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Delphine Masson, Valentin Robin, Emmanuel Joussein, Emmanuel Tertre,
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1 Role of the crystal chemistry on the dissolution kinetics of Fe(III)-rich smectites

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3 D. Masson¹, V. Robin¹, E. Joussein¹, E. Tertre² & F. Baron²

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5 ¹Université de Limoges, E2Lim UR 24133, 123 av. A. Thomas, 87060 Limoges Cedex, France

6 ²Université de Poitiers, IC2MP UMR CNRS 7285, 4 rue M. Brunet, 86022 Poitiers Cedex, France

7 8 Abstract

9 Smectites are reactive minerals that are present in surface environments. Most of the smectite
10 dissolution kinetics reported in the literature are related to Al-rich smectites, whereas Fe(III)-rich
11 smectites, which are commonly found in soils, have not been well studied. In this study, the impact
12 of structural Fe(III) in smectites on the dissolution kinetics is determined under acidic conditions. The
13 dissolution kinetics of three pure Fe(III)-rich smectites with different crystal chemistries
14 $(\text{Si}_{7.16}\text{Fe}^{3+}_{0.84})(\text{Fe}^{3+}_{3.46}\text{Mg}_{0.54})\text{O}_{20}(\text{OH})_4\text{Na}_{1.38}$, $(\text{Si}_{6.86}\text{Fe}^{3+}_{1.14})(\text{Fe}^{3+}_4)\text{O}_{20}(\text{OH})_4\text{Na}_{1.14}$, and
15 $(\text{Si}_{7.34}\text{Fe}^{3+}_{0.66})(\text{Fe}^{3+}_4)\text{O}_{20}(\text{OH})_4\text{Na}_{0.66}$ are investigated at 25°C using flow-through experiments at pH
16 values between 1.8 and 5.5. The measured dissolution rates are compared with published rates for
17 Al-rich smectites. The concentrations of dissolved Si, Fe and Mg are measured as a function of time,
18 and the retrieved residual solids are analyzed via infrared spectroscopy and transmission electron
19 microscopy. The steady-state dissolution rates of the synthetic smectites calculated from the amount
20 of Si release (R_{Si}) decrease with increasing pH. A comparison of the dissolution rates as a function of
21 pH does not allow us to observe major effects of the crystal chemistry among the synthetic
22 smectites. However, the dissolution rates calculated for synthetic Fe(III)-rich smectites are
23 systematically greater than those of Al-rich smectites. The measured dissolution rates decrease as
24 the aqueous system approaches equilibrium. Different behaviors are observed for Fe(III)-rich (i.e., > 4

25 Fe(III)/O₂₀(OH)₄) and Al-rich smectites as the $R_{Si}=f(\Delta G)$ functions differ, with Fe(III)-rich smectites
26 exhibiting greater instability than Al-rich smectites. Under the most acidic conditions investigated (pH
27 1.8 and 2), the crystal chemistry and mineralogy of the smectite changed during dissolution, with a
28 relatively greater loss of tetrahedral Fe than of octahedral Fe and the formation of amorphous silica
29 phases. These results show that the amount and location of structural Fe(III) in smectites impact the
30 stability of the minerals. This suggests that the dissolution rate of smectites as a function of the ionic
31 activity product classically used to describe reactive transport should consider the effects of the
32 crystal chemistry, in particular, the amount of structural Fe(III), which is rather high, especially in soil
33 smectites.

34 Key words: smectite, crystal chemistry, structural Fe(III), dissolution kinetics, acidic conditions

35 Introduction

36 Smectites are ubiquitous in surface environments and are commonly present in the fine fraction (<2
37 μm) of soils and sediments. In these environments, smectite particles can be very small (i.e., <0.2
38 μm) (Laird et al., 1991), with high specific surface areas (e.g., >600 $\text{m}^2 \text{g}^{-1}$) and cation exchange
39 capacity (CEC; e.g., > 80 $\text{cmol}_{(+)} \text{kg}^{-1}$). As a result, smectites in soils and sediments are responsible for
40 most of the capacity to retain cations in these environments (Hubert et al., 2012; Viennet et al.,
41 2015; Martin et al., 2018; Bakker et al., 2018, 2019) and play a key role in the mobility of nutrients
42 and contaminants in these systems (Chorover and Amistadi, 2001; Haack et al., 2008; Vorhies and
43 Gaines, 2009; Ferret et al., 2014; Parrello et al., 2016; Robin et al., 2020).

44 Smectites are 2:1 swelling clays whose layers are composed of one octahedral sheet sandwiched
45 between two tetrahedral sheets. In dioctahedral smectites, the octahedral sheet is mainly occupied
46 by trivalent cations (i.e., aluminum (Al) or ferric iron [Fe(III)]), whereas the tetrahedral sheets are
47 mainly composed of tetravalent silicon (Si). Heterovalent substitutions commonly occur in both the
48 tetrahedral (e.g., Al(III) or Fe(III) for Si(IV) substitutions) and octahedral (e.g., magnesium Mg(II) for
49 Al(III) or Fe(III) substitutions) sheets. The net negative charge of the smectite layers generated by
50 these substitutions is compensated for by the incorporation of cations in the interlayer space.
51 Depending on the nature of the main cations in the octahedral sheet and the location of the main
52 negative charge in the structure (tetrahedral or octahedral), smectites can be defined as beidellite
53 (Al-rich smectite with a predominant tetrahedral charge), nontronite (Fe(III)-rich smectite with a
54 predominant tetrahedral charge), or montmorillonite (Al-rich smectite with a predominant
55 octahedral charge). Note that soil smectites are typically characterized by a rather high structural
56 charge ($>0.45/\text{O}_{10}(\text{OH})_2$), a high tetrahedral charge, and a high Fe(III) content in the octahedral sheet
57 (Tessier and Pédro, 1985; Stucki et al., 1987). Fe-rich clays are ubiquitous minerals in soils, and Fe-
58 rich beidellite is commonly present (Stucki et al., 1987; Badraoui and Bloom, 1990; Wilson, 1999). As

59 a consequence, the properties of Fe-rich smectites play important roles in the chemical and physical
60 properties of soils.

61 In the literature, discussions of the stability of smectites have focused on the kinetic dissolution of
62 bentonites (i.e., materials composed of montmorillonites) due to their excellent application potential
63 in the context of the long-term behavior of engineered clay barriers used for nuclear waste storage
64 (Marty et al., 2011; Kaufhold et al., 2019; Jalal et al., 2021) or chemical and pharmaceutical
65 applications (Jayrajsinh et al., 2017; França et al., 2022). Numerous flow-through experiments have
66 been performed to assess the effects of environmental parameters, such as pH (Metz et al., 2005;
67 Amram and Ganor, 2005; Rozalén et al., 2008; Cappelli et al., 2018), temperature (Amram and Ganor,
68 2005; Rozalen et al., 2009; Marty et al., 2011), ionic strength and the presence of soluble organic
69 acids (Golubev et al., 2006; Ramos et al., 2011, 2014), on the constant dissolution rate of
70 montmorillonites. However, studies that have focused on the kinetics of the Fe-rich smectites
71 commonly found in soils are limited. Gainey et al. (2014) studied the dissolution rate of a natural
72 nontronite (Nau-1 from the Clay Minerals Society) and showed a faster dissolution rate for
73 nontronite than for beidellite (SBId-1 from the Clay Minerals Society) despite the similarity in particle
74 sizes and total layer charges between the two minerals. Thus, the role of the crystal chemistry (i.e.,
75 the amount, nature and location of charge) on the dissolution kinetics of Fe-rich smectites has not
76 been studied in detail.

77 Smectites are commonly mixed with nonclayey minerals in natural samples and/or are interstratified
78 mixed-layer minerals (see discussion in Hubert et al., 2012). Therefore, using natural samples to
79 assess the role of the structural Fe content, structural charge and location of the charge (tetrahedral
80 or octahedral) on the stability of these minerals is not trivial. To overcome this difficulty, a synthesis
81 approach (Baron et al., 2016; Petit et al., 2017) enabling us to control the crystal chemistry of Fe(III)-
82 smectites was applied in this study. The hydrothermal sol-gel synthesis used here allowed us to
83 prepare synthetic particles with a high proportion of Fe(III) and a size comparable to that of soil

84 particles (<100 nm) and to control the amount and location of heterovalent substitutions. The
85 dissolution kinetics of three synthetic Fe(III)-rich smectites, differing in terms of the content and
86 location of structural Fe(III) (tetrahedral vs. octahedral), were studied using flow-through reactors at
87 pH (HNO₃) values between 1.8 and 5.5. The concentrations of Si, Fe, and Mg in solution were
88 analyzed as a function of time and used to calculate the dissolution rates and to elucidate the
89 mechanisms associated with dissolution. Both aqueous concentration measurements and solid-state
90 analysis (FTIR and TEM) allowed us to interpret the effects of crystal chemical parameters on the
91 reactivity of the three Fe(III)-rich smectites at acidic pH. A comparison with published data obtained
92 for smectites with distinct crystal chemistry allowed us to discuss the effect of structural Fe(III) (i) on
93 the stability of these minerals and (ii) for further reactive modelling approach involving smectite
94 data.

95 2. Materials and methods

96 2.1. Synthetic smectites

97 2.1.1. Synthesis

98 Three Fe(III)-rich smectites were synthesized that differ in terms of their heterovalent substitutions,
99 i.e., (i) their amount (permanent layer charge from 0.66 to 1.38 per unit cell) and (ii) their location in
100 the smectite layer (only in tetrahedral sites or in both tetrahedral and octahedral sites). Syntheses
101 were performed according to the procedures described by Baron et al. (2016) and Petit et al. (2017)
102 using a precursor gel obtained by coprecipitation of sodium metasilicate, ferric iron chloride, and
103 magnesium chloride solutions. After precipitation, each precursor gel was collected by filtration at
104 0.45 µm and placed in a PTFE metallic-coated hydrothermal reactor. The amount of Fe(III) for Si(IV)
105 tetrahedral substitutions was controlled by the addition of 0.02 M NaOH solution to adjust the pH
106 (Baron et al., 2016; Petit et al., 2017). Magnesium chloride was added to introduce octahedral
107 substitutions (Mg(II) for Fe(III)). The hydrothermal synthesis was conducted at 150°C for 7 days.
108 Then, the solid materials were recovered by filtration at 0.1 µm, dispersed in a 2 M NaCl solution to

109 achieve Na saturation and rinsed by dialysis to remove the excess salt before being stored as a
110 suspension prior to the dissolution experiments.

111 2.1.2. Solid analysis

112 Infrared (FTIR) analyses were performed to assess the changes in the crystal chemistry in the clay
113 minerals after dissolution and the neoformation of any IR-sensitive minerals. FTIR spectra were
114 obtained in transmission mode at a resolution of 4 cm^{-1} in the mid-infrared (MIR) range (4000-400
115 cm^{-1}) using a Thermo Scientific Nicolet iS50 FTIR spectrometer equipped with a KBr beam splitter, an
116 Ever-Glo source, and a DTGS-KBr detector. MIR spectra were collected from KBr pellets (obtained by
117 mixing 1 mg of sample with 150 mg of KBr) which were pressed in a 10 mm diameter press die for 5
118 min at 8 kbar and dried for 1 day at 110°C .

119 Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy
120 (HRTEM) were performed with a Jeol 2100 UHR (LaB6) transmission electron microscope at 200 kV in
121 conjunction with energy dispersive X-ray spectroscopy (EDS) to observe the particle morphology and
122 structural organization and to perform local chemical analysis. The samples were dispersed in
123 deionized water using sonication, and a droplet of the suspension was then placed on a TEM copper
124 grid and dried at ambient temperature.

125 2.1.3. Description of the three synthetic Fe(III)-rich smectites

126 Preliminary results obtained using infrared spectroscopy and X-ray diffraction (XRD) confirmed the
127 synthesis of 2:1 swelling clay minerals without other detectable mineral phases: neither amorphous
128 silica nor other impurities were formed (see Figs. S1 and S2 and the associated discussion in the
129 supplementary material). The structural formulas of the initial synthetic Fe(III)-rich smectites were
130 determined by either FTIR spectroscopy (Baron et al., 2016) or EDS with scanning electron
131 microscopy (SEM), and the results are reported in Table 1. SEM-EDS analyses were performed on
132 pressed disks (7 mm) of pure synthetic particles. Chemical analyses of individual particles were also
133 performed using TEM-EDS to evaluate the homogeneity of the synthetic Fe(III)-rich smectites.

134 Chemical analyses via either SEM or TEM showed that the synthetic smectite particles were
 135 homogeneous. Fe(III)-rich smectites are named according to their crystal chemical properties; i.e.,
 136 Sm-LC, Sm-HC and Sm-Mg indicate low-charge smectite, high-charge smectite and Mg(II) for Fe(III)
 137 substitutions smectite, respectively.

