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1 **Experimental study of smectite interaction with metal iron**
2 **at low temperature: 1. Smectite destabilization.**

3
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19
20 **KEYWORDS:** nuclear waste disposal, engineered barrier, clay barrier, iron-clay interactions,
21 iron corrosion, clay stability, X-ray diffraction, smectite.

ABSTRACT

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23
24 Interaction between metal iron and a variety of natural and synthetic smectites samples with
25 contrasting crystal chemistry was studied by scanning electron microscopy and X-ray
26 diffraction (XRD) from experiments conducted at 80°C. These experiments demonstrate an
27 important reactivity contrast as a function of smectite crystal chemistry. An XRD
28 quantification method involving the use of an internal standard allowed quantification of the
29 relative proportion of smectite destabilized as a function of initial pH conditions as well as of
30 smectite structural parameters. In mildly acidic to neutral pH conditions, a significant
31 proportion of metal iron is corroded to form magnetite without smectite destabilization. Under
32 basic pH conditions, smectite and metal iron are partly destabilized to form magnetite and
33 newly-formed 1:1 phyllosilicate phases (odinite and crondstedtite). Systematic destabilization
34 of both metal iron and smectite is observed for dioctahedral smectites while trioctahedral
35 smectites are essentially unaffected under similar experimental conditions. Smectite reactivity
36 is enhanced with increasing Fe^{3+} content and with the presence of Na^+ cations in smectite
37 interlayers. A conceptual model for smectite destabilization is proposed. This model involves
38 first the release of protons from smectite structure, $\text{MeFe}^{3+}\text{OH}$ groups being deprotonated
39 preferentially and metal iron acting as proton acceptor. Corrosion of metal iron results from
40 its interaction with these protons. Fe^{2+} cations resulting from this corrosion process sorb on
41 the edges of smectite particles and lead to induce the reduction of structural Fe^{3+} and migrate
42 into smectite interlayers to compensate for the increased layer charge deficit. Interlayer Fe^{2+}
43 cations subsequently migrate to the octahedral sheet of smectite because of the extremely
44 large layer charge deficit. At low temperature, this migration is favored by the reaction time
45 and by the absence of protons within the di-trigonal cavity. Smectite destabilization results

- 46 from the inability of the tetrahedral sheets to accommodate the larger dimensions of the newly
47 formed trioctahedral domains resulting from the migration of Fe^{2+} cations.

INTRODUCTION

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In some of the “multi-barriers” concepts envisaged for the storage of high- and intermediate-level and/or long-lived nuclear waste, metallic containers filled with vitrified nuclear waste are placed in a confinement barrier itself surrounded by a geological barrier. The reactive components of the engineered and geological barriers are clays (mainly smectites) while metallic containers could be made up of iron. To predict the long-term properties of these clay barriers, it is thus essential to study the interactions between clay minerals, and more especially smectite, and metal iron as the corrosion of the metallic canister could induce in turn the destabilization of the clay minerals.

Studies of these iron-clay interactions have shown indeed the partial but systematic destabilization of the initial clay material and the subsequent crystallization of reaction products (Habert, 2000; Perronnet, 2001, 2004; Kohler, 2001; Lantenois, 2003; Guillaume *et al.*, 2003). The nature of these reaction products depends on experimental conditions such as temperature and, to a minor extent, the nature of the initial clay material. When smectite is used, iron-rich chlorite-like species are synthesized at high temperature (300°C - Guillaume *et al.*, 2003) whereas iron-rich serpentine-like species are obtained for temperatures more realistic in the context of nuclear waste disposal (80°C - Habert, 2000; Perronnet, 2001, 2004; Lantenois, 2003). Newly formed 1:1 phyllosilicates with low iron content were also identified by Kohler (2001) after reaction between iron metal and kaolinite/smectite mixtures at 80°C.

As reaction pathways appear to vary significantly as a function of temperature (Guillaume *et al.*, 2003; Lantenois, 2003), it is especially important to work at temperatures similar to those expected during storage lifetimes, thus generally excluding medium-to-high temperature experiments (>200°C). Experimental conditions have been chosen to mimic those of the repository, and experiments were thus performed in an anoxic and reducing

73 environment. The clay materials used for this study were essentially natural smectites which
74 have swelling and self-healing abilities and cation retention properties suitable for engineered
75 barriers. To promote the reactivity of clays so that significant reaction progress could be
76 obtained on a laboratory-compatible timescale, the water/solid ratio was significantly
77 increased.

78 A method has been developed to quantify the amount of smectite destabilized as a
79 result of its interaction with metal iron. The aim of the present study was to determine the role
80 of the nature of clay minerals on the contrasting reactivity observed during their hydrothermal
81 reaction with iron metal by using a variety of starting materials. Specifically, the structural
82 characteristics responsible for these differences were sought, together with the mechanism of
83 clay destabilization. The companion paper (Lantenois *et al.*, 2005) will describe the crystal-
84 chemistry of newly-formed phases.

85

86 MATERIALS AND METHODS

87

88 *Materials*

89

90 A variety of natural and synthetic smectite samples with contrasting crystal chemistry
91 were used in the present study. These samples were selected to include both di- and
92 trioctahedral varieties, smectite with octahedral or tetrahedral substitutions, and to cover a
93 wide range of chemical composition, focusing on the iron content. Chemical compositions of
94 selected samples are reported in Table 1. Untreated bulk samples were ground in an agate
95 mortar to increase their reactivity, but samples were neither size-fractionated nor purified.

96 Synthetic clays were crystallized from gels under hydrothermal conditions. Gels were
97 prepared following a method adapted from Hamilton and Henderson (1968) using tetraethyl

98 orthosilicate (TEOS), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, HNO_3 , Na_2CO_3 ,
99 NH_4OH and ethanol. All reagents had a 99% minimum grade. After dissolution of Al- and
100 Mg-nitrates and of Na_2CO_3 in nitric acid, TEOS and ethanol were added. A precipitate was
101 obtained by neutralizing the resulting solution at $\text{pH} \sim 6$ with addition of NH_4OH . This
102 precipitate was dried at 80°C for 24 hours, ground in an agate mortar and heated to 400°C to
103 remove nitrates and carbonates and to obtain a gel composed essentially of Al, Mg, Si and Na
104 oxides. SapFe08 saponite was synthesized from such gels in a cold-sealed pressure vessel.
105 Gel and deionized water were introduced in a 2:1 weight ratio in a silver tube itself placed in
106 the vessel heated at 400°C for one month at an estimated pressure of 100 MPa (Suquet *et al.*,
107 1977). The SbS-1 beidellite was synthesized in an internally heated pressure vessel. 600 mg
108 of gel were mixed to 1.3 g of a NaOH solution (0.2N) in a gold tube. The tube was then
109 sealed and heated to 350°C under 22 MPa for 10 days (Kloprogge *et al.*, 1999). After cooling
110 of the vessels, the solid products were extracted from the reaction tubes, dried at 80°C
111 overnight, and ground before structural and chemical characterization using X-ray diffraction
112 (XRD) and energy dispersive X-ray fluorescence spectroscopy (EDS) on a transmission
113 electron microscope (TEM).

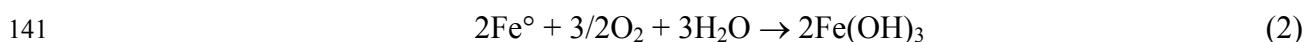
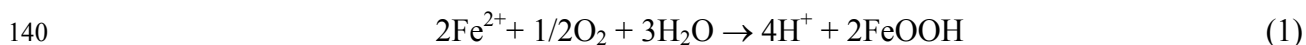
114 To better assess the role of the interlayer composition on the reaction rate K-, Na-, and
115 Ca-saturated specimens were prepared for samples SWy-2, Garfield, and SAz-1. The cation
116 exchange procedure was performed at room temperature by immersing the ground clay
117 sample in 1M KCl, NaCl or CaCl_2 aqueous solutions. After 12 hours of contact, the solid was
118 extracted by centrifugation. The saturation procedure was repeated four times. The excess
119 chloride was then removed by washing the sample five times with distilled water (K- and Ca-
120 saturated samples). Na-saturated samples were washed once in ethanol, and then dialysed in
121 deionized water for one week.

122

123 *Experimental*

124

125 For the iron-clay interactions, 0.6 g of the clay powder were mixed with 0.6 g of metal
126 iron powder (10 μm maximum size, Merck[®] product for analysis) to maximize the contact
127 surface between iron and clay particles. The large amount of metal iron was intended also to
128 promote reducing conditions during the experiments. 30 mL of water were added to this
129 initial mixture. Deionized water (with a resistivity $>18\text{M}\Omega\text{ cm}^{-1}$) was used to allow studying
130 the final solution composition. Samples were prepared in a MBraun[®] glove box equipped with
131 copper catalysts to eliminate O_2 , and a MBraun[®] O_2 control system. Partial pressure of O_2 was
132 lower than 1 ppm during sample preparation. Deionized water was degassed with Argon for
133 one hour prior to its introduction in the glove box and all products were allowed to stay in the
134 glove box for 24 hours to equilibrate with the glove box atmosphere. Starting products were
135 then placed in 40 mL Nalgene[®] reactors. Because these reactors are oxygen porous, a “double
136 enclosure system” was used where the Nalgene[®] reactors were inserted into larger Teflon[®]
137 reactors which contain metal iron powder, FeSO_4 and water. Any oxygen entering the Teflon
138 reactors was thus eliminated according to reactions (1) and (2) with ferrous and metal iron,
139 respectively (Aogaki, 1999).



142 The two reactors were tightly closed within the glove box and subsequently heated at
143 80°C for 45 days outside of the glove box. Additional experiments were also performed for 5,
144 15, 30, 60, 90 and 120 days on selected samples (Garfield, SbId, SWy-2 and SapCa-2). At the
145 end of the reactions, reactors were cooled down to room temperature and opened in air, the
146 solution pH being measured immediately. The solution was subsequently filtered ($0.45\ \mu\text{m}$)

147 and acidified for chemical analysis, whereas the solid fraction was dried at 80°C overnight
148 and ground.

149 Filtered solutions were analyzed for major and trace elements (Si, Al, Fe, Mg, Ti, Na,
150 Ca and K) with an ICP-AES Jobin-Yvon ULTIMA spectrometer. Scanning electron
151 microscopy (SEM) was performed using a JEOL 6400 microscope. Samples were covered
152 with a Au film before observation to avoid charge build up. TEM was performed using a
153 JEOL 2000 FX microscope operated at 200 kV. Samples were prepared as a suspension in
154 deionized water, a drop of this suspension being dried on copper grids covered with a carbon
155 film.

156 Powder XRD patterns were recorded in transmission geometry using $\text{CoK}\alpha$ radiation
157 (35 mA, 35 kV) to avoid iron fluorescence. The use of an INEL CPS 120 curved position
158 sensitive detector allowed recording simultaneously the diffracted intensity over a $4\text{--}50^\circ 2\theta$
159 range with a step size of 0.03° . The non-linearity of the detector was corrected (Roux and
160 Wolfinger, 1996). A 0.5 mm diameter Lindemann glass tube was used to hold the sample
161 powder.

