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► **To cite this version:**

I. Criouet, Jean-Christophe Viennet, Fabien Baron, E. Balan, A. Buch, et al.. Influence of pH on the Hydrothermal Synthesis of Al-Substituted Smectites (Saponite, Beidellite, and Nontronite). *Clays and Clay Minerals*, 2023, 10.1007/s42860-023-00255-3. hal-04300843

HAL Id: hal-04300843

<https://hal.science/hal-04300843>

Submitted on 22 Nov 2023

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

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Accepted: 24 August 2023

Abstract—Smectitic clay minerals are unique indicators of paleoenvironmental conditions and exhibit a unique reactivity in the mineral world. Smectites may exhibit tetrahedral substitutions (Al³⁺ - and sometimes Fe³⁺ - can substitute for Si⁴⁺ 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 CO₂ or H₂ (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,Fe³⁺)–O tetrahedral sheets and in which stacking creates
64 expandable interlayer spaces capable of storing water, organics, and exchangeable cations (mostly Ca²⁺,
65 Mg²⁺, Na⁺, and K⁺) 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 (Al³⁺ - and sometimes Fe³⁺ - can substitute for Si⁴⁺ 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 AlCl_3 solution into a Na_2SiO_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 MgCl_2 , an FeCl_3 , or
110 an 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°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 ± 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 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 Na_2SiO_3 (>95%), AlCl_3 (99%), MgCl_2 (>99%), and FeCl_3 (>99%) were
139 prepared using pure water (milliQ - 18.2 M Ω -cm) for the syntheses reported here, leading to a Na_2SiO_3
140 solution at pH 13.1, a MgCl_2 solution at pH 5.4, an FeCl_3 solution at pH 1.8, and an AlCl_3 solution at
141 pH 3.4 (Table 1). Some NaOH was added to the AlCl_3 and FeCl_3 solutions to obtain an additional FeCl_3
142 solution at pH 2.1 and four additional 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 μL of the AlCl_3 solution at pH 3.4 into 5 mL of the Na_2SiO_3
150 solution, before being mixed with 4.17 mL of the 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 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 AlCl_3 solution at pH 3.9 into 4.25 mL of
165 the Na_2SiO_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 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 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 AlCl_3
179 solution at pH 3.4, a second series of four syntheses was conducted with a gel produced using the 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 AlCl₃ solution at pH 5.3 or a gel produced using the AlCl₃ solution at pH 8. Each starting gel was
182 prepared by pouring 833 μL of the AlCl₃ solution into 7.5 mL of the Na₂SiO₃ solution, before being
183 mixed with 4.17 mL of the FeCl₃ solution, to produce, theoretically, ~165 mg of a gel stoichiometrically
184 identical to a pure nontronite with 0.4 Al in each tetrahedron (Na_{0.4}(Si_{3.6}Al_{0.4})Fe(III)₂O₁₀(OH)₂). The pH
185 of the solution in equilibrium with the gel prepared with the AlCl₃ solution at pH 3.4 was ~4, while the
186 one formed with the AlCl₃ 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 AlCl₃
188 solution at pH 3.4 or the AlCl₃ 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 CO₂) 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 AlCl₃ solution at pH 5.3 or the AlCl₃ 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*₀₀₁ 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⁻¹ 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 νMg₃OH and δMg₃OH vibrations at 3680 and 655 cm⁻¹, respectively; νSi–O vibration near 1000–
217 950 cm⁻¹; ⁴Al–O out of plane near 800 cm⁻¹; perpendicular Si–O–Mg vibrations at 692 and 532 cm⁻¹;
218 and δSi–O–Si vibrations near 500 and 455 cm⁻¹ (Madejová et al., 2017; Kloprogge & Ponce, 2021).
219 Bands corresponding to νMg₃OH and δMg₃OH 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⁻¹ 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⁻¹ 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⁻¹
244 (ν Al₂OH), 3626 cm⁻¹ (ν Al₂OH), 1000–950 cm⁻¹ (ν Si–O), 914 cm⁻¹ (δ Al₂OH), 815 cm⁻¹ (⁴Al–O out of
245 plane), 694 cm⁻¹ (⁶Al–O_{ap}), 520 cm⁻¹ (δ Si–O–⁶Al), and 455 cm⁻¹ (δ Si–O–⁶Al) (Fig. 4; Farmer &
246 Russell, 1964; Klopogge et al., 1990; Zviagina et al., 2004; Lantenois et al., 2008). Under vacuum, the
247 *d*₀₀₁ 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⁻¹ corresponding to ν Si–O–Si and ν Si–O–Al vibrations, and a band at
264 613 cm⁻¹ 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 AlCl₃ solution at pH 10.6 and the syntheses conducted in
269 solutions at pH 12.5 using the gels obtained with the AlCl₃ 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 AlCl₃ 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 ^{[4]Fe³⁺} for ^{[4]Si⁴⁺} 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⁻¹, $\delta\text{Fe}_2^{3+}\text{-OH}$ at 815 cm⁻¹,
292 the 855 cm⁻¹ (not assigned), ^{[4]Fe-O} at 707 cm⁻¹, and ^{[6]Fe³⁺-O_{ap}} ~667 cm⁻¹; 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 AlCl₃ 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 ^{[4]Fe³⁺} for ^{[4]Si⁴⁺} tetrahedral
306 substitutions with increasing pH (Baron et al., 2016a). The additional presence of bayerite (Al(OH)₃)
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⁻¹
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⁻¹ ($\nu\text{Fe}_2\text{OH}$), ~950 cm⁻¹ ($\nu\text{Si-O}$), ~815 cm⁻¹ ($\delta\text{Fe}^{3+}_2\text{OH}$), ~667 cm⁻¹ (^{[6]Fe³⁺-}
312 O_{ap}), 585 cm⁻¹ ($\delta\text{Si-O}$) and ~480 cm⁻¹ (^{[6]Fe-O-Si}) (Goodman et al., 1976; Baron et al., 2016a). The
313 bands at 850 and 707 cm⁻¹ are present commonly in nontronite with large ^{[6]Fe} occupancy, but the band
314 at 707 cm⁻¹ 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⁻¹ 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*₀₀₁ of the
317 nontronite synthesized in the solution at pH 12 with the gel produced using the AlCl₃ solution at pH
318 10.6 collapsed to 10.06 Å (Fig. S1).

319

320

321 *Syntheses from the gels obtained using the AlCl₃ 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⁻¹; Goodman et al., 1976; Baron et al., 2016a; Figs 5, 6). However,
325 a band at 707 cm⁻¹, corresponding to ^[4]Fe–O vibrations, is present in both FTIR spectra, likely indicating
326 ^[4]Fe³⁺ for ^[4]Si⁴⁺ 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 Klopogge and Ponce
342 (2021), with a feature at 800–815 cm⁻¹ attributed to δAl–O of tetrahedral Al (absent from the ATR-FTIR
343 spectrum of talc which contains no tetrahedral Al; Klopogge & Ponce, 2021). Plus, the absence of the
344 FTIR band attributed to νMg₂-Al–OH at 3625 cm⁻¹ is consistent with the absence of octahedral Al
345 (Klopogge & 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*₀₀₁ 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 (Klopogge & Frost, 2000; Klopogge & Ponce, 2021). Still, such a decrease in width may also indicate
352 an increase in the permanent charge, i.e. a higher degree of ^[4]Al³⁺ for ^[4]Si⁴⁺ 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⁻¹ and from 800 to 815 cm⁻¹, respectively, while the νMg₃OH and δMg₃OH
355 absorption bands of the synthesized saponites shifted from 3674 to 3685 cm⁻¹ and from 655 to 640 cm⁻¹,
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)₂), serpentine (Mg₃Si₂O₅(OH)₄), or talc (Si₄Mg₃O₁₀(OH)₂), i.e. an assemblage
360 similar to what is obtained with a gel produced using Na₂SiO₃ and AlCl₃ 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 AlCl₃ solution
367 and the pH of the solution in which gels are immersed. A gel of beidellite composition produced using
368 an AlCl₃ 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 AlCl₃ 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, H₄SiO₄, Al(OH)₂⁺, and Al(OH)²⁺ prevail, and Si and Al ions form
375 tetrahedral and octahedral complexes, respectively, while at high pH (>13), H₂SiO₄⁻ and Al(OH)₄⁻
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).

