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## 1 IRON-RICH CLAY MINERAL SYNTHESIS USING DESIGN OF EXPERIMENTS

### 2 APPROACH

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### 10 Abstract

11 The precipitation of iron-rich clay minerals has been reported in various geologic environments.  
12 However, large quantities of these minerals are not widely accessible to study their  
13 thermodynamic properties and thus improve our understanding of these particular geological  
14 systems. To obtain sufficient amount of iron-rich minerals, their synthesis can be foreseen. A  
15 design of experiments and surface response methodology was used in this study to find  
16 optimum synthesis conditions for these clay minerals. Three parameters were considered:  
17 quantity of OH<sup>-</sup>, synthesis time and temperature. The quantity of OH<sup>-</sup> had the largest influence  
18 on the synthesis result. The amount of 2:1 type clay mineral with respect to 1:1 type clay mineral  
19 increased with OH/Fe molar ratio. Time and temperature had less significant impact on the  
20 synthesis outcome, yet the formation of 2:1 type phase was favored at short synthesis time (1  
21 day) and high temperature (160°C). The findings suggested that the kinetic of 2:1 type clay

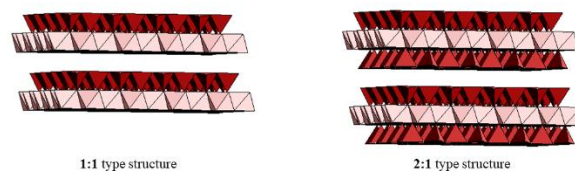
22 mineral phase formation with respect to 1:1 type phase was faster, yet the precipitation was  
23 strongly dependent on the availability of the reactants.

## 24 **Key words**

25 iron-rich clay minerals, design of experiments, synthesis, nontronite, berthierine

## 26 **Introduction**

27 Clay minerals are layered silicate materials, where silica tetrahedra are arranged in continuous  
28 sheet combined with hexagonally coordinated metal-containing octahedral sheet. In general,  
29 two types of structures can be distinguished, a so-called 2:1 type clay mineral where the metal-  
30 containing octahedral sheet is sandwiched between two silicate sheets forming a 2:1 layer, and  
31 a 1:1 type clay mineral, where one silicate sheet is combined with one octahedral sheet forming  
32 a 1:1 layer (Figure 1). These minerals are widely encountered in natural sedimentary rocks and  
33 soils. The most common elements found in natural clay minerals are Si, Al, Mg, Fe, O and H  
34 (i.e., montmorillonite, beidellite, vermiculite, kaolinite, saponite). Minerals containing solely  
35 Si, Fe, O and H are known, but less common (i.e., greenalite, cronstedtite, hisingerite,  
36 nontronite).



37

38

**Figure 1.** Schematic representation of clay mineral structures.

39 The environments where the formation of iron-rich clay minerals have been reported include  
40 deep-sea sediments (Baldermann et al., 2015; Tosca et al., 2016), subduction zones (Beaufort  
41 et al., 2015; Sforza et al., 2018), transform faulting (Kodolányi et al., 2012), the surface of Mars  
42 (Chemtob et al., 2015) and meteorites (Zolotov, 2015). Their presence has also been reported  
43 at the interface between different materials such as steel and glass (Schlegel et al., 2016) and  
44 steel and clay-rich rocks (Lanson et al., 2012) studied for the conception of radioactive waste  
45 repository sites.

46 For the different geological systems, it is of great interest to predict the evolution of these  
47 systems whether millions of years in the past, as in the case of Mars and Earth surfaces, or other  
48 thousands of years in the future as in the case of long-term radioactive waste repository sites.  
49 In order to do this, geochemical modelling is required to predict the evolution with time of the  
50 mineralogical composition of these different systems. The prediction of this evolution is crucial  
51 as it enables assessing the changes of key properties such as porosity and permeability.

52 To assess the clay mineral thermodynamic properties for geochemical modelling, different  
53 approaches were developed (Tardy and Fritz, 1981; Vieillard, 2000). The thermodynamic  
54 properties of clay minerals are particularly challenging to constrain owing to the great chemical  
55 and structural variability of these minerals (Gailhanou et al., 2013). A common approach to  
56 assess them is the summation of oxide/hydroxide parameters, which on the other hand are well-  
57 known. However, the knowledge of experimental thermodynamic and kinetic properties of  
58 iron-rich clay minerals would enhance the robustness of the models, as well as allow the  
59 comparison of experimental data with modelling (Gailhanou et al., 2013).

60 As Fe-rich clay mineral phases and especially tri-octahedral ones are seldom encountered in  
61 environments and as only very small quantities can be extracted, their synthesis can be foreseen.  
62 Two reviews have recently gathered the different methods carried out to prepare iron-rich clay  
63 minerals (Dzene et al., 2018; Petit et al., 2017). The hydrothermal synthesis route remains the

64 preferred one because it is a versatile and easy to use process which allows the attainment of  
65 well crystallized compounds (Jaber et al., 2013; Kloprogge, 1998; Le Forestier et al., 2010;  
66 Reinholdt et al., 2005). The key parameters governing the formation of clay minerals are the  
67 sources of reactants, synthesis time, temperature and the pH of the hydrogel. Regarding the  
68 preparative methods, the formation of a sol followed by a gel is expected to yield a  
69 homogeneous repartition of elements in the final product (Dzene et al., 2018). The use of  $\text{Fe}^{2+}$   
70 source for the preparation of precursor is expected to increase the kinetics of synthesis and to  
71 allow obtaining faster a well-crystallized product compared to the use of  $\text{Fe}^{3+}$  source (Petit et  
72 al., 2017). The three other parameters, pH, time and temperature, have been widely varied in  
73 literature and no particular tendency can be extracted. Thus, the variation from neutral to  
74 alkaline pH has been previously reported, and syntheses have been performed in various time  
75 and temperature ranges. Nevertheless, the three later parameters can significantly influence the  
76 type of synthesized clay mineral and its crystallinity (Jaber et al., 2013; Kloprogge et al., 1999).  
77 For this reason, the three parameters (time, temperature and the initial quantity of  $\text{OH}^-$ ) were  
78 chosen as the variables for this study. In general, time will intervene in reaction kinetics and  
79 crystal growth processes. The increase of synthesis time will allow attaining the equilibrium or  
80 pseudo-equilibrium conditions and will allow growing larger crystals. The temperature will  
81 intervene in both, in reaction kinetics and thermodynamics. On the one hand the increase of  
82 temperature is expected to accelerate the kinetics of reaction. Thus, higher temperature would  
83 lead to shorter synthesis time. On the other hand, the increase of temperature will influence the  
84 thermodynamics of the reaction. As the precipitation of clay minerals is in general an  
85 endothermic process (Giffaut et al., 2014), the increase of the temperature is expected to favor  
86 the formation of products. Finally, the quantity of  $\text{OH}^-$  will influence the condensation reactions  
87 (Cundy and Cox, 2005).