162 Infrared (IR) spectra were recorded over the $650\text{--}4000\text{ cm}^{-1}$ range with a 2 cm^{-1}
163 resolution using a Nicolet Magna-IR Fourier transform spectrometer equipped with a Global
164 SiC source and a DTGS detector. The spectrometer was purged with dry air prior to data
165 collection to remove most of atmospheric H_2O . The sample was finely ground in an agate
166 mortar, and 0.5 mg of the resulting powder was mixed to 150 mg of KBr previously dried at
167 120°C for 24 hours. The mixture was homogenized and pressed in an evacuable die to
168 prepare a 12 mm diameter pellet. Decomposition of the IR spectra in the OH bending region
169 ($700\text{--}900\text{ cm}^{-1}$) was performed with Peak-Fit (v4.05).

170 The cation exchange capacity (CEC) was measured using the copper complex method
171 (Gaboriau, 1991). 600 mg of sample were suspended for 12 hours in 25 mL of a 0.02 N

172 ethylene di-amine copper complex ($\text{Cu}(\text{EDA})_2\text{Cl}_2$) solution. After centrifugation, the Cu
173 concentration in solution was measured using a 905-GBC atomic absorption
174 spectrophotometer from GBC Scientific Equipment.

175

176 *Quantification of the relative proportion of smectite destabilized after reaction*

177

178 To estimate reaction progress, the amount of residual smectite was quantified by XRD
179 using the internal standard technique adapted to clays by Hillier (2000). As recommended by
180 this author, each sample was mixed with 10% of a corundum internal standard (particle size
181 $< 50\mu\text{m}$), dry ground in an agate mortar for 10 minutes and then introduced in the Lindeman
182 glass tube. The use of a glass tube in transmission geometry allows optimizing sample
183 disorientation. Segregation due to particle size and/or particle density was minimized by
184 careful grinding and mixing. Absorption corrections have not been considered because
185 absorption, which is closely related to sample chemical composition, is similar before and
186 after reaction.

187 The (001) reflection of smectite was not selected for quantification, because its
188 intensity strongly depends on smectite hydration state and thus on the chemical composition
189 of smectite interlayers, which can be modified during the reaction. The amount of residual
190 smectites was rather quantified by measuring the integrated intensity of the (02,11) band
191 (between 22.0° and $27.0^\circ 2\theta$ $\text{CoK}\alpha$ - Figure 1) before and after reaction, these intensities
192 being normalized to the (012) reflection of corundum ($29.8^\circ 2\theta$ $\text{CoK}\alpha$ - Figure 1).
193 Background was assumed to be linear between 22.0 and $27.0^\circ 2\theta$ and subtracted. If quartz
194 impurities were present, the (100) reflection of quartz ($\sim 24.3^\circ 2\theta$ $\text{CoK}\alpha$) was fitted, and its
195 integrated intensity subtracted from the total integrated intensity. To assess the validity of
196 XRD results, the relative proportion of reacted smectite was also quantified from CEC

197 measurements performed before and after reaction, the observed CEC decrease being directly
198 linked to the amount of destabilized smectite. This assumption was made possible by the non-
199 swelling character of the reaction products (Lantenois, 2003; Lantenois *et al.*, 2005).

200 The amount of residual smectite was also quantified using IR spectroscopy. Over the
201 OH bending frequency range, three bands at 912-920 cm^{-1} , 874-886 cm^{-1} , and 840-850 cm^{-1}
202 correspond to the Al-Al-OH, Al-Fe-OH and Al-Mg-OH vibrations of smectites, respectively
203 (Farmer, 1974; Goodman *et al.*, 1976; Russell and Fraser, 1994; Vantelon *et al.*, 2001). The
204 position reported in the literature for the Fe-Fe-OH band scatters from 820-795 cm^{-1}
205 (Goodman *et al.*, 1976; Cuadros and Altaner, 1998) and overlaps with the Si-O vibrations of
206 quartz at 780 and 800 cm^{-1} (Madejova and Komadel, 2001). To avoid using this problematic
207 band, reaction progress was quantified using IR spectroscopy for Fe-poor smectites only. The
208 quantification method itself requires subtracting a baseline which corresponds to Si-O
209 vibrations in phyllosilicates (Figure 2a – Vantelon *et al.*, 2001). A cubic spline baseline,
210 similar for all samples, was adjusted on both sides of the region of interest (817-822 cm^{-1} and
211 940-945 cm^{-1} , respectively). The 822-945 cm^{-1} range of the baseline-corrected spectra was
212 then fitted with three Gaussian-shaped curves (Figures 2b) corresponding to Al-Al-OH, Al-
213 Fe-OH and Al-Mg-OH vibration modes. Relative proportion of unaltered smectite was
214 estimated from the ratio between the total surface areas determined for these three
215 contributions before and after reaction.

216

RESULTS

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Qualitative evaluation of the reaction progress

Long-term experiments show that the reaction progress reaches a plateau after about 30 days (see below). Except when specifically notified, reactions described in the following section were thus performed for 45 days, without constraining the solution pH. The observed reaction depends on the nature of the initial smectite sample. In particular di- and trioctahedral smectites exhibit contrasting reactivities and will be described separately.

Diocahedral smectites. Although reaction progress varies considerably as a function of the initial smectite sample, a similar effect was observed for all dioctahedral smectites. After 45 days, solution pH was not significantly modified, whereas the chemical composition of the solutions was altered (Table 2). In particular, the concentration in solution of alkali and alkali-earth cations which were initially present in smectite interlayers (Na^+ , Ca^{2+} , and K^+) was significantly increased after reaction (Table 2) together with that of silicon. For smectite samples reacted without metal iron, Si was not detected in solution, and the concentration in solution of alkali and alkali-earth cations after reaction was lower than in similar experiments performed in presence of metal iron (Table 2). In all reacted samples residual metal iron was systematically present together with newly-formed phases (magnetite and 7 Å phyllosilicates – Figure 1a-e). However, iron particles observed in all reacted samples appear corroded as compared to their initial state (Figure 3a,b). In addition, clay particles with a distinct morphology were observed in all reacted samples (Figure 3c). These particles most likely correspond to the newly-formed phyllosilicate phase. Unreacted clay particles were also observed for both montmorillonite and beidellite samples (Figures 3d,e). Accordingly, residual smectite was identified for montmorillonite and beidellite samples from its (02,11)

242 band at $\sim 23^\circ 2\theta$ CoK α (Figure 1a-d). The intensity of this characteristic band was much
243 reduced after reaction for Garfield nontronite sample (Figure 1e), in agreement with the
244 absence of unreacted clay particles in the reacted Garfield sample (Figure 3f).

245 *Trioctahedral smectites*. For saponite samples, solution pH and composition are not
246 significantly modified after 45 days of iron-clay interactions (Table 2). Accordingly, XRD
247 patterns recorded on both unreacted and reacted samples are alike (Figure 1f). In particular,
248 the (02,11) band ($\sim 23^\circ 2\theta$ CoK α) is similar in both samples, an even the (001) reflection
249 ($\sim 7^\circ 2\theta$ CoK α) is practically unaffected. In addition, no extra reflection was visible after
250 reaction. SEM observations support this lack of reactivity as both iron (not shown) and clay
251 particles (Figures 3g,h) appear unaltered after 45 days.

252

253 *Quantification of the extent of smectite destabilization*

254

255 A quantitative estimate of the relative proportion of smectite destabilized after
256 reaction was obtained from XRD results using the internal standard method (Hillier, 2000).
257 Results of this quantification are presented in Table 1. The absolute precision on the relative
258 proportion of smectite destabilized was estimated to be $\pm 10\%$. This estimate corresponds to
259 the standard deviation of twelve measurements obtained for 45 day experiments performed
260 with sample SWy-2.

261 Using this quantitative XRD method it was possible to demonstrate the reactivity
262 contrast as a function of the nature of initial smectite samples. For the different smectites
263 presented in Figure 1, the relative proportion of destabilized smectite scatters indeed from 0-
264 95%. Trioctahedral smectites (SapCa-2 and SapFe08 samples) were essentially unaffected as
265 a result of their interactions with iron, while the dioctahedral smectites were systematically
266 destabilized. Montmorillonite (20 and 50% of destabilized smectite for SAz-1 sample and

267 SWy-2 samples, respectively) and beidellites (40, 60 and 70% of destabilized smectite for
268 CP4, SbId, and Drayton samples, respectively) were less destabilized than ferruginous
269 smectites or nontronites (90 and 95% of destabilized smectite for SWa-1 and Garfield
270 samples, respectively).

271 These quantification results were positively correlated to the estimates made using
272 CEC measurements (Figure 4a). The precision of the CEC determination ($\pm 10\%$), which
273 corresponds to the standard deviation of six measurements obtained for 45 day experiments
274 performed with sample SWy-2, is similar to that of the XRD method. A good correlation was
275 also obtained with the IR quantification results except for the Drayton sample (Figure 4b)
276 which contains a significant proportion of ferric iron (0.47 per $O_{10}(OH)_2$ – Table 1). Precision
277 was estimated from the standard deviation of six measurements obtained for 45 day
278 experiments performed with sample SWy-2. IR measurements of reaction progress were
279 found to be less precise ($\pm 15\%$) than those using XRD and CEC methods mostly as a result of
280 the uncertainty on the baseline determination. In addition, note that IR results obtained on raw
281 materials may be correlated with XRD data only in the absence of kaolinite which exhibits a
282 band at 911 cm^{-1} which may interfere with the Al-Al-OH, Al-Fe-OH and Al-Mg-OH vibration
283 modes.

284 For the three quantification methods, the possible influence of the newly-formed clay
285 phases was neglected. This approximation was justified by the nature (crondstedtite, odinite)
286 of the newly-formed phases (Lantenois, 2003; Lantenois *et al.*, 2005). These 1:1
287 phyllosilicates were indeed non-swelling species thus exhibiting an extremely low CEC. In
288 addition, these phases include a large amount of structural iron. As a result, the (02,11) band
289 of these iron-rich 1:1 phyllosilicates was significantly shifted towards lower angles (at
290 $\sim 4.7\text{ \AA}$) as compared to the (02,11) band of initial smectite samples (at 4.45-4.56 \AA for the
291 whole compositional range). In addition the intensity of the (02,11) band of these iron-rich 1:1

292 phyllosilicates was found to be extremely low, thus not affecting significantly the XRD
293 measurements (Lantenois, 2003; Lantenois *et al.*, 2005). The OH bending bands observed for
294 these iron-rich 1:1 phyllosilicates were also shifted towards lower frequencies (750-800 cm⁻¹
295 – Lantenois, 2003; Lantenois *et al.*, 2005) as compared to initial Al-rich smectites (820-
296 940 cm⁻¹).

