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# Influence of pH on the hydrothermal synthesis of Al-substituted smectites (Saponite, Beidellite, and Nontronite)

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**Abstract**—Smectitic clay minerals are unique indicators of paleoenvironmental conditions and exhibit a unique reactivity in the mineral world. Smectites may exhibit tetrahedral substitutions (Al<sup>3+</sup> - and sometimes Fe<sup>3+</sup> - can substitute for Si<sup>4+</sup> in tetrahedral sites), resulting in a layer charge increase, thereby impacting their properties (e.g. swelling and sorption capacities, catalytic properties, expandable abilities). The objective of the present study was to determine the influence of pH conditions on the hydrothermal production of smectite end-members exhibiting tetrahedral Al substitutions (saponite, beidellite, and nontronite), using XRD and FTIR methods. The results of a series of syntheses conducted at various pH allowed discussion of the crystallization pathways of these smectites from a mechanistic point of view. Altogether, the present study provided easily reproducible protocols for the hydrothermal production of pure saponite, nontronite, or beidellite (i.e. with no other mineral). The successful synthesis of pure saponite was achieved by exposing the starting gels to 230°C for 4 days in solutions at pH ranging from 5.5 to 14. The successful synthesis of pure beidellite was achieved by exposing the starting gels to 230°C for 9 days in a solution at pH 12. The successful synthesis of pure nontronite was achieved by exposing the starting gels to 150°C for 2.5 days in a solution at pH 12.5. Although extrapolating experimental results to natural settings remains difficult, the results of the present study may be of great help to constrain better the geochemical conditions existing or having existed on extraterrestrial planetary bodies.

**Keywords:** Smectite; pH; hydrothermal synthesis; XRD; FTIR

## Introduction

Smectitic clay minerals are widespread in the Solar System (Hazen et al., 2013) and can form in many contexts, from alteration settings to magmatic systems, in wide ranges of redox and pH conditions

41 (Meunier, 2005; Meunier et al., 2008; Zhou & Keeling, 2013; Viennet et al., 2017, 2020, 2021; Fox et  
42 al., 2021). These strongly anisotropic minerals carry key information about the geochemistry, oxidation  
43 state, and water content of the environments in which they were produced (Ehlmann et al., 2011; Fox et  
44 al., 2021), making them good indicators of paleoenvironmental and paleoclimatic conditions. Their  
45 intrinsic properties (e.g. adsorption capacity, catalytic properties) confer on them a unique reactivity in  
46 the mineral world, explaining their huge number of applications in a variety of domains (e.g. Murray  
47 1991, 2000; Choy et al., 2007; Carniato et al., 2020), including medicine (Ghadiri et al., 2015; Saadat  
48 et al., 2022), pharmaceuticals (Carretero & Pozo, 2009; Corbin et al., 2021; Bello et al., 2022), pollution  
49 control (Churchman et al., 2006; Ewis et al., 2022), the petroleum industry (Abdo & Haneef, 2013; Li  
50 et al., 2023; Salter et al., 2023), and the construction industry (Singh, 2022). It is the exceptional trapping  
51 capabilities of smectites that make possible the geological storage of CO<sub>2</sub> or H<sub>2</sub> (Romanov, 2013; Rother  
52 et al., 2013; de Jong et al., 2014; Abdulelah et al., 2023; Ho et al., 2023) and radioactive waste (Delage  
53 et al., 2010; Landais et al., 2013; Robin et al., 2017; Parrotin et al., 2023). Smectite-rich rocks are also  
54 a major reservoir of Rare Earth Elements (Moldoveanu & Papangelakis, 2012; Abbott et al., 2019), and  
55 the strong affinities of smectites for organic molecules make them the primary agents for organic carbon  
56 sequestration in soils, sediments, and chondrites (Kennedy et al., 2002; Blattmann et al., 2019; Viennet  
57 et al., 2023) and the probable main actors of the origins of life (Viennet et al., 2021; Klopogge &  
58 Hartman, 2022). Being also the main carriers of water in sediments and in the oceanic crust, they play a  
59 great role in subduction settings (Katayama et al., 2015; Hwang et al., 2017). Their anisotropic nature  
60 affects the seismic properties of rocks (Almqvist & Mainprice, 2017), as well as the macroscopic  
61 behavior of faults (Ikari et al., 2009).

62 Smectites are clay minerals with a 2:1 layer silicate structure, each layer being made of an octahedral  
63 sheet sandwiched between two Si(Al,Fe<sup>3+</sup>)–O tetrahedral sheets and in which stacking creates  
64 expandable interlayer spaces capable of storing water, organics, and exchangeable cations (mostly Ca<sup>2+</sup>,  
65 Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) balancing the overall charge (Meunier, 2005; Fox et al., 2021). While trioctahedral  
66 smectites (such as hectorite and saponite) have all octahedral sites filled by mostly divalent cations,  
67 dioctahedral smectites (such as nontronite, montmorillonite, and beidellite) have only two of their three  
68 octahedral sites filled by mostly trivalent cations, the most common octahedral cations being Al, Fe, and  
69 Mg. Depending on the pH conditions under which they crystallize, smectites may exhibit tetrahedral  
70 substitutions (Al<sup>3+</sup> - and sometimes Fe<sup>3+</sup> - can substitute for Si<sup>4+</sup> in tetrahedral sites), resulting in an  
71 increase in layer charge, thereby impacting their properties, such as their swelling or sorption capacities,  
72 catalytic properties, or expandable abilities (Murray, 2000; Komadel et al., 2005; Meunier, 2005; Fox  
73 et al., 2021).

74 Many studies dealing with the synthesis of smectites exist in the literature (Klopogge, 1999; Zhang et  
75 al., 2010; Petit et al., 2017; Dzene et al., 2018; Ponce & Klopogge, 2020). Although smectites could be  
76 synthesized from glasses submitted to high pressure and temperature conditions (Nakazawa et al., 1992;  
77 Yamada, 1994, 1995; Tamura, 2000; Kalo et al., 2010), most syntheses are conducted following the sol-  
78 gel method, i.e. using gels produced at room temperature before being exposed to hydrothermal  
79 conditions. A number of syntheses aimed at producing a suite of smectite samples spanning  
80 compositional ranges between Fe(II), Fe(III), Mg, and Al end-member species to document precisely  
81 their spectroscopic signatures, as recently done by Fox et al. (2021). In parallel, a number of laboratory  
82 studies have investigated how conditions (such as temperature and pH) control cation coordination and  
83 incorporation into the smectite structure and, in turn, their final crystallochemistry (Harder, 1976;  
84 Grauby et al., 1993, 1994; Huertas et al., 2000; Andrieux & Petit, 2010; Petit et al., 2015, 2017; Baron  
85 et al., 2016a, 2016b; Blukis et al., 2022). For instance, Blukis et al. (2022) recently showed that high pH  
86 favors a high degree of crystallinity for saponite. However, those studies were dedicated to a given end-  
87 member or to a given solid solution (i.e. either the Fe(III)–Mg (nontronite–saponite) or the Fe(III)–Al  
88 (nontronite–beidellite) series (Grauby et al., 1993, 1994; Andrieux & Petit, 2010; Petit et al., 2015)).

89 The speciation of Fe, Mg, and Al as a function of pH being different (Millero et al., 1995; Perry &  
90 Shafran, 2001; See et al., 2015; Pierrot & Millero, 2017; de Mello Gabriel et al., 2021), the optimal pH  
91 for the synthesis of saponite, beidellite, and nontronite is anticipated to be different, with pH conditions  
92 strongly influencing their production. The sensitivity of different smectites to pH conditions thus  
93 remains to be investigated. The purpose of the present study, therefore, was to investigate the influence  
94 of pH conditions on the production of smectites, using three different series of hydrothermal syntheses  
95 designed to lead (when conditions are optimal) to the crystallization of three smectite end-members  
96 containing tetrahedral Al, namely a saponite ( $\text{Na}_{0.4}(\text{Si}_{3.6}\text{Al}_{0.4})\text{Mg}_3\text{O}_{10}(\text{OH})_2$ ), a beidellite  
97 ( $\text{Na}_{0.4}(\text{Si}_{3.6}\text{Al}_{0.4})\text{Al}_2\text{O}_{10}(\text{OH})_2$ ), and a nontronite ( $\text{Na}_{0.4}(\text{Si}_{3.6}\text{Al}_{0.4})\text{Fe}^{3+}_2\text{O}_{10}(\text{OH})_2$ ).

## 98 **Experimental**

### 99 Sample Preparation

100 The syntheses reported here were conducted via a sol-gel method, i.e. using gels produced at room  
101 temperature before being exposed to hydrothermal conditions. To explore the influence of pH  
102 conditions, the syntheses reported here used gels produced from solutions at various pH and exposed to  
103 hydrothermal conditions within solutions at various pH. The preparation of the gels was done following  
104 rather classic protocols (Baron et al., 2016a; Petit et al., 2017; Dzene et al., 2018; Fox et al., 2021).  
105 Starting solutions were mixed to obtain gels with the Si:Al:Mg, Si:Al:Al, and Si:Al:Fe molar ratios of  
106 pure Al-substituted smectite end-members (i.e. 3.6:0.4:3 for the saponite, 3.6:0.4:2 for the beidellite,  
107 and 3.6:0.4:2 for the nontronite). For all gels, the first step was to pour an  $\text{AlCl}_3$  solution into a  $\text{Na}_2\text{SiO}_3$   
108 solution under continuous stirring at room temperature, which led to the instantaneous formation of a  
109 white precipitate of amorphous aluminosilicate. Then, a given volume of either a  $\text{MgCl}_2$ , an  $\text{FeCl}_3$ , or  
110 an  $\text{AlCl}_3$  solution was added to provide the exact quantity of cations needed for the octahedral  
111 occupancies. Stirring was stopped soon after this step, and the precipitated gel was filtered and rinsed  
112 with pure water with a vacuum suction filter device to remove excess salts. Each starting gel was  
113 immersed in a solution at a given pH in Teflon acid-digestion bombs which were sealed and placed in  
114 an oven for several days (syntheses were conducted in pure water or in solutions at pH values ranging  
115 from 12 to 14 for saponites and from 12 to 13 for nontronites and beidellites given the high pH sensitivity  
116 of these smectites). The synthesized products were then filtered and rinsed with pure water (resistivity  
117 of  $18.2 \text{ M}\Omega \cdot \text{cm}$ ) to remove any remaining salt. Then, they were dried in an oven at  $50^\circ\text{C}$  for 24 h and  
118 ground in an agate mortar for characterization using X-ray diffraction (XRD) and Fourier-transform  
119 infrared spectroscopy (FTIR) as classically done for smectites (Baron et al., 2016a; Petit et al., 2017;  
120 Dzene et al., 2018; Fox et al., 2021).