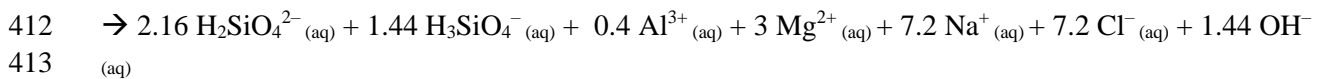
379 The synthesis of ⁴¹Al-nontronite is also very sensitive to the pH of solutions, as is the case for ⁴¹Fe-
380 nontronite as acknowledged earlier (Andrieux & Petit, 2010; Boumaiza et al., 2020; Dzene et al., 2022).
381 Only the gel produced using an AlCl₃ solution at pH 10.6 and immersed in a solution at pH 12.5 leads
382 to pure ⁴¹Al-nontronite. The syntheses conducted at a pH lower than 12.5 from the gels of nontronite
383 composition produced using an AlCl₃ solution at pH 10.6 led to the production of nontronite together
384 with bayerite. Gels produced using an AlCl₃ solution at pH 10.6 and immersed in solutions at pH 13
385 crystallized into pure nontronite, but these are ⁴¹Fe-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 ⁴¹Fe³⁺ for ⁴¹Si⁴⁺ tetrahedral substitutions, as historically suggested by Grubb
388 (1969). The use of gels produced using an AlCl₃ solution at pH 3.4 did not lead to the production of
389 pure, well crystallized ⁴¹Al-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 ⁴¹Fe-nontronite.

394 Mechanistic Considerations

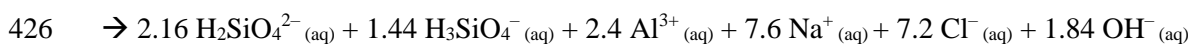
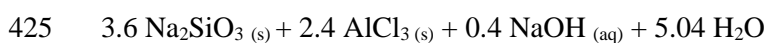
395 This section concerns the reactions that have likely occurred during the syntheses of saponite, beidellite,
396 and nontronite. Please note that the equations presented below refer to the theoretical products of the
397 syntheses carried out in the present study.

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 Mg²⁺ ions did not compete with Al species for tetrahedral substitutions.
402 The major species in the Na₂SiO₃ solution at 0.2 M at pH 13.1 are H₂SiO₄²⁻ and H₃SiO₄⁻ (Table 1).
403 Although Al was present mainly as Al³⁺ in the AlCl₃ solution, it converted to Al(OH)₄⁻ when this
404 solution was poured into the Na₂SiO₃ 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 MgCl₂ solution was responsible for a slight decrease in the pH (down to 10 – Table 2),
407 probably converting the remaining H₂SiO₄²⁻ ions into H₃SiO₄⁻, 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):

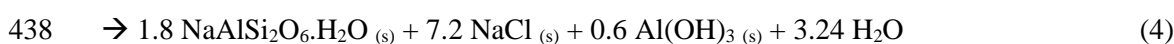
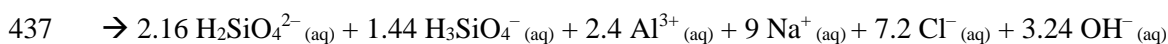
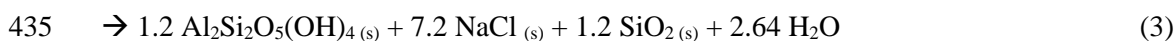
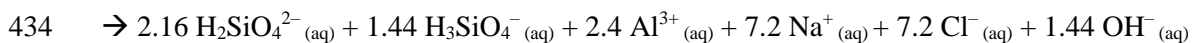
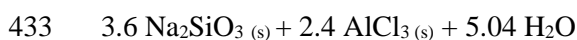




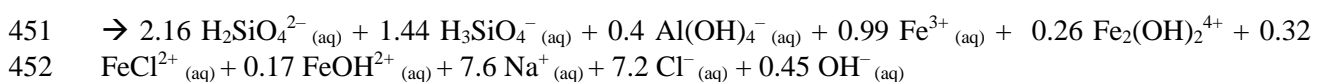
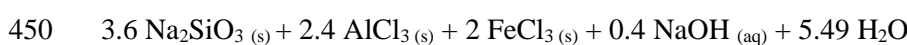
415 Pure beidellite cannot be synthesized over a large range of pH. The pH of the solution in which the gel
 416 is immersed for crystallization has to be precisely controlled. Although the formation of tetrahedral
 417 complexes occurred as for saponite when pouring the AlCl_3 solution at pH 3.9 into the Na_2SiO_3 solution
 418 at 0.2 M at pH 13.1, the subsequent addition of the second 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 H_4SiO_4 and the $\text{Al}(\text{OH})_4^-$ ions into $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})^{2+}$, and Al^{3+} . The
 421 gel obtained with the starting 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):

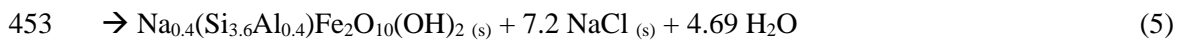


428 If the gel is immersed into a solution at pH lower than 12, only kaolins will be produced following Eq. 3,
 429 while if the gel is immersed into a solution at pH higher than 12, only zeolites will be produced following
 430 Eq. 4 (together with SiO_2 or $\text{Al}(\text{OH})_3$, respectively, which are likely leached during filtration). Note that
 431 a starting 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 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 AlCl_3 solution does not seem to be critical, given that pure ^{54}Fe -nontronite or ^{27}Al -nontronite
 442 were produced here from AlCl_3 solutions at either pH 3.4 or 10.6. However, here, only the use of an
 443 AlCl_3 solution at pH 10.6 led to the production of ^{27}Al -Nontronite. As for saponite and beidellite, the
 444 formation of tetrahedral complexes occurred when pouring the AlCl_3 solution into the 0.2 M Na_2SiO_3
 445 solution at pH 13.1. The subsequent addition of the 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}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 H_3SiO_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 $^{[4]}\text{Al}$ -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 $^{[4]}\text{Fe}$ -nontronite rather than $^{[4]}\text{Al}$ -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 $^{[4]}\text{Fe}$ -
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 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 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

DECLARATIONS

507 **Funding**

508 This work was made possible thanks to financial support from the ATM program at MNHN (Project
509 BioMars; PI: S. Bernard), from the Institut des Matériaux of Sorbonne Université (IMat) (Project Ageing
510 on Mars; PI: S. Bernard) and from the European Research Council (ERC Consolidator Grant No.
511 819587: HYDROMA; PI: L. Remusat).

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

523 **ACKNOWLEDGMENTS**

524 The authors acknowledge the spectroscopic and X-ray diffraction facilities of the Institut de
525 Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC) and Elisabeth Malassis for
526 administrative support.

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REFERENCES

529

530 Abbott, A.N., Löhr, S., & Trethewy, M. (2019) Are Clay Minerals the Primary Control on the Oceanic
531 Rare Earth Element Budget? *Frontiers in Marine Science*, 6, 504.

532 Abdulelah, H., Keshavarz, A., Hoteit, H., Abid, H., Goudeli, E., Ennis-King, J., & Iglauer, S. (2023)
533 Hydrogen physisorption in earth-minerals: Insights for hydrogen subsurface storage. *Journal of*
534 *Energy Storage*, 66, 107440.

535 Abdo, J., & Haneef, M.D. (2013) Clay nanoparticles modified drilling fluids for drilling of deep
536 hydrocarbon wells. *Applied Clay Science*, 86, 76-82.