297

298 *Kinetics of smectite destabilization*

299

300 XRD quantification of the relative proportion of smectite destabilized after reaction
301 also allowed deriving the kinetics of this destabilization reaction. For example, XRD patterns
302 obtained for samples SbId reacted for 0, 5, 15, 30 and 45 days are presented in Figure 5.
303 These experimental patterns are normalized to the (012) reflection of corundum so that the
304 relative intensity of the (02,11) band can be compared for all samples. The relative proportion
305 of smectite destabilized was estimated from the intensity decrease of this (02,11) band as a
306 function of reaction time (0-120 days). Results are plotted in Figure 6 for four samples (SbId,
307 Garfield, SWy-2 and SapCa-2). As described qualitatively, no reaction was observed for
308 sample SapCa-2. For dioctahedral smectites, the relative proportion of destabilized smectite
309 increases with time to reach a steady-state plateau after 30-45 days. The amount of
310 destabilized smectite obtained after 45 days can be considered as the final one for all
311 smectites. As was qualitatively observed the extent of smectite destabilization varies
312 significantly as a function of the initial samples (50%, 60% and 95% of destabilized smectite
313 for the SWy-2, SbId and Garfield samples, respectively)

314

DISCUSSION

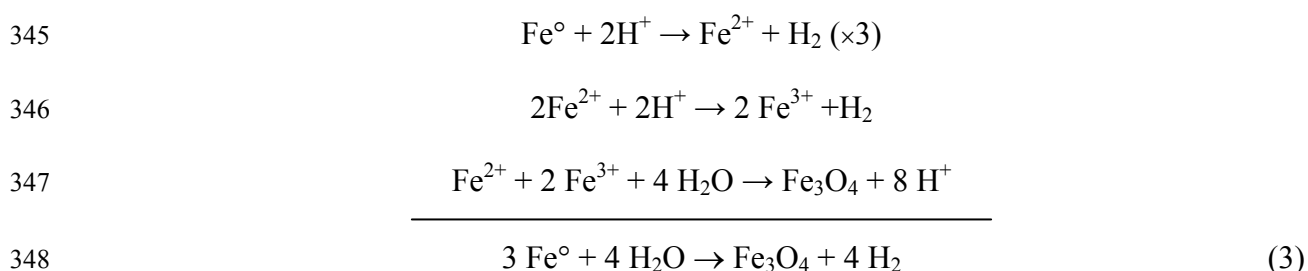
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Quantification by XRD of the relative proportion of destabilized smectite allowed demonstrating that reaction progress strongly depends on the nature of the initial smectite sample, and that reaction kinetics cannot account for the reactivity contrast between different smectite samples. In the following discussion, the origin of these contrasting reactivities will be sought, and the influence of some structural characteristics of smectites will be discussed to hypothesize reaction mechanisms for the destabilization of smectite.

Influence of pH on smectite destabilization

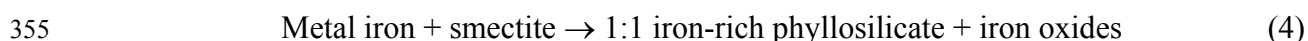
The initial solution pH, which is obtained by equilibrating the different smectite samples in water, depends on the nature of the smectite, and varies from 7.5-10.5 (SbId-1 and SWy-2, respectively – Table 2). To assess the impact of this parameter on reaction progress, the relative proportion of destabilized smectite was determined as a function of the initial pH for sample SWy-2. Initial pH was adjusted by adding HCl or NaOH to the initial mixture. Relative proportion of destabilized smectite is reported in Table 3. When initial pH is basic (8-12 pH range), the nature of the reaction products and the reaction progress are independent on pH (Table 3). Conversely, reaction is dramatically different when initial pH is mildly acidic to neutral. In such case, a large proportion of metal iron is dissolved, whereas iron oxides, identified as magnetite using XRD (data not shown), precipitate extensively. In addition, smectite appears unaffected (Table 3). A similar reaction, with the precipitation of magnetite and the stability of smectite, was observed for SapCa-2 and Garfield samples when initial pH was mildly acidic to neutral (Table 3).

339 Under mildly acidic to neutral pH conditions such as those of the present study
 340 (pH = 6), smectite remains unaltered in presence of metal iron whatever its nature. However,
 341 smectite plays a catalytic role as in the same experimental conditions (45 days, 80°C , initial
 342 pH = 6) metal iron is not destabilized in the absence of smectite whereas in presence of
 343 smectite metal iron is oxidized, most likely from its interaction with solution protons, to form
 344 magnetite according to the following reaction:



349 In our experiments, the production of gaseous H₂ during the reaction was not
 350 observed as Nalgene[®] reactors were H₂ porous.

351 Under more basic pH conditions (pH > 7 obtained from the addition of NaOH if
 352 necessary), the reaction is dramatically different as dioctahedral smectites are involved in the
 353 reaction. Dioctahedral smectites are then destabilized to form new clay phases according to
 354 the following reaction:



356 Under these basic pH conditions, destabilization of dioctahedral smectite is
 357 systematic but the amount of destabilized smectite varies significantly from one sample to the
 358 other most likely as a function of the initial smectite crystal chemistry. Note that except for K-
 359 saturated smectites the equilibration pH of smectite with water is basic. The pH is essentially
 360 unaffected by iron-clay interactions.

361

362 *Influence of smectite crystal chemistry on smectite destabilization*

363

364 *Influence of the di- or tri-octahedral character.* Although initial pH values are alike, and
365 basic, for both di- and tri-octahedral smectites, the reactivity of trioctahedral smectites is
366 strikingly different from that of dioctahedral ones. Dioctahedral smectites are indeed
367 systematically destabilized as the result of their interaction with metal iron whereas
368 trioctahedral smectites remain unaffected under similar experimental conditions (Figures 1,
369 6). This lack of reactivity is independent on the iron content of trioctahedral smectites and on
370 the nature of the interlayer cation.

371 *Influence of structural Fe^{3+} .* As can be seen in Figure 6 and in Table 1, nontronite and
372 ferruginous smectites are thoroughly destabilized as the result of their interaction with metal
373 iron. In both cases, Fe^{3+} is the predominant cation in the octahedral sheet of these 2:1
374 expandable phyllosilicates which exhibit mostly tetrahedral substitutions (Table 1). By
375 contrast, the extent of the destabilization is much reduced for smectites that are not iron-rich,
376 whatever the origin of the layer charge deficit. However, this decrease of reactivity is less
377 important for beidellites (tetrahedral layer charge) than for montmorillonites (octahedral layer
378 charge) for a given Fe^{3+} content. To illustrate further the influence of the amount of structural
379 iron on smectite destabilization, XRD patterns of reacted and unreacted samples are compared
380 in Figures 1 and 7 for dioctahedral smectites with predominant tetrahedral charges
381 (beidellites). Their octahedral Fe^{3+} content which ranges from 0.0-1.9 per $O_{10}(OH)_2$. Relative
382 proportions of destabilized smectites are reported as a function of the Fe^{3+} content in Figure 8.
383 No reaction is observed when no structural Fe^{3+} is present in dioctahedral smectites, and
384 smectite is not destabilized (Figures 7a, 8). The presence of structural Fe^{3+} is thus an essential
385 condition for the destabilization of dioctahedral smectites when in contact with metal iron.
386 The minimum amount of structural Fe^{3+} necessary to induce this destabilization is extremely

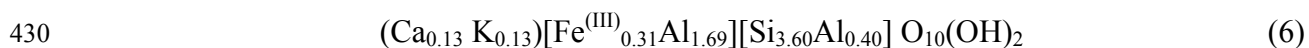
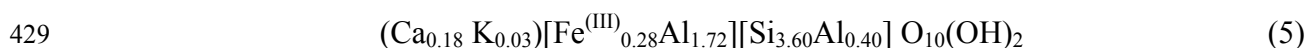
387 low as 60% of samples SbId is destabilized after 45 days of reaction with metal iron, in spite
388 of its limited Fe^{3+} content (0.1 atom per $\text{O}_{10}(\text{OH})_2$). In addition to this essential triggering
389 role, the reactivity of dioctahedral smectite is clearly enhanced by an increased content of
390 octahedral Fe^{3+} (Figure 8). However, this parameter is not the only structural parameter
391 influencing smectite reactivity as, for example, the relative proportion of destabilized smectite
392 is much higher for sample SbId than for sample CP4, in spite of the higher Fe^{3+} content in the
393 latter sample (Figures 1c,d, 8 – Table 1).

394 *Influence of the interlayer cation composition.* The cation composition of smectite interlayers
395 appears as an additional parameter influencing the reactivity of dioctahedral smectites. All
396 samples used in the experiments reported to this point were unprocessed, and Ca^{2+} was
397 usually predominant in their interlayer spaces (Table 1). However, K^+ was also present in CP4
398 and SbId, whereas Na^+ was present in several samples (SbId, SWy-2, SAz-1), and Mg^{2+} in
399 Drayton sample. To assess the influence of the interlayer cation composition on smectite
400 reactivity, three smectite samples (SWy-2, SAz-1 and Garfield) were reacted with metal iron
401 following their saturation with Na^+ , Ca^{2+} , and K^+ . XRD patterns of reacted SWy-2 samples
402 are presented in Figure 9, whereas the relative proportions of smectite destabilized after 45
403 days of reaction with metal iron are reported in Table 4. If Ca-saturated smectites are used as
404 a reference, smectite destabilization is enhanced for Na-saturated smectites whereas it is
405 decreased for K-saturated samples.

406 The reactivity contrast observed as a function of the interlayer cation composition is most
407 likely related to the hydration of smectite which varies as a function of the interlayer cation
408 (Norrish, 1954; Pons *et al.*, 1981). The $d_{(001)}$ basal spacing of K^+ -saturated smectites varies
409 indeed from 12.5-15.5 Å in aqueous solution (Mamy, 1968; Besson and Tchoubar, 1980),
410 whereas that of Ca^{2+} -saturated smectites is 18.6-19.2 Å (Suquet, 1978). The $d_{(001)}$ basal
411 spacing of Na^+ -saturated smectites is not limited (osmotic swelling – Suquet *et al.*, 1981). No

412 significant collapse of smectite interlayers is expected as the ionic strength of the solutions,
 413 and more specifically the concentration of alkali and alkali-earth cations, remains low after
 414 reaction (Table 2). The enhanced reactivity observed for the most hydrated samples ($\text{Na}^+ >$
 415 $\text{Ca}^{2+} > \text{K}^+$) indicates that the ability of solution cations to access smectite interlayers is a key
 416 parameter to smectite destabilization.

417 Accordingly, the interlayer cation composition of samples CP4 and SbId is likely
 418 responsible for their contrasting reactivity which does not seem to be consistent with their
 419 respective Fe^{3+} contents (Figure 8, Table 1). Specifically, the presence of Na^+ in the
 420 interlayers of sample SbId most likely enhances its reactivity as compared to sample CP4 in
 421 spite of the higher iron content in the latter sample. The influence of the cation interlayer
 422 composition may also account for the different reactivity exhibited by populations of particles
 423 observed in sample CP4. Using TEM-EDX, two populations of particles were indeed
 424 differentiated from their morphology, as “rolled” and “flat” particles were identified in this
 425 sample (Figure 10). The chemical analysis of these two types of particles revealed that
 426 although the composition of the 2:1 layers was identical in both cases, the two populations
 427 differed by their interlayer cation composition as the following structural formulae were
 428 derived for “rolled” and “flat” particles, respectively (average values from twelve analyses):



431 After reaction with metal iron, no remnant “rolled” particles were observed and only
 432 “flat” particles persisted. This is likely due to the increased proportion of K^+ in the interlayer
 433 of the latter particles which reduces their reactivity. Note that because long-term experiments
 434 were not performed on homoionic samples, it is not clear if the relative proportion of smectite
 435 ultimately destabilized varies from one cation to the other, or if the nature of the interlayer
 436 cation essentially influences the destabilization rate.