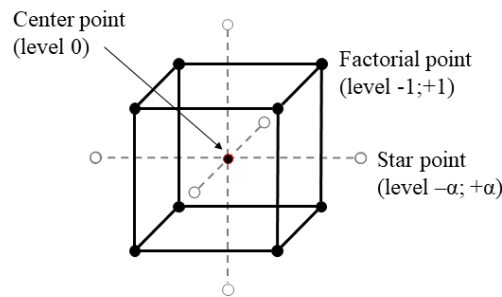
88 The complexity of the studied reactions, make the systematic exploration rather challenging.  
89 Therefore, the design of experiments (DOE) can be used. This approach largely applied in  
90 natural sciences and engineering has been only recently explored in the synthesis of inorganic  
91 materials such as zeolite, aluminophosphate and glass (Carvalho et al., 2013; Cichocki and  
92 Kościelniak, 1999; Ji et al., 2014; Katovic et al., 2001; Zhang et al., 2009). This approach has  
93 allowed to eliminate insignificant parameters and reveal the most significant ones, which  
94 influence material properties such as crystallinity, ion exchange capacity and solubility of the  
95 product. However, the method has not yet been explored for lamellar silicate synthesis. This  
96 might be due to the fact, that the characterization of synthesis products requires a set of several  
97 analytical techniques, thus choosing the response variable(s) for the DOE is not trivial. By using  
98 oriented preparation for X-ray diffraction, we took advantage of a particular feature of lamellar  
99 materials to characterize them. The objective of this study then is to test this characterization  
100 technique for the design of experiments and explore in an efficient way, how, the three  
101 parameters: quantity of OH<sup>-</sup>, synthesis time and temperature, influence the type of synthesized  
102 clay mineral and its crystallinity.

## 103 **Materials and methods**

### 104 2.1. Design of experiments

105 Preliminary experiments identified the three parameters that influence the type and amount of  
106 obtained clay mineral: synthesis time  $t$ , temperature  $T$  and  $(\text{OH}/\text{Fe})_{\text{ini}}$  molar ratio. They allowed  
107 also to set the relevant range of each of these three parameters ( $T=80\text{ }^{\circ}\text{C} - 180\text{ }^{\circ}\text{C}$ ,  $t=1 - 7$  days  
108 and  $(\text{OH}/\text{Fe})_{\text{ini}}=2 - 4$ ) for the design of experiments. To analyze the results in terms of synthesis  
109 parameters, a methodology based on Design Of Experiments (DOE) and Response Surface  
110 Methodology (RSM) was used (Myers et al., 2016).

111 For this, a central composite design for  $k = 3$  factors (T, t, (OH/Fe)<sub>ini</sub>) was used (Anderson and  
 112 Whitcomb, 2016). It consists of three sets of experimental points:  $2^k$  points coming from  
 113 classical factorial design (two levels),  $2k$  axial points (“star points”) and a center point, i.e.  
 114  $8+6+1$  experimental tests in this case (Figure 2). Thus, the center point in our study is [130 °C;  
 115 4 days; (OH/Fe)<sub>ini</sub>=3]. The eight points (factorial points) define the domain of the study, which  
 116 is also the domain of the validity to consider for the numerical interpretation of results, i.e.  
 117 (T=100 °C -160 °C, t=2.3 - 5.7 days) and (OH/Fe)<sub>ini</sub>=2.4 - 3.6). The “star points” are additional  
 118 points required to increase the efficiency of the quadratic fitting.



119

120 **Figure 2.** Scheme representing central composite design for  $k=3$  factors.

121 The main objective of DOE is to obtain the maximum of information from a minimum of  
 122 experiments. RSM enables to explore relationships between the studied functions and the  
 123 operating factors. To obtain an optimal response a linear quadratic model with 10 parameters  
 124 is used to numerically approximate the response function. For this, a system of 15 equations  
 125 with 10 variables is statistically solved by minimizing a quadratic criterion, i.e.  
 126  $\sum_{i=1}^n (y_{exp}(i) - y_{calc}(i))^2$ , where  $y_{exp}$  and  $y_{calc}$  are the experimental and calculated variable,  
 127 respectively. The studied parameters (T, t and OH/Fe molar ratio) are standardized in the range  
 128 [-1,1] to analyze the sensitivity of the calculated response functions. Additional experiments  
 129 were performed to investigate experimental error. The relevance of the response functions

130 (presented in paragraph 2.3.) was studied by statistical analysis via the calculation of five  
131 criteria, as follows:

132 - The determination coefficient  $r^2$

133 - The standard error of estimate  $S = \sqrt{\frac{\sum_{i=1}^n (y_{exp}(i) - y_{calc}(i))^2}{n-6}}$

134 - The Marquard's percent standard deviation MPSD =  $\sqrt{\frac{1}{n-6} \sum_{i=1}^n \frac{(y_{exp}(i) - y_{calc}(i))^2}{y_{exp}(i)^2}}$

135 - The mean absolute error EABS =  $\frac{1}{n} \sum_{i=1}^n |y_{exp}(i) - y_{calc}(i)|$

136 - The mean relative error RE =  $\frac{1}{n} \sum_{i=1}^n \left| \frac{y_{exp}(i) - y_{calc}(i)}{y_{exp}(i)} \right|$

137 The five criteria are used to assess the pertinence of the numerical approximation. The studied  
138 functions are studied directly and in power, logarithmic, exponential, hyperbolic, etc. forms.  
139 According to the five studied criteria, the best function is chosen and used for the numerical  
140 approximation.