- 537 Allard, T., Balan, E., Calas, G., Fourdrin, C., Morichon, E. , & Sorieul, S. (2012) Radiation-induced
538 defects in clay minerals: A review. *Nuclear Instruments and Methods in Physics Research B*,
539 277, 112-120.
- 540 Almqvist, B.S.G., & Mainprice, D. (2017) Seismic properties and anisotropy of the continental crust:
541 Predictions based on mineral texture and rock microstructure. *Reviews of Geophysics*, 55, 367-
542 433.
- 543 Andrieux, P., & Petit, S. (2010) Hydrothermal synthesis of dioctahedral smectites: The Al-Fe³⁺
544 chemical series. *Applied Clay Science*, 48, 5-17.
- 545 Balan, E., Allard, T., Morin, G., Fritsch, E., & Calas, G. (2020) Crystallochemistry of Clay Minerals,
546 Weathering Processes and Evolution of Continental Surfaces. In: *Electron Paramagnetic*
547 *Resonance Spectroscopy*. Springer, 109-135.
- 548 Baron, F., Petit, S., Tertre, E., & Decarreau, A. (2016a) Influence of Aqueous Si and Fe Speciation on
549 Tetrahedral Fe(III) Substitutions in Nontronites: a Clay Synthesis Approach. *Clays and Clay*
550 *Minerals*, 64, 230-244.
- 551 Baron,F., Pushparaj, S.S.C., Fontaine C., Sivaiah, M.V., Decarreau, A., & Petit., S. (2016b) Microwave-
552 Assisted Hydrothermal Synthesis of Ni-Mg Layered Silicate Clays. *Current Microwave*
553 *Chemistry*, 3, 85-89.
- 554 Bello, M.L., Junior, A.M., Freitas, C.A., Moreira, M.L.A., da Costa, J.P., de Souza, M.A., Santos,
555 B.A.M.C., de Sousa, V.P., Castro, H.C., Rodrigues, C.R., & Cabral, L.M. (2022) Development
556 of novel montmorillonite-based sustained release system for oral bromopride delivery.
557 *European Journal of Pharmaceutical Sciences*, 175, 106222.
- 558 Besselink, R., Stawski, T.M., Freeman, H.M., Hövelmann, J., & To, D.J. (2020) Mechanism of saponite
559 crystallization from a rapidly formed amorphous intermediate. *Crystal Growth & Design*, 20(5),
560 3365-3373.
- 561 Blattmann, T.M., Liu, Z., Zhang, Y., Zhao, Y., Haghypour, N., Montluçon, D.B., Plötze, M., & Eglinton,
562 T.I. (2019) Mineralogical control on the fate of continentally derived organic matter in the
563 ocean. *Science*, 366, 742-745.
- 564 Blukis, R., Schindler, M., Couason, T., & Benning, L.G. (2022) Mechanism and Control of Saponite
565 Synthesis from a Self-Assembling Nanocrystalline Precursor. *Langmuir*, 38, 7678-7688.
- 566 Boonruang, C., & Sanumang, W. (2021) Effect of nano-grain carbide formation on electrochemical
567 behavior of 316L stainless steel. *Scientific Reports*, 11, 12602.
- 568 Brown, G., & Brindley, G.W. (1980) X-ray Diffraction Procedures for Clay Mineral Identification. In:
569 *Crystal Structures of Clay Minerals and Their X-Ray Identification* (G.W. Brindley and G.
570 Brown, editors). Mineralogical Society of Great Britain and Ireland.
- 571 Carniato, F., Gatti G., & Bisio C. (2020) An overview of the recent synthesis and functionalization
572 methods of saponite clay. *New Journal of Chemistry*, 44, 9969-9980.
- 573 Carter, J., Poulet, F., Bibring, J.P. Mangold, N., & Murchie, S. (2013) Hydrous minerals on Mars as
574 seen by the CRISM and OMEGA imaging spectrometers: Updated global view. *Journal of*
575 *Geophysical Research: Planets*, 118, 831-858.
- 576 Carretero, M.I., & Pozo, M. (2009) Clay and non-clay minerals in the pharmaceutical industry. *Applied*
577 *Clay Science*, 46, 73-80.

- 578 Carroll, D. (1970) *Clay Minerals: A Guide to Their X-ray Identification*. In.: Geological Society of
579 America, 528 pp.
- 580 Choy, J.-H., Choi, S.-J., Oh, J.-M., & Park, T. (2007) Clay minerals and layered double hydroxides for
581 novel biological applications. *Applied Clay Science*, 36, 122-132.
- 582 Churchman, G.J., Gates, W.P., Theng, B.K.G., & Yuan, G. (2006) Chapter 11.1 Clays and Clay Minerals
583 for Pollution Control. In: *Developments in Clay Science*. Elsevier, pp 625-675.
- 584 Corbin, G., Vulliet, E., Lanson, B., Rimola, A., & Mignon, P. (2021) Adsorption of Pharmaceuticals
585 onto Smectite Clay Minerals: A Combined Experimental and Theoretical Study. *Minerals*, 11,
586 62.
- 587 De Kimpe, C.R. (1976) Formation of Phyllosilicates and Zeolites from Pure Silica-Alumina Gels. *Clays
588 and Clay Minerals*, 24, 200-207.
- 589 Decarreau, A., & Petit, S. (2014) Fe³⁺/Al³⁺ partitioning between tetrahedral and octahedral sites in
590 dioctahedral smectites. *Clay Minerals*, 49, 657-665.
- 591 Decarreau, A., Grauby, O., & Petit, S. (1992) The actual distribution of octahedral cations in 2:1 clay
592 minerals: Results from clay synthesis. *Applied Clay Science*, 7, 147-167.
- 593 Decarreau, A., Petit, S., Martin, F., Farges, F., Vieillard, P., & Joussein, E. (2008) Hydrothermal
594 Synthesis, Between 75 and 150°C, of High-Charge, Ferric Nontronites. *Clays and Clay
595 Minerals*, 56, 322-337.
- 596 Delage, P., Cui, Y.J., & Tang, A.M. (2010) Clays in radioactive waste disposal. *Journal of Rock
597 Mechanics and Geotechnical Engineering*, 2, 111-123.
- 598 Delvaux, B., Mestdagh, M.M., Vielvoye, L., & Herbillon, A.J. (1989) XRD, IR and ESR study of
599 experimental alteration of Al-nontronite into mixed-layer kaolinite/smectite. *Clay Minerals*, 24,
600 617-630.
- 601 Dzene, L., Brendlé, J., Limousy, L., Dutournié, P., Martin, C., & Michau, N. (2018) Synthesis of iron-
602 rich tri-octahedral clay minerals: A review. *Applied Clay Science*, 166, 276-287.
- 603 Dzene, L., Dutournie, P., Brendle, J., Limousy, L., Le Meins, J.-M., Michelin, L., Vidal, L., Gree, S.,
604 Abdelmoula, M., Martin, C., & Michau, N. (2022) Characterization of Iron-Rich Phyllosilicates
605 Formed at Different Fe/Si Ratios. *Clays and Clay Minerals*, 70, 580-594.
- 606 Eggleton, R.A. (1998) Hisingerite: A Ferric Kaolin Mineral with Curved Morphology. *Clays and Clay
607 Minerals*, 46, 400-413.
- 608 Ehlmann, B.L., & Edwards, C.S. (2014). Mineralogy of the Martian Surface. *Annual Review of Earth
609 and Planetary Sciences*, 42(1), 291-315.
- 610 Ehlmann, B.L., Mustard, J.F., Clark, R.N., Swayze, G.A., & Murchie, S.L. (2011) Evidence for low-
611 grade metamorphism, hydrothermal alteration, and diagenesis on Mars from phyllosilicate
612 mineral assemblages. *Clays and Clay Minerals*, 59, 359-377.
- 613 Ewis, D., Ba-Abbad, M.M., Benamor, A., & El-Naas, M.H. (2022) Adsorption of organic water
614 pollutants by clays and clay minerals composites: A comprehensive review. *Applied Clay
615 Science*, 229, 106686.
- 616 Farmer, V.C. (1974) *The Infrared Spectra of Minerals*. Mineralogical Society, London.