437

438 *Towards a possible model for smectite destabilization*

439

440 *Experimental constrains.* From the above observations, several structural features appear as
441 essential to the destabilization of smectite when in contact with metal iron. First, the smectite
442 should be dioctahedral and should contain octahedral Fe³⁺. In addition, the accessibility of its
443 interlayer space is a key parameter for the apparent reactivity of the dioctahedral smectite.
444 Finally, when comparing experiments run at different pH values, structural protons of the
445 smectite are likely involved in the oxidation of metal iron under neutral-to-alkaline
446 conditions. In mildly acidic to neutral conditions, solution protons are abundant enough so
447 that smectite is used essentially as a catalyst but is not directly involved in the corrosion of
448 iron following Reaction (3). Under high pH conditions, protons are essentially present as OH
449 groups in smectite, as both smectite interlayer and edge sites are essentially deprotonated
450 under such pH conditions.

451 Deprotonation of these hydroxyl groups may occur under a variety of physico-
452 chemical conditions for dioctahedral smectites (Russel, 1979; Jaymes and Bigham, 1987;
453 Heller-Kallai and Rozenson, 1981; Heller-Kallai, 2001 – Figure 11a). In particular, the
454 presence of inorganic proton acceptors, usually alkali halides or alkali hydroxides, has been
455 reported to induce such a deprotonation reaction (Heller-Kallai, 1975a, 1975b, 2001; Russel,
456 1979; Heller-Kallai and Rozenson, 1981; Heller-Kallai and Mosser, 1995). In our case, metal
457 iron is likely the proton acceptor triggering smectite deprotonation. Metal iron is oxidized in
458 turn as the result of its interaction with protons (Figure 11b) according to Reaction (3). The
459 high affinity of metal iron for smectite and their resulting interactions have for example been
460 recognized as causing the oxidation of steel pipes when using clay-containing drilling fluids
461 (Tomoe *et al.*, 1999; Cosultchi *et al.*, 2003). According to this model, both the oxidation of

462 metal iron and the deprotonation of smectite are strongly favored by the accessibility of metal
463 iron to smectite interlayer. With this respect the osmotic swelling commonly observed for Na-
464 saturated smectites significantly enhances the accessibility of metal iron particles to smectite
465 interlayers, thus favoring the deprotonation reaction. In turn, deprotonation increases
466 considerably the layer charge deficit in smectite octahedral sheet and thus enhances their
467 reactivity.

468 Deprotonation thus appears as the driving force for the oxidation of metal ion, and for
469 the initiation of smectite destabilization. Accordingly, the presence of Fe^{3+} in the octahedral
470 sheet of smectite appears as an essential parameter for these two reactions as $\text{MeFe}^{3+}\text{OH}$
471 groups are known to deprotonate preferentially in dioctahedral smectites (Heller-Kallai,
472 1975a, 2001; Russel, 1979; Jaymes and Bigham, 1987). It is not clear however if
473 deprotonation of Fe^{3+} -free dioctahedral smectites is not occurring, or is extremely limited, or
474 if deprotonation is not the limiting step for the destabilization of Fe^{3+} -free dioctahedral
475 smectites. However, although Heller-Kallai (1975a) showed that deprotonation occurs even in
476 Fe^{3+} -free dioctahedral smectite, we have not observed iron corrosion resulting from this
477 process in the SbS-1 experiments.

478 *Destabilization of smectite.* Following its initial deprotonation, destabilization of smectite is
479 probably favored by the presence of Fe^{2+} in solution as a result of the oxidation of metal iron.
480 Specifically, the high affinity of Fe^{2+} for smectite edge surface sites (Tournassat *et al.*, 2005 –
481 Figure 11c) is likely a key factor for the subsequent destabilization of smectite. Following
482 their sorption on these edge sites, Fe^{2+} cations are readily oxidized as shown by Tournassat *et*
483 *al.* (2005), the electron acceptors being octahedral Fe^{3+} from smectite structure (Figure 11c).
484 Note that following their oxidation, sorbed Fe cations may also accept electrons either from
485 solution Fe^{2+} cations or from iron metal to restore their +II valency (Figure 11d). As a result
486 of both its initial deprotonation and of the subsequent reduction of its structural Fe^{3+} , the

487 charge deficit in the octahedral sheet of smectite is dramatically increased and Fe^{2+} cations
488 likely migrate in its interlayers to compensate for the increased layer charge (Figure 11d). The
489 increased concentration of Fe^{2+} in solution resulting from the oxidation of the metal iron also
490 favors a Fe^{2+} -for- Na^+ cation exchange. Such Fe^{2+} -for- Na^+ cation exchange has been shown to
491 occur in reducing environments cations (Kamei *et al.*, 1999).

492 The effective ionic radius of Fe^{2+} cations (0.78 Å – Shannon, 1976) is smaller than the
493 limit size approximated by Heller-Kallai (2001) at 0.85 Å allowing migration of the cations
494 into the silicate layer. It is thus likely that interlayer Fe^{2+} cations actually migrate either into
495 the di-trigonal cavities of smectite tetrahedral sheets or in smectite octahedral sheet (Figure
496 11e). This migration is similar to that of Li^+ cations (0.76 Å – Shannon, 1976) involved in the
497 Hofmann-Klemen test (Hofmann and Klemen, 1950; Greene-Kelly, 1955). The migration of
498 Li^+ from the interlayer to the di-trigonal cavity and further to the octahedral sheet of
499 montmorillonites has been extensively documented (Hofmann and Klemen, 1950; Greene-
500 Kelly, 1955 ; Glaeser and Fripiat, 1976; Madejova *et al.*, 1996, 2000a, 2000b, among others).
501 Heating to 300°C for 24 hours represent optimum experimental conditions for this migration.
502 Migration of other divalent cations with an effective ionic radius similar to that of Li^+ cations
503 has also been described. For example, Cu^{2+} , Ni^{2+} and Zn^{2+} cations (0.73, 0.69 and 0.74 Å,
504 respectively) migrate from montmorillonite interlayers to the di-trigonal cavity between 100-
505 300°C (Heller-Kallai and Mosser, 1995; Mosser *et al.*, 1997; Madejova *et al.*, 1999; Palkova
506 *et al.*, 2003) and to the octahedral sheet at higher temperature (Brindley and Ertem, 1971;
507 McBride and Mortland, 1974; Heller-Kallai and Mosser, 1995; Emmerich *et al.*, 1999).

508 These conditions are much more energetically favorable than those involved in our
509 experiments. However, partial migration of Li at least to the di-trigonal cavity has been
510 reported for Li-saturated montmorillonite heated to 105°C for 24 hours (Madejova *et al.*,
511 1996). In our experiments, three factors compensate for the low thermal energy available. The

512 first one is the extremely strong layer charge deficit which, according to the structural model
513 proposed for smectite destabilization occurring in our experiments, arises both from the
514 deprotonation of hydroxyl groups and from the reduction of structural Fe^{3+} . Note that the need
515 for an octahedral layer charge deficit is the fundamental basis for the migration of Li^+ cations
516 involved in the Hofmann-Klemen test (Hofmann and Klemen, 1950). Furthermore, the
517 positive influence of an increased layer charge deficit on the migration of divalent cations has
518 been reported by Heller-Kallai and Mosser (1995, e.g.). These authors observed indeed an
519 increased amount of Cu in samples that were deprotonated first. As described by Heller-Kallai
520 and Mosser (1995), the positive effect of the initial deprotonation is not restricted to the
521 increased layer charge deficit and the second factor favoring the migration of Fe^{2+} cations is
522 the absence of protons inside the di-trigonal cavity. As a consequence, there is no electrostatic
523 repulsion to the migration of Fe^{2+} cations into the octahedral sheet. Reaction time represents
524 the third factor compensating for the low thermal energy in our experiments. Our experiments
525 lasted indeed for 45 days whereas the common duration of experiments leading to the
526 formation of reduced-charge smectites is 24 hours. Initial migration of Fe^{2+} cations to the di-
527 trigonal cavity is likely favored by an increased undersaturation of the oxygen atoms present
528 at the surface of the 2:1 layers, that is by the existence of layer charge deficit in smectite
529 tetrahedral sheets. Such location of layer charge deficit favors indeed the initial partial
530 dehydration of interlayer Fe^{2+} cations, allowing for the formation of an inner-sphere complex
531 necessary for their migration, and thus accounts for the increased reactivity of beidellite
532 samples as compared to montmorillonite ones for a given iron content (see for example SAz-1
533 and SbId samples – Table 1). The formation of such inner-sphere complexes has been widely
534 documented in hydrated beidellites for monovalent interlayer cations, both from XRD (Ben
535 Brahim *et al.*, 1983a, 1983b, 1984), and infrared (Pelletier *et al.*, 2003) studies, and from
536 Monte-Carlo modeling (Chang *et al.*, 1995; Skipper *et al.*, 1995).

537 In our experiments, migration of Fe^{2+} cations in the octahedral sheet of smectite does
538 not induce a collapse of smectite interlayers as these new octahedral Fe^{2+} compensate
539 essentially for the layer charge deficit resulting from the deprotonation of hydroxyl groups
540 and from the reduction of structural Fe^{3+} , but not for the initial charge deficit of the 2:1 layers.
541 The presence of hydrated interlayer cations, part of which are Fe^{2+} , still compensates for this
542 initial charge deficit, and keeps the smectite interlayers expanded. The migration of Fe^{2+}
543 cations in the octahedral sheet of smectite is rather thought to be responsible for the
544 destabilization of smectites induced by their interaction with metal iron. Destabilization is
545 indeed thought to result from the presence of trioctahedral domains in the octahedral sheet of
546 reacted smectite (Figure 11e). The coexistence of both dioctahedral and trioctahedral domains
547 is widely reported in natural 1:1 phyllosilicates but is limited in 2:1 phyllosilicates (Bailey,
548 1980). The existence of 2:1 phyllosilicates with a mixed di- and tri-octahedral occupancy is
549 indeed essentially limited to mica species exhibiting a tetrahedral charge (muscovite-
550 zinnwaldite or muscovite-phlogopite series – Monier and Robert, 1986). In such species the
551 increased dimensions of the octahedral sheet in the **ab** plane is accommodated by the
552 reduction of the tetrahedral tilt angle. In smectites, and more especially in montmorillonites,
553 the amount of tetrahedral substitutions is limited and the tetrahedral tilt angle is thus
554 minimum. As a consequence, such 2:1 phyllosilicates are unable to accommodate the
555 presence of trioctahedral domains containing large cations and are thus destabilized by the
556 migration of Fe^{2+} cations in their octahedral sheet.

557 According to the conceptual model hypothesized for smectite destabilization, the lack
558 of reactivity of trioctahedral smectites results from three main factors. The first two are
559 related to the absence of Fe^{3+} cations in the octahedral sheet of these smectite samples. The
560 first effect of this absence is to make deprotonation of hydroxyl groups more difficult as, in
561 dioctahedral smectites, $\text{MeFe}^{3+}\text{OH}$ groups are known to deprotonate preferentially (Heller-

562 Kallai, 1975a, 2001; Russel, 1979; Jaymes and Bigham, 1987). The second effect is the
563 absence of cations that may be reduced in the octahedral sheet of trioctahedral smectites. The
564 combination of these two effects prevents building a strong layer charge deficit in the
565 octahedral sheet of trioctahedral smectites. The third factor leading to the lack of reactivity of
566 trioctahedral smectite is the obvious impossibility for cations to migrate in this octahedral
567 sheet which is fully occupied.

