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Characterization of Iron-Rich Phyllosilicates Formed at Different Fe/Si Ratios

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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 μm (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°C)
58 compared to the one of greenalite (up to 150°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 ($18.2 \text{ M}\Omega \cdot \text{cm}$), 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 Fe^{2+} oxidation.
119 Next, a certain amount of sodium orthosilicate (Na_4SiO_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 (pH_{ini}) and then again in an aliquot of the supernatant withdrawn
 126 after the synthesis (pH_{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 (Eh_{ini}) in an aliquot withdrawn from the suspension and in the aliquot of the supernatant
 131 after the synthesis (Eh_{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	pH_{ini}	Eh_{ini} (mV/SHE)	$(\text{Fe/Si})_{\text{solid}}$ molar	pH_{f}	Eh_{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 ($12,860\times g$) 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 θ - θ
 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°) 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 Ca^{2+} using
158 1 M 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°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 ~ 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° , 0.125° , and 2.3° , 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 cm^{-1} with a resolution
184 of 4 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}Co in a Rh matrix. Data were obtained from appropriate amounts (10 mg of Fe per 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}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 μm 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.

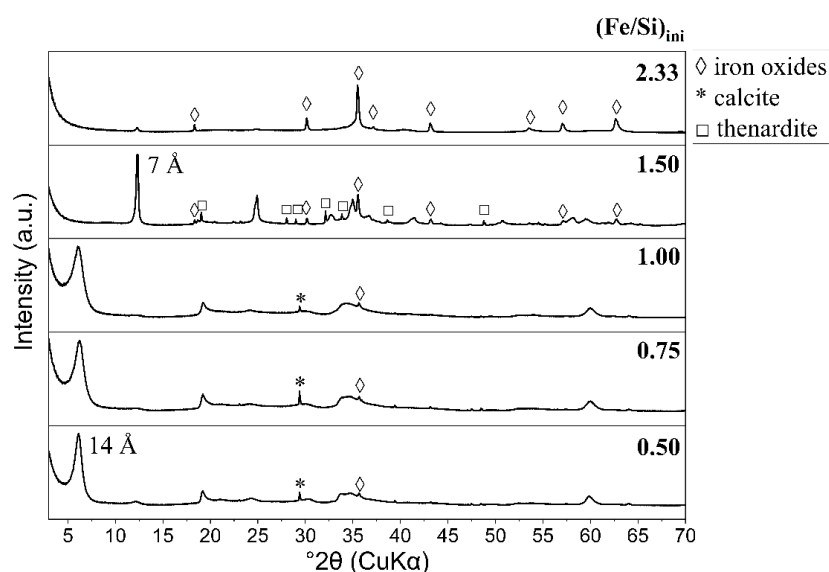
205 *Transmission electron microscopy coupled with energy dispersive X-ray spectroscopy.* For the
206 observations under transmission electron microscopy (TEM), a few particles of sample were
207 dispersed in chloroform using ultrasound and deposited on a 300-mesh copper TEM grid.
208 Images were acquired 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 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*

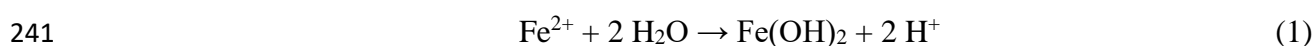
221 Crystalline phase analysis of synthesis products showed that for $(\text{Fe}/\text{Si})_{\text{ini}} \leq 1.00$, 2:1
222 phyllosilicate was formed (Fig. 1). The 2:1 phyllosilicate was identified in XRD by its
223 characteristic reflections at $6.26; \sim 19.20\text{--}19.30; \sim 34.00,$ and $60.06^\circ 2\theta$ (i.e. $14.11, 4.62\text{--}4.58,$
224 $2.60,$ and $1.54\ \text{\AA}$, respectively) (Brindley & Brown, 1982). Calcite (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 (Na_2SO_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 $0.50 \leq (\text{Fe}/\text{Si})_{\text{ini}} \leq 2.33$