138 The structural formulas of Sm-HC and Sm-LC show that the net negative permanent layer charge
 139 (100%) originated from Fe(III) substitutions for Si(IV) in the tetrahedral sheets, whereas for Sm-Mg,
 140 the negative charge was distributed between the tetrahedral (61% Fe(III) for Si(IV)) and octahedral
 141 (39%) sheets due to Mg(II) substitutions for Fe(III) (Table 1). Sm-HC and Sm-Mg exhibited high
 142 permanent layer charges of 1.14 and 1.38 per unit formula, respectively, while the permanent layer
 143 charge was only 0.66 for Sm-LC (Table 1). The size of the synthetic smectite particles was fairly
 144 homogeneous and was estimated to be approximately 100 nm using TEM observations.

145 2.2. Flow-through experiments

146 Fifteen dissolution experiments were performed using flow-through reactors with input acidic
 147 solutions (pH between 1.80 and 5.50) prepared using a 69% HNO₃ (AR grade) solution and Milli-Q
 148 water. NaNO₃ salt (AR grade) was added to the input solutions as a background electrolyte to achieve
 149 ionic strength of 10⁻³ M. Given the small size of the synthetic particles, to avoid membrane clogging
 150 or loss of particles from the reactor, two open reactor types were used according to the approach
 151 proposed by Köhler et al. (2005) (Fig. 1). The first type of reactor (Fig. 1A) consisted of a PTFE cell
 152 with a total volume of 30 mL. The input solution was in contact with the smectite particles. The
 153 suspension in the system was homogenized by continuous stirring with a suspended Teflon-coated
 154 magnetic bar. The outlet solution was filtered through a 0.22 μm PVDF membrane.

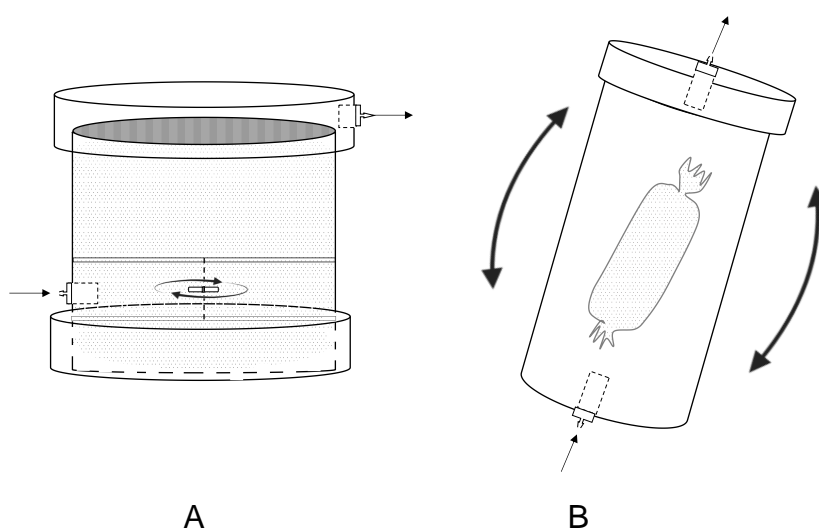
155 Table 1. Details related to the structural formula of the three synthetic Fe(III)-rich smectites.

Structural formulas of synthetic Fe(III)-rich smectites	Global charge (per O ₂₀ (OH) ₄)	Nature and % tetrahedral charge	Nature and % octahedral charge	Tetrahedral Si/Fe ratio	Global Si/Fe ratio

Sm-HC	1.14	Fe (III) → Si	0	6.02	1.33
$(\text{Si}_{6.86}\text{Fe}^{3+}_{1.14})(\text{Fe}^{3+}_4)\text{O}_{20}(\text{OH})_4\text{Na}_{1.14}$		100			
Sm-LC	0.66	Fe (III) → Si	0	11.12	1.58
$(\text{Si}_{7.34}\text{Fe}^{3+}_{0.66})(\text{Fe}^{3+}_4)\text{O}_{20}(\text{OH})_4\text{Na}_{0.66}$		100			
Sm-Mg	1.38	Fe (III) → Si	Mg → Fe (III)	8.52	1.66
$(\text{Si}_{7.16}\text{Fe}^{3+}_{0.84})(\text{Fe}^{3+}_{3.46}\text{Mg}_{0.54})\text{O}_{20}(\text{OH})_4\text{Na}_{1.38}$		61	39		

156 The second type of reactor (Fig. 1B) consisted of a 180 mL polycarbonate column. Smectite particles
 157 were enclosed in a dialysis bag with a 7000 Dalton (≈ 1.5 nm) pore size. The dialysis bag was sealed
 158 tightly and placed inside the column in contact with the input solution. In the type B reactor, the fluid
 159 was mixed by placing the columns on an oscillating shaker. Table S1 lists the experimental conditions.

160 All the experiments were performed at $20 \pm 1^\circ\text{C}$ in a temperature-controlled room. The flow rate of
 161 the input solution was set at $1.07 \times 10^{-3} \pm 6.00 \times 10^{-5}$ for type A reactors or $7.68 \times 10^{-4} \pm 2.20 \times 10^{-5}$ mL.s⁻¹
 162 for type B reactors using an Ismatec® peristaltic pump. Since steady-state dissolution of clay minerals
 163 may not occur (Kohler et al., 2005), we proposed that a steady state was achieved when the output
 164 Si concentration remained approximately constant, i.e., differing by less than 6% across six
 165 consecutive samples collected every 24 h, as proposed in previous studies (Rozalén et al., 2008;
 166 Robin et al., 2016; Cappelli et al., 2018).



167

168 Fig. 1. Schematic illustration of the two types of reactors (A and B) used in this study. Reactor B was adapted from Kohler et al. (2005).

169

170 2.3. Solution analysis

171 Output solutions were collected every day or every two days. The collected solutions were analyzed
172 for pH, oxidation potential (ORP) and total aqueous Si, Fe, and Mg concentrations. The pH was
173 measured immediately after sample collection using precalibrated pH combination electrode
174 (Accumet® 13-620-AE6). A WTW-SenTix® ORP electrode standardized with an ORP test solution (240
175 mV) was used to measure the ORP. The Si, Fe and Mg concentrations were determined for acidified
176 samples (2% HNO₃ v/v).

177 At pH 1.80 and 2, the aqueous concentrations of Si, Fe and Mg were determined via microwave
178 plasma-atomic emission spectroscopy (MP-AES, Agilent MP 4100). The limits of quantification were
179 2.71 μM, 1.27 μM and 0.5 μM for Si, Fe, and Mg, respectively. For samples collected between pH 3
180 and 5.5, the aqueous Si concentration was determined by colorimetry using the molybdate blue
181 method (Strickland and Parsons, 1972), and the absorbance at 810 nm was measured in 5 cm cells
182 with a Shimadzu UV-1800 UV-Vis spectrophotometer. The limit of quantification was 0.02 μM.
183 Aqueous Fe and Mg concentrations were measured using inductively coupled plasma mass
184 spectrometry (Agilent Technology 7700× ICP-MS from Santa Clara, CA, USA) using ⁴⁵Sc and ¹¹⁵In as
185 internal standards. The limits of quantification were 0.03 μM for Fe and Mg.

186 2.4. Calculations

187 *Dissolution rate.* The steady-state dissolution rate R (mol g⁻¹ s⁻¹) was calculated from aqueous Si (or
188 Fe) concentrations by using the following equation (Metz et al., 2005):

$$189 \quad R_j = \frac{-1}{\nu_j} \frac{q}{m} C_j \quad (1)$$

190 where ν is the stoichiometric coefficient of component j (i.e., Si or Fe) in the dissolution reaction, q is
191 the flow rate (L s⁻¹), m is the sample mass (g) (obtained by subtracting the amount of dissolved

192 element from the initial amount of sample), and C is the concentration of component j (i.e., Si or Fe)
193 in the output solution (mol L^{-1}).

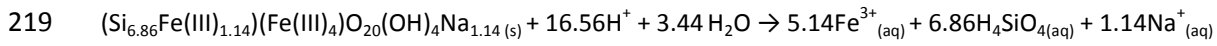
194 A common practice in some experimental dissolution kinetics studies of clay minerals is to normalize
195 the dissolution rate to their specific surface areas (e.g., either partial or total surface including
196 interlayer, external surface or edge surface; Metz and Ganor, 2001; Cama et al., 2002; Bibi et al.,
197 2011; Daval et al., 2013). However, several studies on phyllosilicates (and with silicates in general)
198 revealed that dissolution reactions at different specific sites (e.g., etch-pits opening on basal surfaces
199 or edge retreat) may differ, indicating that reactive and overall surface areas are not equivalent
200 (Grybos et al., 2010; Cappelli et al., 2020; N'Guessan et al., 2021). As the relative reactivity of each
201 surface type remains unknown, the dissolution rates of smectites were normalized in the present
202 study to the mass, as proposed by Metz et al. (2005), Amram and Ganor (2005), Robin et al. (2016)
203 and Cappelli et al. (2018) (among others); this choice allowed us to compare the dissolution rates of
204 smectites or other phyllosilicates (Marty et al., 2005; Rozalén et al., 2008) without being impacted by
205 the choice of surface normalization. The propagated error associated with the calculated dissolution
206 rate was estimated according to the Gaussian error propagation method for independent variables
207 (Wells and Krakiwsky, 1971). The error in the calculated rate was less than 5% and was dominated by
208 the uncertainty in the measured Si (or Fe) concentration in the output solution.

209 *Thermodynamic calculations.* PHREEQC software version 4 (Parkhurst and Appelo, 1999) and the
210 Thermoddem thermodynamic database (Blanc et al., 2012) were used to calculate the aqueous
211 speciation and the saturation state of the output solutions.

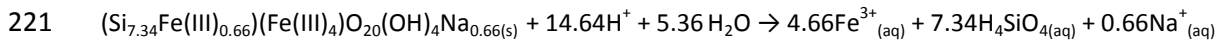
212 The saturation indexes (SI) of the output solutions with respect to the phases of interest were
213 calculated using the ion activity product (IAP) of the solution and the equilibrium constant (K_{eq}) (2).

$$SI = \log \frac{IAP}{K_{eq}} \quad (2)$$

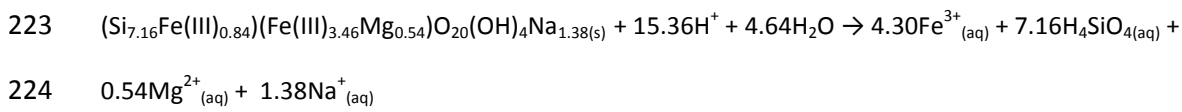
216 The dissolution K_{eq} values of the three synthetic Fe(III)-rich smectites at 25°C and 1 atm were
 217 computed according to the method proposed by Blanc et al. (2021) (a brief description of this
 218 approach is provided in the supplementary material) according to the following dissolution reactions:



220 $\text{Log } K_{eq} = -9$



222 $\text{Log } K_{eq} = -10.07$



225 $\text{Log } K_{eq6} = -2.55$

226 The degree of saturation of the output solutions with respect to the different smectites was
 227 calculated in terms of the Gibbs free energy of reaction $\Delta_r G$ (in kcal mol⁻¹), which was defined as

228
$$\Delta G_r = RT \ln \left(\frac{IAP}{K_{eq}} \right) \quad (3)$$

229 where R is the gas constant (8.314 J mol⁻¹ K⁻¹) and T is the absolute temperature (K).