568 *Influence of structural Fe on smectite destabilization.* In the above conceptual model for
569 smectite destabilization, the effect of an increased proportion of structural iron on smectite
570 destabilization is dual. The first effect arises from the increased proportion of $\text{MeFe}^{3+}\text{OH}$
571 groups that will readily deprotonate when in contact with metal iron. The larger number of
572 deprotonated hydroxyl groups requires in turn the presence of a larger number of Fe^{2+} cations
573 in smectite interlayers to balance the charge. The second effect is directly related to the
574 increased proportion of structural Fe^{3+} in smectite octahedral sheet. This allows for a larger
575 proportion of smectite octahedral sheets to present dramatic charge deficit leading to the
576 migration of interlayer Fe^{2+} in the 2:1 layer, thus destabilizing it. On the other hand, the
577 presence of Fe^{3+} in smectite tetrahedral sheet does not enhance smectite reactivity as these
578 cations cannot be reduced because of steric constrains arising from their tetrahedral
579 environment.

580

581 CONCLUSION

582

583 The present study aimed at assessing the stability of smectites, which represent the
584 reactive components of engineered and geological barriers, when in contact with metal iron at
585 temperatures realistic in the context of nuclear waste disposal (80°C). Dioctahedral smectites
586 are thoroughly destabilized under such conditions, leading to the precipitation of magnetite

587 and of 1:1 iron-rich phyllosilicates [odinite, crondstedtite – Lantenois (2003), Lantenois *et al.*
588 (2005)]. Smectite destabilization is systematic for neutral-to-basic pH conditions (pH > 7),
589 whereas in mildly acidic to neutral pH conditions, a significant proportion of metal iron is
590 corroded to form magnetite without smectite destabilization.

591 An XRD method was developed to quantify the extent of smectite destabilization. This
592 method was validated against CEC measurements and IR spectroscopy results. Structural and
593 crystal-chemical factors favoring smectite destabilization were thus determined. These
594 parameters include the amount of octahedral iron, the presence of tetrahedral substitutions,
595 and the nature of interlayer cations, and a conceptual model was hypothesized to account for
596 smectite destabilization. According to this model, the formation of trioctahedral clusters
597 resulting from the migration of Fe²⁺ cations into the octahedral sheet of the 2:1 layer is
598 responsible for smectite destabilization as tetrahedral sheets are unable to accommodate the
599 larger dimensions of these domains.

600 In agreement with experimental results, the dioctahedral character of the initial
601 smectite is an essential condition for its destabilization in the proposed model. As a result the
602 non-reactivity of trioctahedral smectites appears as an important point for the conception of
603 engineered barriers for nuclear waste disposal, although natural deposits of trioctahedral
604 smectite are uncommon.

605

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607

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772

FIGURE CAPTIONS

773

774

775 **Figure 1.** XRD patterns obtained on unreacted and reacted smectite samples (upper and lower
776 patterns, respectively). Montmorillonite, beidellite, nontronite and saponite samples were
777 reacted for 45 days with metal iron at 80°C (see text for details) (a) Sample SWy-2 ,(b)
778 Sample SAz-1, (c) Sample SbId, (d) Sample CP4, (e) Sample Garfield, (f) Sample SapCa-2,
779 and (g) Sample SapFe08. Scale factor (x3) over the 20-35°2 θ CoK α range. Patterns were
780 normalized by pairs to the integrated intensity of corundum (012) reflection (solid line, S).
781 The (001) reflection and the (02,11) band of the clay samples are labeled. Q indicates the
782 presence of quartz impurities in some samples (dashed lines). Dotted lines indicate the
783 reflections of newly-formed phases. These phases are labeled M, L, and P for magnetite
784 (Fe₃O₄), lepidocrocite (γ -FeOOH), and a newly formed 1:1 phyllosilicate, respectively.

785 **Figure 2.** Method for quantifying the relative proportion of destabilized smectite using IR
786 spectroscopy. (a) IR spectrum of sample SWy-2 (unreacted) before subtraction of the
787 baseline. Si-O indicates the Si-O vibrations in phyllosilicates whereas Al-Al-OH, Al-Fe-OH
788 and Al-Mg-OH refer to the OH bending mode of the respective hydroxyl groups. Q denotes
789 the two vibrations bands of quartz. (b) Decomposition assuming three Gaussian-shaped
790 contributions of the OH bending zone after baseline subtraction (sample SWy-2 unreacted).

791 **Figure 3.** SEM micrographs of unreacted and reacted samples. Metal iron particles in
792 unreacted and reacted SWy-2 sample are shown on (a) and (b), respectively. (c) and (d)
793 Smectite particles in the reacted sample SWy-2. (e) Smectite particles in the initial sample
794 SWy-2. (f) Smectite particles in the reacted Garfield sample. (g) Smectite particles in the
795 initial sample SapCa-2. (h) Smectite particles in the reacted sample SapCa-2.

796 **Figure 4.** Relative proportion of destabilized smectite calculated by XRD and CEC methods
797 (a) and by XRD and infrared methods (b). Solid square: sample SapCa-2; solid triangle:

798 sample SAz-1; solid circle: sample SWy-2; solid diamond: Garfield sample; open diamond:
799 Drayton sample. The (1:1) line is shown as a solid line.

800 **Figure 5.** XRD patterns obtained for unreacted SbId sample (a) and for reacted SbId sample
801 (b-e). (b), (c), (d) and (e) correspond to 5, 15, 30 and 45 day experiments, respectively. Scale
802 factor (x3) over the 20-35°2θ CoKα range. Patterns were normalized as in Figure 1. Other
803 labels and patterns as in Figure 1.

804 **Figure 6.** Evolution of the relative proportion of destabilized smectite as a function of
805 reaction time. Symbols as in Figure 4. Open triangles: sample SbId.

806 **Figure 7.** XRD patterns obtained on unreacted and reacted beidellite samples (upper and
807 lower patterns, respectively). Patterns are ranked as a function of their structural Fe³⁺ content
808 (Table 1). Samples were reacted for 45 days with metal iron at 80°C without controlling the
809 initial pH. (a) Sample SbS-1, (b) Drayton sample, and (c) sample SWa-1. Scale factor (x3)
810 over the 20-35°2θ CoKα range. Patterns were normalized as in Figure 1. Other labels and
811 patterns as in Figure 1.

812 **Figure 8.** Relative proportion of destabilized smectite after reaction with metal iron as a
813 function of their content of structural Fe³⁺ (Table 1) Relative proportion of destabilized
814 smectite amounts was estimated using XRD on 45 day experiments.

815 **Figure 9.** XRD patterns recorded on sample SWy-2 reacted with metal iron after K-, Ca-, and
816 Na-saturation (b, c, and d, respectively). Unreacted Na-saturated sample corresponds to the
817 raw SWy-2 sample (a). Scale factor (x3) over the 20-35°2θ CoKα range. Patterns were
818 normalized as in Figure 1. Other labels and patterns as in Figure 1.

819 **Figure 10.** Transmission electron micrographs of smectite particles from sample CP4.
820 “rolled” and “flat” particles are labeled (1) and (2), respectively.

821 **Figure 11.** Conceptual model leading to the destabilization of dioctahedral smectites as a
822 result of their interaction with metal iron. (a) Deprotonation of MeFe³⁺OH groups. (b)

823 Oxidation of metal iron as a result of its interaction with released protons. (c) Sorption of Fe^{2+}
824 cations on the edges of smectite particles and reduction of structural Fe^{3+} cations. (d)
825 Migration of solution Fe^{2+} cations in smectite interlayers to compensate for the layer charge
826 deficit. Part of this migration results from a Fe^{2+} -for- Na^+ exchange. With time, interlayer Fe^{2+}
827 cations migrate to the di-trigonal cavity and further to the octahedral sheet to compensate
828 locally for the charge deficit. (e) Coexistence of di- and tri-octahedral domains in the
829 octahedral sheet of smectite leads to its destabilization.

830

Table 1: Chemical composition of the initial smectite materials (structural formulae calculated per $O_{10}(OH)_2$) and relative proportion of smectite destabilized after reaction with metal iron for 45 days.

Sample	Garfield ^a	SWa-1 ^a	Drayton ^b	CP4 ^b	Sbld ^c	SbS-1 ^{c,d}	SWy-2 ^c	SAz-1 ^c	SapCa-2 ^c	SapFe08 ^{c,d}
Nature ^e	N	FS	B	B	B	B	M	M	S	S
Tetrahedral										
Si	3.51	3.70	3.69	3.60	3.71	3.66	3.95	4.00	3.58	3.62
Al	0.49	0.30	0.31	0.40	0.29	0.34	0.05	-	0.39	-
Fe ³⁺	-	-	-	-	-	-	-	-	0.03	0.38
charge	-0.49	-0.30	-0.31	-0.40	-0.29	-0.34	-0.05	-	-0.42	-0.38
Octahedral										
Al	0.11	0.55	1.11	1.70	1.80	2.00	1.56	1.37	-	-
Fe ³⁺	1.86	1.31	0.47	0.30	0.12	-	0.21	0.07	-	0.00
Mg	0.02	0.13	0.44	-	0.08	-	0.23	0.56	3.00	3.00
occupancy	1.99	1.99	2.02	2.00	2.00	2.00	2.00	2.00	3.00	3.00
charge	-0.05	-0.16	-0.38	0.00	-0.08	0.00	-0.23	-0.56	0.00	0.00
Interlayer										
Na	0.09	0.03	-	-	0.08	0.33	0.14	0.05	0.34	0.39
Ca	0.20	0.20	0.17	0.15	0.10	-	0.05	0.24	0.05	-
Mg	-	-	0.18	-	-	-	-	-	-	-
K	0.04	0.05	-	0.09	0.08	-	0.01	0.01	0.02	-
charge	0.53	0.48	0.70	0.39	0.36	0.33	0.25	0.54	0.46	0.39
Smectite destabil. (wt %)	95	90	70	40	60	0	50	20	0	0

Note: ^a From Gates *et al.* (2002). Interlayer composition of raw materials was determined from electron microprobe analysis, ^b EDX analysis on a transmission electron microscope, ^c electron microprobe analysis, ^d synthetic clays. ^e N, FS, B, M, S correspond to nontronite, ferruginous smectite, beidellite, montmorillonite and saponite respectively.

Table 2: Chemical composition of the solution after reaction of smectite samples with metal iron for 45 days.

	Si	Al	Fe	Mg	Na	Ca	K	Initial pH	Final pH
SapCa-2	0.0	0.0	0.0	0.0	10.0	4.0	0.0	9.5	10.0
SapCa-2 Ref	0.0	0.0	0.0	0.0	7.0	2.0	0.0	9.5	9.5
SWy-2	6.5	0.1	0.0	0.3	115	3.5	3.0	10.0	10.5
SWy-2 Ref	0.0	0.0	0.0	0.0	11.0	0.0	0.0	10.0	10.0
Sbld	2.0	0.4	0.0	0.3	17.0	28.0	14.0	7.5	7.5
Sbld Ref	0.0	0.0	0.0	0.0	1.0	2.0	1.0	7.5	7.5
Garfield	0.0	0.0	0.0	0.0	17.5	22.5	1.0	8.5	9.5
Garfield Ref	0.0	0.0	0.0	0.0	10.0	1.0	2.0	8.5	9.0

Note: Concentrations are given in mg.L⁻¹. Initial and final pH values were measured before and after reaction, respectively. Regular sample names correspond to the reaction of a given smectite sample with metal iron for 45 days at 80°C. Ref samples correspond to the reaction of a given smectite sample for 45 days at 80°C without metal iron.