### 121 Measurements and Characterization

122 The pH of each starting solution, i.e. the solution in equilibrium with the gel and the solution in  
123 equilibrium with the products of syntheses, was measured using a Fisher Scientific (Hampton, New  
124 Hampshire, USA) Accumet XL600 pH/mV/Temp/ISE/DO/Conductivity Meter calibrated with three  
125 buffers (pH 7, 10, and 12). The uncertainty for each measurement was estimated to be  $\pm 0.05$  pH units.  
126 The *PhreeqC* code associated with the minteq.v4 database was used to determine the major species in  
127 the starting solutions used for the production of gels.

128 The XRD data reported here were collected on unoriented powders at room temperature with a step size  
129 of  $0.033^\circ 2\theta$  over the  $4\text{--}75^\circ 2\theta$   $\text{CoK}\alpha_{1,2}$  (40 mA, 45 kV) angular range and a counting time of 300 ms per  
130 step using an X'Pert Pro instrument from Malvern PANalytical (Malvern, UK), operating at the Institut  
131 de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC, Paris, France).

132 The FTIR data shown here were collected on unoriented powders in attenuated total reflection mode  
133 (ATR) with a diamond internal reflexion element with a  $4 \text{ cm}^{-1}$  resolution in the mid-infrared (MIR)  
134 range ( $4000\text{--}400 \text{ cm}^{-1}$ ) using a Fisher Scientific (Hampton, New Hampshire, USA) Nicolet 6700 FTIR

135 spectrometer equipped with a KBr beamsplitter and DTGS-KBr detector and operating at the Institut de  
136 Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC, Paris, France).

### 137 Starting Solutions

138 Dilute solutions (0.2 M) of  $\text{Na}_2\text{SiO}_3$  (>95%),  $\text{AlCl}_3$  (99%),  $\text{MgCl}_2$  (>99%), and  $\text{FeCl}_3$  (>99%) were  
139 prepared using pure water (milliQ - 18.2 M $\Omega$ -cm) for the syntheses reported here, leading to a  $\text{Na}_2\text{SiO}_3$   
140 solution at pH 13.1, a  $\text{MgCl}_2$  solution at pH 5.4, an  $\text{FeCl}_3$  solution at pH 1.8, and an  $\text{AlCl}_3$  solution at  
141 pH 3.4 (Table 1). Some NaOH was added to the  $\text{AlCl}_3$  and  $\text{FeCl}_3$  solutions to obtain an additional  $\text{FeCl}_3$   
142 solution at pH 2.1 and four additional  $\text{AlCl}_3$  solutions at pH 3.9, 5.3, 8.0, and 10.6 (Table 1). These  
143 additional solutions were used to test the influence of the pH of the starting solutions on the synthesis  
144 of nontronite and beidellite. All chemicals were obtained from Sigma Aldrich (St. Louis, Missouri,  
145 USA).

### 146 Detailed Protocols

#### 147 *Saponite syntheses*

148 Four different syntheses were conducted from the gel of saponite composition for the present study. The  
149 starting gels were prepared by pouring 556  $\mu\text{L}$  of the  $\text{AlCl}_3$  solution at pH 3.4 into 5 mL of the  $\text{Na}_2\text{SiO}_3$   
150 solution, before being mixed with 4.17 mL of the  $\text{MgCl}_2$  solution, to produce, theoretically, about  
151 100 mg of a gel stoichiometrically identical to a pure saponite with 0.4 Al in each tetrahedron ( $\text{Na}_{0.4}$   
152  $(\text{Si}_{3.6}\text{Al}_{0.4})\text{Mg}_3\text{O}_{10}(\text{OH})_2$ ). The pH of the solution in equilibrium with the gel was about 10. After  
153 filtration, the produced gel was placed into 23 mL Teflon reactors before drying and immersed in  
154 16.5 mL of pure water at pH 5.5 (i.e. pure water in equilibrium with atmospheric  $\text{CO}_2$ ) or in 16.5 mL of  
155 a solution composed of pure water in which was added NaOH to reach a pH of 12, 13, or 14 (cf Table 2).  
156 All reactors were then put in an oven at 230°C (~28 bar) for 4 days, following the recommendations of  
157 Zhang et al. (2020) for the synthesis of pure saponites. During syntheses above 200°C, saponite particles  
158 grow faster during the first 3 days than during the subsequent 10 (Zhang et al., 2020). Of note, although  
159 saponites can be produced at low temperature (i.e. 90°C; Meyer et al., 2020; Ponce & Klopogge, 2020),  
160 high temperature conditions inhibit the incorporation of Al into octahedral sheets, while enhancing  
161  $^{[4]}\text{Al}^{3+}$  for  $^{[4]}\text{Si}^{4+}$  tetrahedral substitutions, as reported by Klopogge and Ponce (2021).

#### 162 *Beidellite syntheses*

163 Four different syntheses were conducted from the gel of beidellite composition for the present study.  
164 The starting gels were prepared by pouring 2.833 mL of the  $\text{AlCl}_3$  solution at pH 3.9 into 4.25 mL of  
165 the  $\text{Na}_2\text{SiO}_3$  solution to produce theoretically ~80 mg of a gel stoichiometrically identical to a pure  
166 beidellite with 0.4 Al in each tetrahedron ( $\text{Na}_{0.4}(\text{Si}_{3.6}\text{Al}_{0.4})\text{Al}_2\text{O}_{10}(\text{OH})_2$ ). The pH of the solution at room  
167 temperature in equilibrium with the gel was ~4.5. After filtration, the produced gel was kept hydrated  
168 and placed into 23 mL Teflon reactors and immersed into 12.5 mL of pure water at pH 5.5 (i.e. pure  
169 water in equilibrium with atmospheric  $\text{CO}_2$ ) or into 12.5 mL of a solution composed of pure water in  
170 which was added NaOH to reach a pH of 12, 12.5, or 13 (cf Table 2). Only 12.5 mL of pure water or  
171 solution at pH 12, 12.5, or 13 were used rather than 16.5 mL to prevent overpressure related to the  
172 swelling of the gel containing a lot of highly hydrated  $\text{Al}^{3+}$ . All reactors were then put in an oven at  
173 230°C (~28 bar) for 9 days, previous successful syntheses having been conducted over 8 to 10 days from  
174 175–200°C (De Kimpe, 1976; Klopogge et al., 1993) to well above 300°C (Klopogge et al., 1990;  
175 Lantenois et al., 2008).

#### 176 *Nontronite syntheses*

177 Three different series of syntheses were conducted from four different gels of nontronite composition  
178 for the present study. A first series of four syntheses was conducted with a gel produced using the  $\text{AlCl}_3$   
179 solution at pH 3.4, a second series of four syntheses was conducted with a gel produced using the  $\text{AlCl}_3$

180 solution at pH 10.6, and a third series of two syntheses was conducted with either a gel produced using  
181 the AlCl<sub>3</sub> solution at pH 5.3 or a gel produced using the AlCl<sub>3</sub> solution at pH 8. Each starting gel was  
182 prepared by pouring 833 μL of the AlCl<sub>3</sub> solution into 7.5 mL of the Na<sub>2</sub>SiO<sub>3</sub> solution, before being  
183 mixed with 4.17 mL of the FeCl<sub>3</sub> solution, to produce, theoretically, ~165 mg of a gel stoichiometrically  
184 identical to a pure nontronite with 0.4 Al in each tetrahedron (Na<sub>0.4</sub>(Si<sub>3.6</sub>Al<sub>0.4</sub>)Fe(III)<sub>2</sub>O<sub>10</sub>(OH)<sub>2</sub>). The pH  
185 of the solution in equilibrium with the gel prepared with the AlCl<sub>3</sub> solution at pH 3.4 was ~4, while the  
186 one formed with the AlCl<sub>3</sub> solution at pH 10.6 reached a pH of 9. After filtration, all the produced gels  
187 were kept hydrated and placed into 23 mL Teflon reactors. The gels produced using either the AlCl<sub>3</sub>  
188 solution at pH 3.4 or the AlCl<sub>3</sub> solution at pH 10.6 were immersed into 16.5 mL of pure water at pH 5.5  
189 (i.e. pure water in equilibrium with atmospheric CO<sub>2</sub>) or into 16.5 mL of a solution composed of pure  
190 water in which was added NaOH to reach a pH of 12, 12.5, or 13, while the two gels produced using  
191 either the AlCl<sub>3</sub> solution at pH 5.3 or the AlCl<sub>3</sub> solution at pH 8 were immersed only into 16.5 mL of a  
192 solution composed of pure water in which was added NaOH to reach a pH of 12.5 (cf Table 2). All  
193 reactors were then put in an oven at 150°C (4.75 bar) for 2.5 days, following the recommendations of  
194 Andrieux & Petit (2010), Baron et al. (2016a), and Dzene et al. (2022). In fact, higher temperatures  
195 (>200°C) may favor the formation of kaolinite, hematite (akaganeite), or aegirine (Delvaux et al., 1989;  
196 Decarreau et al., 2008; Andrieux & Petit, 2010)

## 197 **Results**

### 198 Saponite Syntheses

199 Each of the four syntheses produced a translucent, gelatinous solid residue immersed in a transparent  
200 solution at a pH close to that of the solutions in which the starting gels were immersed (i.e. 7.5 for the  
201 synthesis conducted in pure water, 10.4 in the solution at pH 12, 12.9 in the solution at pH 13, and 13.7  
202 in the solution at pH 14; cf Table 2). These residues turned white upon drying.

