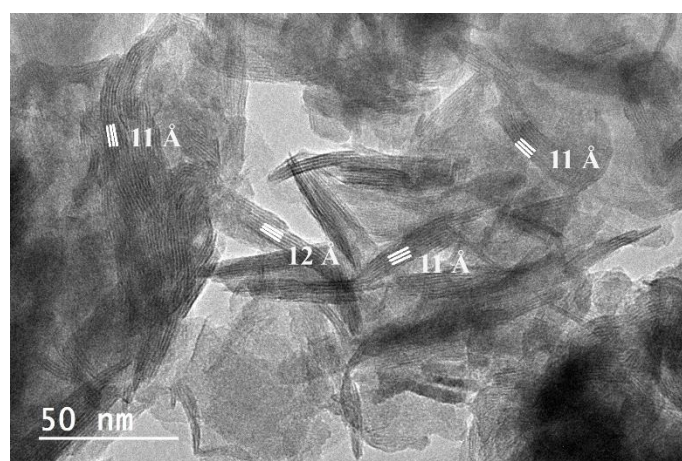
366

367 **Fig. 8.** FTIR spectra for samples with  $(\text{Fe}/\text{Si})_{\text{ini}} = 0.50, 0.75$  and  $1.00$

368 **Table 6.** Identified FTIR bands and corresponding vibration modes for (Fe/Si)<sub>ini</sub> from 0.50 to  
 369 1.00

Wavenumber (cm <sup>-1</sup> )	Vibration mode
3560	O–H stretching
980	Si–O stretching
808	O–H bending
706	Fe <sup>3+</sup> <sub>tet</sub> –O stretching
663	Fe <sup>3+</sup> <sub>oct</sub> –O <sub>apical</sub> out-of-plane deformation / Si–O
595	Fe <sup>3+</sup> <sub>oct</sub> –O <sub>ap</sub> –Si <sup>4+</sup> <sub>tet</sub> coupled lattice deformation band
455	Si–O bending

370  
 371 Observation of the sample under TEM revealed the presence of platy-like particles (Fig. 9). A  
 372 clear layer-type structure could be distinguished, characteristic of phyllosilicates. The measured  
 373 distances between layers were in the range 11 to 12 Å, corresponding to one of 2:1  
 374 phyllosilicates. In contrast to the (Fe/Si)<sub>ini</sub> = 1.50 sample, all observed particles were just a few  
 375 layers thick.



376  
 377 **Fig. 9.** TEM image of synthesis product with (Fe/Si)<sub>ini</sub> = 0.75

378 The measured chemical composition for the zones corresponding to phyllosilicates showed  
 379 homogeneous distribution of elements (Table 7) contrary to two distinct zones observed  
 380 previously for the sample (Fe/Si)<sub>ini</sub> = 1.50. The calculated average (Fe/Si)<sub>EDX</sub> = 1.1 ± 0.2

381 suggests that the average chemical composition for smectite should be  $^{\text{INT}}\text{Ca}_{0.50}$ -  
 382  $_{0.75}^{\text{VI}}[\text{Fe}^{3+}_2]^{\text{IV}}[\text{Si}_{2.5-3}\text{Fe}^{3+}_{1.0-1.5}]\text{O}_{10}(\text{OH})_2$ . This result is in agreement with the experiments  
 383 reported by Baron et al. (2016). They reported a synthesis of high-charge nontronite with  
 384 tetrahedral Fe(III) between 1.0 and 1.5 atoms per formula unit when  $\text{pH} > 13$ .