Table3: Relative proportion of smectite destabilized (weight %) as a function of the initial solution pH.

pH	SWy-2	SapCa-2	Garfield
6	0%	0%	0%
8	50%	-	95%
10	50%	0%	-
12	50%	-	-

Note: Relative proportion of destabilized smectite is estimated using the XRD method.

Table 4: Relative proportion of smectite destabilized (weight %) as a function of the cation interlayer composition.

	SAz-1	SWy-2	Garfield
K	-	0%	50%
Ca	20%*	20%	95%*
Na	40%	50%*	-

Note: Relative proportion of destabilized smectite is estimated using the XRD method. * indicate raw samples, with the corresponding predominant interlayer cation.

Figure 1 :

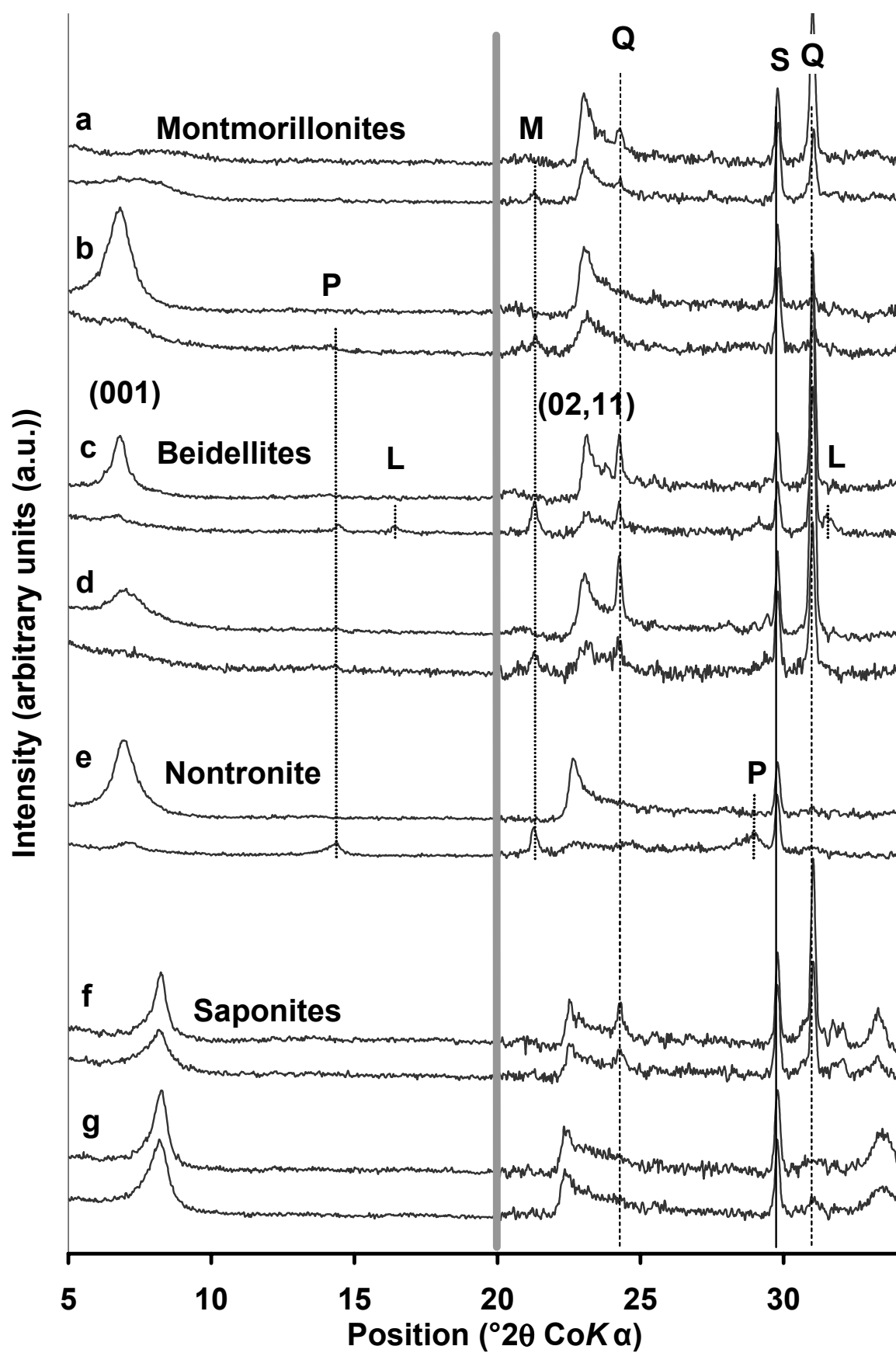
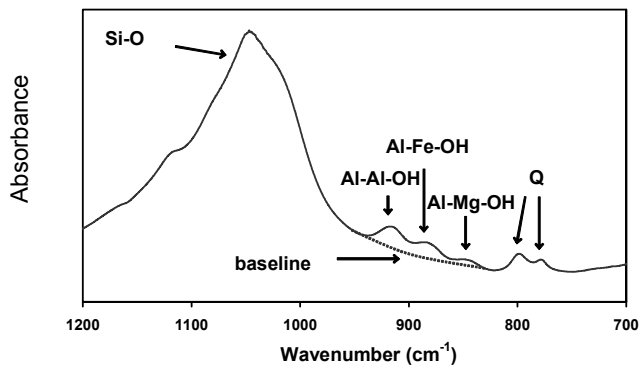
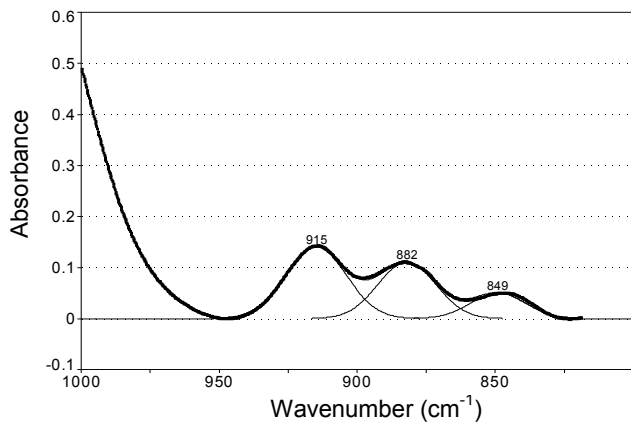


Figure 2 :



a



b

Figure 3 :

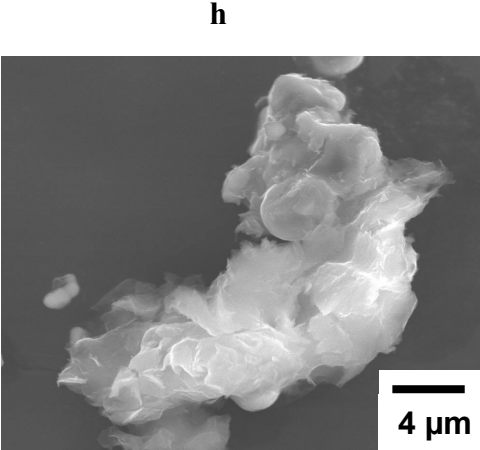
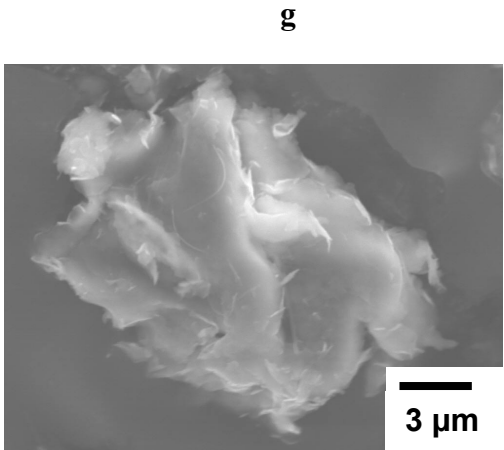
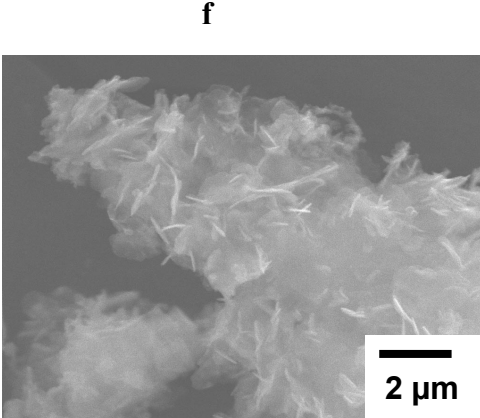
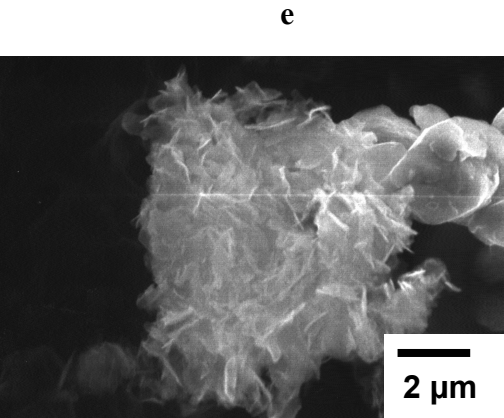
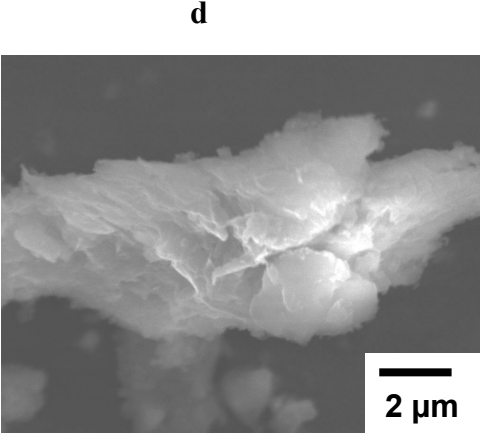
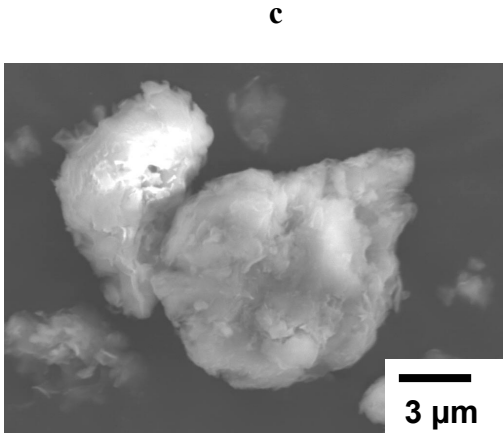
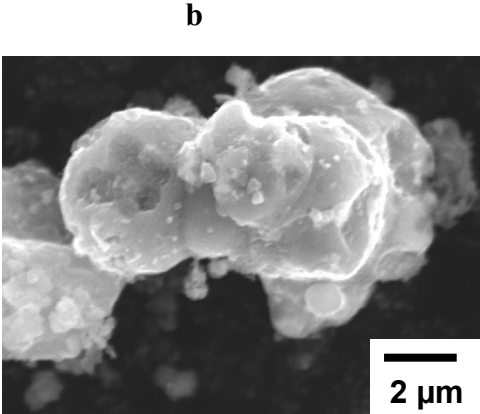
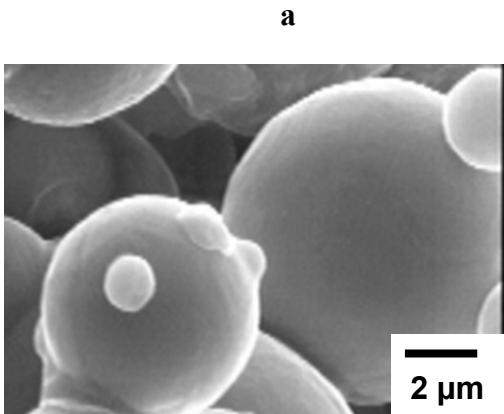