203 Whatever the pH of the solution used for the syntheses, the XRD patterns of the synthetic products  
204 exhibited peaks typical of the *hkl* reflections of 2:1 trioctahedral saponites (Grauby *et al.*, 1994), i.e.  
205 peaks at ~12.7 Å (001), 4.55 Å (02,11), ~3.10 Å (004), 2.60 Å (13,20), 1.73 Å (15,24,31), and ~1.53 Å  
206 (06,33) (Fig. 1). The 06,33 reflection of these saponites confirmed their trioctahedral nature (>1.51 Å;  
207 Brown & Brindley, 1980; Decarreau et al., 1992; Grauby et al., 1994), and the position of the 001  
208 reflections indicated that they were mainly monohydrated (Brown & Brindley, 1980, Ferrage et al.,  
209 2005, 2007). Under vacuum, the *d*<sub>001</sub> of the saponite synthesized in pure water collapsed to 10.45 Å  
210 (Fig. S1). The 02,11 and 06,33 reflections of the saponite synthesized in solution at pH 14 shifted to  
211 lower angles compared to saponites synthesized in solutions at lower pH (4.58 to 4.55 Å and 1.533 to  
212 1.526 Å).

213 All synthetic products had a FTIR spectrum exhibiting a broad band near 3420 cm<sup>-1</sup> typical of the νOH  
214 vibrations of the water adsorbed within the interlayer spaces of smectites (Fig. 2; Madejová et al., 2017).  
215 In addition, the FTIR spectra of all synthetic products showed the characteristic bands of saponite, i.e.  
216 νMg<sub>3</sub>OH and δMg<sub>3</sub>OH vibrations at 3680 and 655 cm<sup>-1</sup>, respectively; νSi–O vibration near 1000–  
217 950 cm<sup>-1</sup>; <sup>4</sup>Al–O out of plane near 800 cm<sup>-1</sup>; perpendicular Si–O–Mg vibrations at 692 and 532 cm<sup>-1</sup>;  
218 and δSi–O–Si vibrations near 500 and 455 cm<sup>-1</sup> (Madejová et al., 2017; Kloprogge & Ponce, 2021).  
219 Bands corresponding to νMg<sub>3</sub>OH and δMg<sub>3</sub>OH vibrations in the FTIR spectra of the saponite  
220 synthesized in solution at pH 14 shifted towards higher and lower wavenumbers compared to FTIR  
221 spectra of saponites synthesized in solutions at lower pH. The band near 3612–3634 cm<sup>-1</sup> is related to  
222 the stretching vibration of interlayer water molecules (Fig. S2). In this case, the two OH groups of the  
223 molecule are not equivalent and this signal is assigned to the OH group weakly bonded to the surface  
224 oxygens (Farmer, 1974).

225

226

## 227 Beidellite Syntheses

228 Each of the four syntheses produced solid residues immersed in a colorless transparent solution at a pH  
229 close to that of the solutions in which the starting gels were immersed (i.e. 7.2 for the synthesis  
230 conducted in pure water at pH 5.5, 9.4 in the solution at pH 12, 11 in the solution at pH 12.5, and 12 for  
231 the synthesis at pH 13; Table 2).

232 The synthesis conducted in pure water produced a white and pasty solid residue which became very soft  
233 upon drying, showing an XRD pattern typical of kaolins, with peaks at 7.17 Å (001), 4.43 Å (020),  
234 4.34 Å (110), 4.41 Å (111), 3.57 Å (002), 3.39 Å (111), 2.55 Å (201), 2.35 Å (003), 1.79 Å (004), and  
235 1.486 Å (060) (Fig. 3; Carroll, 1970). The bands at 3621 and 3692 cm<sup>-1</sup> in the FTIR spectrum of this  
236 solid confirms the presence of kaolins (Fig. 4; Kodama, 1962; Zhang et al., 2010; Madejovà et al., 2017).

237 The synthesis conducted in the solution at pH 12 produced a translucent, gelatinous solid residue that  
238 turned white, with a paper texture, upon drying. The XRD pattern of this synthetic product revealed the  
239 presence of reflections typical of smectitic clay minerals, with peaks at 12.17 Å (001), 6.12 Å (002),  
240 4.43 Å (02,11), 3.09 Å (004), 2.53 Å (13,20), 2.04 Å (006), 1.68 Å (15,24,31), and 1.488 Å (06,33)  
241 (Fig. 3). In addition, the basal spacing of the *d*(06,33) is typical of dioctahedral Al-rich smectites such  
242 as beidellite (1.48–1.50 Å; Grauby et al., 1994; Petit et al., 2015). Its presence was suggested also by  
243 the FTIR spectrum exhibiting characteristic bands of Al-rich smectites, i.e. the bands at 3670 cm<sup>-1</sup>  
244 ( $\nu$ Al<sub>2</sub>OH), 3626 cm<sup>-1</sup> ( $\nu$ Al<sub>2</sub>OH), 1000–950 cm<sup>-1</sup> ( $\nu$ Si–O), 914 cm<sup>-1</sup> ( $\delta$ Al<sub>2</sub>OH), 815 cm<sup>-1</sup> (<sup>4</sup>Al–O out of  
245 plane), 694 cm<sup>-1</sup> (<sup>6</sup>Al–O<sub>ap</sub>), 520 cm<sup>-1</sup> ( $\delta$ Si–O–<sup>6</sup>Al), and 455 cm<sup>-1</sup> ( $\delta$ Si–O–<sup>6</sup>Al) (Fig. 4; Farmer &  
246 Russell, 1964; Kloprogge et al., 1990; Zviagina et al., 2004; Lantenois et al., 2008). Under vacuum, the  
247 *d*<sub>001</sub> of the beidellite synthesized in the solution at pH 12 collapsed down to 9.78 Å (Fig. S1).

248 The synthesis conducted in the solution at pH 12.5 produced a solid residue with an XRD pattern  
249 exhibiting peaks at 10.96 Å (001), 4.42 Å (02,11), 2.52 Å (13,20), and 1.481 Å (06,33), likely indicating  
250 the presence of beidellite (i.e. the *d*(06,33) diffracts between 1.48 and 1.50 Å; Fig. 3). The weak and  
251 broad peak of the (001) reflection indicates its poorly crystalline and dehydrated state (Ferrage et al.,  
252 2007). This beidellite cohabits with two zeolites (which are the main phases of the residue): analcime  
253 (diffraction peaks at 5.58, 4.83, 3.65, 3.42, 2.91, 2.42, 2.22, 2.15, 1.90, 1.86, 1.74, 1.71, and 1.59 Å) and  
254 a Na-garronite-like zeolite (diffraction peaks at 7.04, 5.75, 5.02, 4.91, 4.08, 3.51, 3.32, 3.18, 3.12, 3.03,  
255 2.68, 2.65, 2.04, 1.97, 1.96, and 1.78 Å; Oleksiak et al., 2016; Tayraukham et al., 2020).

256 The synthesis conducted in the solution at pH 13 produced a grainy solid residue with an XRD pattern  
257 typical of analcime, with peaks at 6.20 Å, 5.62 Å (011), 4.86 Å (020), 3.79 Å, 3.67 Å (021), 3.41 Å  
258 (222), 3.24 Å, 2.91 Å (112), 2.80 Å (022), 2.69 Å (130), 2.51 Å (231), 2.43 Å (040), 2.23 Å (032),  
259 2.17 Å (032), 2.12 Å, 2.02 Å, 1.94 Å, 1.90 Å (151), 1.87 Å (141), 1.83 Å, 1.74 Å (051), 1.71 Å (444),  
260 1.69 Å (223), 1.66 Å, 1.62 Å, 1.59 Å (043), and 1.50 Å and 1.48 Å (233) (Fig. 3). Peaks at 2.08 and 1.81 Å  
261 (also present in the XRD pattern of the saponite produced in the solution at pH 14; Fig. 1) were attributed  
262 to an austenitic steel from a spatula used during preparation for XRD. The FTIR spectrum (Fig. 4) shows  
263 two bands at 735 and 664 cm<sup>-1</sup> corresponding to  $\nu$ Si–O–Si and  $\nu$ Si–O–Al vibrations, and a band at  
264 613 cm<sup>-1</sup> attributed to 4-membered rings vibrations of analcime (Mozgawa et al., 2011).

265

## 266 Nontronite Syntheses

267 Each of the syntheses conducted in solutions at pH lower than 13 produced red solid residues, with the  
268 exception of the syntheses conducted with the AlCl<sub>3</sub> solution at pH 10.6 and the syntheses conducted in  
269 solutions at pH 12.5 using the gels obtained with the AlCl<sub>3</sub> solutions above pH 5.4. The latter produced  
270 gelatinous solid residues that were green on top and orange below. In contrast, the syntheses conducted  
271 in solutions at pH 13 produced gelatinous solid residues green on top and yellow below.

272

273 *Syntheses from the gels obtained using the AlCl<sub>3</sub> solution at pH 3.4*

274 Each of the four syntheses produced solid residues immersed in a reddish solution at a pH lower than  
275 that of the solution in which the starting gel was immersed (i.e. 4.7 for the synthesis conducted in pure  
276 water, 8.3 in the solution at pH 12, 10.7 at pH 12.5, and 12.7 at pH 13; Table 2). The XRD patterns of  
277 the synthetic products are very different from one another (Fig. 5). The solid produced in pure water  
278 exhibited XRD peaks at 8.96 Å (001), 4.50 Å (02,11), 3.52 Å (002), 2.54 Å (20,13), 2.32 Å (04,22),  
279 2.15 Å, 1.91 Å, 1.53 Å (06,33), and 1.50 Å, likely corresponding to hisingerite (i.e. a precursor of  
280 nontronite containing no Al, nontronite-like phase; Kohyama, 1975; Farmer et al., 1994; Eggleton,  
281 1998), while the solid produced in the solution at pH 12 exhibited only two broad bands near 3.58 and  
282 1.93 Å, maybe indicating the presence of a semi-amorphous hisingerite). The solid produced in the  
283 solution at pH 12.5 showed a broad peak at ~12.3 Å (001) and weak peaks at 4.52 Å (02,11), 3.14 Å  
284 (004), 2.59 Å (13,20), 1.72 Å (15,24,31), and 1.524 Å (06,33) corresponding to nontronite (Baron et al.,  
285 2016a). The solid produced in the solution at pH 13 contained sharper, rather crystalline nontronite  
286 (XRD peaks at 12.18 Å (001), 4.54 Å (02,11), 3.09 Å (004), 2.61 Å (13,21), and 1.530 Å (06,33);  
287 Fig. 5) mixed with analcime (XRD peaks at 5.55, 4.81, 3.67, 3.41, 2.91, 2.68, 2.49, 2.41, 2.22, 1.89,  
288 1.86, 1.73, 1.71, and 1.68 Å; Fig. 5). Note that the 06,33 reflection of this nontronite was shifted towards  
289 lower angles (greater *d* spacings) possibly indicating <sup>[4]Fe<sup>3+</sup></sup> for <sup>[4]Si<sup>4+</sup></sup> tetrahedral substitutions and, thus,  
290 an increase of its charge (Baron et al., 2016a). The FTIR data (Fig. 6) confirmed the interpretations of  
291 the XRD patterns; the bands typical of nontronite (i.e.  $\nu\text{Fe}_2^{3+}\text{-OH}$  at ~3560 cm<sup>-1</sup>,  $\delta\text{Fe}_2^{3+}\text{-OH}$  at 815 cm<sup>-1</sup>,  
292 the 855 cm<sup>-1</sup> (not assigned), <sup>[4]Fe-O</sup> at 707 cm<sup>-1</sup>, and <sup>[6]Fe<sup>3+</sup>-O<sub>ap</sub></sup> ~667 cm<sup>-1</sup>; Goodman et al., 1976;  
293 Baron et al., 2016a; Dzene et al., 2022) were stronger in the FTIR spectrum of the solid produced in the  
294 solution at pH 13 than in the FTIR spectrum of the solid produced in the solution at pH 12.5, indicating  
295 that the nontronite produced at pH 12.5 was poorly crystallized. No band typical of nontronite was  
296 observed in the FTIR spectra of the solids produced in solutions at pH lower than 12.5 (Fig. 6).