385 **Table 7.** Semi-quantitative chemical composition of sample with  $(\text{Fe}/\text{Si})_{\text{ini}} = 0.75$  determined  
 386 by TEM-EDX

Element mass (%)	
O	38±1
Ca	7.2±0.3
Si	17±2
Fe	37±2
Molar ratio	
$(\text{Fe}/\text{Si})_{\text{EDX}}$	1.1 ± 0.3

387

388

## DISCUSSION

389 Initially, the choice was made to perform the synthesis at hydrothermal conditions in an attempt  
 390 to increase the yield and crystallinity of the final synthesis product. On the one hand, this  
 391 objective was reached as crystalline phyllosilicates were produced in most of the samples  
 392 during synthesis. Their amount and crystallinity allowed a sufficiently detailed characterization  
 393 to be carried out. On the other hand, the use of hydrothermal conditions led to processes which  
 394 were difficult to control at this temperature and pressure, and which caused the experimental  
 395 variables to evolve. This resulted in a rather complex mineralogy: phyllosilicates, magnetite,  
 396 and/or hematite were identified in synthesis products. In addition, for the sample with  $(\text{Fe}/\text{Si})_{\text{ini}}$   
 397 = 2.33, a large decrease in pH occurred during the precipitation of the precursor and as the  
 398 hydrothermal treatment “moved” this system out of the phyllosilicate stability field. The  
 399 synthesis performed at lower temperatures, closer to room temperature, enabled better and  
 400 continuous control of experimental conditions, and thus a precipitation of a single mineralogical

401 phase, as was shown in the experiments of Tosca et al. (2016) and Hinz et al. (2021). However,  
402 such an experiment requires a significantly longer time (3 months in the case of Tosca et al.,  
403 2016) or a subsequent hydrothermal treatment at higher temperatures as in the case of Hinz et  
404 al. (2021) to obtain sufficient quantities of the material for further characterization, while yield  
405 products were still very low in crystallinity.

406 Despite the complex mineralogy obtained, study of the phyllosilicates was still possible, as well  
407 as verifying the current hypothesis that a single phyllosilicate would form at a given initial  
408 Fe/Si. For  $(\text{Fe/Si})_{\text{ini}} < 1.50$ , a 2:1 phyllosilicate, a high-charge nontronite was synthesized. Very  
409 similar samples were obtained regardless of the  $(\text{Fe/Si})_{\text{ini}}$  for this range. The formula unit found  
410 in this study was in agreement with nontronite synthesized by Baron et al. (2016) at the same  
411 pH. This suggested that in the case of nontronite the pH could be the main governing factor  
412 determining the formation of this Fe(III)-rich smectite as evidenced by Baron et al. (2016).  
413 Their results and the current study are also in agreement with previous findings (Boumaiza et  
414 al., 2020). Those authors showed that among three synthesis parameters, namely, time,  
415 temperature, and initial OH/Fe molar ratio, the last named (and consequently the pH) had the  
416 most important effect on the final synthesis product.

417 Another conclusion of the Boumaiza et al. (2020) study was that the kinetics of the formation  
418 of 2:1 phyllosilicate in the Fe–Si–O–H system for a given  $(\text{Fe/Si})_{\text{ini}}$  was faster compared to 1:1  
419 phyllosilicate. As discussed already in the Introduction, this could then explain, for a given  
420  $(\text{Fe/Si})_{\text{ini}}$ , why the stoichiometry corresponds to a 2:1 phyllosilicate rather to a 1:1 phyllosilicate.  
421 Therefore, a compromise between the increase in temperature and yield, yet limiting the  
422 formation of a 2:1 phyllosilicate, must be found.

423 In the current study, the formation of the 1:1 phyllosilicate was achieved for  $(\text{Fe/Si})_{\text{ini}} \geq 1.50$ .  
424 However, the phyllosilicate phase which formed was rather heterogeneous, showing two  
425 chemical compositions, and thus possibly two types of phases, cronstedtite and greenalite. A  
426 more rigorous control of synthesis conditions (Eh, pH) may be necessary in this particular  
427 system to synthesize a homogeneous phyllosilicate. Indeed, Pignatelli et al. (2014) presented  
428 the calculated stability fields of hematite, cronstedtite, magnetite, and greenalite, and showed  
429 that the stability field of cronstedtite at 150°C is very narrow.