Figure 4 :

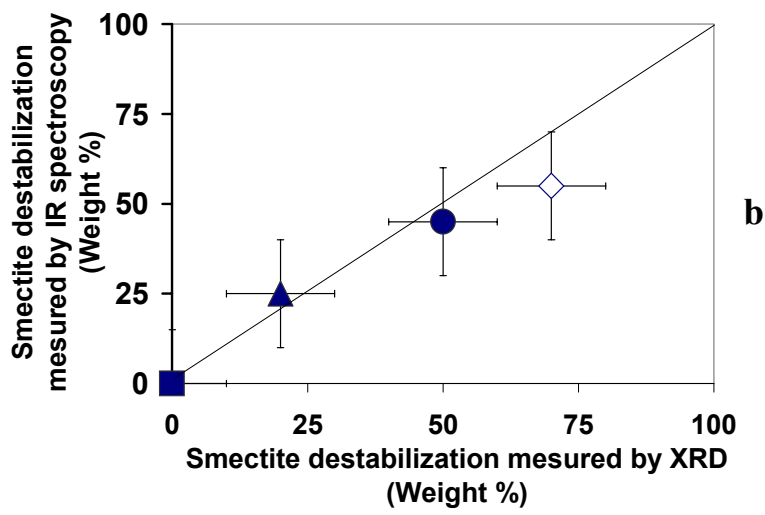
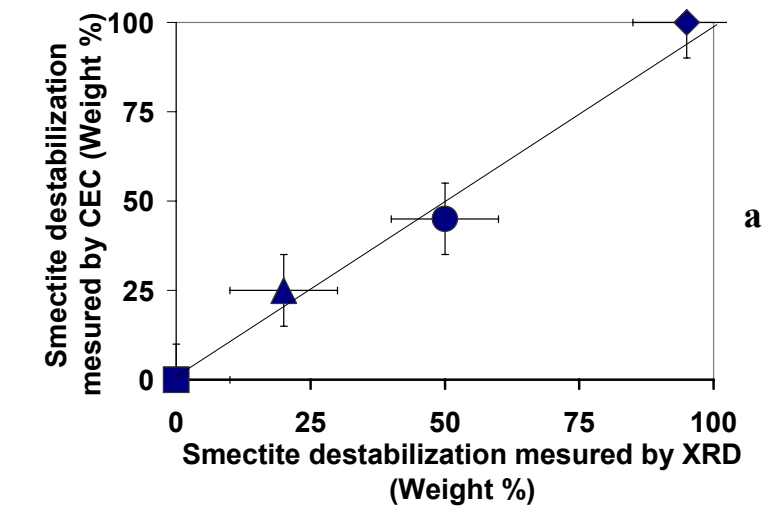


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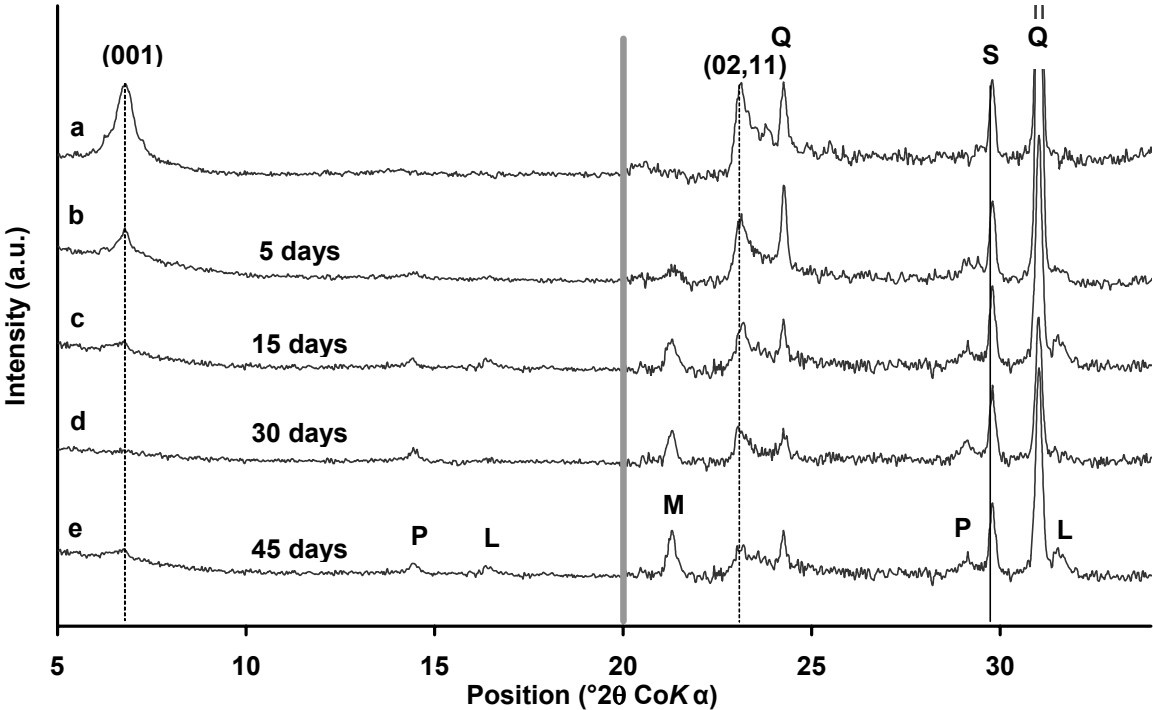


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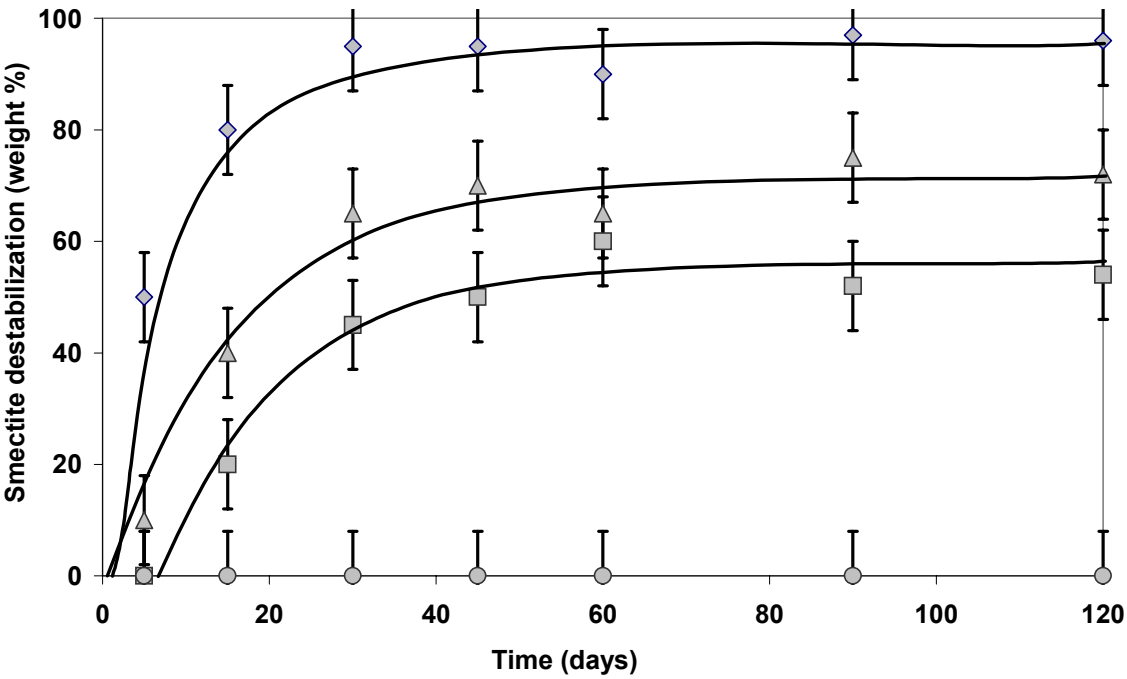


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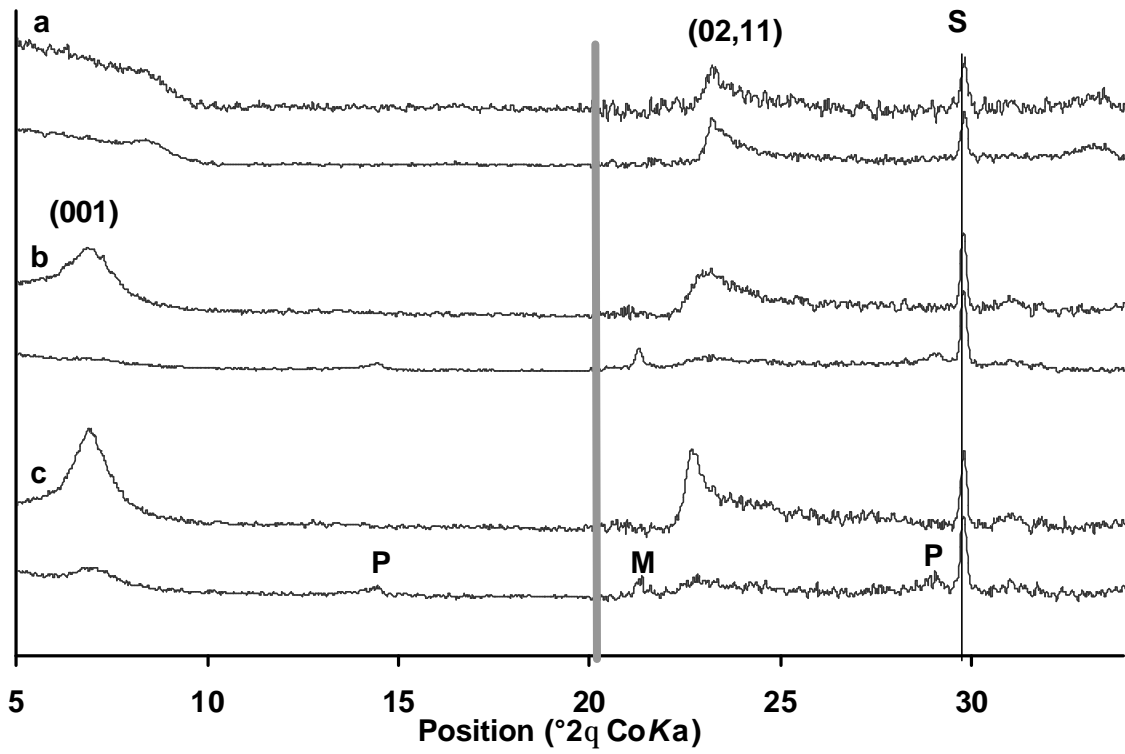