297 *Syntheses from the gels obtained using the AlCl<sub>3</sub> solution at pH 10.6*

298 Each of the four syntheses produced solid residues immersed in solutions ranging from reddish to  
299 colorless; the lower the pH of the solution in which the synthesis was conducted, the more reddish the  
300 solution at the end of the synthesis (Table 2). With the exception of the final solution of the synthesis  
301 conducted in pure water at pH which ended at pH 9.7, the final solutions had pH values close to those  
302 of the solutions in which the starting gels were immersed (Table 2). The XRD patterns of all the solids  
303 show the presence of nontronite, i.e. XRD peaks at 12.43–13.07 Å (001), 4.53–4.56 Å (02,11), 3.10–  
304 3.14 Å (004), 2.58–2.62 Å (13,20), 1.73 Å (13,24,31), and 1.522–1.537 Å (06,33) (Baron et al., 2016a;  
305 Fig. 5). The increase of the 06,33 reflection position may indicate increasing <sup>[4]Fe<sup>3+</sup></sup> for <sup>[4]Si<sup>4+</sup></sup> tetrahedral  
306 substitutions with increasing pH (Baron et al., 2016a). The additional presence of bayerite (Al(OH)<sub>3</sub>)  
307 can be inferred from the solid produced in pure water, as well as from the solid produced in the solution  
308 at pH 12 (although in lower abundance), from the XRD peaks at 4.68, 4.35, 3.18, 2.21, 1.71, and 1.59 Å  
309 (Milligan, 1951; Lefevre & Fedoroff, 2002) and the FTIR bands at 3651, 3545, 3461, and 3418 cm<sup>-1</sup>  
310 (Phambu et al., 2002 – Figs 5, 6). FTIR spectra of all solid residues showed bands typical of nontronite  
311 (i.e. bands at ~3560 cm<sup>-1</sup> ( $\nu\text{Fe}_2\text{OH}$ ), ~950 cm<sup>-1</sup> ( $\nu\text{Si-O}$ ), ~815 cm<sup>-1</sup> ( $\delta\text{Fe}^{3+}_2\text{OH}$ ), ~667 cm<sup>-1</sup> (<sup>[6]Fe<sup>3+</sup>-</sup>  
312  $\text{O}_{\text{ap}}$ ), 585 cm<sup>-1</sup> ( $\delta\text{Si-O}$ ) and ~480 cm<sup>-1</sup> (<sup>[6]Fe-O-Si</sup>) (Goodman et al., 1976; Baron et al., 2016a). The  
313 bands at 850 and 707 cm<sup>-1</sup> are present commonly in nontronite with large <sup>[6]Fe</sup> occupancy, but the band  
314 at 707 cm<sup>-1</sup> is present only in the FTIR spectrum of the nontronite produced in the solution at pH 13. Of  
315 note, the weak band at ~3635 cm<sup>-1</sup> observed in the FTIR spectra of the solids produced in the solutions  
316 at pH 12 and 12.5 corresponds to OH vibrations from water (cf Fig. S2). Under vacuum, the *d*<sub>001</sub> of the  
317 nontronite synthesized in the solution at pH 12 with the gel produced using the AlCl<sub>3</sub> solution at pH  
318 10.6 collapsed to 10.06 Å (Fig. S1).

319

320



321 *Syntheses from the gels obtained using the AlCl<sub>3</sub> solutions at pH 5.3 and pH 8*

322 Both syntheses conducted in the solution at pH 12.5 produced nontronite as revealed by XRD (peaks at  
323 ~12.7 Å, 4.55 Å / 4.54 Å, 3.1 Å, 2.6 Å, 1.73 Å, 1.528 Å / 1.527 Å; Baron et al., 2016a) and FTIR (bands  
324 at 3564, 812, 855, 707, and 665 cm<sup>-1</sup>; Goodman et al., 1976; Baron et al., 2016a; Figs 5, 6). However,  
325 a band at 707 cm<sup>-1</sup>, corresponding to <sup>[4]Fe</sup>–O vibrations, is present in both FTIR spectra, likely indicating  
326 <sup>[4]Fe</sup><sup>3+</sup> for <sup>[4]Si</sup><sup>4+</sup> tetrahedral substitutions.

327

## 328 **Discussion**

329

330 Results show that the conditions required for the syntheses of pure (i.e. with no other mineral) Al-  
331 substituted smectite end-members (saponite, beidellite, and nontronite) are very different, even though  
332 these smectites differ only by the cation present at their octahedral sites. In this article the sensitivity to  
333 pH conditions of the production of pure saponite, beidellite, and nontronite is discussed and the various  
334 protocols leading to their successful syntheses are summarized.

### 335 Influence of pH

336 The results reported here show that the synthesis of pure saponite does not depend strongly on the pH  
337 of the solution in which the gels of saponite composition are immersed (saponite was obtained in  
338 solutions at pH ranging from 5.5 to 14). This can be due to the stability of the starting gel of trioctahedral  
339 smectites, as previously observed by Huertas et al. (2000). Of note, the saponites produced in the present  
340 study contain tetrahedral Al and no octahedral Al. In fact, the ATR-FTIR spectra of the saponites  
341 produced were very similar to the ATR-FTIR spectrum of saponite presented in Kloprogge and Ponce  
342 (2021), with a feature at 800–815 cm<sup>-1</sup> attributed to δAl–O of tetrahedral Al (absent from the ATR-FTIR  
343 spectrum of talc which contains no tetrahedral Al; Kloprogge & Ponce, 2021). Plus, the absence of the  
344 FTIR band attributed to νMg<sub>2</sub>-Al–OH at 3625 cm<sup>-1</sup> is consistent with the absence of octahedral Al  
345 (Kloprogge & Ponce, 2021).

346 The XRD pattern of the saponite synthesized in solutions at pH 14 exhibited narrower 001 reflections  
347 than those of the saponites synthesized in solutions at lower pH. Such a decrease in width indicates a  
348 decrease in the *d*<sub>001</sub> distance and can be interpreted as an increase in crystallinity (Zhang et al., 2022).  
349 Consistently, high pH conditions during syntheses have been reported to improve both the crystallinity  
350 and crystallization rate of saponites (Blukis et al., 2022), as is the case of high temperature conditions  
351 (Kloprogge & Frost, 2000; Kloprogge & Ponce, 2021). Still, such a decrease in width may also indicate  
352 an increase in the permanent charge, i.e. a higher degree of <sup>[4]Al</sup><sup>3+</sup> for <sup>[4]Si</sup><sup>4+</sup> tetrahedral substitutions.  
353 Consistently, with increasing pH (from 5.5 to 14), the νSi–O–Si and δAl–O absorption bands shifted  
354 from 960 to 944 cm<sup>-1</sup> and from 800 to 815 cm<sup>-1</sup>, respectively, while the νMg<sub>3</sub>OH and δMg<sub>3</sub>OH  
355 absorption bands of the synthesized saponites shifted from 3674 to 3685 cm<sup>-1</sup> and from 655 to 640 cm<sup>-1</sup>,  
356 respectively (Fig. 2), such shifts having been interpreted previously as an increase of the permanent  
357 charge (Pelletier et al., 2003; Meyer et al., 2020). Note that the production of saponites with a higher  
358 charge should leave available Si and Mg in the system, possibly leading to the production of other phases  
359 such as brucite (Mg(OH)<sub>2</sub>), serpentine (Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), or talc (Si<sub>4</sub>Mg<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub>), i.e. an assemblage  
360 similar to what is obtained with a gel produced using Na<sub>2</sub>SiO<sub>3</sub> and AlCl<sub>3</sub> solutions at pH 14 (Fig. S3).  
361 The absence of these minerals in the final residue (only saponite is present according to XRD and FTIR  
362 data; Figs 1, 2) suggests either that both Si and Mg in excess have been leached during filtration or that  
363 some Mg has replaced Na as the interlayer cation. Additional data (such as elemental or NMR data)  
364 would be required to determine if the saponite produced by immersing the gel in a solution at pH 14 has  
365 exactly the same composition as those produced at lower pH.

366 In contrast to that of saponite, the synthesis of beidellite is highly sensitive to the pH of the AlCl<sub>3</sub> solution  
367 and the pH of the solution in which gels are immersed. A gel of beidellite composition produced using  
368 an AlCl<sub>3</sub> solution at pH 3.4 seems to be very unstable and does not lead to the formation of pure  
369 beidellite, irrespective of the pH of the solution used for the synthesis (cf Fig. S4). In contrast, a gel of  
370 beidellite composition produced using an AlCl<sub>3</sub> solution at pH 10.6 will lead systematically to the  
371 formation of boehmite (cf Fig. S4). Syntheses using gels of beidellite composition immersed in pure  
372 water will lead to the formation of kaolins, while only zeolites form in solutions at high pH, as also  
373 reported by De Kimpe (1976) and Huertas et al. (2000). The cause resides in the (pH-dependent) form  
374 of Si and Al species. In pure water, H<sub>4</sub>SiO<sub>4</sub>, Al(OH)<sub>2</sub><sup>+</sup>, and Al(OH)<sup>2+</sup> prevail, and Si and Al ions form  
375 tetrahedral and octahedral complexes, respectively, while at high pH (>13), H<sub>2</sub>SiO<sub>4</sub><sup>-</sup> and Al(OH)<sub>4</sub><sup>-</sup>  
376 prevail, leading to the formation of only tetrahedral complexes (Table 1). Thus, the successful synthesis  
377 of pure beidellite occurs only at a very specific pH (i.e. 12), where 4-fold and 6-fold coordinated Al  
378 species exist, as previously suggested (De Kimpe, 1976).