430 In summary, the 2:1 phyllosilicate seemed to be less sensitive to redox conditions. For the 1:1  
431 phyllosilicate, its formation also depended on pH, and also was strongly dependent on the redox  
432 conditions of the system. Indeed, Rivard et al. (2013) had shown that, in a kaolinite-iron system

433 under anoxic conditions, a berthierine-like phase was formed which dissolved upon  
434 introduction of O<sub>2</sub> into the system. It has to be noted that, even if a synthesis of homogeneous  
435 phyllosilicate could be achieved, the synthesis time was relatively short compared to the  
436 expected formation of such phyllosilicate analogues in Nature. As a consequence, synthetic iron  
437 rich phyllosilicates could be expected to be more heterogeneous than natural ones (Baker &  
438 Strawn, 2014).

439 Implication of the results of this study are important for engineered systems, where soluble  
440 silicon and iron species might be present. The study showed that the  $(\text{Fe}/\text{Si})_{\text{ini}} \leq 1.50$  in aqueous  
441 solution can lead to the precipitation of phyllosilicates, and thus possibly induce corrosion or  
442 scale formation. Three cases can be mentioned regarding engineered systems where such  
443 conditions might occur: (1) the scale formation in solution-conducting pipes, (2) the corrosion  
444 of steel containers or pipes, and (3) the corrosion of glass. First, regarding scale formation in  
445 solution-conducting pipes, such conditions can occur for basic solutions where the  
446 concentration of silica is high, and iron can be present such as in hyper-saline brines (Manceau  
447 et al., 1995). Such scale formation can then clog pipes and damage other equipment. Second,  
448 corrosion of the metal container or pipe can occur in an environment where such pipes or  
449 containers are surrounded by cement material. The pH of cement material is basic. As a result,  
450 some dissolved silica is expected to be present if the material is wet and porous. In contact with  
451 metal where some Fe<sup>2+</sup> could be leached, the formation of phyllosilicates can then be expected,  
452 leading to further dissolution of steel. Indeed, previous studies of such a system reported the  
453 presence of phyllosilicates (Lanson et al., 2012). Third, most glass compositions contain a large  
454 amount of silica. Thus, on the glass surface a significant amount of Si–OH species can be  
455 present. In contact with steel or dissolved Fe<sup>2+</sup>, phyllosilicate precipitation can then be expected  
456 due to a high Si/Fe ratio (i.e. low Fe/Si ratio). Silica consumption can then lead to glass  
457 corrosion. Indeed, the study of Carriere et al. (2021) identified phyllosilicate phases on the  
458 glass–steel interface.

## 459 CONCLUSIONS

460 The synthesis performed in the Fe–Si–H<sub>2</sub>O system at 150°C showed that the initial Fe/Si molar  
461 ratio and the pH are critical parameters with regard to specificity of neoformed phases. The  
462 formation of ferrous serpentine (Fe(II)-containing) appears to be restricted to high iron  
463 concentration in solution and a very low redox range at high temperature (i.e. 150°C). In  
464 addition, a heterogeneity of formed phases (cronstedite or greenalite) was identified. For lower  
465 initial Fe/Si molar ratio, formation of a single high-charge nontronite phase was observed. The

466 ion exchange experiments with  $\text{NH}_4^+$  suggested some layer heterogeneity. Thus, the hypothesis  
467 of the formation of a single one type homogeneous clay mineral was not proven. However, for  
468 lower initial Fe/Si molar ratios, one kind of mineral, nontronite, was formed. Progress is still  
469 needed to achieve better selectivity, purity, and yield for structural, chemical, and  
470 thermodynamic characterizations. The findings and study in general are of interest for  
471 engineering systems where soluble iron and silicon species might be found, in glass and steel  
472 corrosion, and scale formation in pipes.

## 473 DECLARATIONS

### 474 *Funding*

475 The study was conducted within the framework of R&D project between the French National  
476 Agency for Radioactive Waste Management (ANDRA) and CNRS.

### 477 *Conflicts of interest/Competing interests*

478 On behalf of all authors, the corresponding author states that there is no conflict of interest.

### 479 *Availability of data and material*

480 All data generated or analyzed during this study are included in this published article and its  
481 supplementary information files.

### 482 *Code availability*

483 Not applicable.

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