230 3. Results

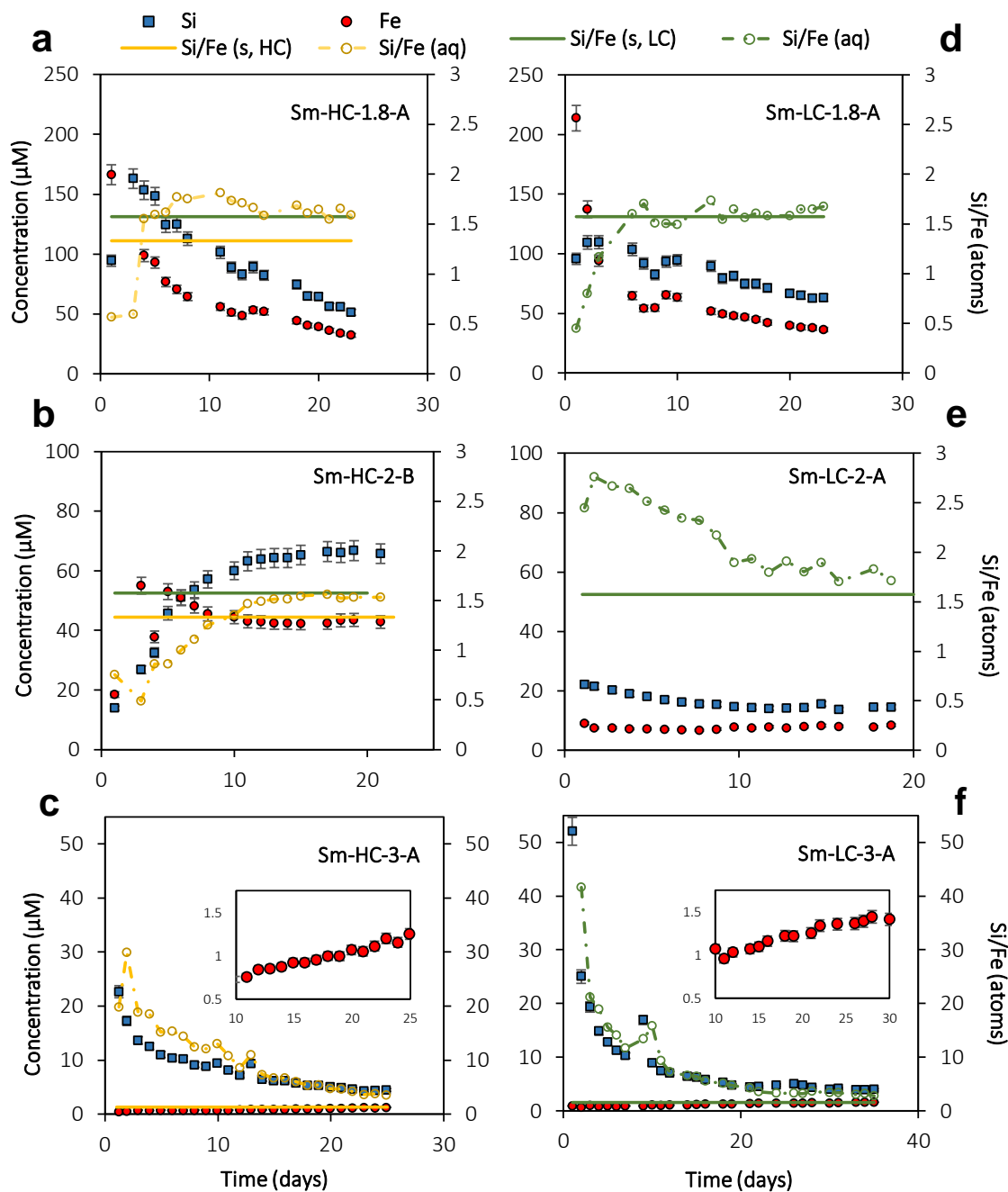
231 3.1. Output solution analysis

232 Good reproducibility of the dissolution rates was achieved between experiments performed with the
 233 two reactor types under the same conditions (pH, starting material). The differences between the
 234 experimental dissolution rates obtained with reactor A and reactor B varied from 3% to 12% (Table
 235 S1). These differences are acceptable and allowed a comparison of the results regardless of the
 236 reactor used.

237 Fig. 2 shows the output Si, Fe and Mg concentrations and the aqueous Si/Fe and solid Si/Fe
 238 stoichiometric ratios for the three samples at pH 1.8, 2 and 3. The results of the experiments

239 performed at pH 4 and 5 are shown only for LC smectite (representative experiments). The data
 240 obtained under other experimental conditions are reported in Fig. S3 (supplementary material).

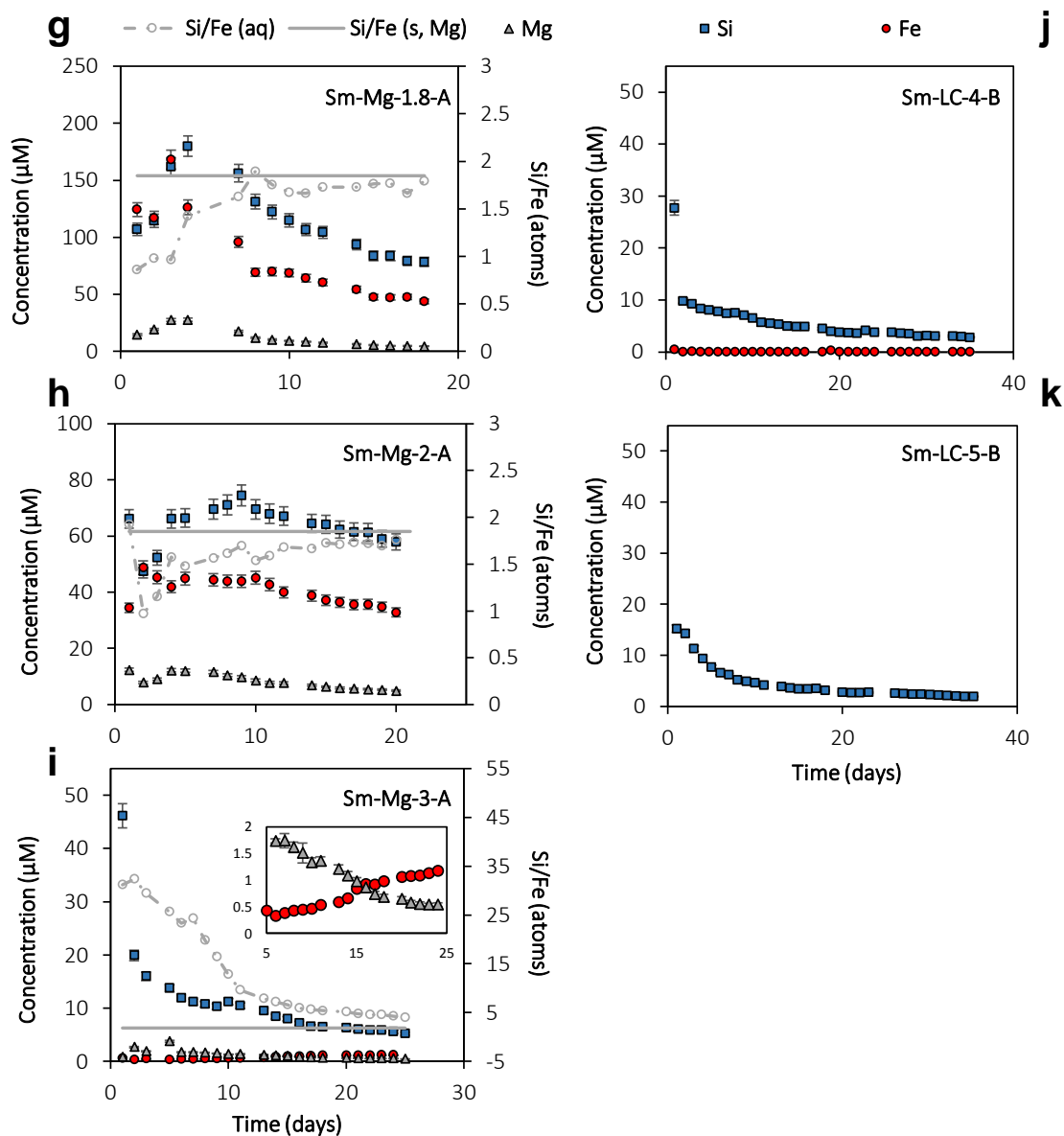
241



242

243 Fig. 2. Variation in the Si (blue square), Fe (red circle) and Mg (gray triangle) concentrations and the Si/Fe atomic ratio as a
 244 function of time in the output solutions (connected circles) of selected dissolution experiments. The first two characters in
 245 the names of the experiments denote the smectite crystal chemistry used, the next digit in the name is the pH, and the last
 246 letter indicates the type of reactor used. The solid Si/Fe ratio of the synthetic Fe(III)-rich smectites is represented by a

247 horizontal line. The concentrations of aqueous Fe in the experiments performed at pH 4 and 5 were below the
 248 quantification limit.



249

250 Fig. 2. (continued)

251 For the dissolution experiments performed at pH 1.8 and 2, all output Si concentrations (except for
 252 those in the Sm-HC-2-B experiment; Fig. 2b) increased during the first days of the experiment
 253 (between two and nine days) (Fig. 2 a, d, e, g and h). Afterward, the aqueous Si concentration
 254 decreased until it reached a steady state (between 12 and 15 days at pH 1.8 and between 10 and 12
 255 days at pH 2). This evolution was not observed for experiments at $\text{pH} \geq 3$, which instead showed a

256 continuous decrease in the output Si concentration from the beginning of the experiments until a
257 steady state was reached (Fig. 2 c, f, i, j and k). For the experiments performed at pH 1.8 and 2
258 (except Sm-HC-2-B), the release of Fe in solution exhibited a trend similar to that of Si. At the
259 beginning of the experiments performed at pH 3, the amount of Fe released was less than 0.6 μM
260 but increased slowly with time. At steady state, the aqueous Fe concentration was twice the
261 concentration measured in the first days (see insets in Figs. 2 c, f, i). For experiments performed at
262 $\text{pH} \geq 4$, the Fe concentrations were below the quantification limit ($< 0.03 \mu\text{M}$). For the experiments
263 performed with Sm-Mg, the aqueous Mg concentration exhibited the same trend as that for the
264 experiments carried out at $\text{pH} \leq 3$, with an increase in concentration in solution for six days, followed
265 by a progressive decrease. The Mg release remained at a value of half of the Fe release, consistent
266 with the low Mg content in the smectite structure (see Table 1). The average Si, Fe and Mg aqueous
267 concentrations measured at the steady state in all the experiments are presented in Table S1. The
268 output concentrations approached a steady state between 10 and 30 days depending on the
269 dissolution conditions and/or crystal chemistries of the starting smectite. The time to reach the
270 steady state was the longest for the Sm-LC sample under all pH conditions.

271 For the output solutions, different changes in the Si/Fe ratios were observed depending on the
272 sample and the pH of the input solution. For the dissolution of Sm-LC at pH 1.8 (Fig. 2 d) and the
273 dissolution of Sm-Mg at pH 1.8 and 2 (Fig. 2 g, h), the evolution of the Si/Fe ratios was divided into
274 two steps. First, the Si/Fe ratios increased for 10 days, remaining lower than the solid stoichiometry
275 values. Second, constant Si/Fe ratios close to the solid stoichiometry ratios were observed. The same
276 trend was observed in the Sm-HC experiments, in which the first step lasted 12 days; however,
277 during the second step, the constant Si/Fe ratios were not close to the Sm-HC solid stoichiometry but
278 were instead close to the Sm-LC solid stoichiometry (see Fig. 2 a, b). Two steps were also observed in
279 the Sm-LC experiment at pH 2 (Fig. 2 e); however, in that case, the Si/Fe ratio decreased toward the
280 solid stoichiometry but remained slightly greater (9%). The same trend was observed at pH 3 for the

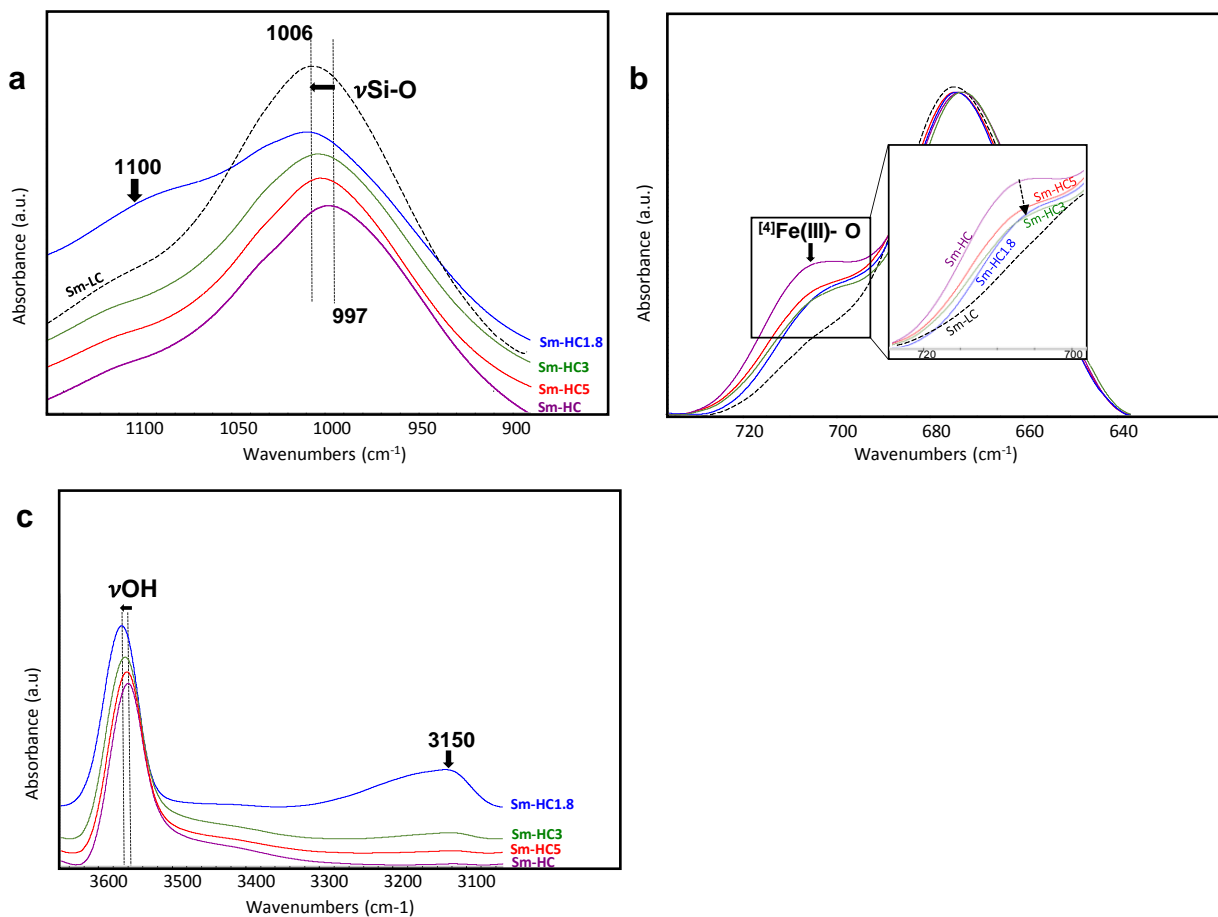
281 three smectite samples, but the time to reach a constant Si/Fe value was longer (more than 16 days),
282 and the solid stoichiometry was never reached during the experiment (maximum of 35 days).