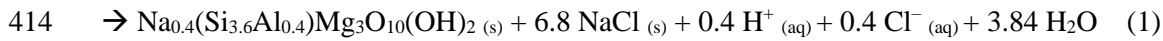
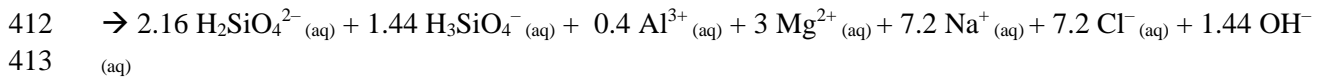
379 The synthesis of <sup>41</sup>Al-nontronite is also very sensitive to the pH of solutions, as is the case for <sup>41</sup>Fe-  
380 nontronite as acknowledged earlier (Andrieux & Petit, 2010; Boumaiza et al., 2020; Dzene et al., 2022).  
381 Only the gel produced using an AlCl<sub>3</sub> solution at pH 10.6 and immersed in a solution at pH 12.5 leads  
382 to pure <sup>41</sup>Al-nontronite. The syntheses conducted at a pH lower than 12.5 from the gels of nontronite  
383 composition produced using an AlCl<sub>3</sub> solution at pH 10.6 led to the production of nontronite together  
384 with bayerite. Gels produced using an AlCl<sub>3</sub> solution at pH 10.6 and immersed in solutions at pH 13  
385 crystallized into pure nontronite, but these are <sup>41</sup>Fe-nontronites as indicated by the shift of the 06,33  
386 reflection to lower angles and the shift of the νSi–O to lower wavelengths (Baron et al., 2016a). A high  
387 pH, thus, seems to favor <sup>41</sup>Fe<sup>3+</sup> for <sup>41</sup>Si<sup>4+</sup> tetrahedral substitutions, as historically suggested by Grubb  
388 (1969). The use of gels produced using an AlCl<sub>3</sub> solution at pH 3.4 did not lead to the production of  
389 pure, well crystallized <sup>41</sup>Al-nontronite (only poorly crystalline nontronite is obtained at pH 12.5). The  
390 immersion of such gels in solutions at lower pH leads to the production of hisingerite (i.e. a precursor  
391 of nontronite containing no Al; Kohyama, 1975; Farmer et al., 1994; Eggleton, 1998; Milliken & Bish,  
392 2014), while their immersion in solutions at higher pH leads to the production of a zeolite (analcime)  
393 together with <sup>41</sup>Fe-nontronite.

#### 394 Mechanistic Considerations

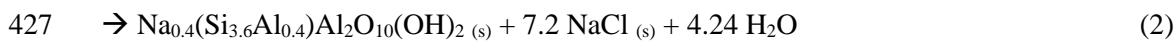
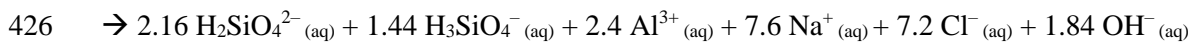
395 This section concerns the reactions that have likely occurred during the syntheses of saponite, beidellite,  
396 and nontronite. Please note that the equations presented below refer to the theoretical products of the  
397 syntheses carried out in the present study.

398 Pure saponite can be synthesized following various protocols, at various temperatures (Kloprogge &  
399 Frost, 2000; Meyer et al., 2020) and for different durations (Zhang et al., 2020), whatever the pH (Blukis  
400 et al., 2022). Here, saponite was obtained by immersing gels in solutions at pH ranging from 5.5 to 14,  
401 probably because the rather large Mg<sup>2+</sup> ions did not compete with Al species for tetrahedral substitutions.  
402 The major species in the Na<sub>2</sub>SiO<sub>3</sub> solution at 0.2 M at pH 13.1 are H<sub>2</sub>SiO<sub>4</sub><sup>2-</sup> and H<sub>3</sub>SiO<sub>4</sub><sup>-</sup> (Table 1).  
403 Although Al was present mainly as Al<sup>3+</sup> in the AlCl<sub>3</sub> solution, it converted to Al(OH)<sub>4</sub><sup>-</sup> when this  
404 solution was poured into the Na<sub>2</sub>SiO<sub>3</sub> solution, leading to the polymerization of an aluminosilicate  
405 network (i.e. tetrahedral complexes) at high pH (as suggested by Besselink et al., 2020). The subsequent  
406 addition of the MgCl<sub>2</sub> solution was responsible for a slight decrease in the pH (down to 10 – Table 2),  
407 probably converting the remaining H<sub>2</sub>SiO<sub>4</sub><sup>2-</sup> ions into H<sub>3</sub>SiO<sub>4</sub><sup>-</sup>, thereby leading to the polymerization of  
408 Mg-rich octahedral complexes. The produced gel crystallized into saponite whatever the pH of the  
409 solution into which it will be immersed, following the overall simplified reaction, written with respect  
410 to the main species present in each starting solution at 20°C (cf Table 1):

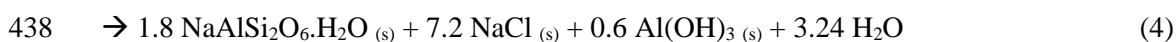
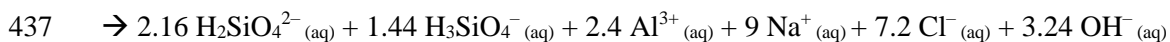
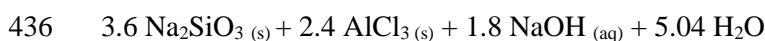
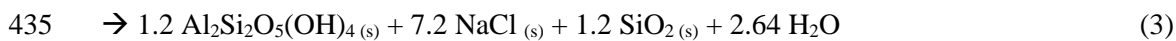
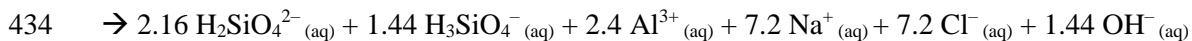
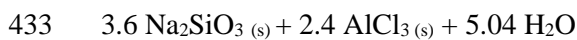




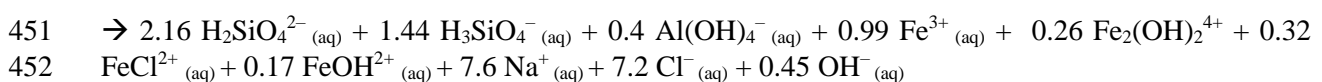
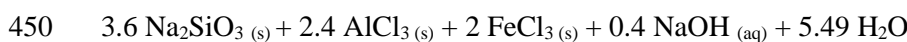
415 Pure beidellite cannot be synthesized over a large range of pH. The pH of the solution in which the gel  
 416 is immersed for crystallization has to be precisely controlled. Although the formation of tetrahedral  
 417 complexes occurred as for saponite when pouring the  $\text{AlCl}_3$  solution at pH 3.9 into the  $\text{Na}_2\text{SiO}_3$  solution  
 418 at 0.2 M at pH 13.1, the subsequent addition of the second  $\text{AlCl}_3$  solution was responsible for a large  
 419 decrease in the pH (down to 4.5 – Table 2), destabilizing the tetrahedral complexes already formed and  
 420 converting the  $\text{H}_2\text{SiO}_4^{2-}$  ions into  $\text{H}_4\text{SiO}_4$  and the  $\text{Al}(\text{OH})_4^-$  ions into  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})^{2+}$ , and  $\text{Al}^{3+}$ . The  
 421 gel obtained with the starting  $\text{AlCl}_3$  solution at pH 3.9 will crystallize into pure beidellite only if  
 422 immersed in solutions at pH 12 (allowing the conversion of Al species into  $\text{Al}(\text{OH})_4^-$ , and thus the  
 423 incorporation of tetrahedral Al) followed the overall simplified reaction, written with respect to the main  
 424 species present in each starting solution at 20°C (cf Table 1):

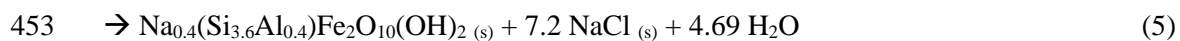


428 If the gel is immersed into a solution at pH lower than 12, only kaolins will be produced following Eq. 3,  
 429 while if the gel is immersed into a solution at pH higher than 12, only zeolites will be produced following  
 430 Eq. 4 (together with  $\text{SiO}_2$  or  $\text{Al}(\text{OH})_3$ , respectively, which are likely leached during filtration). Note that  
 431 a starting  $\text{AlCl}_3$  solution at pH above 8, which would contain  $\text{Al}(\text{OH})_4^-$  ions, cannot be used to produce a  
 432 gel because of the inevitable precipitation of  $\text{AlOOH}$  or  $\text{Al}(\text{OH})_3$  (Fig. S4).