## 141 2.2. Synthesis protocol and chemicals used

142 The following chemicals were used: iron (II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , Merck,  
143 99.9 %) as Fe(II) source, fumed silica ( $\text{SiO}_2$ , Aerosil<sup>®</sup> 380, Evonik) as silicon source, sodium  
144 hydroxide (NaOH, Sigma Aldrich, 97 wt.%) to provide an alkaline medium and sodium  
145 dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ , Sigma Aldrich, ca. 85 wt.%) to maintain reducing conditions. Double  
146 distilled water (DDW, 18.2 M $\Omega$ ·cm) was used for all the experiments.

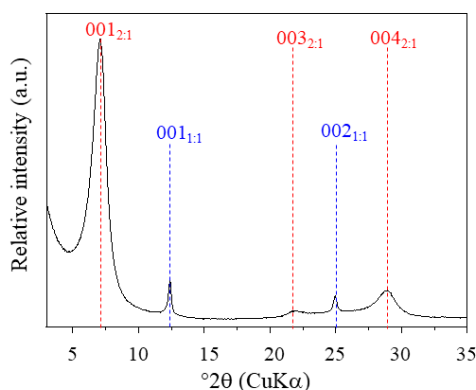
147 The procedure is based on a hydrothermal synthesis starting from a suspension having an Fe to  
148 Si molar ratio equal to 1.5. The procedure consisted of dissolving successively in 70 mL of  
149 distilled water 0.041 g of  $\text{Na}_2\text{S}_2\text{O}_4$ , 4.510 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.647 g of  $\text{SiO}_2$  and a given quantity



150 of NaOH at the desired OH/Fe molar ratio corresponding to each run of experiment (Table 1).  
151 Thus, the initial theoretical concentrations were  $c(\text{Fe}^{2+}) = 0.23 \text{ mol}\cdot\text{L}^{-1}$ ,  $c(\text{Si})=0.15 \text{ mol}\cdot\text{L}^{-1}$  and  
152  $c(\text{OH}^-)=0.45 - 1.00 \text{ mol}\cdot\text{L}^{-1}$ . The mixture was stirred during 2 hours at room temperature before  
153 being sealed in a Teflon-lined stainless-steel autoclaves (Top Industrie ®, 150 mL) and put at  
154 the desired temperature (T) ranging from 80 °C to 180 °C and time (t) ranging from 1 to 7 days.  
155 After the synthesis, the autoclaves were cooled down at room temperature. The run products  
156 were then recovered and washed by centrifugation (8000 rpm for 10 min), and dried at 60 °C.

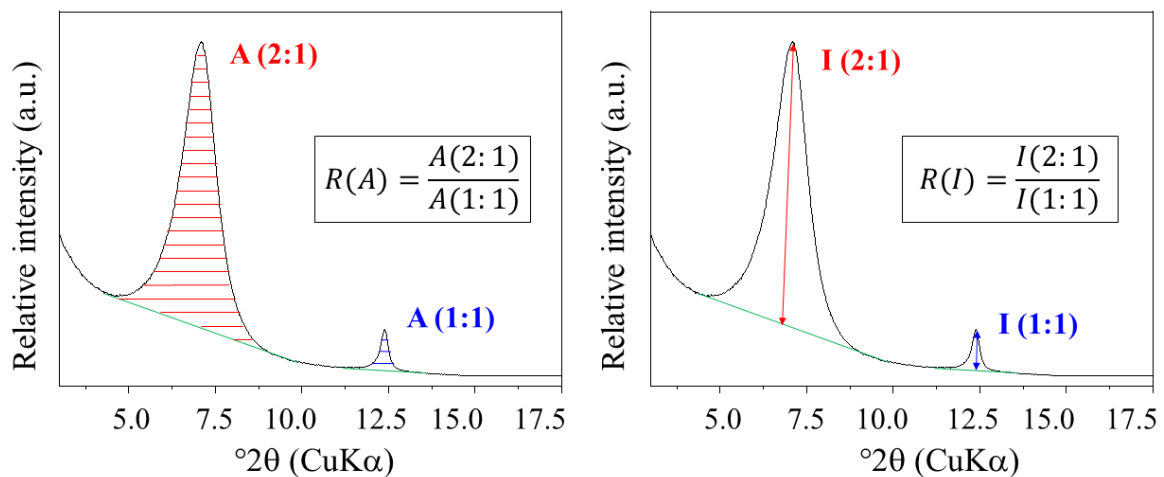
### 157 2.3. Choice of response for the design of experiments

158 Clay minerals are highly anisotropic, therefore, it is challenging to obtain truly un-oriented  
159 sample for powder XRD. To overcome this drawback, oriented preparations can be made,  
160 recording solely (00 $\ell$ ) reflections, which are characteristic for different clay mineral types. An  
161 example of X-ray diffractogram of oriented preparation is shown in Figure 3. Thus, 1:1 type  
162 structure would have  $d_{(001)}$  value of ca. 7 Å and 2:1 type structure would have  $d_{(001)}$  value in the  
163 range of 10 Å to 15 Å.



164  
165 **Figure 3.** Example of XRD pattern of oriented preparation (Run N°01). Red dashed lines  
166 indicate (00 $\ell$ ) plane reflections of 2:1 type clay mineral and blue dashed lines indicate (00 $\ell$ )  
167 plane reflections of 1:1 type clay mineral.