283 For each steady state obtained experimentally, the saturation indexes of the output solutions were
284 calculated with respect to the amorphous silica, Fe-bearing (ferrihydrite), and Mg-bearing (brucite)
285 phases using the measured aqueous chemical composition (Table S1). The results were plotted
286 against the output pH in the supplementary material file (Fig. S4 a, b, c). Saturation indexes for
287 amorphous silica were reported as a function of time for experiments performed at pH 1.8 and pH 2
288 (Fig. S4 d). For all the experiments, the output solutions were undersaturated with respect to the
289 amorphous silica, Fe-bearing, and Mg-bearing phases and Fe-rich smectites.

290 3.2. Solid analysis

291 The FTIR spectra of the initial Sm-HC and acidified Sm-HC samples retrieved at the end of the
292 experiments are shown in Fig. 3. The spectra of Sm-LC and Sm-Mg are not shown, but the band
293 positions of interest are listed in Table S2 (supplementary material). The spectra of the three crystal
294 chemistries displayed an intense band in the Si-O stretching (ν) region (997 to 1015 cm^{-1}) at different
295 positions depending on the crystal chemistry and pH (Fig. 3 a, Table S2). In the spectra on the initial
296 Fe(III)-rich smectites, $\nu\text{Si-O}$ vibrations were observed at 997, 1005, and 1006 cm^{-1} for Sm-HC
297 (tetrahedral charge = 1.14), Sm-Mg (tetrahedral charge = 0.84) and Sm-LC (tetrahedral charge =
298 0.66), respectively. Overall, for the dissolved samples, the position of the $\nu\text{Si-O}$ band shifted toward
299 higher wavenumbers from the initial positions as the pH decreased (see Fig. 3 a, Table S2). The
300 spectrum of the Sm-HC samples showed the greatest continuous shift, from 997 to 1010 cm^{-1} (Fig. 3
301 a), while that of Sm-Mg displayed a shift from 1005 to 1015 cm^{-1} . The spectra of these two samples
302 displayed shifts at pH 5, whereas the spectra of the Sm-LC samples exhibited a significant shift from
303 1006 to 1012 cm^{-1} only at pH 1.8 (Table S2). The spectra showed a shoulder at approximately 1100
304 cm^{-1} for Sm-HC-1.8 and Sm-Mg-1.8 with similar intensities (Table S2, Fig. 3 a), but this feature was
305 not present in the Sm-LC-1.8 spectrum. The Sm-HC (altered or not) spectra exhibited a band at 707

306 cm^{-1} (Fig. 3 b), which was attributed in part to tetrahedral $^{[4]}\text{Fe(III)-O}$ vibrations (Decarreau et al.,
 307 2008). The intensity of the $^{[4]}\text{Fe(III)-O}$ band increased as the tetrahedral Fe(III) content of the smectite
 308 samples increased (Fig. 4, Table S2). For the Sm-HC samples dissolved at acidic pH, the $^{[4]}\text{Fe(III)-O}$
 309 band continuously decreased in intensity as the pH decreased (Fig. 3 b).



310
 311 Fig. 3. MIR spectra of initial and altered Sm-HC samples at pH 1.8, 3, and 5 in the $\nu\text{Si-O}$ region (a), in the $^{[4]}\text{Fe(III)-O}$ vibration
 312 region (b) and in the νOH region (c). The black arrows indicate the shoulders and the shifts associated with the main
 313 modifications upon alteration. To help interpret the changes in the spectra of the Sm-HC sample upon alteration, the initial
 314 spectrum of the Sm-LC sample is also shown. For clarity, only the results of Sm-HC alteration experiments are shown here,
 315 and the data for Sm-LC and Sm-Mg alteration are reported in Table S2 in the supplementary material file.

316 The spectra of the initial Fe(III)-rich smectites exhibited an absorption band in the νOH region at 3559
 317 cm^{-1} for Sm-HC and Sm-LC and at 3555 cm^{-1} for Sm-Mg (Table S2), which was attributed to
 318 $\nu\text{Fe(III)}_2\text{OH}$. The small difference among samples was due to the presence of Mg atoms in the
 319 octahedral sheet. In the spectra of all the altered samples, the position of this band shifted toward

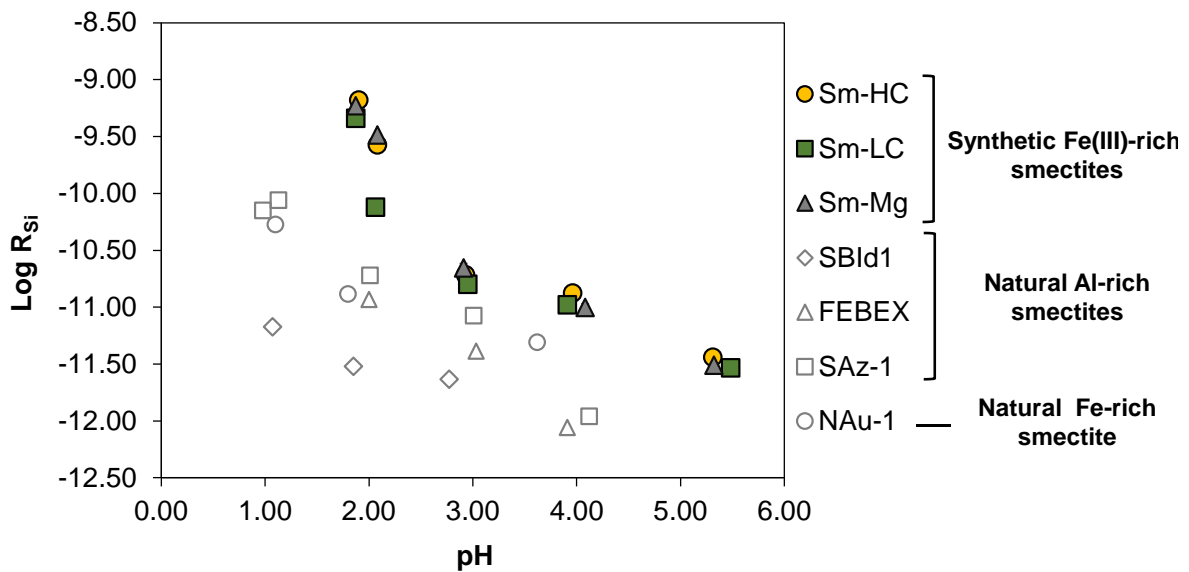
320 higher wavenumbers (Fig. 3c), and the shifts were similar among the three samples ($\approx 8 \text{ cm}^{-1}$)
321 between the initial and dissolved smectite phases at pH 1.8).

322 In the spectra of the three samples, a shoulder progressively appeared at 3150 cm^{-1} (identified by the
323 black arrow in Fig. 3c). The intensity of this shoulder increased continuously as the pH decreased,
324 with greater intensity for the samples dissolved at pH 1.8 and 2 (Table S2).

325 TEM observations of the Sm-LC initial particles and the Sm-LC samples dissolved at pH 3 and 1.8
326 revealed the morphological evolution of the particles (Fig. S5). The initial particles presented a lath
327 shape that evolved after the dissolution experiments to form a rounded shape, accompanied by a
328 decrease in the particle size (Fig. S5). HRTEM images of the altered Sm-HC particles at pH 3 showed
329 alterations in the basal surface (Fig. S6b). A higher magnification image of Sm-HC-3 (Fig. S6d) showed
330 a decrease in the crystallinity of some parts of the basal surface relative to the initial particles (Fig.
331 S6a, c). No discrete Si-rich or amorphous phases were observed at the scale of the observation;
332 however, their presence could not be completely excluded.

333 3.3. Fe(III)-rich smectite dissolution rates

334 The steady-state dissolution rates of Fe(III)-rich smectites are plotted as a function of pH in Fig. 4. The
335 dissolution rates decreased with increasing pH. The dissolution rates for Sm-LC were lower than
336 those for the Sm-HC samples, regardless of the pH. Note that greater differences between
337 dissolution rates were observed at pH 1.8 and 2. The dissolution rates of the Sm-Mg samples were
338 between those obtained for the two other smectites.



339 Fig. 4. Dissolution rates of Sm-HC, Sm-LC and Sm-Mg calculated in this study using equation (1) compared to the dissolution
 340 rates of natural SBId1, FEBAX, SAz-1, and NAu-1 from Robin et al. (2016), Cappelli et al. (2018), Amram and Ganor (2005)
 341 and Gaaney et al. (2014), respectively.
 342

343 The variations in the dissolution rates of Sm-HC, Sm-LC and Sm-Mg are plotted as a function of Gibbs
 344 free energy ($\Delta_r G$) in Fig. 4a. In the Sm-LC experiments performed between pH 2.06 and 5.5, the
 345 calculated values of $\Delta_r G$ deviated from equilibrium as the rates increased. However, for the highest
 346 dissolution rate measured at pH 1.87 ($R_{Si} = 4.47 \cdot 10^{-10} \text{ g mol}^{-1} \text{ s}^{-1}$), the associated $\Delta_r G$ value was closer
 347 to equilibrium ($-5.24 \text{ kcal mol}^{-1}$) than the $\Delta_r G$ value calculated for Sm-LC at pH 4. This deviation of the
 348 $\Delta_r G$ values toward equilibrium was also observed for the experiments performed with Sm-HC and
 349 Sm-Mg. However, for these samples, the deviation was observed for two dissolution rates, namely,
 350 those measured at pH 2.08 and pH 1.90 for Sm-HC and those measured at pH 2.08 and 1.87 for Sm-
 351 Mg samples, for which the $\Delta_r G$ values were closer to equilibrium than those measured in the
 352 experiments carried out with Sm-HC and Sm-Mg at pH 4 (Fig. 4a).

353

354 4. Discussion

355 4.1. Effect of the crystal chemistry of synthetic Fe(III)-rich smectites on the dissolution rate

356 The variation in $\log R_{Si}$ as a function of pH for the three synthetic Fe(III)-rich smectites followed the
357 same trend (Fig. 4). The rates decreased from pH 1.8 to 5.5, as observed for silicate dissolution rates
358 at acidic pH (Marty et al., 2015). Similar $\log R_{Si}$ values were calculated (Fig. 4), even though Sm-LC
359 tended to have lower dissolution rates than Sm-HC and Sm-Mg. In particular at pH 2, the dissolution
360 rate of Sm-LC was three times lower than the dissolution rates of Sm-HC and Sm-Mg (Table S1). The
361 common representation of dissolution rates on a log scale as a function of pH did not highlight
362 important differences between the chemical reactivity of the three Fe(III)-rich smectites.

363 4.2. Evolution of the crystal chemistry during dissolution.

364 The steady-state aqueous Si/Fe ratios of Sm-HC at pH 1.8 and 2 were higher than the stoichiometric
365 ratio of the starting material, while the Si/Fe aqueous ratio was stoichiometric for Sm-LC and Sm-Mg,
366 characterized by a lower Fe(III) content (Fig. 2). This finding demonstrated the instability of Fe(III)-
367 rich smectite with a high tetrahedral charge and high iron content and the preferential loss of Fe
368 during dissolution (nonstoichiometric dissolution). FTIR analyses of the Sm-HC and Sm-Mg samples
369 also revealed a significant decrease in the $^{54}Fe(III)$ content with respect to the total Fe content under
370 all pH conditions, as determined from the continuous shift in the $\nu Si-O$ band in the spectra of the
371 Sm-Mg samples and the continuous shift in the $\nu Si-O$ band in conjunction with a decrease in the
372 intensity of the $^{54}Fe(III)-O$ band in the spectra of the Sm-HC samples (Baron et al., 2016) (Table S2). In
373 contrast, for the Sm-LC samples, the shift in the $\nu Si-O$ vibration was significant only for the
374 experiment at pH 1.8, and a decrease in the intensity of the $^{54}Fe(III)-O$ vibration was not observed
375 (Table S2). These results indicated that Sm-HC and, to a lesser extent, Sm-Mg were subject to
376 changes in crystal chemistry during dissolution at acidic pH. A higher reactivity of the Sm-HC sample
377 was also determined from the TEM images, which showed partial disorganization of the crystal
378 structure after acidic dissolution at pH 3 (Fig. S6b and d). The decrease in the crystalline order was
379 not homogeneous over the basal surface but was localized (Fig. S6d). Specifically, 5 nm spots with
380 low structural order covered all the particles (white spots in Fig. S6b) and were attributed to

381 reorganization of the crystal structure in response to the loss of tetrahedral Fe(III), as observed via
382 aqueous and FTIR measurements. This uncommon feature of smectites was attributed to the high
383 amount of tetrahedral Fe(III) substitutions for Si(IV), which caused a large distortion of the
384 tetrahedral layer and consequently a high local energy environment that favored dissolution on the
385 basal surface of the smectites. Cappelli et al. (2020) observed the formation of etch-pits during
386 biotite dissolution at pH 1-2, in the presence of oxalic acid (at 0.01 M and 0.1 M) and at temperature
387 between 25°C and 70°C. The alteration of biotite occurred far from equilibrium ($-138 \text{ kcal mol}^{-1} < \Delta_r G$
388 $< -131 \text{ kcal mol}^{-1}$). In the present study, dissolution features comparable to those observed by
389 Cappelli et al. (2020) were observed after the dissolution of the synthetic Fe(III)-rich smectites under
390 less drastic conditions (HNO_3 0.001 M, 25°C) and closer to equilibrium conditions ($-10 \text{ kcal mol}^{-1} < \Delta_r G$
391 $< -1 \text{ kcal mol}^{-1}$) (Fig. 5a), revealing the high reactivity of these minerals.