439 Pure nontronite also cannot be synthesized over a large pH range. As for beidellite, the pH of the solution  
 440 in which the gel is immersed for crystallization has to be controlled precisely, even though the pH of the  
 441 starting  $\text{AlCl}_3$  solution does not seem to be critical, given that pure  $^{54}\text{Fe}$ -nontronite or  $^{27}\text{Al}$ -nontronite  
 442 were produced here from  $\text{AlCl}_3$  solutions at either pH 3.4 or 10.6. However, here, only the use of an  
 443  $\text{AlCl}_3$  solution at pH 10.6 led to the production of  $^{27}\text{Al}$ -Nontronite. As for saponite and beidellite, the  
 444 formation of tetrahedral complexes occurred when pouring the  $\text{AlCl}_3$  solution into the 0.2 M  $\text{Na}_2\text{SiO}_3$   
 445 solution at pH 13.1. The subsequent addition of the  $\text{FeCl}_3$  solution was responsible for only a slight  
 446 decrease in the pH (down to 9; Table 2), leading to the production of Fe-rich octahedral complexes  
 447 forming a gel which would crystallize into pure  $^{27}\text{Al}$ -nontronite only if immersed in solutions at pH 12.5  
 448 following the overall simplified reaction, written with respect to the main species present in each starting  
 449 solution at 20°C (cf Table 1):





454 At high pH, the major species in solution were  $\text{H}_3\text{SiO}_4^-$ ,  $\text{H}_2\text{SiO}_4^{2-}$ ,  $\text{Al}(\text{OH})_4^-$ , and  $\text{Fe}(\text{OH})_4^-$  (Perry &  
455 Shafran, 2001; Guan et al., 2009), with  $\text{Al}(\text{OH})_4^-$  competing with  $\text{Fe}(\text{OH})_4^-$  for tetrahedral substitutions  
456 (Decarreau & Petit, 2014). According to the present results, if the gel is immersed in a solution at pH  
457 12.5,  $\text{Al}(\text{OH})_4^-$  is preferentially incorporated into tetrahedral sites over  $\text{Fe}(\text{OH})_4^-$ , leading eventually to  
458 the production of  $^{41}\text{Al}$ -nontronite. In contrast, if the gel is immersed in a solution at pH higher than 12.5,  
459  $\text{Fe}(\text{OH})_4^-$  is incorporated preferentially into tetrahedral sites over  $\text{Al}(\text{OH})_4^-$ , eventually leading to the  
460 production of  $^{41}\text{Fe}$ -nontronite rather than  $^{41}\text{Al}$ -nontronite (cf Fig. 6). At pH lower than 12.5, Al seems  
461 to be incorporated neither in tetrahedral nor octahedral sites and bayerite is produced together with  $^{41}\text{Fe}$ -  
462 nontronite (Fig. 6).

## 463 **Concluding Remarks**

### 464 **Optimal pH for the Synthesis of Saponite, Beidellite, and Nontronite**

465 The successful synthesis of saponite was achieved by exposing the starting gels to 230°C for 4 days in  
466 solutions at pH ranging from 5.5 to 14, confirming the pH non-sensitivity of saponite production (Blukis  
467 et al., 2022). Of note, the gel-to-solution ratio is an important parameter. Here, a mass of about 100 mg  
468 of gel was immersed into 16.5 mL of solution. In a similar volume of solution, a smaller (50 mg) or a  
469 larger (200 mg) mass of gel led to the formation of less crystalline saponites (data not shown here).

470 The successful synthesis of beidellite was achieved by exposing the gel obtained using the  $\text{AlCl}_3$  solution  
471 at pH 3.9 to 230°C for 9 days in a solution at pH 12. The gel-to-solution ratio is also an important  
472 parameter. Here, a mass of about 80 mg of gel was immersed into 12.5 mL of solution at pH 12. In a  
473 similar volume of solution, a lower mass of gel (60 mg) led to the formation of zeolites, while a larger  
474 mass of gel (100 mg) led to the formation of kaolins and aluminum hydroxides (data not shown here).

475 The successful synthesis of nontronite was achieved by exposing the starting gels to 150°C for 2.5 days  
476 in solutions at pH between 12.5 and 13. Pure nontronite was obtained by immersing gels prepared with  
477 an  $\text{AlCl}_3$  solution at a pH above 5 in solutions at pH 12.5 (confirming the results of Andrieux and Petit,  
478 2010). Here, a mass of about 165 mg of gel was immersed into 16.5 mL of solution. Of note, changing  
479 this ratio will influence the pH and may lead to the additional production of either analcime or aluminum  
480 hydroxides (data not shown here).

### 481 **Implications for Natural Systems**

482 Smectites carry key information on the geochemistry, oxidation state, and water content of the  
483 environments in which they were produced (Ehlmann et al., 2011; Fox et al., 2021), making them good  
484 indicators of paleoenvironmental and paleoclimatic conditions. Although further characterization (such  
485 as elemental or NMR analyses) would be required to ascertain the exact structure and composition of  
486 the various products more precisely, the present study shows that the optimal pH for the synthesis of  
487 saponite, beidellite, or nontronite is different; pH conditions influence strongly the purity and the final  
488 crystallochemistry of the smectites produced. Although extrapolating experimental results to natural  
489 settings remains complicated, the present results suggest that the crystallochemistry of natural smectites  
490 could also be used (a priori) as a paleo-pH proxy. However, smectitic clay minerals are rarely pure in  
491 natural settings, and most often exist in a complicated assemblage of various (more or less interstratified)  
492 clay mineral phases. Plus, natural clay minerals, either terrestrial or extraterrestrial, have usually  
493 experienced a complex history, including possible transport, mixing, reworking, and alteration, without  
494 mentioning interactions with organic compounds which may influence the crystallization and the final  
495 crystallochemistry of clay minerals (Jacquemot et al., 2019; Viennet et al., 2019, 2022). Last, the precise  
496 estimation of an age is fundamental for a proxy to be useful, and it remains very difficult to date smectitic  
497 clay minerals other than relying on certain impurities (transition ions) and point defects (radicals) which  
498 may be probed using electron paramagnetic resonance spectroscopy (Allard et al., 2012; Balan et al.,

499 2020). Still, there is no doubt that the results of the present study will be of great help to constrain better  
500 the geochemical conditions existing or having existed on extraterrestrial planetary bodies such as Mars,  
501 on which the production of clay minerals has been intense (Carter et al., 2013; Ehlmann & Edwards,  
502 2014), or on rocky and/or icy small bodies such as Ceres, Enceladus, or Europa on which the production  
503 of (likely smectitic) clay minerals have recently been reported (Waite et al., 2017; Nordheim et al., 2018;  
504 Marchi et al., 2019).

505

506

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### 512 **Conflicts of interest**

513 The authors declare that they have no known competing financial interests or personal relationships that  
514 could have appeared to influence the work reported in this article.

### 515 **Availability of data and material (data transparency)**

516 All data are available at

517 <https://drive.google.com/drive/folders/1prbEh1-XBEL-Qcb8NxvS1qzrygQ873yZ?usp=sharing>

### 518 **Authors' contributions**

519 IC, JCV, and SB designed the present study. IC and JCV performed the FTIR and the XRD analyses,  
520 with the help of LD and MG. All authors contributed to the interpretation of the data and discussed their  
521 implications. IC, JCV, and SB wrote the present manuscript, with critical inputs from FB, AB, and EB.

522

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## TABLES & FIGURES

819

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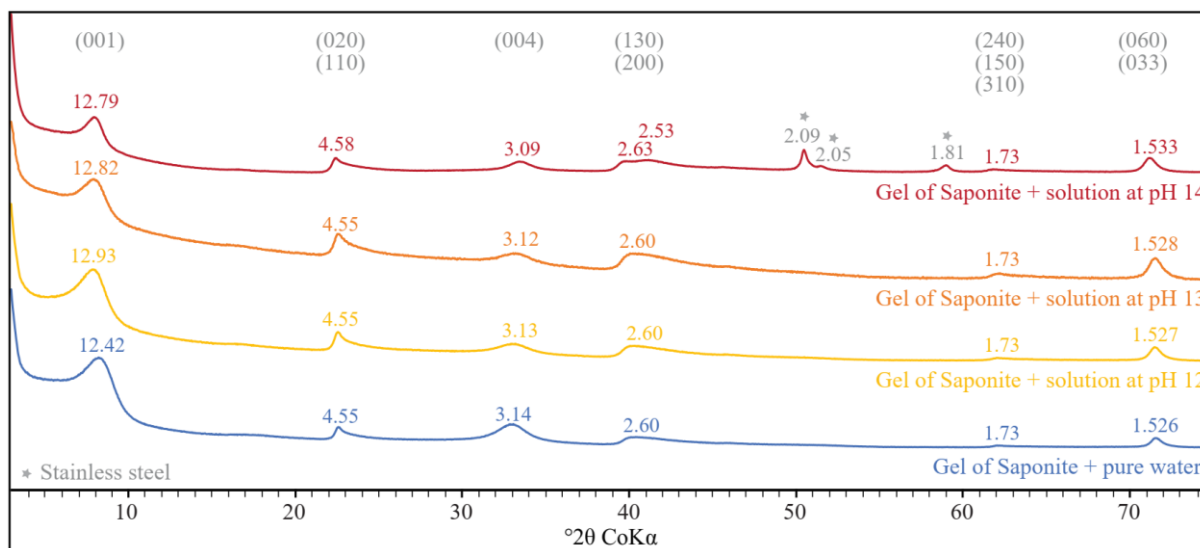
821 Table 1. pH of the solutions (0.2 mol.L<sup>-1</sup>) and the main Si, Al, Fe, and Mg species in solution at 20°C  
 822 (calculated using *Phreeqc*)

Solutions	pH	Major species in solution	Visual aspect
Na <sub>2</sub> SiO <sub>3</sub> (0.2 M)	13.1	H <sub>2</sub> SiO <sub>4</sub> <sup>2-</sup> /H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup>	Transparent liquid
AlCl <sub>3</sub> (0.2 M)	3.4	Al <sup>3+</sup>	Transparent liquid
FeCl <sub>3</sub> (0.2 M)	1.8	Fe <sup>3+</sup>	Yellow liquid
MgCl <sub>2</sub> (0.2 M)	5.4	Mg <sup>2+</sup>	Transparent liquid
FeCl <sub>3</sub> (0.2 M) + NaOH	2.1	Fe <sup>3+</sup> >Fe <sub>2</sub> (OH) <sub>2</sub> <sup>4+</sup> >FeCl <sup>2+</sup> >FeOH <sup>2+</sup>	Orange liquid
AlCl <sub>3</sub> (0.2 M) + NaOH	3.9	Al <sup>3+</sup> >>>Al(OH) <sup>2+</sup>	Transparent liquid
AlCl <sub>3</sub> (0.2 M) + NaOH	5.3	Al <sup>3+</sup> >Al(OH) <sup>2+</sup> >Al(OH) <sub>2</sub> <sup>+</sup>	White liquid (+ solid Al(OH) <sub>3</sub> )
AlCl <sub>3</sub> (0.2 M) + NaOH	8	Al(OH) <sub>4</sub> <sup>-</sup>	White and very viscous liquid (+ solid Al(OH) <sub>3</sub> )
AlCl <sub>3</sub> (0.2 M) + NaOH	10.6	Al(OH) <sub>4</sub> <sup>-</sup>	White viscous liquid (+ solid Al(OH) <sub>3</sub> )