- 617 Farmer, V.C., & Russell, J.D. (1964) The infra-red spectra of layer silicates. *Spectrochimica Acta*, 20,
618 1149-1173.
- 619 Farmer, V.C., McHardy, W.J., Elsass, F., & Robert, M. (1994) hk-Ordering in Aluminous Nontronite
620 and Saponite Synthesized Near 90°C: Effects of Synthesis Conditions on Nontronite
621 Composition and Ordering. *Clays and Clay Minerals*, 42, 180-186.
- 622 Ferrage, E., Lanson, B., Sakharov, B.A., & Drits, V.A. (2005) Investigation of smectite hydration
623 properties by modeling experimental X-ray diffraction patterns: Part I. Montmorillonite
624 hydration properties. *American Mineralogist*, 90, 1358-1374.
- 625 Ferrage, E., Lanson, B., Sakharov, B.A., Geoffroy, N., Jacquot, E., & Drits, V.A. (2007) Investigation
626 of dioctahedral smectite hydration properties by modeling of X-ray diffraction profiles:
627 Influence of layer charge and charge location. *American Mineralogist*, 92, 1731-1743.
- 628 Fox, V.K., Kupper, R.J., Ehlmann, B.L., Catalano, J.G., Razzell-Hollis, J., Abbey, W.J., Schild, D.J.,
629 Nickerson, R.D., Peters, J.C., Katz, S.M., & White, A.C. (2021) Synthesis and characterization
630 of Fe(III)-Fe(II)-Mg-Al smectite solid solutions and implications for planetary science.
631 *American Mineralogist*, 106, 964-982.
- 632 Ghadiri, M., Chrzanowski, W., & Rohanizadeh, R. (2015) Biomedical applications of cationic clay
633 minerals. *RSC Advances*, 5, 29467-29481.
- 634 Goodman, B.A., Russell, J.D., Fraser, A.R., & Woodhams, F.W.D. (1976) A Mössbauer and I.R.
635 Spectroscopic Study of the Structure of Nontronite. *Clays and Clay Minerals*, 24, 53-59.
- 636 Grauby, O., Petit, S., Decarreau, A., & Baronnet, A. (1993) The beidellite-saponite series: an
637 experimental approach. *European Journal of Mineralogy*, 5, 623-636.
- 638 Grauby, O., Petit, S., Decarreau, A., & Baronnet, A. (1994) The nontronite-saponite series: An
639 experimental approach. *European Journal of Mineralogy*, 6, 99-112.
- 640 Grubb, P.L.C. (1969) Phase changes in aged sesquioxide gels and some analogies with katamorphic
641 processes. *Mineralium Deposita*, 4, 30-51.
- 642 Guan, X., Dong, H., Ma, J., & Jiang, L. (2009) Removal of arsenic from water: Effects of competing
643 anions on As(III) removal in KMnO₄-Fe(II) process. *Water Research*, 43, 3891-3899.
- 644 Harder, H. (1976) Nontronite synthesis at low temperatures. *Chemical Geology*, 18, 169-180.
- 645 Hazen, R.M., Sverjensky, D.A., Azzolini, D., Bish, D.L., Elmore, S.C., Hinnov, L., & Milliken, R.E.
646 (2013) Clay mineral evolution. *American Mineralogist*, 98, 2007-2029.
- 647 Ho, T.A., Jove-Colon, C.F., & Wang, Y. (2023) Low hydrogen solubility in clay interlayers limits gas
648 loss in hydrogen geological storage. *Sustainable Energy & Fuels*, 7, 3232-3238.
- 649 Huertas, F.J., Cuadros, J., Huertas, F., & Linares, J. (2000) Experimental study of the hydrothermal
650 formation of smectite in the beidellite-saponite series. *American Journal of Science*, 300, 504-
651 527.
- 652 Hwang, H., Seoung, D., Lee, Y., Liu, Z., Liermann, H.-P., Cynn, H., Vogt, T., Kao, C.-C., & Mao, H.-
653 K. (2017) A role for subducted super-hydrated kaolinite in Earth's deep-water cycle. *Nature*
654 *Geoscience*, 10, 947-953.
- 655 Ikari, M.J., Saffer, D.M., & Marone, C. (2009) Frictional and hydrologic properties of clay-rich fault
656 gouge. *Journal of Geophysical Research: Solid Earth*, 114, B05409.

- 657 Jacquemot, P., Viennet, J.C., Bernard, S., Le Guillou, C., Rigaud, B., Delbes, L., Georgelin, T., & Jaber
658 M. (2019) The degradation of organic compounds impacts the crystallization of clay minerals
659 and vice versa. *Scientific Reports*, 9, 20251.
- 660 de Jong, S.M., Spiers, C.J., & Busch, A. (2014) Development of swelling strain in smectite clays through
661 exposure to carbon dioxide. *International Journal of Greenhouse Gas Control*, 24, 149-161.
- 662 Kalo, H., Möller, M.W., Ziadeh, M., Dolejš, D., & Breu, J. (2010) Large scale melt synthesis in an open
663 crucible of Na-fluorohectorite with superb charge homogeneity and particle size. *Applied Clay
664 Science*, 48, 39-45.
- 665 Katayama, I., Kubo, T., Sakuma, H., & Kawai, K. (2015) Can clay minerals account for the behavior of
666 non-asperity on the subducting plate interface? *Progress in Earth and Planetary Science*, 2, 30.
- 667 Kennedy, M.J., Pevear, D.R., & Hill, R.J. (2002) Mineral Surface Control of Organic Carbon in Black
668 Shale. *Science*, 295, 657-660.
- 669 Klopogge, J.T. (1999) Synthesis of Smectite Clay Minerals: A Critical Review. *Clays and Clay
670 Minerals*, 47, 529-554.
- 671 Klopogge, J.T., & Frost, R.L. (2000) The effect of synthesis temperature on the FT-Raman and FT-IR
672 spectra of saponites. *Vibrational Spectroscopy*, 23, 119-127.
- 673 Klopogge, J.T., & Ponce, C.P. (2021) Spectroscopic Studies of Synthetic and Natural Saponites: A
674 Review. *Minerals*, 11, 112.
- 675 Klopogge, J.T., & Hartman, H. (2022) Clays and the Origin of Life: The Experiments. *Life*, 12, 259.
- 676 Klopogge, J.T., Jansen, J.B.H., & Geus, J.W. (1990) Characterization of Synthetic Na-Beidellite. *Clays
677 and Clay Minerals*, 38, 409-414.
- 678 Klopogge, J.T., van der Eerden, A.M.J., Jansen, J.B.H., Geus, J.W., & Schuiling, R.D. (1993) Synthesis
679 and Paragenesis of Na-Beidellite as a Function of Temperature, Water Pressure, and Sodium
680 Activity. *Clays and Clay Minerals*, 41, 423-430.
- 681 Kodama, H. (1962) Identification of Kaolin Minerals in the Presence of Chlorite by X-ray Diffraction
682 and Infrared Absorption Spectra. *Clays and Clay Minerals*, 11, 236-249.
- 683 Kohyama, N. (1975) Hisingerite Occurring as a Weathering Product of Iron-Rich Saponite. *Clays and
684 Clay Minerals*, 23, 215-218.
- 685 Komadel, P., Madejová, J., & Bujdák, J. (2005) Preparation and properties of reduced-charge smectites
686 - a review. *Clays and Clay Minerals*, 53, 313-334.
- 687 Landais, P., Dohrmann, R., & Kaufhold, S. (2013) Overview of the clay mineralogy studies presented
688 at the 'Clays in natural and engineered barriers for radioactive waste confinement' meeting,
689 Montpellier, October 2012. *Clay Minerals*, 48, 149-152.
- 690 Lantenois, S., Muller, F., Bény, J.-M., Mahiaoui, J., & Champallier, R. (2008) Hydrothermal synthesis
691 of beidellites: Characterization and study of the cis- and trans-vacant character. *Clays and Clay
692 Minerals*, 56, 39-48.
- 693 Lefevre, G., & Fedoroff, M. (2002) Synthesis of bayerite (β -Al(OH)₃) microrods by neutralization of
694 aluminate ions at constant pH. *Materials Letters*, 56(6), 978-983.