168 The absence of other ( $hkl$ ) plane reflections was systematically checked in the analyzed  
 169 samples. The measured peak areas of different phases then represent the relative abundance of  
 170 each phase in the sample. Moreover, it is also possible to assess the information regarding the  
 171 coherent scattering domain size (CSDS) in the direction perpendicular to the corresponding  
 172 ( $00\ell$ ) plane. In conventional powder X-ray diffraction, this information can be obtained from  
 173 the Full Width at Half Maximum (FWHM) of a reflection. However, in this particular case of  
 174 oriented preparations, the simplifications can be done so that the peak intensity can provide this  
 175 information on the CSDS in the direction perpendicular to the corresponding ( $00\ell$ ) plane. The  
 176 chosen synthesis protocol revealed the formation of both types of clay minerals (1:1 and 2:1).  
 177 The assumption was made that the chemical composition of 2:1 type phase is very similar in all  
 178 samples and the chemical composition of 1:1 type phase is very similar in all samples. The  
 179 objective of the study was to find optimum synthesis conditions for each type of phase. For this  
 180 reason, the area and intensity ratios of (001) reflection, (respectively  $R(A)$  and  $R(I)$ ), between  
 181 1:1 and 2:1 type structures were chosen as the studied responses in the design of experiments  
 182 (Figure 4).



183

184

**Figure 4.** Illustration of  $R(A)$  and  $R(I)$  between 1:1 and 2:1 type clay minerals.

185

## 186 2.4. X-ray diffraction

187 The mineralogical composition of the samples and, more specifically, the type of clay mineral  
188 was determined using X-ray diffraction of powder and oriented preparations. The powders were  
189 previously ground and then introduced into PMMA sample holder with a cavity 25 mm in  
190 diameter and 1.2 mm deep, whereas the thin films of oriented samples were prepared from  
191 diluted suspensions by deposition onto a glass slide. All the samples, powder and oriented, were  
192 characterized on a Bruker D8 Advance X-ray diffractometer with a LYNXEYE XE-T high  
193 resolution energy dispersive 1-D detector (CuK $\alpha_{1,2}$ ) fully opened (2.938°). This kind of detector  
194 allows to avoid Fe fluorescence effects with Cu X-ray tube.

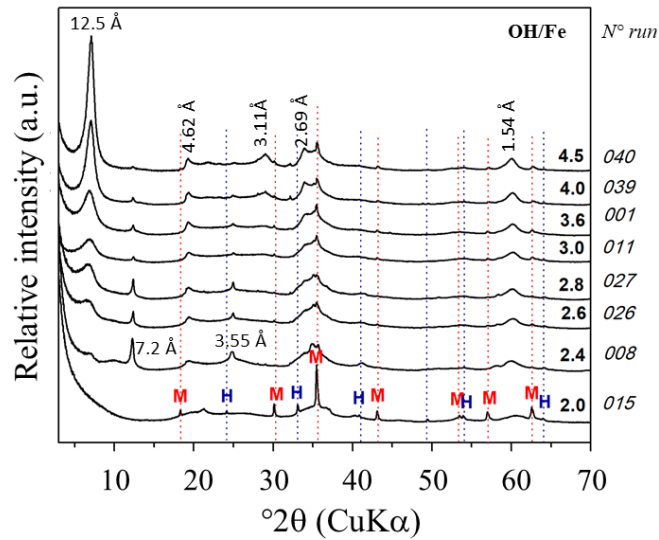
195 For the powder samples, the X-ray diffractograms were recorded from 3° to 70° 2 $\theta$  at a step  
196 scan of 0.017° 2 $\theta$ , a step time of 1.80 s with variable divergence slits that ensure that the  
197 irradiated sample length (*i.e.*, 15 mm) is kept equal over a measured range of 2 $\theta$ . For the  
198 oriented samples, the XRD patterns were recorded in the range from 3 to 40° 2 $\theta$  at a step scan  
199 of 0.017° 2 $\theta$ , a step time of 3.3 s with a fixed divergence slits width of 0.08°. For both kind of  
200 samples (powder and oriented), automatic motorized anti-scatter screen is used for effective  
201 suppression of air-scatter at low angles 2 $\theta$ .

## 202 **Results**

### 203 3.1. Experiments used for modelling

204 Examples of powder XRD patterns for selected experiments are given in Figure 5. The  
205 experimental synthesis conditions corresponding to each run N° are reported in Table 1. The  
206 formed reaction products were not pure phases, but containing also iron oxides: hematite and  
207 magnetite/maghemite. Two sets of experiments were performed in order to extract the optimal  
208 conditions to obtain a single type of clay mineral. The first set of experiments was designed

209 considering the central composite model. It contained a minimal number of experiments equal  
 210 to 15 performed for OH/Fe molar ratio [2.0 – 4.0].



211  
 212 **Figure 5.** Powder XRD patterns of selected experiments. For the experimental conditions  
 213 corresponding to each run N° see Table 1.

214 The first set of experiments produced satisfactory results in the validity range (2.4 – 3.6, i.e.  
 215 standardized parameters = +1 / -1), but the errors increased significantly at the boundaries of  
 216 the studied range ( $r^2 = 0.94$  for OH/Fe = [2.4 – 3.6] and 0.89 for OH/Fe = [2 – 4]). The addition  
 217 of a second set was consequently necessary in order to extract the optimal conditions from the  
 218 quadratic equation. In fact, when calculating the extracted responses R(A) and R(I), different  
 219 tendencies were noticed between the experiments performed for high OH/Fe molar ratios [2.4  
 220 – 4.0] in comparison with the lower values [2.0 – 2.4]. The studied response could therefore not  
 221 be estimated based on the same model. The second set of experiment was then focused on high  
 222 OH/Fe ratios, up to 4.5, and the linear quadratic model was studied accordingly in the range  
 223 [2.4 – 4.5]. In order to improve the relevance of the model, 4 tests were added (N°26, N°27,  
 224 N°39 and N°40) for the calculation of R(A) and R(I).