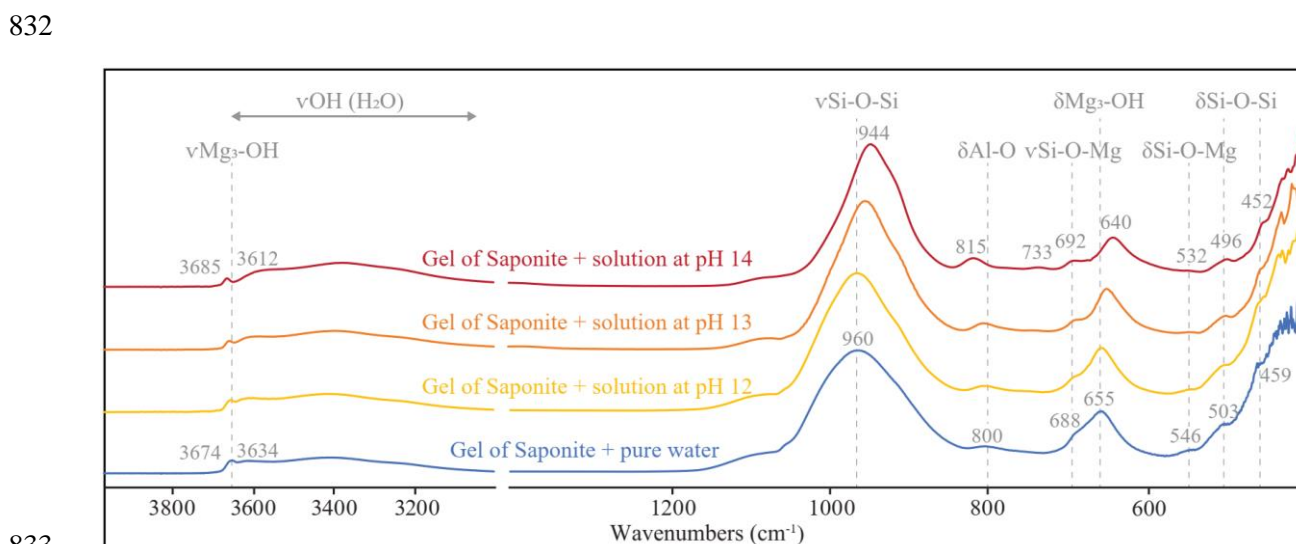
823

824 Table 2. Starting materials, conditions of synthesis of smectites, and synthesized products (pH<sub>i</sub> corresponds to the pH of the solutions in equilibrium with the  
 825 gel; pH<sub>f</sub> corresponds to the pH of the solutions in equilibrium with the final products)

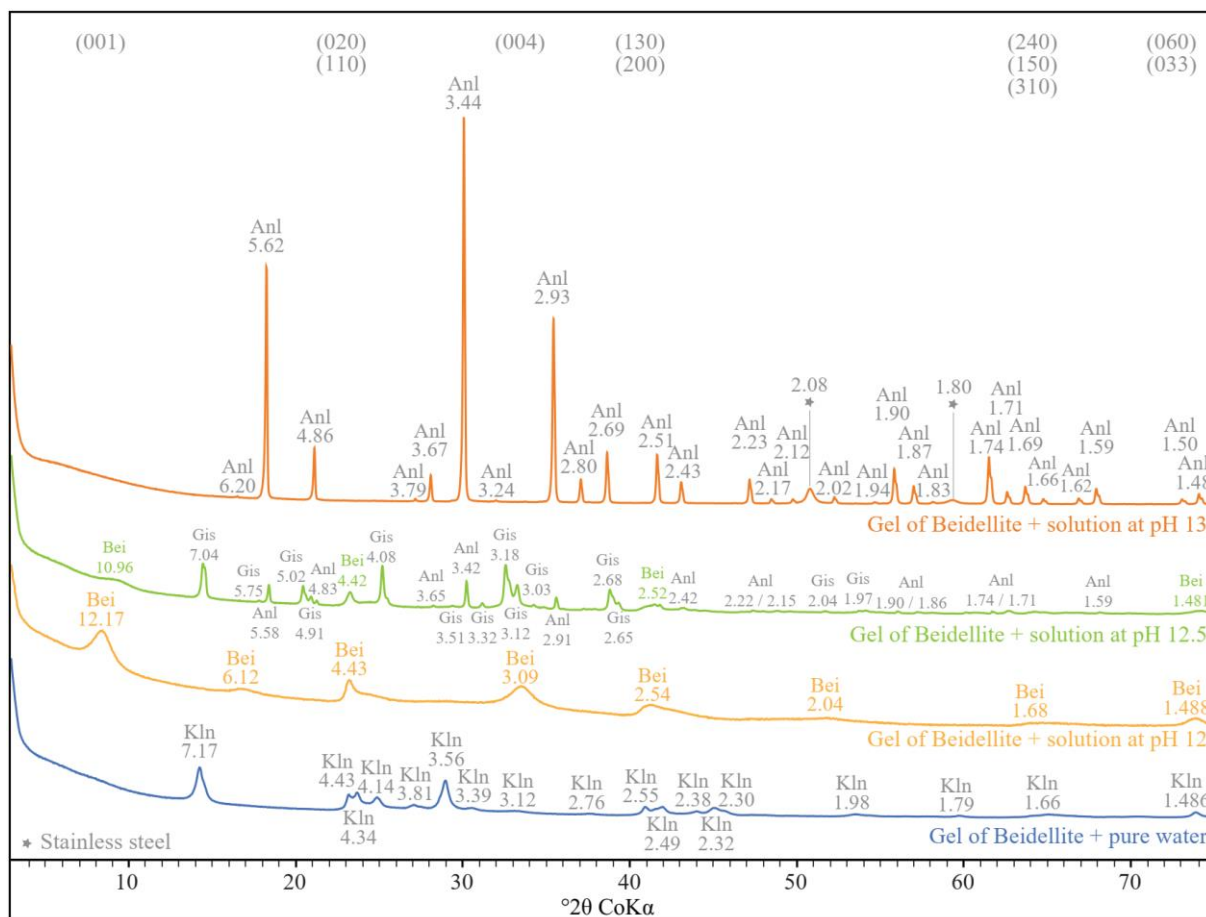
Theoretical Starting Gel	pH of the Na <sub>2</sub> SiO <sub>3</sub> solution	pH of the AlCl <sub>3</sub> solution	pH of the 3 <sup>rd</sup> solution	Theoretical mass of gel (mg)	pH <sub>i</sub>	Volume of the added solution (mL)	pH of the added solution	T°C	Synthesis duration (days)	pH <sub>f</sub>	Products
Saponite	13.1	3.4	MgCl <sub>2</sub> - pH 5.4	100	10	16.5	5.5	230	4	7.5	[ <sup>4</sup> ]Al-Saponite
Saponite	13.1	3.4	MgCl <sub>2</sub> - pH 5.4	100	10	16.5	12	230	4	10.4	[ <sup>4</sup> ]Al-Saponite
Saponite	13.1	3.4	MgCl <sub>2</sub> - pH 5.4	100	10	16.5	13	230	4	12.9	[ <sup>4</sup> ]Al-Saponite
Saponite	13.1	3.4	MgCl <sub>2</sub> - pH 5.4	100	10	16.5	14	230	4	13.7	[ <sup>4</sup> ]Al-Saponite
Beidellite	13.1	3.9	AlCl <sub>3</sub> - pH 3.9	80	4.5	12.5	5.5	230	9	7.2	Kaolins
Beidellite	13.1	3.9	AlCl <sub>3</sub> - pH 3.9	80	4.5	12.5	12	230	9	9.4	[ <sup>4</sup> ]Al-Beidellite
Beidellite	13.1	3.9	AlCl <sub>3</sub> - pH 3.9	80	4.5	12.5	12.5	230	9	11	[ <sup>4</sup> ]Al-Beidellite+Analcime
Beidellite	13.1	3.9	AlCl <sub>3</sub> - pH 3.9	80	4.5	12.5	13	230	9	12	Analcime
Nontronite	13.1	3.4	FeCl <sub>3</sub> - pH 2.1	165	4	16.5	5.5	150	2.5	4.7	Hisingerite
Nontronite	13.1	3.4	FeCl <sub>3</sub> - pH 2.1	165	4	16.5	12	150	2.5	8.3	Amorphous Gel
Nontronite	13.1	3.4	FeCl <sub>3</sub> - pH 2.1	165	4	16.5	12.5	150	2.5	10.7	[ <sup>4</sup> ]Fe-Nontronite
Nontronite	13.1	3.4	FeCl <sub>3</sub> - pH 2.1	165	4	16.5	13	150	2.5	12.7	[ <sup>4</sup> ]Fe-Nontronite+Analcime
Nontronite	13.1	5.3	FeCl <sub>3</sub> - pH 2.1	165	-	16.5	12.5	150	2.5	-	[ <sup>4</sup> ]Fe-Nontronite+Hisingerite
Nontronite	13.1	8.0	FeCl <sub>3</sub> - pH 2.1	165	-	16.5	12.5	150	2.5	-	[ <sup>4</sup> ]Fe-Nontronite
Nontronite	13.1	10.6	FeCl <sub>3</sub> - pH 2.1	165	9	16.5	5.5	150	2.5	9.7	[ <sup>4</sup> ]Fe-Nontronite+Bayerite
Nontronite	13.1	10.6	FeCl <sub>3</sub> - pH 2.1	165	9	16.5	12	150	2.5	12.1	[ <sup>4</sup> ]Fe-Nontronite+Bayerite
Nontronite	13.1	10.6	FeCl <sub>3</sub> - pH 2.1	165	9	16.5	12.5	150	2.5	12.5	[ <sup>4</sup> ]Al-Nontronite
Nontronite	13.1	10.6	FeCl <sub>3</sub> - pH 2.1	165	9	16.5	13	150	2.5	12.9	[ <sup>4</sup> ]Fe-Nontronite