- 695 Li, K., Wang, Q., Ma, H., Huang, H., Lu, H., & Peng, P. (2023) Effect of Clay Minerals and Rock Fabric
696 on Hydrocarbon Generation and Retention by Thermal Pyrolysis of Maoming Oil Shale.
697 *Processes*, 11, 894.
- 698 Madejová, J., Gates, W.P., & Petit, S. (2017) IR Spectra of Clay Minerals. In: *Developments in Clay*
699 *Science*. Elsevier, pp. 107-149.
- 700 Marchi, S., Raponi, A., Prettyman, T.H., Sanctis, M.C.D., Castillo-Rogez, J., Raymond, C.A.,
701 Ammannito, E., Bowling, T., Ciarniello, M., Kaplan, H., Palomba, E., Russell, C.T.,
702 Vinogradoff, V., & Yamashita, N. (2019) An aqueously altered carbon-rich Ceres. *Nature*
703 *Astronomy*, 3, 140.
- 704 de Mello Gabriel, G.V., Machado Pitombo, L., Tavares Rosa, L.M., Aparecido Navarrete, A., Botero,
705 W.G., do Carmo, J.B., & Camargo de Oliveira, L. (2021) The environmental importance of iron
706 speciation in soils: evaluation of classic methodologies. *Environmental Monitoring and*
707 *Assessment*, 193, 63.
- 708 Meunier, A. (2005) *Clays*. Springer-Verlag, Berlin/Heidelberg.
- 709 Meunier, A., Mas, A., Beaufort, D., Patrier, P., & Dudoignon, P. (2008) Clay minerals in basalt-hawaiite
710 rocks from Mururoa atoll (French Polynesia). II. Petrography and Geochemistry. *Clays and*
711 *Clay Minerals*, 56, 730-750.
- 712 Meyer, S., Bennici, S., Vaultot, C., Rigolet, S., & Dzene, L. (2020) Influence of the precursor and the
713 temperature of synthesis on the structure of saponite. *Clays and Clay Minerals*, 68, 544-552.
- 714 Millero, F.J., Yao, W., & Aicher, J. (1995) The speciation of Fe(II) and Fe(III) in natural waters. *Marine*
715 *Chemistry*, 50(1-4), 21-39.
- 716 Milligan, W.O. (1951) Recent X-Ray Diffraction Studies on the Hydrrous Oxides and Hydroxides. *The*
717 *Journal of Physical Chemistry*, 55, 497-507.
- 718 Moldoveanu, G.A., & Papangelakis, V.G. (2012) Recovery of rare earth elements adsorbed on clay
719 minerals: I. Desorption mechanism. *Hydrometallurgy*, 117-118, 71-78.
- 720 Mozgawa, W., Krol, M., & Barczyk, K. (2011) FT-IR studies of zeolites from different structural groups.
721 *Chemik*, 65, 667-674.
- 722 Murray, H.H. (1991) Overview - Clay mineral applications. *Applied Clay Science*, 5, 379-395.
- 723 Murray, H.H. (2000) Traditional and new applications for kaolin, smectite, and palygorskite: a general
724 overview. *Applied Clay Science*, 17, 207-221.
- 725 Nakazawa, H., Yamada, H., & Fujita, T. (1992) Crystal synthesis of smectite applying very high
726 pressure and temperature. *Applied Clay Science*, 6, 395-401.
- 727 Nordheim, T.A., Hand, K.P., & Paranicas, C. (2018) Preservation of potential biosignatures in the
728 shallow subsurface of Europa. *Nature Astronomy*, 2, 673.
- 729 Oleksiak, M.D., Ghorbanpour, A., Conato, M.T., McGrail, B.P., Grabow, L.C., Motkuri, R.K., & Rimer,
730 J.D. (2016) Synthesis Strategies for Ultrastable Zeolite GIS Polymorphs as Sorbents for
731 Selective Separations. *Chemistry - A European Journal*, 22, 16078-16088.
- 732 Parrotin, F., Robin, V., Beaucaire, C., Descostes, M., & Tertre, E. (2023) Competitive ion-exchange
733 reactions of Pb(II) (Pb²⁺/PbCl⁺) and Ra(II) (Ra²⁺) on smectites: Experiments, modeling, and

- 734 implication for $^{226}\text{Ra(II)}/^{210}\text{Pb(II)}$ disequilibrium in the environment. *Chemosphere*, 313,
735 137369.
- 736 Pelletier, M., Michot, L.J., Humbert, B., Barrès, O., de la Caillerie, J.B.D., & Robert, J.L. (2003)
737 Influence of layer charge on the hydroxyl stretching of trioctahedral clay minerals: A vibrational
738 study of synthetic Na- and K-saponites. *American Mineralogist*, 88, 1801-1808.
- 739 Perry, C.C., & Shafran, K.L. (2001) The systematic study of aluminium speciation in medium
740 concentrated aqueous solutions. *Journal of Inorganic Biochemistry*, 87(1-2), 115-124.
- 741 Petit, S., Decarreau, A., Gates, W., Andrieux, P., & Grauby, O. (2015) Hydrothermal synthesis of
742 dioctahedral smectites: The Al-Fe³⁺ chemical series. Part II: Crystal-chemistry. *Applied Clay
743 Science*, 104, 96-105.
- 744 Petit, S., Baron, F., & Decarreau, A. (2017) Synthesis of nontronite and other Fe-rich smectites: a critical
745 review. *Clay Minerals*, 52, 469-483.
- 746 Phambu, N., Humbert, B., & Burneau, A. (2002) Use of Diffuse Reflectance Infrared Spectroscopy to
747 Monitor Purification. *Journal of Chemical Education*, 79(9), 1117.
- 748 Pierrot, D., & Millero, F.J. (2016) The Speciation of Metals in Natural Waters. *Aquatic Geochemistry*,
749 23, 1-20.
- 750 Ponce, C.P., & Kloprogge, J.T. (2020) Urea-Assisted Synthesis and Characterization of Saponite with
751 Different Octahedral (Mg, Zn, Ni, Co) and Tetrahedral Metals (Al, Ga, B), a Review. *Life*, 10,
752 168.
- 753 Robin, V., Tertre, E., Beaucaire, C., Regnault, O., & Descostes, M. (2017) Experimental data and
754 assessment of predictive modeling for radium ion-exchange on beidellite, a swelling clay
755 mineral with a tetrahedral charge. *Applied Geochemistry*, 85, 1-9.
- 756 Romanov, V.N. (2013) Evidence of irreversible CO₂ intercalation in montmorillonite. *International
757 Journal of Greenhouse Gas Control*, 14, 220-226.
- 758 Rother, G., Ilton, E.S., Wallacher, D., Hauß, T., Schaef, H.T., Qafoku, O., Rosso, K.M., Felmy, A.R.,
759 Krukowski, E.G., Stack, A.G., Grimm, N., & Bodnar, R.J. (2013) CO₂ Sorption to Subsingle
760 Hydration Layer Montmorillonite Clay Studied by Excess Sorption and Neutron Diffraction
761 Measurements. *Environmental Science & Technology*, 47, 205-211.
- 762 Saadat, S., Rawtani, D., & Parikh, G. (2022) Clay minerals-based drug delivery systems for anti-
763 tuberculosis drugs. *Journal of Drug Delivery Science and Technology*, 76, 103755.
- 764 Salter, T.L., Watson, J.S., & Sephton, M.A. (2023) Effects of minerals (phyllosilicates and iron oxides)
765 on the responses of aliphatic hydrocarbon containing kerogens (Type I and Type II) to analytical
766 pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 170, 105900.
- 767 See, K.A., Chapman, K.W., Zhu, L., Wiaderek, K.M., Borkiewicz, O.J., Barile, C.J., Chupas, P.J., &
768 Gewirth, A.A. (2015) The Interplay of Al and Mg Speciation in Advanced Mg Battery
769 Electrolyte Solutions. *Journal of the American Chemical Society*, 138, 328-337.
- 770 Singh, N.B. (2022) Clays and Clay Minerals in the Construction Industry. *Minerals*, 12, 301.
- 771 Tamura, K. (2000) Stepwise Hydration of High-Quality Synthetic Smectite with Various Cations. *Clays
772 and Clay Minerals*, 48, 400-404.