392 4.3. The role of aqueous Fe and Si on the Fe(III)-rich smectite dissolution

393 Regarding the fate of Fe during dissolution, no Fe-rich phase was detected. The output solutions
394 were continuously undersaturated with respect to Fe-hydroxide over the full pH range investigated
395 (Fig. S4). However, the Si/Fe aqueous ratios measured at steady state were at least two times greater
396 than the Si/Fe ratios of the starting materials (Fig. 2) for all the experiments performed at pH 3 (Sm-
397 HC-3, Sm-LC-3, Sm-Mg-3). For all the experiments performed at pH 4 and pH 5, the Fe concentrations
398 were below the detection limits, regardless of the crystal chemistry of the smectite, which indicated
399 an Fe deficit during the dissolution experiments (Fig. 2, Fig. S3). Several authors have attributed the
400 Al or Fe deficit in solution to the adsorption of dissolved metals on cation exchanger sites during
401 smectite dissolution experiments (Golubev et al., 2006; Rozalén et al., 2008; Gainey et al., 2014;
402 Robin et al., 2016).

403 An initial increase in the Si aqueous concentration has been observed for natural smectites (Metz et
404 al., 2005; Amram and Ganor 2005; Gainey et al., 2014) and other clay minerals (Cama et al., 2002;
405 Viennet et al., 2016; Smith et al., 2017). The rapid release of Si in the first days of the experiment

406 may have been caused by the dissolution of ultrafine amorphous silica particles, which dissolve
407 faster than smectite under acidic conditions (Metz et al., 2005; Amram and Ganor, 2005). In the
408 present study, even though the presence of amorphous silica particles in the initial smectite samples
409 could not be excluded, amorphous silica particles were not detected in the initial samples by FTIR or
410 TEM (Fig. S1, Fig. S5). It is likely that the release of Si was caused by the dissolution of smaller
411 smectite particles, considering the similar release of Si and Fe during the first days of the
412 experiments (Fig. 2). However, during these initial days, the dissolution was not stoichiometric at pH
413 1.8 or 2. A deficit of Si with respect to Fe was observed (except for in Sm-LC-2), as was the case for Fe
414 and/or Al during dissolution experiments performed with natural smectites (Cama et al., 2000;
415 Rozalén et al., 2008; Robin et al., 2016). In our study, no distinct Si-rich particles were observed by
416 TEM after dissolution, and all the output solutions were undersaturated with respect to amorphous
417 silica (Fig. S4). However, the FTIR spectra of the Sm-HC-1.8 and Sm-Mg-1.8 samples displayed a
418 shoulder at 1100 cm^{-1} on the large $\nu\text{Si-O}$ bands and a continuous increase in the intensity of the band
419 at 3150 cm^{-1} as the pH decreased. These two bands were observed during the dissolution
420 experiments of smectites under acidic conditions and were attributed to the presence of a hydrated
421 amorphous silica layer (Komadel, 1996; Madejová et al., 2009; Robin et al., 2016). Therefore, despite
422 undersaturation with respect to amorphous silica, these results indicated the potential formation of
423 an amorphous Si-rich phase in the samples with the highest total layer charge at acidic pH ($\text{pH} < 3$)
424 (Table S2). While precipitation of amorphous silica has commonly been observed during the
425 dissolution of smectites at $\text{pH} \leq 1$ and 35°C (Komadel, 1996; Barrios et al., 2001; Shaw and Jim
426 Hendry, 2009; Madejová et al., 2009), the present study demonstrates the potential formation of a
427 Si-rich layer under less acidic conditions ($1.8 \leq \text{pH} \leq 3$). Previous studies have shown that the
428 formation of an amorphous layer on the surface of smectite particles results in a coating that affects
429 the release of elements (Turpault and Trotignon, 1994; Metz et al., 2005; Kameda et al., 2009; Schott
430 et al., 2012). Even if such a layer did not form in our experiments, as demonstrated by the
431 stoichiometric ratios at steady state, the potential formation of a Si-rich layer at acidic pH is

432 important for achieving a better understanding of the alteration of smectites under natural
433 conditions.

434 4.4. Effects of crystal chemistry on smectite reactivity: insights from comparisons with natural 435 smectites from the literature

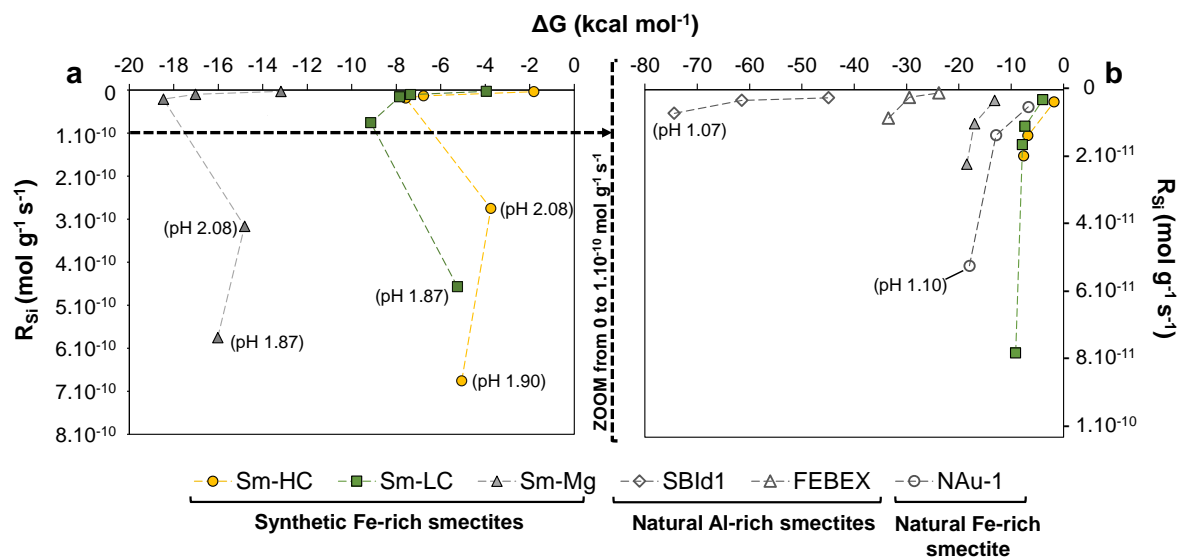
436 The dissolution rates (R_{Si}) of the three Fe(III)-rich synthetic smectites at different pH values were
437 comparable to those of natural dioctahedral smectites (particle size ≤ 200 nm, similar to the
438 synthetic smectites used in this study) containing Al and Fe (Fig. 4). The natural smectites were two
439 montmorillonites (SAz-1 and FEBEX; Amram and Ganor 2005, Cappelli et al., 2018), a beidellite
440 (SBld1; Robin et al., 2016) and a nontronite (NAu-1; Gainey et al., 2014). These studies were selected
441 because of the variety of smectite crystal chemical properties included and because the experimental
442 procedures used were similar to those used in the current study . Details of their respective
443 structural formulas are available in the supplementary material (Table S3).

444 *Dissolution rates of Fe(III)-rich smectites.* The nontronite NAu-1 contains a slightly lower content of
445 total Fe than the synthetic samples presented here (Table S3, Table 1). It has a total charge (1.06)
446 similar to that of Sm-HC (1.14) and a predominant tetrahedral charge (96%) similar to those of Sm-HC
447 and Sm-LC (Table 1). Despite these similarities, the dissolution rates of NAu-1 were reported to be 2
448 to 35 times lower than those of Sm-LC and between 3 and 50 times lower than those of Sm-HC (Fig.
449 4). Furthermore, the Sm-Mg synthetic smectite was found to have a different layer charge
450 distribution than that of NAu-1. Similarly, the dissolution rate of synthetic smectite was greater (2 to
451 44 times) than that of natural smectite (Fig. 4). For Fe(III)-rich smectites, neither the location nor the
452 amount of total charge could explain the significant difference in dissolution rates. However, in NAu-
453 1, the tetrahedral charge was caused by the substitutions of Al(III) for Si(IV) and a small amount of
454 Al(III) was in the octahedral sheets, while no Al(III) was present in the synthetic samples. The total
455 amount of structural Fe and/or the nature of the tetrahedral substitution (Al or Fe) had a significant
456 impact on the dissolution rate of Fe(III)-rich smectites.

457 *Comparison between Fe(III)-rich and Al-rich smectites.* FEBEX and SAz-1, two montmorillonites,
458 exhibited similar dissolution rates (Fig. 4) despite a significant difference in total charge (SAz-1 has a
459 total charge 1.8 times greater than that of FEBEX; Table S3). However, their dissolution rates at pH 2
460 were 4 times greater than those of SBId1 beidellite (Fig. 4), whose total charge was between those of
461 the two montmorillonites (Table S3). The natural Fe(III)-rich smectite (NAu-1) displayed higher
462 dissolution rates than SBId1 beidellite (8 to 4 times higher at pH 1.1 and pH 2, respectively) despite a
463 similar total charge, which was mainly attributed to tetrahedral substitutions, but the observed rate
464 was within the range of rates exhibited by other Al-rich smectites with varying amounts of octahedral
465 charge. The synthetic Fe(III)-rich smectites exhibited systematically higher dissolution rates than the
466 Al-rich smectites, regardless of the charge location or total charge value (Fig. 5 Fig. 4). Thus, neither
467 the total structural charge nor its location could explain the different reactivities of the smectites.
468 This study highlights the effect of the structural Fe(III) content on mineral reactivity (i.e., the amount
469 of Fe(III) in the octahedral sheets was 16 times greater in NAu-1 than in SBId1). A low content of
470 structural Fe(III) combined with the stabilizing effect of tetrahedral Al(III) led to the strong stability of
471 the Al-rich smectites. This is consistent with the behaviors of NAu-1 and FEBEX, which have similar
472 dissolution rates but different crystal chemistries (more Fe(III) and more tetrahedral Al in NAu-1
473 versus less tetrahedral Al and more octahedral Mg in FEBEX). These results confirmed the stabilizing
474 effect of Al described by Novák and Čížel (1978), Gainey et al. (2014) and Robin et al. (2016). These
475 authors suggested that the substitutions could be considered as localized defects, that cause
476 deformation and/or weakening of the structure, which impacts the reactivity of the particles, with
477 different effects depending on the substituted ion. Additionally, Gainey et al. (2014) suggested that
478 Al-rich and Fe(III)-rich smectites may have different behaviors as a result of surface protonation,
479 which may also lead to different dissolution rates. The increasing reactivity of smectites as the Fe
480 content increases could account for the systematically higher dissolution rates and strong instability
481 of synthetic Fe(III)-rich smectites. The synthetic Fe(III)-rich smectites contained between 33% and
482 43% structural Fe(III) and no structural Al, which could result in stabilization (tetrahedral charges

483 were caused by only Fe(III) substitutions for Si(IV)). Note that other substitutions, with Mg, seemed
 484 to affect the smectite reactivity. Indeed, our results showed that with a relatively similar amount of
 485 tetrahedral iron, Sm-Mg showed greater crystal chemical evolution than Sm-LC (Table S2). In
 486 addition, among the natural Al-rich smectites, it was the smectite richest in Mg (SAz-1) which reacted
 487 the fastest (Fig. 4).

488 5. Smectite dissolution rates laws



489
 490 Fig. 5: Variation in dissolution rates (R_{Si} normalized to the mass) as a function of Gibbs free energy ($\Delta_r G$) for (a) Sm-HC, Sm-
 491 LC and Sm-Mg at pH 1.8-5.5 (the pHs for which abnormal behaviors were observed are highlighted) and (b) Sm-HC and Sm-
 492 Mg at pH 3-5.5 and Sm-LC at pH 2-5.5 (zoom of Fig. 5a) and for three natural smectites, i.e., SBId1, FEBEX, and NAu-1, for
 493 which the values were calculated from the studies of Robin et al. (2016), Cappelli et al. (2018) and Gainey et al. (2014),
 494 respectively (see details in the supplementary material file, Table S4).