**Table 1.** Experimental conditions and obtained R(I) and R(A) corresponding to each run.

Set	Run N°	T (°C)	(OH/Fe) <sub>ini</sub>	t (days)	R(I)	R(A)
<b>1</b>	01	160	3.6	2.3	6.9	29.2
	01-R				13.1	44.3
	02	160	2.4	2.3	0.1	1.2
	03	100	3.6	2.3	5.3	15.9
	04	100	2.4	2.3	0.2	2.0
	05	130	3.0	1.0	2.1	8.3
	06	130	3.0	7.0	1.4	5.9
	07	160	3.6	5.7	3.0	11.2
	08	160	2.4	5.7	0.2	0.4
	09	100	3.6	5.7	2.5	10.1
	10	100	2.4	5.7	0.9	5.1
	11	130	3.0	4.0	2.5	10.7
	11-R1				3.9	18.1
	11-R2				2.8	13.0
	12	180	3.0	4.0	1.1	6.0
13	80	3.0	4.0	7.4	17.0	
14	130	4.0	4.0	13.1	31.8	
15	130	2.0	4.0	-	-	
<b>2</b>	16	150	3.0	7.0	0.6	11.4
	26	130	2.6	5.0	0.8	3.5
	26-R				0.9	4.1
	27	130	2.8	5.0	0.6	3.5
	39	180	4.0	1.0	24.6	64.8
	40	180	4.5	1.0	32.1	68.2

226

227 4 runs (N°01-R, N°11-R1, R2 and N°26-R) were repeated to investigate the experimental error.

228 These tests were chosen to have an experiment corresponding to predominant 2:1 type clay

229 mineral (test N°01), an experiment resulting in a majority of 1:1 type clay mineral (test N°26)

230 and an experiment with intermediate proportions of 2:1 and 1:1 type clay minerals (test N°11).

231 The obtained experimental error was important but all the repeated tests show a parallel trend.

232 The relevance of RSM is studied on the basis of all the experimental tests. In the run N°15,

233 which was repeated several times, the only crystalline phases identified were iron oxides. No

234 crystalline clay minerals were identified in powder XRD pattern (Figure 5) of this run, thus no

235 values of R(A) and R(I) could be obtained for oriented preparations.

236 3.2. Study of response function R(A): ratio between relative quantities of 2:1 and 1:1 clay  
237 minerals

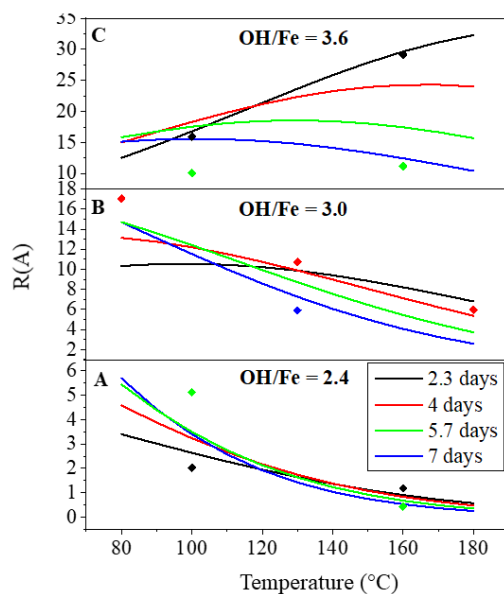
238 This function is proportional to the relative quantity of each phase in the sample. The obtained  
239 quadratic model for the studied function R(A) is given below (eq. 1). The analysis of sensitivity  
240 of the quadratic model for R(A) shows that the response function is highly dependent on OH/Fe  
241 molar ratio (coefficients before linear  $\frac{\overline{OH}}{Fe}$ , square  $\frac{\overline{OH}^2}{Fe}$  and coupled  $\bar{T} \times \frac{\overline{OH}}{Fe}$  variables). In the  
242 same way, linear, quadratic and coupled coefficients relative to time are relatively small, unlike  
243 the coupled coefficient  $\bar{T} \times \bar{t}$ .

$$\begin{aligned} 244 \quad \ln(R(A)) = & 2.292 - 0.268\bar{T} - 0.059\bar{T}^2 + 1.275\frac{\overline{OH}}{Fe} - 0.46\frac{\overline{OH}^2}{Fe} - 0.062\bar{t} - 0.064\bar{t}^2 + \\ 245 \quad & 0.409\bar{T} \times \frac{\overline{OH}}{Fe} - 0.143\bar{T} \times \bar{t} - 0.059\frac{\overline{OH}}{Fe} \times \bar{t} \quad (\text{eq.1}) \end{aligned}$$

246 The pertinence of the model is investigated from all trials (20) except run N°15. Averages of  
247 tests N°01, N°11 and N°26 are used for the calculation of all the tests for the experimental error.

$$248 \quad r^2 = 0.961, S = 4.706, \text{MPSD} = 0.512, \text{EABS} = 2.754, \text{RE} = 0.308$$