- 773 Tayraukham, P., Jantarit, N., Osakoo, N., & Wittayakun, J. (2020) Synthesis of Pure Phase NaP2 Zeolite
774 from the Gel of NaY by Conventional and Microwave-Assisted Hydrothermal Methods.
775 *Crystals*, 10, 951.
- 776 Viennet, J.C., Bultel, B., Riu, L., & Werner, S.C. (2017) Dioctahedral Phyllosilicates Versus Zeolites
777 and Carbonates Versus Zeolites Competitions as Constraints to Understanding Early Mars
778 Alteration Conditions. *Journal of Geophysical Research: Planets*, 122, 2328-2343.
- 779 Viennet, J.C., Bernard, S., Le Guillou, C., Jacquemot, P., Balan, E., Delbes, L., Rigaud, B., Georgelin,
780 T., & Jaber, M. (2019) Experimental clues for detecting biosignatures on Mars. *Geochemical
781 Perspectives Letters*, 12, 28-33.
- 782 Viennet, J.C., Bernard, S., Le Guillou, C., Sautter, V., Schmitt-Kopplin, P., Beyssac, O., Pont, S., Zanda,
783 B., Hewins, R., & Remusat, L. (2020) Tardi-magmatic precipitation of Martian Fe/Mg-rich clay
784 minerals via igneous differentiation. *Geochemical Perspectives Letters*, 14, 47-52.
- 785 Viennet, J.C., Bernard, S., Le Guillou, C., Sautter, V., Grégoire, B., Jambon, A., Pont, S., Beyssac, O.,
786 Zanda, B., Hewins, R., & Remusat, L. (2021) Martian Magmatic Clay Minerals Forming
787 Vesicles: Perfect Niches for Emerging Life? *Astrobiology*, 21, 605-612.
- 788 Viennet, J.C., Le Guillou, C., Baron, F., Balan, E., Criouet, I., Delbes, L., Blanchenet, A., Laurent, B.,
789 Remusat, L., & Bernard, S. (2022) Experimental investigation of Fe-clay/organic interactions
790 under asteroidal conditions. *Geochimica et Cosmochimica Acta*, 318, 352-365.
- 791 Viennet, J.C., Roskosz, M., Nakamura, T., Beck, P., Baptiste, B., Lavina, B., Alp, E., Hu, M.Y., Zhao,
792 J., Gounelle, M., Brunetto, R., Yurimoto, H., Noguchi, T., Okazaki, R., Yabuta, H., Naraoka,
793 H., Sakamoto, K., Tachibana, S., Yada, T., & Tsuda, Y. (2023) Interaction between clay
794 minerals and organics in asteroid Ryugu. *Geochemical Perspectives Letters*, 25, 8-12.
- 795 Whaite, J.H., Glein, C.R., Perryman, R.S., Teolis, B.D., Magee, B.A., Miller, G., Grimes, J., Perry,
796 M.E., Miller, K.E., Bouquet, A., Lunine, J.I., Brockwell, T., & Bolton S.J. (2017) Cassini finds
797 molecular hydrogen in the Enceladus plume: Evidence for hydrothermal processes. *Science*,
798 356, 155-159.
- 799 Yamada, H. (1994) Formation of Smectite Crystals at High Pressures and Temperatures. *Clays and Clay
800 Minerals*, 42, 674-678.
- 801 Yamada, H. (1995) Cooling Rate Dependency of the Formation of Smectite Crystals from a High-
802 Pressure and High-Temperature Hydrous Melt. *Clays and Clay Minerals*, 43, 693-696.
- 803 Zhang, C., Petit, S., He, H., Villi ras, F., Razafitianamaharavo, A., Baron, F., Tao, Q., & Zhu, J. (2020)
804 Crystal Growth of Smectite: A Study Based on the Change in Crystal Chemistry and
805 Morphology of Saponites with Synthesis Time. *ACS Earth and Space Chemistry*, 4, 14-23.
- 806 Zhang, D., Zhou, C.H., Lin, C.X., Tong, D.S., & Yu, W.H. (2010) Synthesis of clay minerals. *Applied
807 Clay Science*, 50, 1-11.
- 808 Zhang, L., Fu, X., Wang, A., & Ling, Z. (2022) Crystallinity effects on the vibrational spectral features
809 of saponite: Implications for characterizing variable crystalline phyllosilicates on Mars. *Icarus*,
810 379, 114951.
- 811 Zhou, C.H., & Keeling, J. (2013) Fundamental and applied research on clay minerals: From climate and
812 environment to nanotechnology. *Applied Clay Science*, 74, 3-9.

813 Zviagina, B.B., McCarty, D.K., Srodonón, J., & Drits, V.A. (2004) Interpretation of infrared spectra of
 814 dioctahedral smectites in the region of OH-stretching vibrations. *Clays and Clay Minerals*, 52,
 815 399-410.

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TABLES & FIGURES

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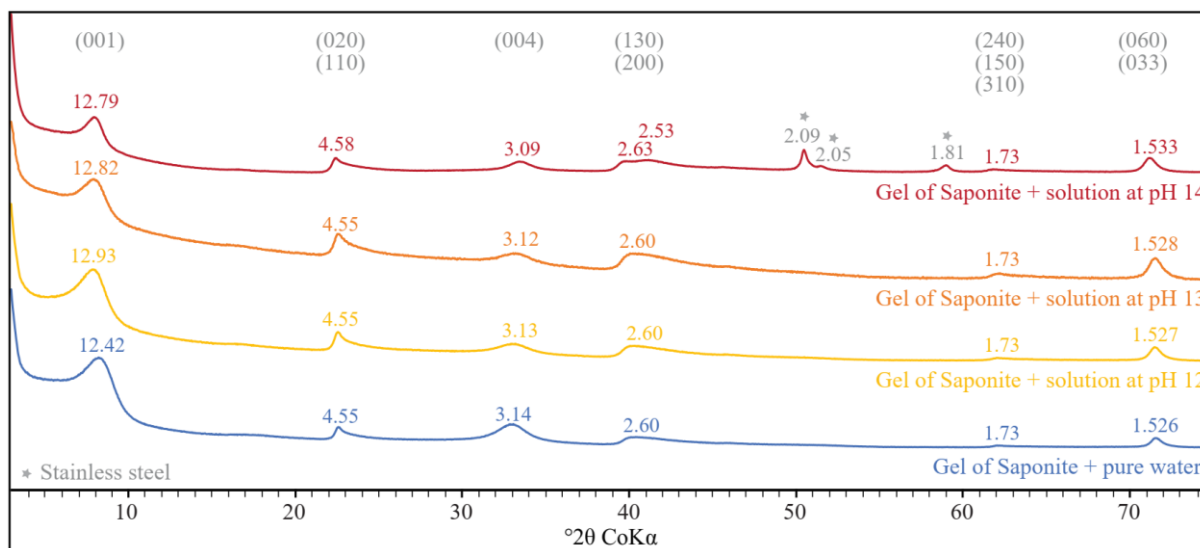
821 Table 1. pH of the solutions (0.2 mol.L⁻¹) and the main Si, Al, Fe, and Mg species in solution at 20°C
 822 (calculated using *Phreeqc*)

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

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824 Table 2. Starting materials, conditions of synthesis of smectites, and synthesized products (pH_i corresponds to the pH of the solutions in equilibrium with the
 825 gel; pH_f corresponds to the pH of the solutions in equilibrium with the final products)