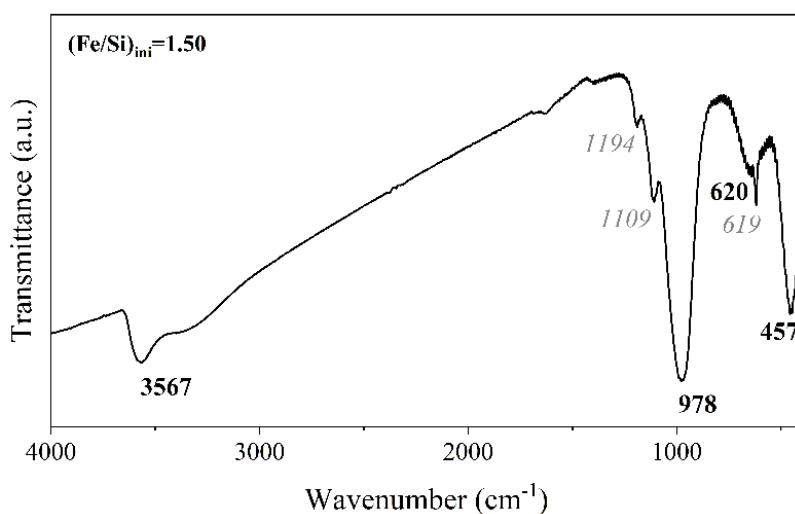
235 Analysis by XRF of synthesis products showed that the (Fe/Si) molar ratio after the synthesis
236 was higher than the (Fe/Si) molar ratio introduced in the mixture, suggesting only partial iron-
237 rich phyllosilicate precipitation and the formation of other Fe-bearing phases (Table 1). This is
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 $(\text{Fe/Si})_{\text{ini}} = 1.50$ and hematite in samples
246 with $(\text{Fe/Si})_{\text{ini}} \leq 1.00$. 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 $(\text{Fe/Si})_{\text{ini}} = 1.50$ was chosen for a more detailed characterization as it indicated
251 a superior phyllosilicate phase crystallinity compared to the sample with $(\text{Fe/Si})_{\text{ini}} = 2.33$
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 cm^{-1} correspond to thenardite, which
254 was also identified by pXRD (Farmer, 1974). The 620 cm^{-1} band could be a combination of O-
255 H deformation and Fe(III)-O_{apical} 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 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

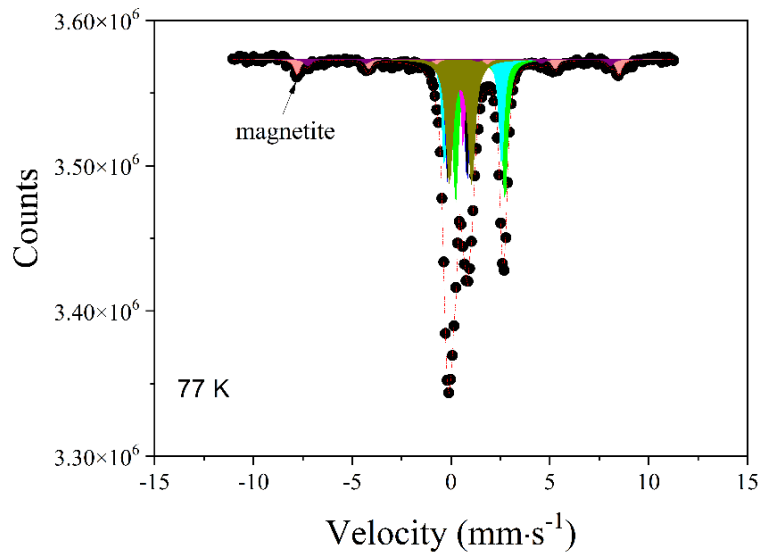
Table 2. Identified FTIR bands and corresponding vibration modes for $(\text{Fe/Si})_{\text{ini}} = 1.50$

Wavenumber (cm^{-1})	Vibration mode
3567	O–H stretching
978	Si–O stretching
620	O–H bending / Fe(III)–O _{ap} 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)_{ini} = 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)_{ini} = 1.50 at 77 K

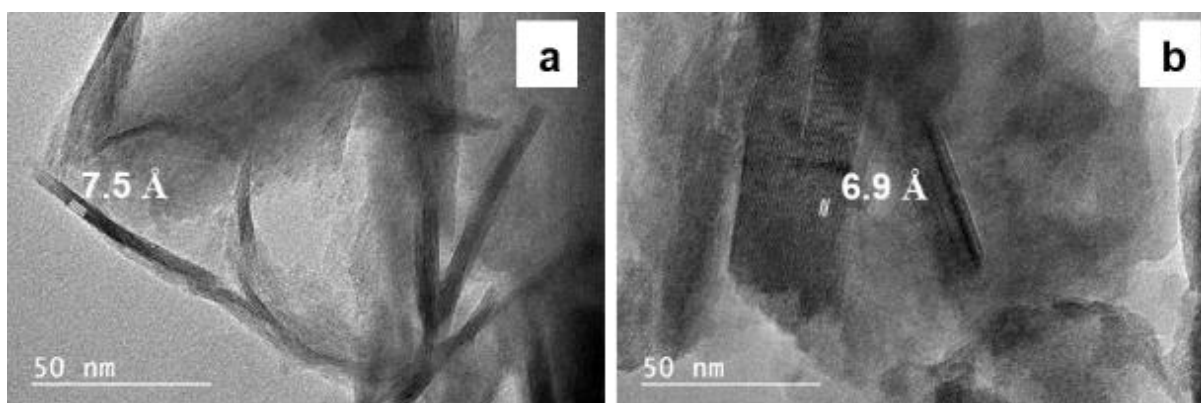
281 In total, five doublets and two sextets were necessary to describe the experimentally obtained
282 spectra (Table 3). The two sextets corresponded to magnetite (Stucki, 2013), which was
283 identified also by pXRD. It is generally agreed that below the Verwey temperature the magnetite
284 spectrum 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, Δ is quadrupole splitting, H is hyperfine field, and R.A. is relative abundance