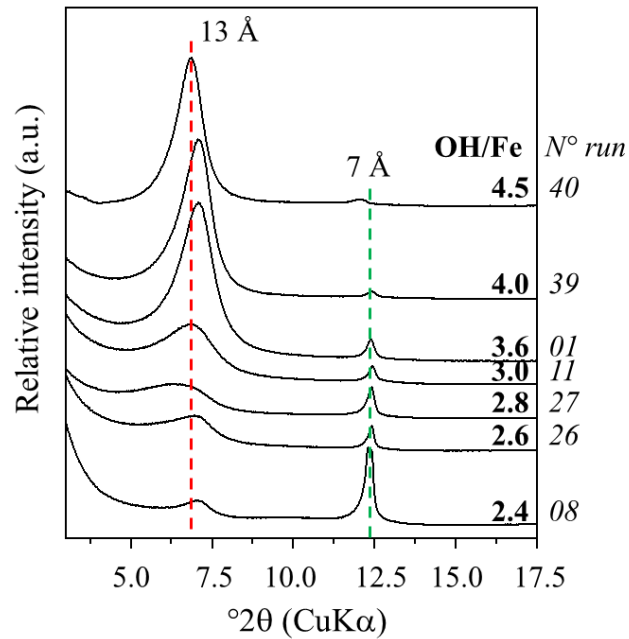
249 Figure 6 shows the area ratio versus temperature for different times for a low OH/Fe molar ratio  
250 (Figure 6A), an average OH/Fe molar ratio (Figure 6B) and a high OH/Fe molar ratio (Figure  
251 6C). The function increases significantly with OH/Fe molar ratio while it increases with time  
252 at low temperature and decreases at high temperature. The same applies for temperature, since  
253 an increase of temperature decreases the area ratio except for high OH/Fe molar ratio values.  
254 The model represents well experimentally observed tendencies. Considering the significant  
255 experimental error, the tendencies given by the model are the same as for the experimental  
256 points thus validating the obtained model.



257

258 **Figure 6.** Time and temperature influence on the obtained R(A) for (OH/Fe)<sub>ini</sub> molar ratios  
 259 equal to 2.4 (A), 3.0 (B) and 3.6 (C). Diamonds represent experimental points from Table 1,  
 260 Set I.

261 For illustration, selected XRD patterns of oriented preparations are given in Figure 7. In  
 262 agreement with results obtained from R(A) investigation, it can be seen that the initial (OH/Fe)  
 263 molar ratio significantly influences the type of clay mineral obtained. For low (OH/Fe)<sub>ini</sub> molar  
 264 ratios the formation of 1:1 type clay mineral is favored, whereas for high (OH/Fe)<sub>ini</sub> molar ratios  
 265 the 2:1 type clay mineral phase is dominant. The relative quantity of 2:1 clay mineral (with  
 266 respect to 1:1 type clay mineral) increases significantly with (OH/Fe)<sub>ini</sub>.



267

268 **Figure 7.** XRD patterns of oriented preparations for selected experiments (red dashed line 2:1  
 269 clay mineral type, green dashed line 1:1 type). For the experimental conditions corresponding  
 270 to each run N° see Table 1.

### 271 3.3. Study of phase abundance and crystallinity: response function R(I)

272 This response function gives additional quantitative information and results about crystallinity.  
 273 For R(I) (eq.2), it is noted that the conclusions about the sensitivity analysis are almost the  
 274 same, except for time contribution, which is, in this present case, more significant, especially,  
 275 the coupled terms with temperature and initial OH/Fe molar ratio. Indeed, the diffracted  
 276 intensity in the particular case of oriented preparations among other factors also includes the  
 277 contribution of the size of coherent scattering domain. It is expected that the synthesis time  
 278 influences the size of formed particles, and thus the coherent scattering domain (Carrado et al.,  
 279 2006). Thus, the contribution of time in the function of R(I) being more important than in R(A)  
 280 function is in agreement with expected results.



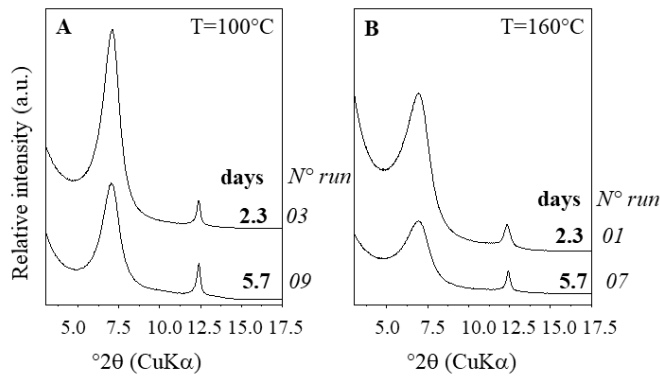
281 
$$R(I) = 2.146 - 0.283\bar{T} + 0.531\bar{T}^2 + 3.127\frac{\overline{OH}}{Fe} + 1.100\frac{\overline{OH}^2}{Fe} - 0.734\bar{t} - 0.141\bar{t}^2 +$$

282 
$$0.928\bar{T} \times \frac{\overline{OH}}{Fe} - 0.819\bar{T} \times \bar{t} - 1.834\frac{\overline{OH}}{Fe} \times \bar{t} \quad (\text{eq.2})$$

283 The pertinence of the model is investigated from all trials (20):

284  $r^2 = 0.962$ ,  $S = 2.014$ ,  $MPSD = 3.232$ ,  $EABS = 1.403$ ,  $RE = 1.422$

285 For high OH/Fe molar ratio, i.e.  $(OH/Fe)_{ini} = 3.6$ , it has to be underlined that whatever the  
 286 temperature T, R(I) decreases with time (Figure 8). Likewise, the temperature increases the  
 287 contribution of time on R(I) (Figure 8B). That is to say, the ratio of diffracted peak intensity  
 288 increases with respect to the background (with no curvature, see Figure 4) without the increase  
 289 of peak full-width at half-maximum when time decreases and temperature increases. It leads  
 290 then to a conclusion that 2 : 1 type clay mineral phase formation is favored in short times, and  
 291 this becomes even more important with the increase of temperature.



292

293 **Figure 8.** XRD patterns of oriented preparations obtained for  $(OH/Fe)_{ini}$  molar ratio = 3.6 at  
 294 two different temperatures T=100°C (A) and T=160°C (B) for two different times of 2.3 and  
 295 5.7 days (Runs N° 01, N°03, N°07 and N° 09 *cf.* Table 1).