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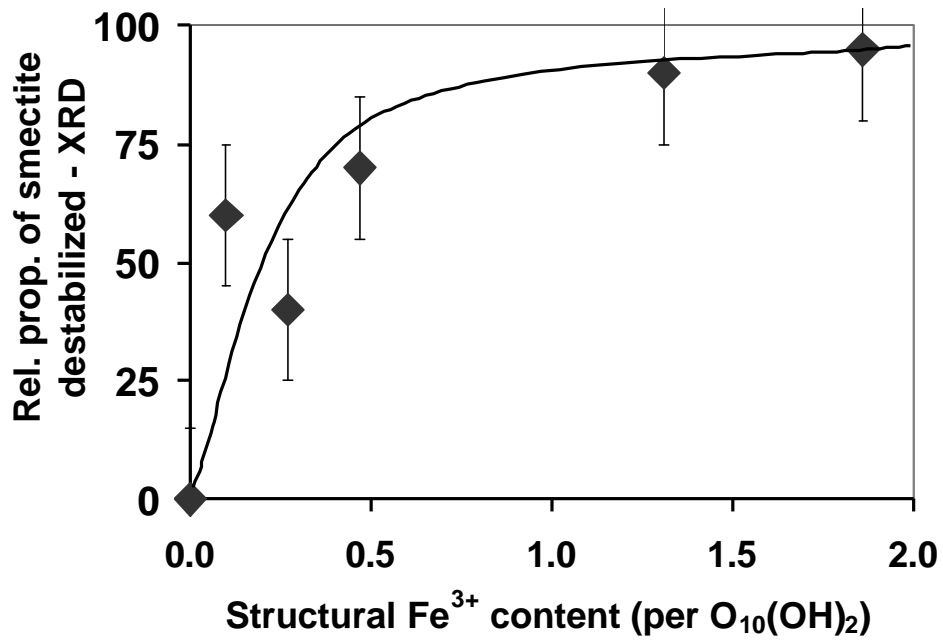


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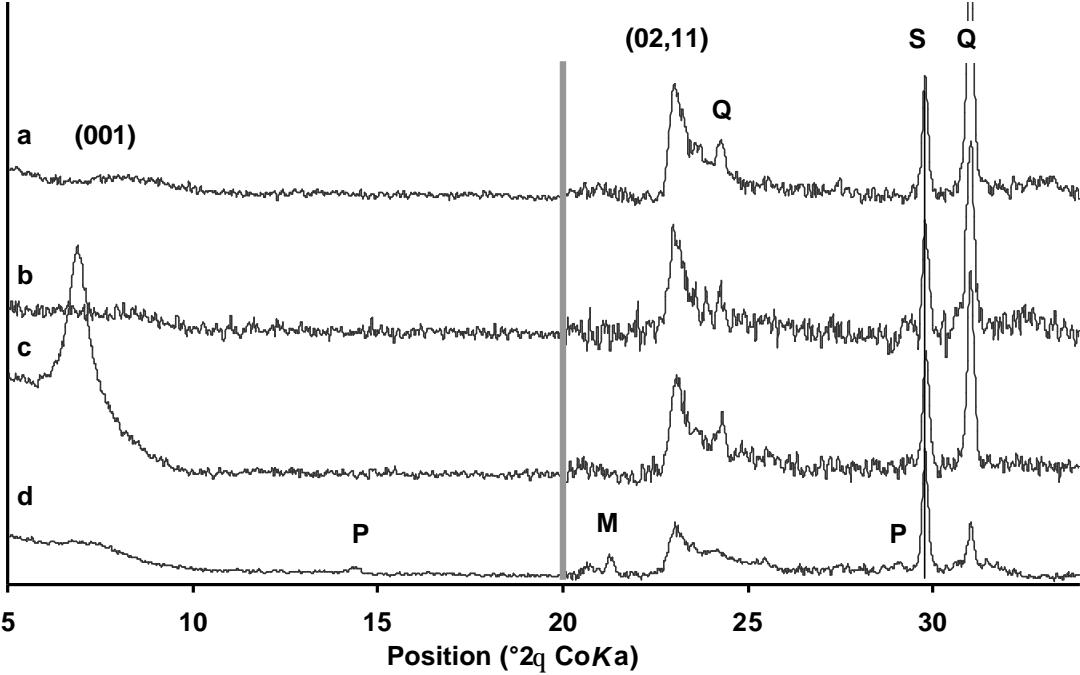


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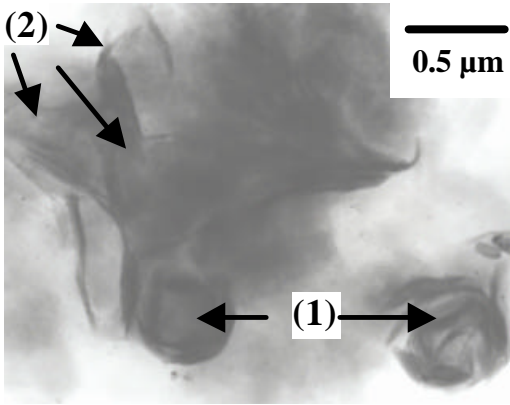
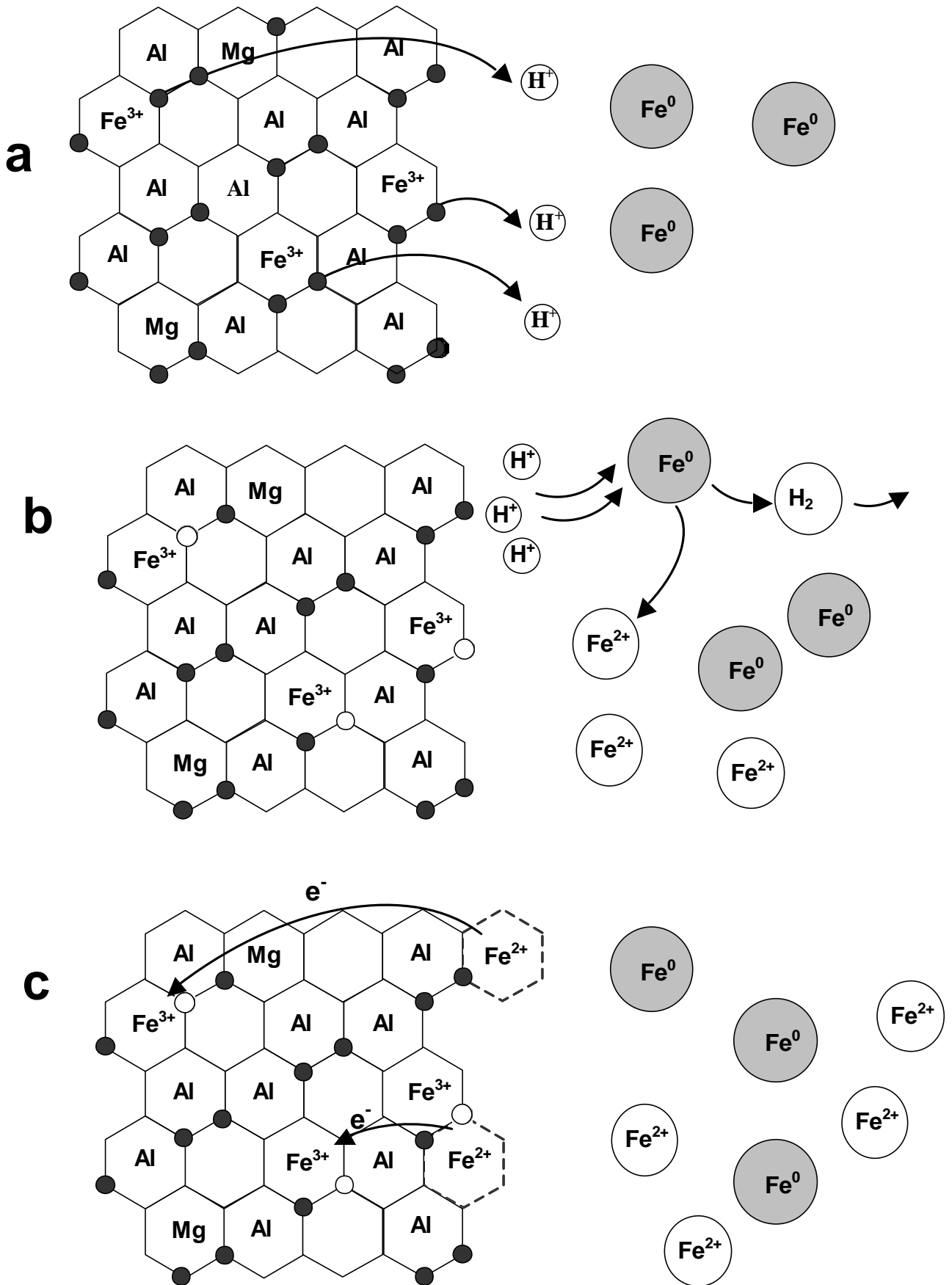
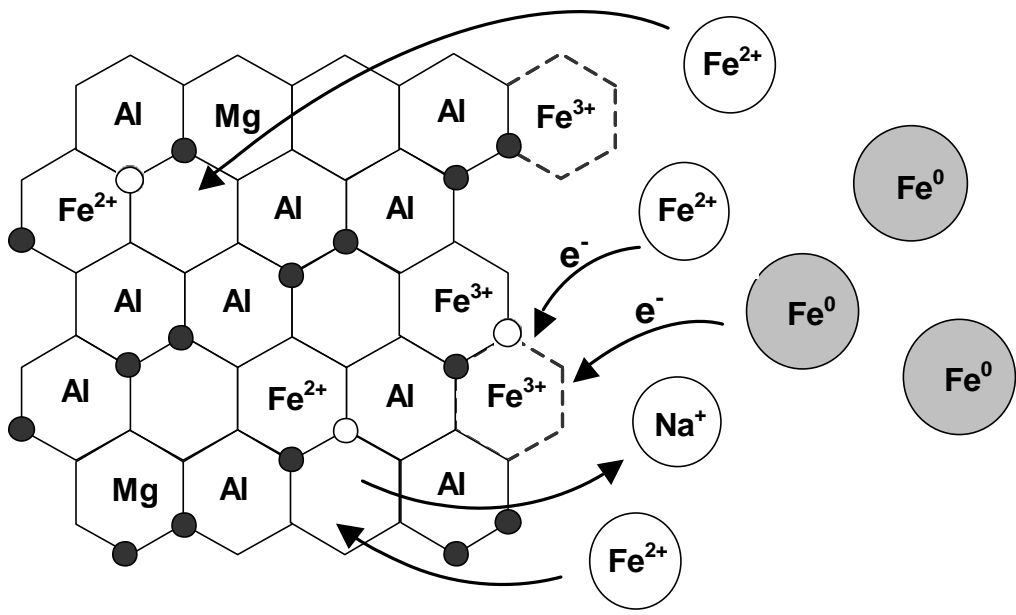


Figure 11



d



e