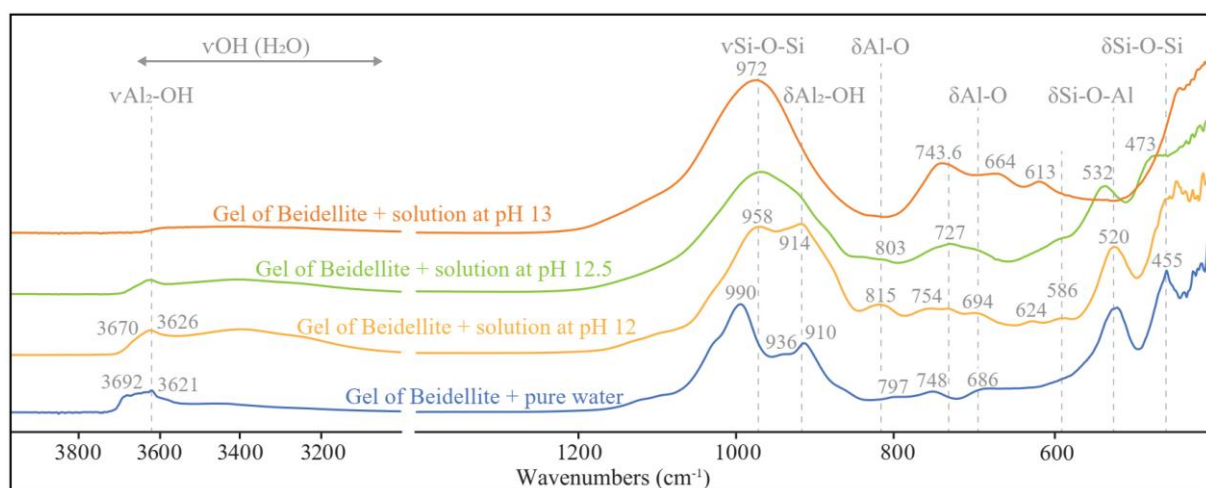
828  
 829 Figure 1. XRD patterns of products of syntheses conducted with the gels of saponite composition. Peaks  
 830 at 2.09, 2.05, and 1.80 Å are attributed to contamination by austenitic stainless steel during XRD sample  
 831 preparation (Boonruang & Sanumang, 2021)



833  
 834 Figure 2. FTIR spectra of products of syntheses conducted with the gels of saponite composition

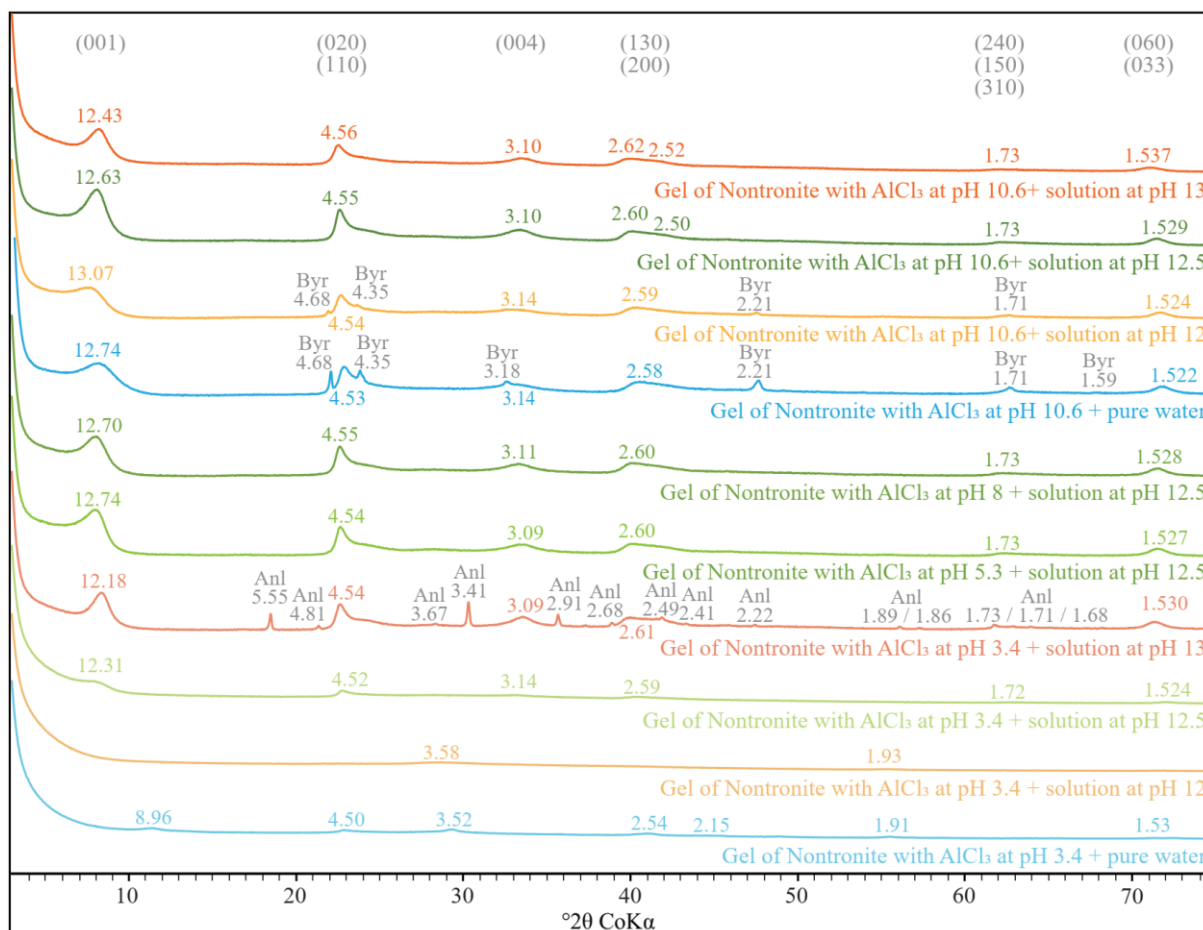


835  
 836 Figure 3. XRD patterns of products of syntheses conducted with the gels of beidellite composition. Bei:  
 837 Beidellite. Anl: Analcime. Gis: Gismondine. Kln: Kaolinite. Peaks at 2.08 Å and 1.80 Å are attributed  
 838 to contamination by austenitic stainless steel during XRD sample preparation (Boonruang & Sanumang,  
 839 2021)



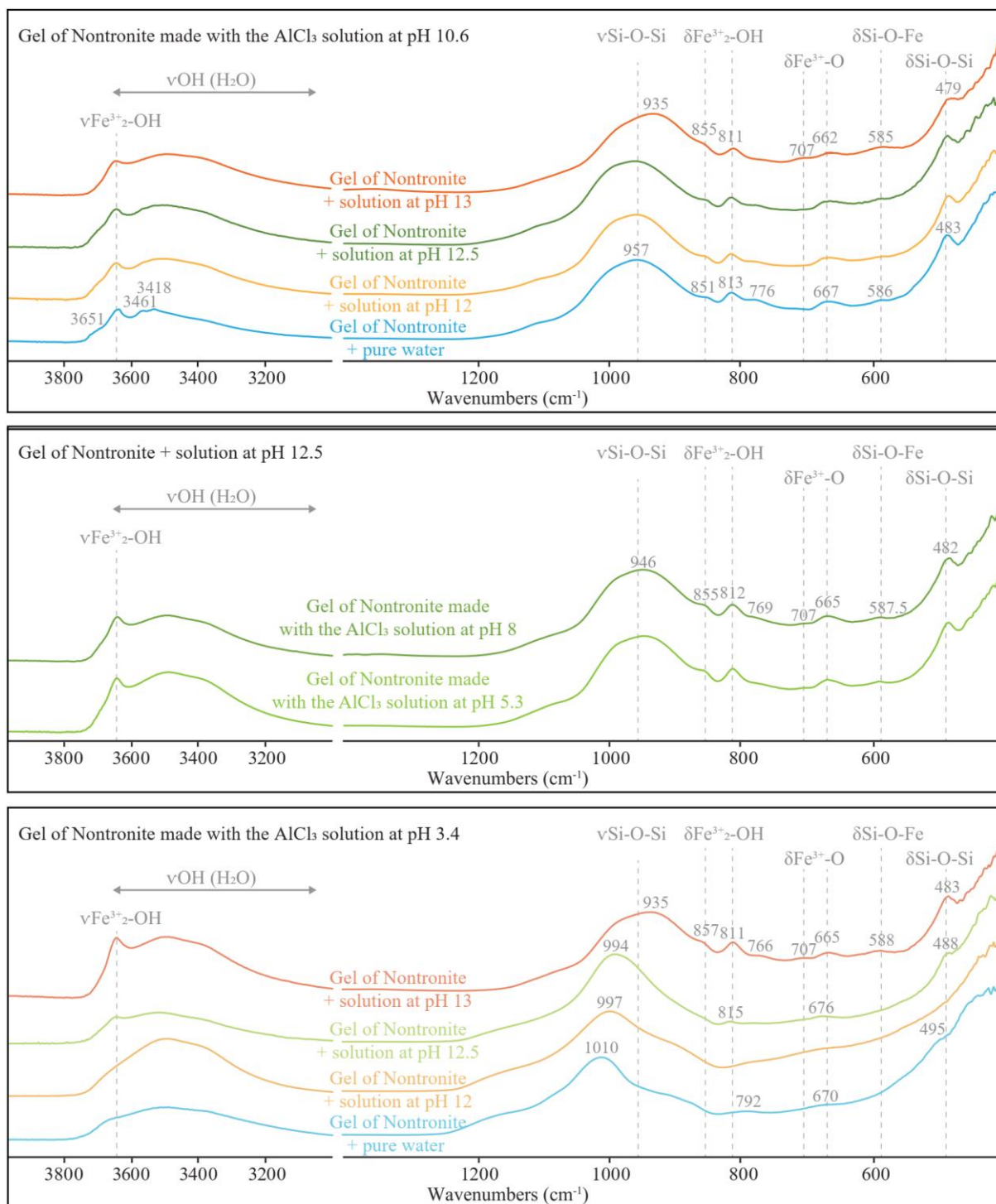
840  
 841 Figure 4 FTIR spectra of products of syntheses conducted with the gels of beidellite composition  
 842





843  
 844 Figure 5. XRD patterns of products of syntheses conducted with the gels of nontronite composition.  
 845 Byr: Bayerite. Anl: Analcime

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Figure 6. FTIR spectra of products of syntheses conducted with the gels of nontronite composition