296 With this function (R(I)), the interpretation is limited for results obtained with low initial OH/Fe  
 297 molar ratio because R(I) is close to zero (Table 1). To overcome this drawback, the last response

298 function ( $1/R(I)$ ) was defined and studied to investigate the favoring of 1:1 type clay formation.  
299 All the studied parameters influence this function and no contribution can be neglected (eq.3).

$$\begin{aligned} 300 \quad \ln\left(1 + \frac{1}{R(I)}\right) &= 0.453 + 0.188\bar{T} - 0.019\bar{T}^2 - 0.726\frac{\overline{OH}}{Fe} + 0.386\frac{\overline{OH}^2}{Fe} - 0.060\bar{t} + 0.058\bar{t}^2 - \\ 301 \quad &0.217\bar{T} \times \frac{\overline{OH}}{Fe} + 0.139\bar{T} \times \bar{t} + 0.267\frac{\overline{OH}}{Fe} \times \bar{t} \quad (\text{eq.3}) \end{aligned}$$

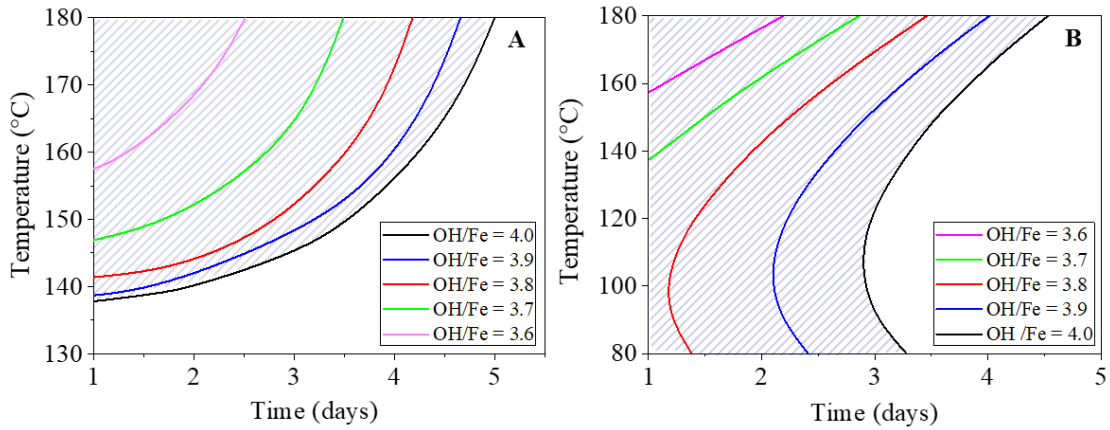
302 The pertinence of the model is investigated from 18 trials (set 1 + tests N°26 and N°27):

$$303 \quad r^2 = 0.981, S = 0.472, \text{MPSD} = 1.192, \text{EABS} = 0.310, \text{RE} = 0.621$$

304 Starting from these 3 mathematical models, optimal solutions are searched by minimizing an  
305 objective function.

#### 306 3.4 Optimum parameters favoring the 2:1 type clay mineral formation

307 The study of the favored formation of 2:1 type clay mineral requires to investigate the  
308 parameters (T, time and initial OH/Fe molar ratio) resulting in high values of R(A) and R(I). It  
309 was considered that R(A) > 30 and R(I) > 12 (objective functions) are representative values of  
310 investigated conditions. Figure 9 shows in a temperature / time diagram the optimal solutions  
311 for having a vast majority of 2:1 type clay for R(A) > 30 (Figure 9A) and for R(I) > 12 (Figure  
312 9B) for  $(OH/Fe)_{ini} = [3.6 - 4.0]$ . The objective function is reached in the hatched area. This  
313 objective (R(A) > 30) is reached for high OH/Fe molar ratio and especially for short synthesis  
314 time and high temperature. The same trend is observed for R(I) with temperature but the  
315 influence of time is more moderate at low temperatures below 120 °C.



316

317 **Figure 9.** Conditions of temperature and time favoring the formation of the 2:1 type clay

318 mineral with  $R(A) > 30$  (A) and for  $R(I) > 12$  (B) for  $(OH/Fe)_{ini} = [3.6 - 4.0]$ .

319 3.5 Optimum parameters favoring the 1:1 type clay mineral formation

320 The favored formation of 1:1 type clay mineral, corresponding to the very low values of  $R(A)$

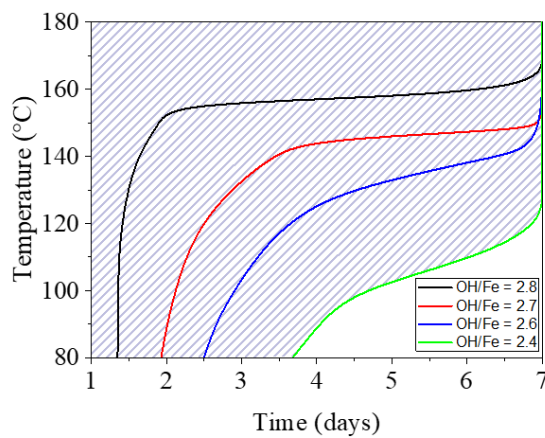
321 and  $R(I)$  is studied with response function  $(1/R(I))$ . It was considered that  $1/R(I) > 2$  are

322 representative values of investigated conditions. It was not possible to fix a higher value for

323  $1/R(I) > 2$  due to the experimental error. This objective is reached, when OH/Fe molar ratio is

324 as low as possible, i.e., OH/Fe=2.4 (Figure 10). It is important to mention, that at OH/Fe < 2.2,

325 the formation of crystalline 1:1 type clay mineral phase was not observed (Table 1).



326

327 **Figure 10.** Conditions of temperature and time favoring the formation of the 1:1 type clay  
328 mineral with  $1/R(I) > 2$  for  $(OH/Fe)_{ini} = [2.4 - 2.8]$ .