495 The variation in dissolution rates as a function of Gibbs free energy was similar between the three
 496 synthetic Fe(III)-rich smectites (Fig. 5a). Between pH 3 and 5.5, the dissolution rates increased as the
 497 system shifted further from equilibrium, with a nonlinear change in R_{Si} as a function of $\Delta_r G$, as for
 498 other natural minerals (Fig. 5a, b). Then, at pH 1.8 and 2 for Sm-HC and Sm-Mg, and only at pH 1.87
 499 for Sm-LC, the R_{Si} increased as the $\Delta_r G$ shifted toward equilibrium (Fig. 5a). Thus, for these samples,
 500 the relation between R_{Si} and $\Delta_r G$ did not follow the positive correlation between the dissolution rate

501 and the distance from equilibrium expected for such a system. These deviations from the expected
502 behavior of a silicate mineral observed at more acidic pH occurred because of important structural
503 changes (decrease in permanent charge) and the formation of an amorphous silica phase (see
504 discussion section 3.2, Fig. 3, and Table S2). A significant change in the solid during the reaction could
505 explain the difficulty to compute a consistent Δ_rG .

506 Only the dissolution rates of Sm-HC and Sm-Mg at pH 3–5.5 and those of Sm-LC at pH 2–5.5 (the
507 samples with the lowest changes in crystal chemistry) are shown in Fig. 5b, as are those of beidellite,
508 nontronite and Al-rich montmorillonite for further comparison. A different behavior was observed
509 between the Fe(III)-rich and Al-rich smectites; i.e., the Fe(III)-rich smectites exhibited the highest
510 dissolution closer to equilibrium. This highlights the greater reactivity of Fe(III)-rich smectites than of
511 Al-rich smectites. The expected evolution of the $R_{Si}=f(\Delta_rG)$ function at pH 1.1 for Nau-1, i.e., a
512 continuous increase in dissolution rate as a function of decreasing Δ_rG , demonstrates the important
513 role of Al substitutions in the tetrahedral sheets, allowing structural stabilization, and confirms that
514 the high instability of Fe(III)-rich smectites is mainly due to Fe(III) substitutions for Si(IV) in clay
515 sheets. The destabilizing effect of the substitutions by Mg in the octahedral sheets was confirmed by
516 the change in behavior observed for Sm-Mg from pH 2.08 (Fig 5a). Nevertheless, additional
517 experimental data are needed to quantify the exact effect of the presence of structural Mg
518 compared with that of structural Fe. Thus, Fe(III)-rich smectites do not systematically satisfy the
519 conditions for proposing a general dissolution rate law allowing us to extrapolate their behavior
520 because of the evolution of their crystal chemistry during dissolution.

521 Cappelli et al. (2018) proposed a dissolution rate law for an Al-rich montmorillonite used in an
522 engineered clay barrier. However, according to our results, a different dissolution rate law is required
523 for Fe(III)-rich smectites, which may be present in many environments, particularly in soils.

524 5. Conclusion and Perspectives

525 The effects of the crystal chemistry and pH on the dissolution rates of Fe(III)-rich smectites with small
526 particle sizes (<100 nm) were studied at pH values between 1.8 and 5.5 and at room temperature.
527 The permanent charge and the amount of Fe in the structure were the main parameters affecting the
528 reactivity of Fe(III)-rich smectites. An initial high total charge (>0.6 by $O_{20}(OH)_4$) resulted in the
529 instability of smectites in solution, with mineral evolution characterized by a loss of tetrahedral
530 charge and the potential formation of a Si-rich layer. When the pH decreased, the Fe(III)-rich
531 smectites formed a common lower charge structure. Additionally, natural Al-bearing smectites were
532 found to exhibit greater stability than Fe-rich smectites under conditions far from equilibrium. These
533 results indicated the significant effect of the crystal chemistry of the smectites on their dissolution
534 (dissolution rate, dissolution stoichiometry) under acidic conditions.

535 Thus, the use of a single rate law to describe the dissolution rate of smectites must be considered
536 with caution. It is important to consider the crystal chemistry of smectites, i.e., the amount and
537 nature of the isomorphic substitutions, to account for the reactivity of these clays. This study showed
538 that the use of a rate law may be limited to acidic pH. Therefore, it might be interesting to complete
539 these observations with other synthetic samples with greater heterogeneity between the nature,
540 location, and amount of isomorphic substitutions to assess the sensitivity of the effects of the crystal
541 chemistry on the variability between rate laws. However, particular attention must be given to the
542 transformations that can occur on solids (crystal-chemical changes, precipitation) even at moderate
543 pH and temperature before predicting the evolution of minerals. Conclusions put forward by Kohler
544 et al. (2004) reinforce this conclusion, indicating that the steady state condition needs to be clearly
545 defined during the experimental approach because clay mineral dissolution may not attain a "true"
546 steady state due to the morphological modifications of solids over time, i.e., the relative increase in
547 the average basal surface compared to edge surfaces. In any case, this study clearly shows the rapid
548 evolution of Fe(III)-rich clay minerals in the environment even for slight physicochemical variations,
549 which is a critical issue at a larger scale toward global changes through the evolution of the
550 availability of nutrients and other elements in soils and surface environments.

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554 Data Availability

555 Data are available through Mendeley Data at <https://data.mendeley.com/datasets/r7sz6d2sww/1>.

556 Appendix A. Supplementary material

557 The Supplementary Materials contains Supplementary Figure 1 and Supplementary Figure 2,
558 providing infrared spectra and X-ray diffraction patterns of unaltered synthetic samples, respectively;
559 Supplementary Table 1, indicating the experimental conditions and the results of the experiments;
560 Supplementary Figure 3, showing the evolution of the concentrations of aqueous Si, Fe, and Mg
561 measured as a function of time in the output solutions during dissolution experiments performed at
562 pH 4 and 5.5 with Sm-HC and Sm-Mg; Supplementary Figure 4, illustrating the saturation indexes of
563 the output solutions with respect to amorphous silica and Fe- and Mg- bearing phases and each
564 synthetic smectite; Supplementary Table 2, indicating the FTIR spectra of dissolved Fe(III)-rich
565 smectites; Supplementary Figures 5 and 6, showing the TEM and HRTEM observations of unaltered
566 and altered Fe(III)-rich smectites; Supplementary Table 3, indicating the crystal chemical properties
567 of the natural smectites mentioned in this study; and Supplementary Table 4, providing data related
568 to the dissolution of SBId1 and Nau-1, which were obtained from the literature and used to calculate
569 the Gibbs free energies (shown in Figure 6).

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718 **Role of the crystal chemistry on the dissolution kinetics of Fe(III)-rich smectites**

719 D. Masson¹, V. Robin¹, E. Joussein¹, E. Tertre² & F. Baron²

720 ¹Université de Limoges, E2Lim UR 24133, 123 av. A. Thomas, 87060 Limoges Cedex, France

721 ²Université de Poitiers, IC2MP UMR CNRS 7285, 4 rue M. Brunet, 86022 Poitiers Cedex, France

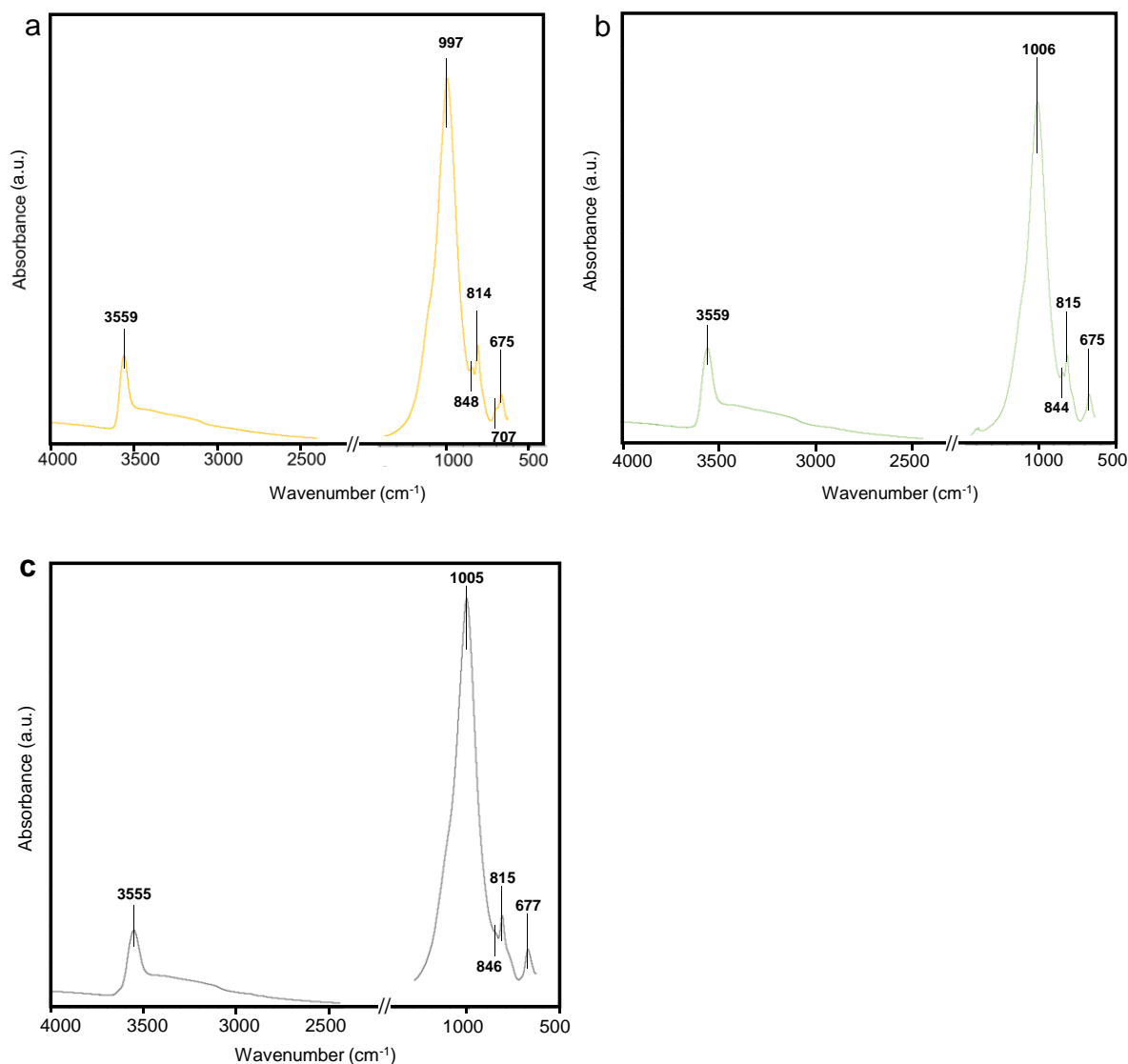
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SUPPLEMENTARY MATERIAL

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725 1. Additional description of initial Fe(III)-rich smectites
726 1.1. Infrared spectroscopy analysis



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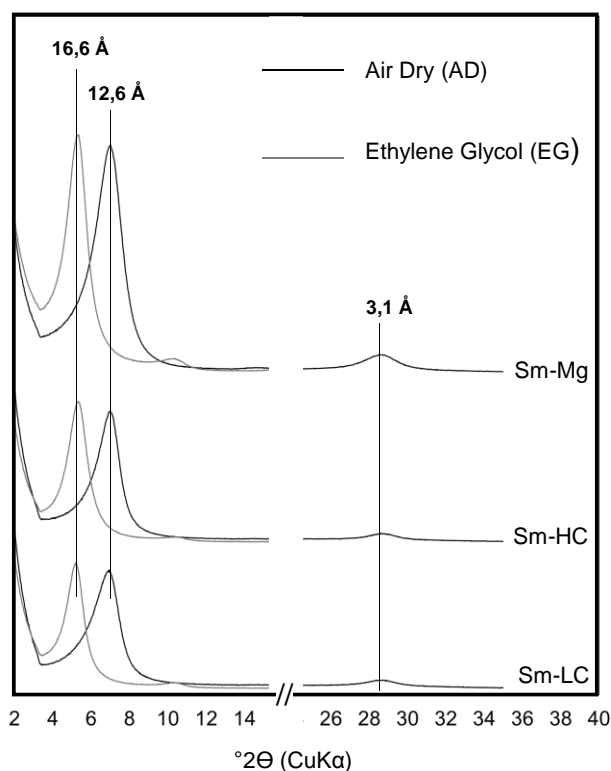
729 Figure S2: MIR Spectra of synthetic samples corresponding to Sm-HC (charge = 1.14) (a), Sm-LC (charge = 0.66) (b) and Sm-
730 Mg (charge = 1.38) (c).

731 The vibrations at 3560 cm⁻¹, 816 cm⁻¹ and 845 cm⁻¹ are characteristic of di-octahedral environment.
732 The stretching $\nu\text{Fe}^{3+}\text{-OH-Fe}^{3+}$ vibration and the bending $\delta\text{Fe}^{3+}\text{-OH-Fe}^{3+}$ vibration correspond to the
733 3560 cm⁻¹ and 816 cm⁻¹ positions respectively. Also, the 845 cm⁻¹ band was usually observed for
734 nontronite. The bands in 1000 cm⁻¹ region correspond to the $\nu\text{Si-O}$ vibration. This vibration shifts
735 toward higher wavenumbers as amount of Fe(III) for Si(IV) substitutions increases. The 677 cm⁻¹ and
736 707 cm⁻¹ bands are also linked in part to the amount of tetrahedral Fe(III). Intensity of 707 cm⁻¹ band
737 increases as the amount of tetrahedral Fe increases. So, the band was displayed on Sm-HC spectrum
738 but was not visible on Sm-Mg and Sm-LC spectra as a result of lower amount of tetrahedral Fe(III) in
739 these two structures. The low content of Mg in Sm-Mg sample not allowed to observe bands
740 involving Mg.