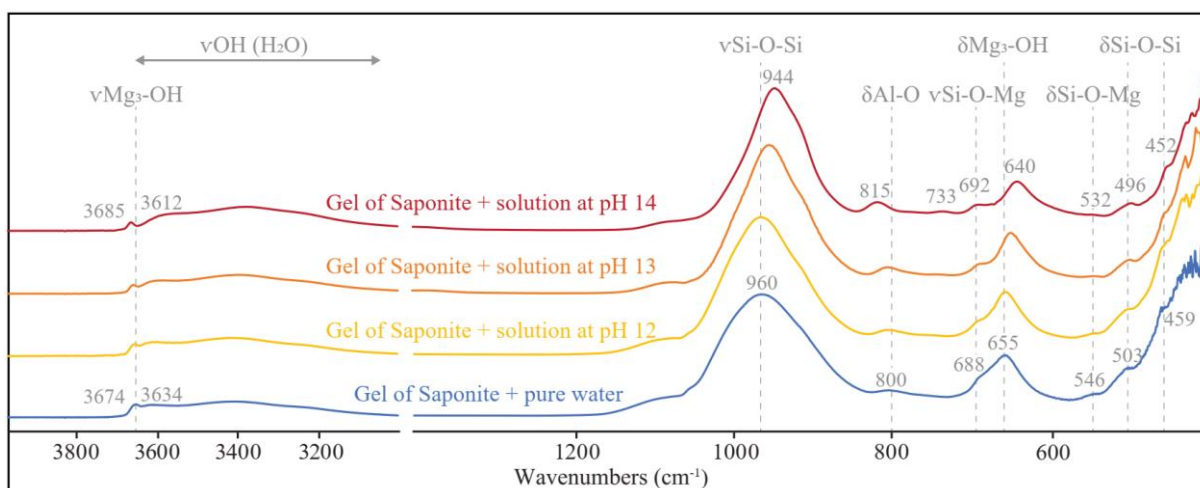
Theoretical Starting Gel	pH of the Na ₂ SiO ₃ solution	pH of the AlCl ₃ solution	pH of the 3 rd solution	Theoretical mass of gel (mg)	pH _i	Volume of the added solution (mL)	pH of the added solution	T°C	Synthesis duration (days)	pH _f	Products
Saponite	13.1	3.4	MgCl ₂ - pH 5.4	100	10	16.5	5.5	230	4	7.5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



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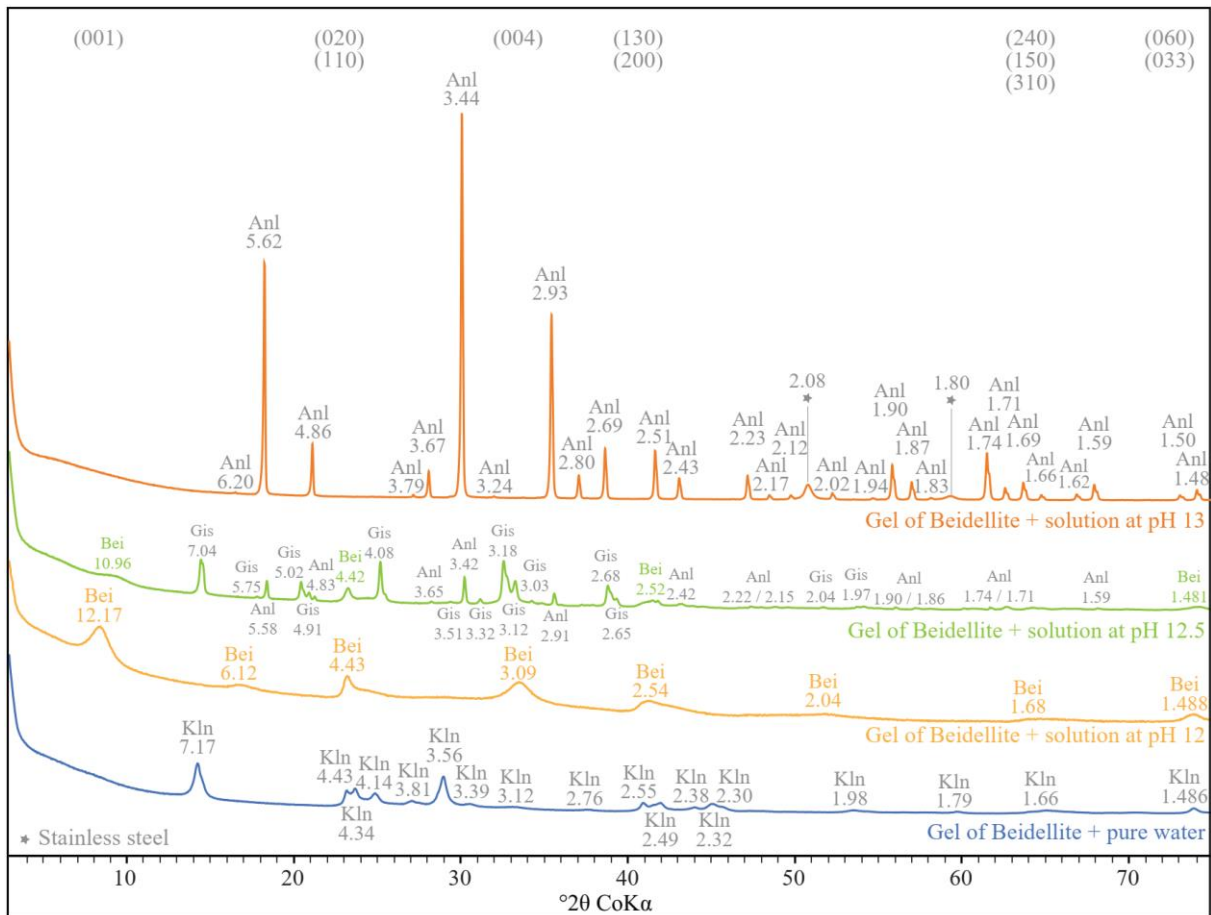
829 Figure 1. XRD patterns of products of syntheses conducted with the gels of saponite composition. Peaks
 830 at 2.09, 2.05, and 1.80 Å are attributed to contamination by austenitic stainless steel during XRD sample
 831 preparation (Boonruang & Sanumang, 2021)

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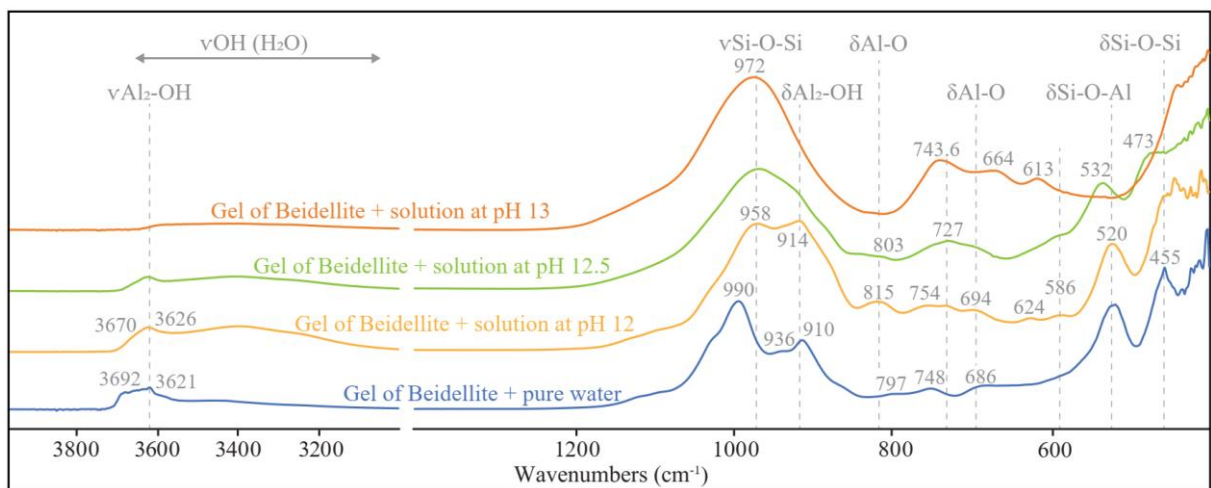
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834 Figure 2. FTIR spectra of products of syntheses conducted with the gels of saponite composition