	CS (mm/s)	Δ (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

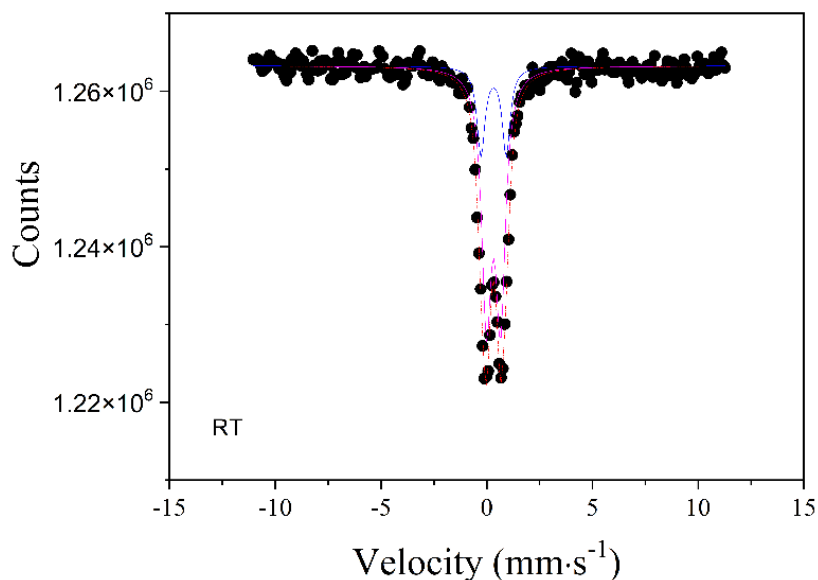
	Set I	Set II
Element mass (%)		
O	40±1	41±1
Na	0.9±0.3	0.9±0.3
Si	10.5±0.5	17±1
Fe	48±2	41±1
Molar ratio		
$(\text{Fe}/\text{Si})_{\text{EDX}}$	2.3±0.2	1.2±0.1

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 (Fe/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).



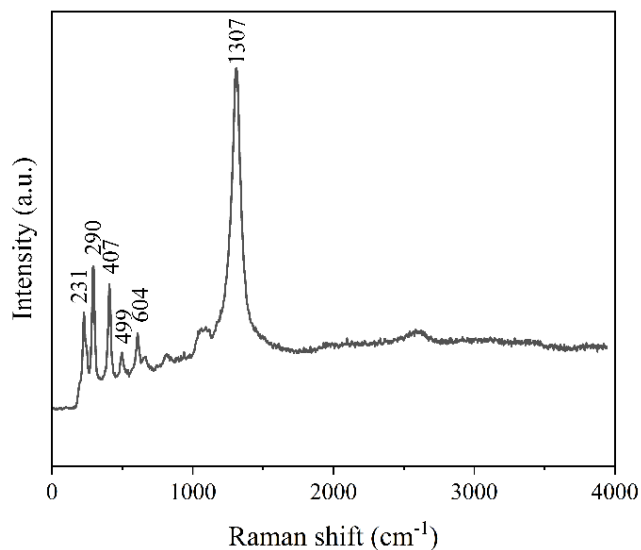
333
 334 **Fig. 5.** Mössbauer spectrum for synthesis product with $(\text{Fe}/\text{Si})_{\text{ini}} = 0.75$ at 290 K

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, Δ is quadrupole splitting, ε quadrupole shift, H is hyperfine field, and R.A.
 337 is relative abundance

	CS (mm/s)	Δ or ε (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 cm^{-1} (Hanesch,
344 2009).