741 1.2. X-ray diffraction analysis

742 The oriented preparation was used to analyze the synthetic clays to ensure the expression of
743 reflections corresponding to the 001 plan. The diluted suspensions of synthetic Na-saturated samples
744 were placed on a glass slide; so, clays were oriented according to their c-axis.

745 The XRD patterns of oriented preparations of initial minerals in the air-dried (AD) conditions, and
746 after the ethylene-glycol (EG) solvation were recorded using a Bruker D8 advance diffractometer
747 (CuK α , 40 kV, 40 mA). The XRD patterns were obtained using a step size of 0.025 $^{\circ}2\theta$ over the 2-35 $^{\circ}2\theta$
748 range and a counting time of 0.6 s as acquisition conditions.



749
750 Figure S3: XRD patterns recorded for the oriented preparations of synthetic samples after Na saturation. Patterns recorded
751 in air-dry (AD) and after ethylene-glycol solvation (EG) are represented by black line and grey line, respectively.

752 The oriented preparation of the three synthetic samples exhibited a 001 reflection at 12.6 Å and a
753 004 reflection at 3.1 Å in air-dry (AD) condition. These two reflections were rational and the apparent
754 001 distance indicated that most of the layers were in mono-hydrated state. No other crystalline
755 phases were detected. After ethylene-glycol (EG) solvation, the XRD patterns of Na-saturated
756 samples exhibited a d_{001} of 16.6 Å, which corresponds to two layers of EG molecules. All observations
757 confirm the synthesis of minerals with a smectitic behavior.

758 1.3. Thermodynamic constants

759 An equilibrium constant was associated with each dissolution equation for Fe(III)-rich smectites. The
760 equilibrium constants were determined using a computer tool (ClayTherm) developed by Blanc et al.
761 (2021). This tool is dedicated to estimating the thermodynamic properties of anhydrous and
762 hydrated clay minerals. It combines several previously published estimation models (Blanc et al.,
763 2015; Gailhanou et al., 2017; Vieillard et al., 2019) and is used to predict equilibrium constants for
764 clay minerals and to compare the calculated thermodynamic properties with solubility data selected
765 from the literature. It is based on a combination of determination of anhydrous (Enthalpy, entropy
766 and heat capacity), hydration (enthalpy and entropy of hydration reactions) and bulk water

767 thermodynamic properties. The model for entropy and heat capacity estimation is based on a
768 method of decomposition in polyhedral units, while it is based on the electronegativity scale for
769 enthalpy.

770 2. Experiments performed with the synthetic Fe(III)-rich smectites.

771 A total of 15 flow experiments were carried out with Fe(III)-rich synthetic smectites. Additional
772 experiments were carried out to assess the reproducibility of the results obtained from the two
773 reactors.

774

775 Table S2: Experimental conditions and results of flow-through dissolution experiments at steady state.

Experiment †	Mass (mg)	Flow rate (mL.s ⁻¹).10 ⁻³	SS days	pe output	pH input	pH output	[Si] μM	[Fe] μM	[Mg] μM	Log R _{Si}	Log R _{Fe}	ΔG kcal.mol ⁻¹
Sm-HC-1.8-A	40	1.08	12	13.5	1.85	1.87	83.47	53.53		-9.17	-9.09	--5.05
Sm-LC-1.8-A	40	1.05	17	13.6	1.85	1.90	67.24	41.50		-9.34	-9.26	-5.24
Sm-LC-1.8-B	40	0.77	13	13.7	1.80	1.84	85.08	56.58		-9.40		
Sm-Mg-1.8-A	40	1.01	14	13.7	1.82	1.87	83.78	51.43	5.25	-9.23	-9.05	-16.02
Sm-HC-2-A	30	1.08	10	13.5	2.04	2.08	37.16	24.93		-9.59	-9.63	
Sm-HC-2-B	30	0.73	14	13.3	2.01	2.06	63.14	43.05		-9.58	-9.69	-3.74
Sm-LC-2-A	30	1.06	12	13.3	2.04	2.08	14.38	7.71		-10.12	-10.21	-9.14
Sm-Mg-2-A	40	1.09	10	13.7	2.01	2.08	64.61	38.43	6.56	-9.48	-9.43	-14.81
Sm-HC-3-A	40	1.06	19	11.9	3.03	2.95	4.57	1.15		-10.72	-	-7.57
Sm-HC-3-B	40	0.75	24	12	3.03	2.97	6.72			-10.71	-	
Sm-LC-3-A	40	1.09	31	12.3	3.03	2.93	3.93	1.38		-10.80	-	-7.84
Sm-Mg-3-A	45	1.13	18	12.1	2.96	2.91	6.05	1.12	0.48	-10.65	-	-18.47
Sm-HC-4-A	45	1.08	19	10.8	4.00	3.91	3.65	0.02*		-10.88	-	-6.78
Sm-LC-4-A	45	1.11	30	11.2	4.00	3.96	2.99	0.03*		-10.96	-	-7.36
Sm-Mg-4-B	60	0.76	16	10.2	4.01	4.08	5.69	0.02*	0.15	-11.00	-	-17.03
Sm-Mg-4-A	45	1.10	18	10.2	4.01	4.06	3.15			-10.96		
Sm-HC-5-B	70	1.09	21	9.4	5.4	5.48	1.55	bdl		-11.45	-	-1.81
Sm-LC-5-B	85	0.79	28	9.4	5.49	5.31	2.26	bdl		-11.54	-	-3.96
Sm-Mg-5-B	85	0.75	20	8.5	5.49	5.32	2.51	bdl	0.05	-11.51	-	-13.19

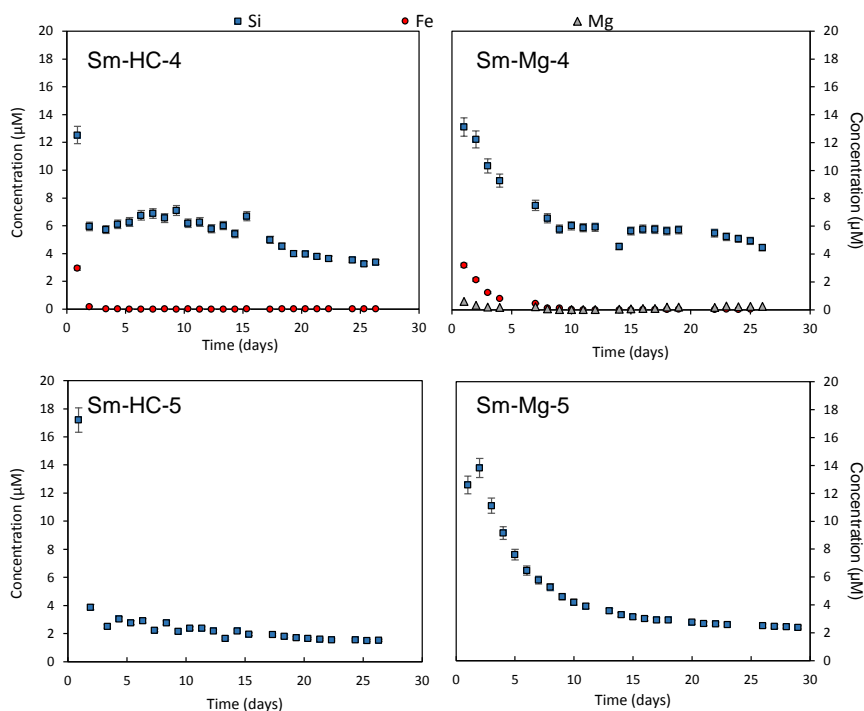
† Labels indicate: Sm = smectite; HC = high charge; LC = low charge, Mg = magnesium; 1, 2, 3, 4, 5 = pH; A = reactor type A, B = reactor type B.
SS: days from the beginning of the experiment to steady state.

pe: redox potential

*Semi quantitative concentrations measured between limit of quantification and limit of detection (LD_{Fe} and LD_{Mg} = 0.01 μM).

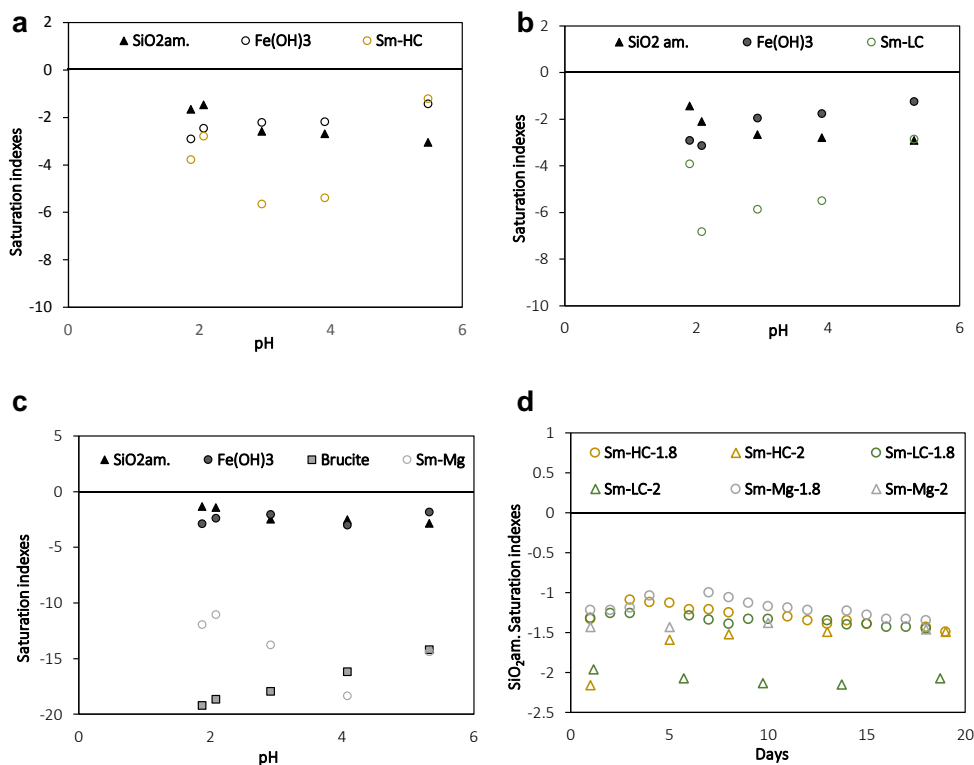
bdl: below detection limit.

777 3. Output solution analysis: experiments performed at pH 4 and pH 5.5 with Sm-HC and Sm-Mg.



778
779 Figure S4: Evolution of Si, Fe, and Mg aqueous concentrations, measured as a function of time in the output solutions for
780 dissolution experiments performed at pH 4 and 5.5 with Sm-HC and Sm-Mg. Concentrations of Fe and Mg are below
781 quantification limits (1.27 μM and 0.5 μM respectively).

782 4. Saturation indexes of the output solutions



783
784 Figure S5: Variation with pH of the saturation indexes of the output solutions obtained at the stationary state for
785 experiments performed with (a) Sm-HC (b) Sm-LC and (c) Sm-Mg. Variation with time of saturation indexes of output

786 solutions relative to amorphous silica for experiments carried out with the three synthetic clay minerals and performed at
787 pH 1.8 and pH 2 (d).

788 Saturation indexes of the output solutions with respect to amorphous silica, Fe ($\text{Fe}(\text{OH})_3$) and Mg
789 (Brucite) -bearing phases and each synthetic smectite were determined at steady state for each pH
790 condition (Fig. S4 a, b, c). Iron oxide $\text{Fe}(\text{OH})_3$ was chosen as Fe-bearing phase due to their highest
791 instability among the iron oxyhydroxides available in Thermoddem database. Saturation indexes of
792 the output solutions with respect to the amorphous silica were determined in function of time for
793 experiments performed at pH 1.8 and 2 (Fig. S4d), to control the solution saturation when the Si
794 concentration measured in output solution was maximal. Throughout the experiments, output
795 solutions were always undersaturated with respect to these phases.