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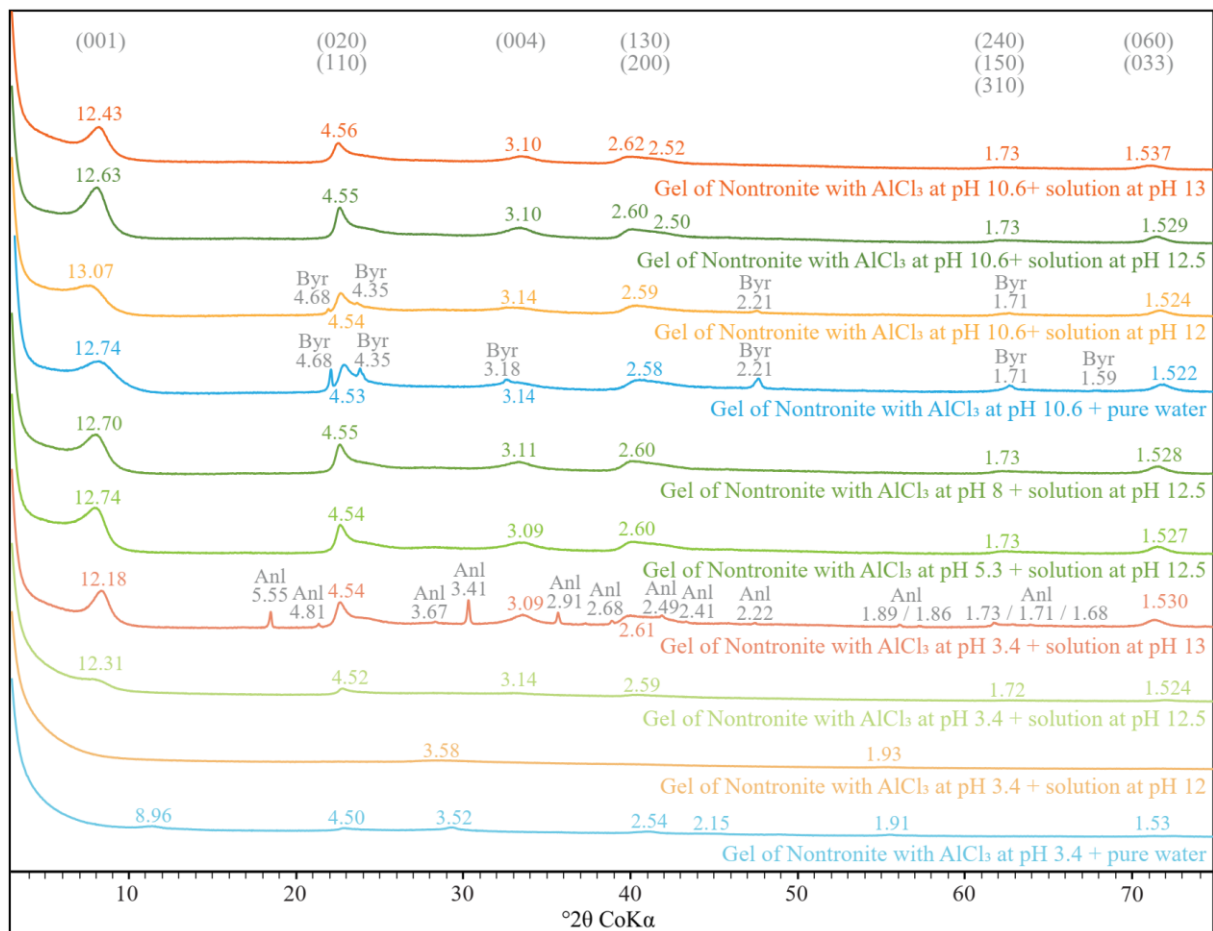
836 Figure 3. XRD patterns of products of syntheses conducted with the gels of beidellite composition. Bei:
 837 Beidellite. Anl: Analcime. Gis: Gismondine. Kln: Kaolinite. Peaks at 2.08 Å and 1.80 Å are attributed
 838 to contamination by austenitic stainless steel during XRD sample preparation (Boonruang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



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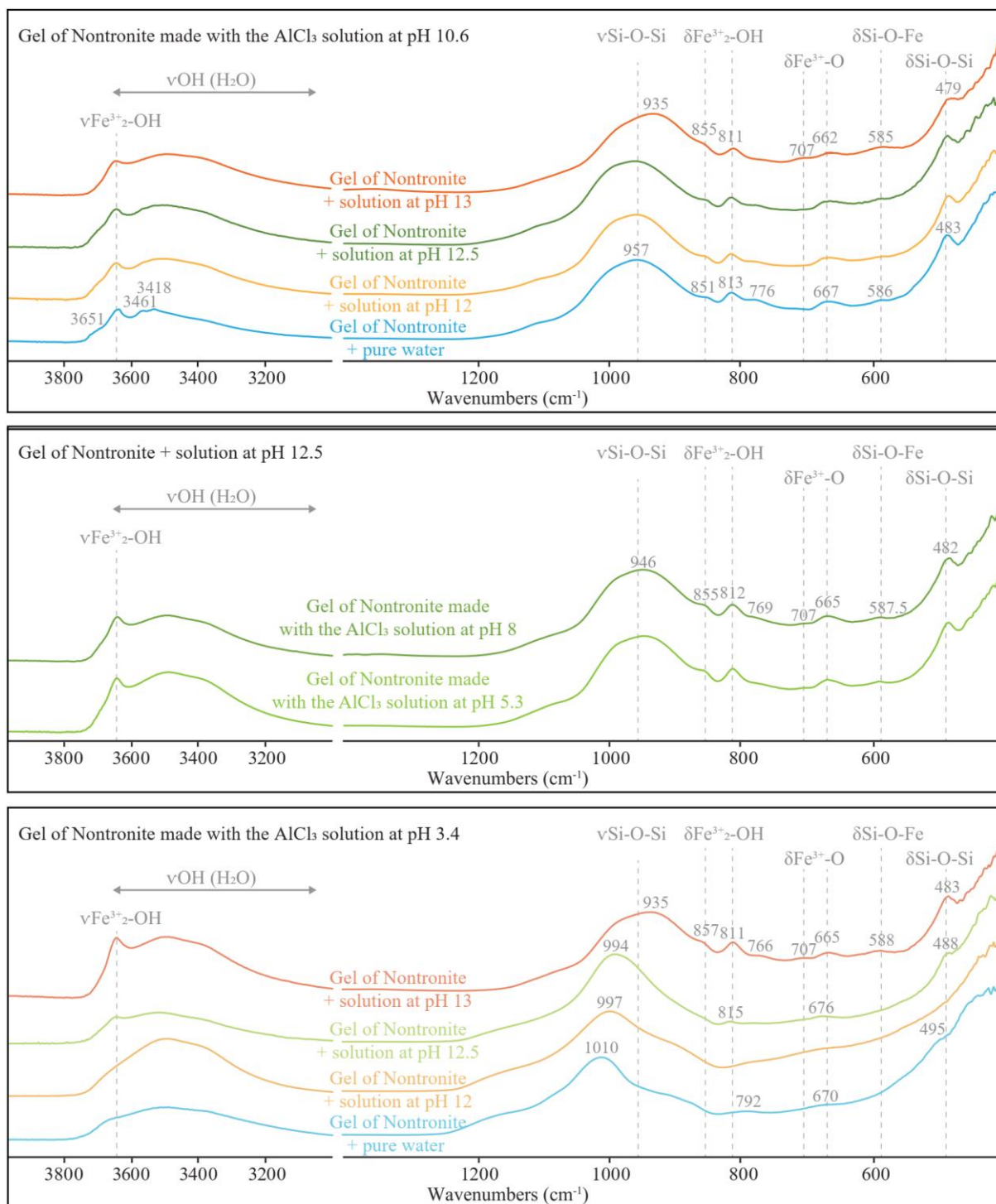
841 Figure 4 FTIR spectra of products of syntheses conducted with the gels of beidellite composition

842



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

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