329 The optimal conditions for the formation of 1:1 type clay mineral phase (with respect to 2:1  
330 phase) are reached for short time and high temperature. Interestingly, the formation of 1:1 type  
331 clay mineral phase can also be achieved at low temperature (below 140 °C) and short times  
332 (less than 3 days) with low OH/Fe molar ratio. In comparison, the synthesis of 2:1 phase is  
333 favored only at high temperatures and high OH/Fe molar ratio. This aspect can be relevant to  
334 environmentally friendly synthesis procedure, as less resources (chemicals and energy) are  
335 consumed.

## 336 **Discussion**

337 The observed tendencies in this study are in agreement with previously reported studies. Indeed,  
338 Fe-serpentines (1:1 type clay mineral) were observed for the experiments at low temperatures  
339 below 150°C (Bertoldi et al., 2005; Lantenois et al., 2005; Pignatelli et al., 2014; Rivard et al.,  
340 2013; Tosca et al., 2016), whereas Fe-rich chlorites (2:1 type clay mineral) were identified at  
341 higher temperature of 300 °C (Mosser-Ruck et al., 2016). However, it has to be noted that in  
342 other studies the duration of experiments was different. The experiments reported in Pignatelli  
343 et al. (2014) lasted 6 months and the experiment of Mosser-Ruck et al. (2016) went for 25  
344 months. Also, in these experiments additional phenomena were in operation such as the  
345 dissolution of iron from metallic plates, which could have been the limiting step regarding the  
346 precipitation of clay mineral phase.

347 It can be expected that the formation of phyllosilicate phases is strongly governed by sol-gel  
348 process as in the case of other silicates such as zeolites. An important step is the precipitation  
349 of dissolved silicon. This condensation reaction is strongly governed by the amount of hydroxyl  
350 ions (Cundy and Cox, 2005). Then, it is not surprising that the quantity of OH<sup>-</sup> has the most

351 significant impact on both studied functions. It has been noted previously that Si speciation in  
352 solution, influence the structure of synthesized nontronite (2:1 type clay mineral) (Baron et al.,  
353 2016). In a similar way here, the quantity of  $\text{OH}^-$  acts on the species and their amount in solution  
354 during the synthesis. Also, the study of Tosca et al. (2016) notes the influence of pH. They  
355 performed the study at three different pH (7.0, 7.5 and 8.0), and they noted that the concentration  
356 of  $\text{Fe}^{2+}$  and  $\text{SiO}_2$  in solution decreased faster when pH increased. Thus, the precipitation of  
357 greenalite-like phase occurred faster when pH increased. Although the pH in our study was  
358 very different (13 to 14) compared to the study of Tosca et al. (2016), both studies note the  
359 important influence of this parameter towards the precipitation of clay minerals.

360 For synthesis at high OH/Fe ratio, a high temperature favors the formation of 2:1 type clay  
361 mineral. Indeed, the thermodynamic constant of the precipitation reaction increases with  
362 temperature and favors the formation of clays (enthalpy of precipitation reactions being  
363 positive) (Giffaut et al., 2014). In the same way, the reaction kinetics increase with the increase  
364 of temperature and the preferential precipitation of 2:1 type clay mineral can be attributed to a  
365 faster kinetic. It is in agreement with observations reported in the study of Grubb (1971), which  
366 used 1N NaOH solution in his experiments and observed that minnesotaite (2:1 type clay  
367 mineral) become the dominant constituent in the three year experiments. Nevertheless, in our  
368 study, when synthesis time increases this tendency is reversed (R(A) decreases) possibly due to  
369 a limited species (intermediate reaction leading to the precipitation of 2:1 phase clay mineral).  
370 This indicates a decrease of the ratio R(A) but the amounts can probably increase.

371 For synthesis performed at low OH/Fe ratios, the quantity of  $\text{OH}^-$  is limited. There is no  
372 thermodynamic limitation but the kinetics are decreased by the limiting reactant. The reaction  
373 leading to the precipitation of 2:1 type clay mineral is favored at high pH and disfavored in  
374 these operating conditions. So, the reaction of precipitation of 1:1 phase clay mineral becomes  
375 dominating.

376 To summarize, the ratio of reaction kinetics ( $k_{2:1} / k_{1:1}$ ) increases with temperature and decreases  
377 when the available amount of hydroxyl ion in solution decreases. This amount of hydroxyl ion  
378 decreases as the precipitation reactions advances (time dependent).

## 379 **Conclusion**

380 The feasibility of synthesis of 2:1 and 1:1 type clay minerals was demonstrated at given  
381 physicochemical conditions. Depending on these conditions, the synthesis can be tailored  
382 towards favoured formation of one or another type of phases. To optimize the number of  
383 experiments and the amount of information, which can be extracted from them, a design of  
384 experiments was used. From few synthesis experiments, the predominant operating parameters  
385 and the conditions leading to the formation of 2:1 and 1:1 type clay minerals were identified.  
386 From RSM (Response Surface Methodology) investigations the optimal conditions of synthesis  
387 were estimated for each type of phase.

388 Among the studied parameters (synthesis temperature, time and ratio OH/Fe), the ratio OH/Fe  
389 (proportional to the available amount of hydroxyl ions in solution) is preponderant. At high  
390 OH/Fe ratio, the precipitation of 2:1 type clay mineral is favoured with respect to 1:1 type clay  
391 mineral. The decrease of available hydroxyl ions with time slowed down the kinetic. For the  
392 same reason, the formation of 1:1 type clay mineral was favoured when the availability of  
393 hydroxyl ions decreased (low OH/Fe ratio).

394 From these results, synthesis of several grams of desired products will be carried out to perform  
395 detailed characterizations (full set of thermodynamic properties, different spectroscopic  
396 measurements, structural model ...). These investigations will allow to improve the  
397 understanding of many aspects related to the presence of either or both 2:1 and 1:1 type iron  
398 bearing clays in natural or anthropized environments: identification of each type of phases in  
399 experimental products or natural samples, understanding of their neoformation mechanisms,

400 sensitivity to relevant or discriminant physico-chemical parameters, thermos-kinetic modelling  
401 of geochemical systems.

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