796

797 5. FTIR spectroscopy analysis of dissolved Fe(III)-rich smectites

798 Table S3: Positions of ν Si-O and ν OH bands and relative intensities of $[4]Fe(III)-O$, 1100 cm^{-1} , and 3150 cm^{-1} bands for
799 initial and

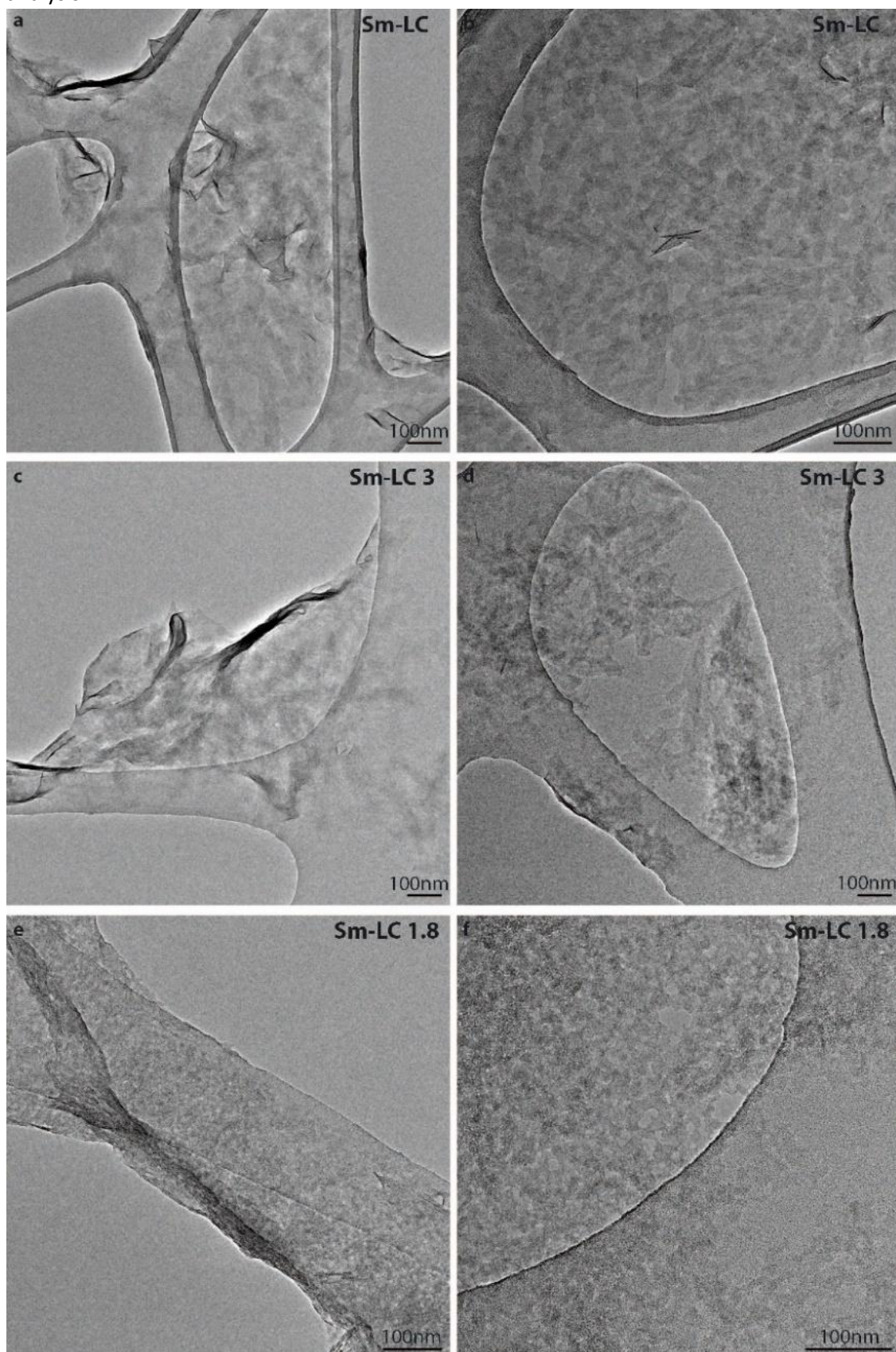
Samples	νSi-O	νOH	$[4]Fe(III)-O$	1100 cm^{-1}	3150 cm^{-1}
Sm-HC	997	3559	++++	ABS	-
Sm-HC-5	1003	3561	+++	ABS	-
Sm-HC-4	1005	3566	+++	ABS	-

800 altered synthetic Fe(III)-rich smectites samples at various pH values.

801	Sm-HC-3	1004	3563	++	ABS	+
802	Sm-HC-2	1004	3565	+	ABS	++++
	Sm-HC-1,8	1010	3567	+	+++	+++
	Sm-LC	1006	3559	-	ABS	-
	Sm-LC-5	1004	3560	-	ABS	+
	Sm-LC-4	1008	3564	-	ABS	+
	Sm-LC-3	1008	3565	-	ABS	+
	Sm-LC-2	1008	3567	-	ABS	+++
	Sm-LC-1,8	1012	3568	-	ABS	++
	Sm-Mg	1005	3555	ABS	ABS	-
	Sm-Mg-5	1010	3558	ABS	ABS	-
	Sm-Mg-4	1009	3558	ABS	ABS	-
	Sm-Mg-3	1010	3558	ABS	ABS	-
	Sm-Mg-2	1012	3562	ABS	ABS	++++
	Sm-Mg-1,8	1015	3563	ABS	+++	+++

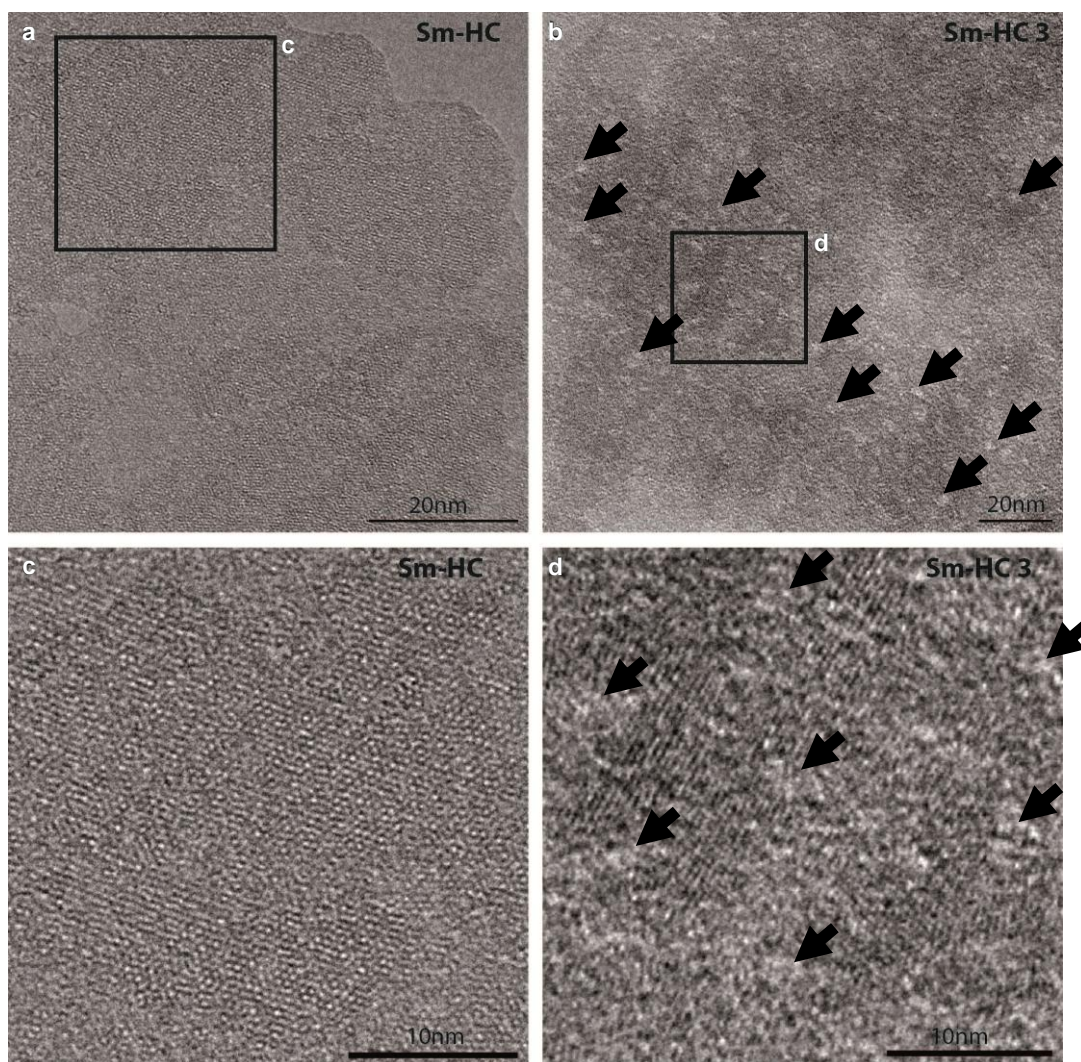
ABS: band is not present on the spectrum.

803 6. Morphological and crystal chemical evolutions of Fe(III)-rich particles observed by (HR)TEM
804 analysis



805
806 Figure S6: TEM Observations of initial Sm-LC particles (a, b) and of Sm-LC particles altered at pH 3 (c, d) and 1.8 (e, f).

807



808

809 Figure S7: HRTEM Observations of (a) initial Sm-HC particles, (b) altered Sm-HC particles at pH 3, (c) zoom on the structure
810 of Sm-HC initial particles, and (d) zoom on the structure of Sm-HC particles altered at pH 3. Arrows point at the zones where
811 amorphization is observed (loss of well-arranged atomic structure), corresponding to whitish spots on figure (b).

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815 7. Properties of natural smectites mentioned in this study

816 Table S4: Details relative to the structural formula of the natural smectites taken from the literature.

Structural formulas of Natural Fe(III)-rich smectite	Global charge (per O₂₀(OH)₄)	Nature and % tetrahedral charge	Nature and % octahedral charge	Tetrahedral Si/Fe ratio	Global Si/Fe ratio
NAu-1 $(\text{Si}_{6.98}\text{Al}_{1.02})(\text{Al}_{0.29}\text{Fe}_{3.68}\text{Mg}_{0.04})\text{O}_{20}(\text{OH})_4\text{M}^{+}_{1.06}$ (Gainey et al., 2014)	1.06	Al (III) → Si 96	Mg → Fe (III) 4		1.89
Structural formulas of Natural Al-rich smectites					
SBId1 $(\text{Si}_{7.148}\text{Al}_{0.852})(\text{Al}_{3.624}\text{Fe}_{0.224}\text{Mg}_{0.18})\text{O}_{20}(\text{OH})_4\text{M}^{+}_{0.948}$ (Robin et al., 2016)	0.95	Al (III) → Si 90	Mg → Al (III) 10		31.9
FEBEX $(\text{Si}_{7.82}\text{Al}_{0.18})(\text{Al}_{2.9}\text{Fe}_{0.36}\text{Mg}_{0.88})\text{O}_{20}(\text{OH})_4\text{M}^{+}_{0.68}$ (Cappelli et al., 2018)	0.68	Al (III) → Si 26.5	Mg → Al (III) 73.5		21.7
SAz-1 $(\text{Si}_{7.70}\text{Al}_{0.30})(\text{Al}_{2.77}\text{Fe}_{0.17}\text{Mg}_{1.11})\text{O}_{20}(\text{OH})_4\text{M}^{+}_{1.25}$ (Amram and Ganor, 2005)	1.25	Al (III) → Si 24	Mg → Al (III) 76		45.3

817

818

819 8. Data from studies used to calculate the Gibbs free energies for dissolution of natural smectites
 820 Data related to the dissolution of FEBEX smectite were directly extracted from Cappelli et al. (2018)
 821 study.

Natural Smectites	Beidellite SBId1 Robin et al., 2015	Nontronite NAU-1 Gainey et al., 2014
Dissolution equations	$(\text{Fe}_{0.224}\text{Si}_{7.148}\text{Al}_{4.476}\text{Mg}_{0.18}\text{O}_{20}(\text{OH})_4)^{-0.948} + 15.408\text{H}^+ + 4.592\text{H}_2\text{O} = 0.224\text{Fe}^{3+} + 4.476\text{Al}^{3+} + 0.18\text{Mg}^{2+} + 7.148\text{H}_4\text{SiO}_4$	$(\text{Fe}_{3.68}\text{Si}_{6.98}\text{Al}_{1.31}\text{Mg}_{0.04}\text{O}_{20}(\text{OH})_4)^{-1.03} + 16.08\text{H}^+ + 3.92\text{H}_2\text{O} = 3.68\text{Fe}^{3+} + 1.31\text{Al}^{3+} + 0.04\text{Mg}^{2+} + 6.98\text{H}_4\text{SiO}_4$
Log $K_{(25^\circ\text{C})}$ *	7.58	-4.05
[Si] mM	$9.86 \cdot 10^{-3}$, $4.56 \cdot 10^{-3}$, $3.20 \cdot 10^{-3}$	3.248, 0.830, 0.315
[Al] mM	$7.08 \cdot 10^{-3}$, $3.74 \cdot 10^{-3}$, $1.90 \cdot 10^{-3}$	0.752, 0.573, LD [‡]
[Mg] mM	LD [‡] , LD [‡] , LD [‡]	0.01, 0.01, 0.18
pH	1.07, 1.85, 2.77	1.10, 1.88, 3.62

822 Table S5: Data related to the dissolution of SBId1 and Nau-1 at 25°C

823 * The equilibrium constants for the natural smectites were computed following the method
 824 proposed by Blanc et al. (2021).

825 ‡ LD=limit detection: when the concentrations of elements were not available in the study, the
 826 detection limit values were used.

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