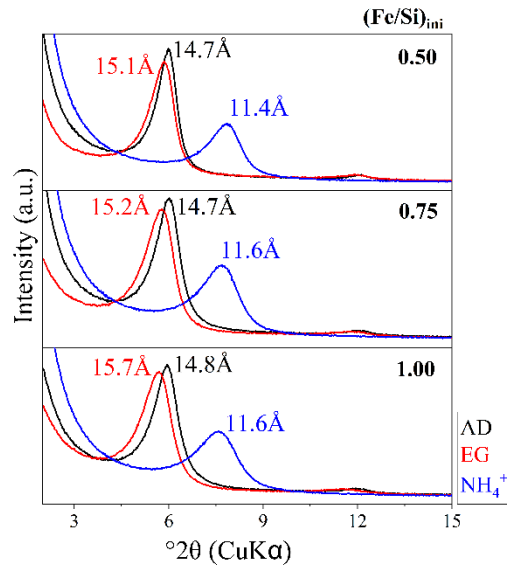


345

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.

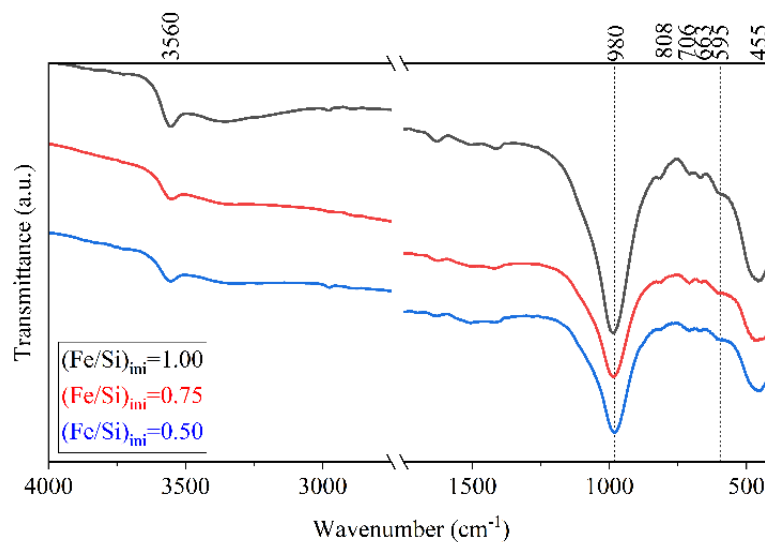
352 Regarding the 2:1 phyllosilicate, air-dried oriented preparations (AD) treated with ethylene
353 glycol (EG) did not exhibit significant swelling, suggesting high-charge smectite or chlorite
354 (Fig. 7). The exchange with NH_4^+ allowed the hypothesis of chlorite to be discarded; however,
355 the 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 NH_4^+ –
 360 exchanged with 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 cm^{-1} suggested Fe(III) substitution in the tetrahedral sheet
 363 (Baron et al., 2016). The band of O–H stretching at 3560 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).



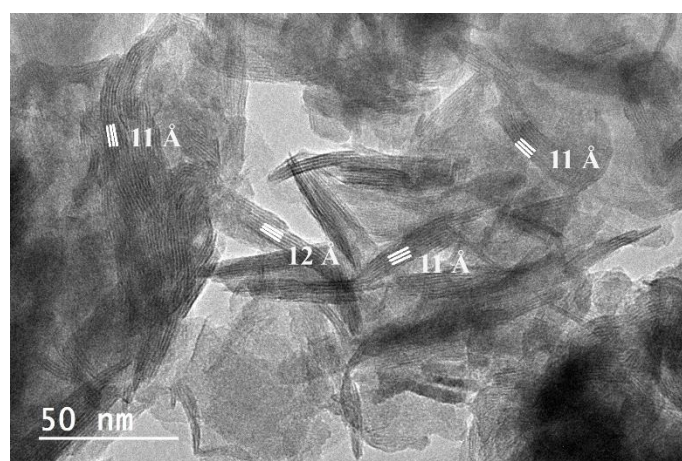
366

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)_{ini} from 0.50 to
 369 1.00

Wavenumber (cm ⁻¹)	Vibration mode
3560	O–H stretching
980	Si–O stretching
808	O–H bending
706	Fe ³⁺ _{tet} –O stretching
663	Fe ³⁺ _{oct} –O _{apical} out-of-plane deformation / Si–O
595	Fe ³⁺ _{oct} –O _{ap} –Si ⁴⁺ _{tet} 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)_{ini} = 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)_{ini} = 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)_{ini} = 1.50. The calculated average (Fe/Si)_{EDX} = 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 O₂ 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 Fe²⁺ 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 Fe²⁺, 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–H₂O 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 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

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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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