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1	Diagenetic smectite-to-illite transition in clay-rich sediments:
2	A reappraisal of X-ray diffraction results using the multi-specimen method
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17	Key words: Clay minerals, Clay diagenesis, Illite-smectite, Mixed-layering, interstratification,

18 XRD, Gulf Coast.

19 ABSTRACT. Smectite illitization is a common mineralogical reaction occurring 20 during the burial diagenesis of clav-rich sediments and shales, and has thus attracted 21 sustained interest over the last fifty years. Prior studies have concluded that smectite 22 illitization proceeds through a steady set of homogeneous reactions involving 23 intermediate mixed layers of varying compositions. In these intermediate structures, 24 illite and smectite, or, more generally, expandable layers (I and Exp layers, respectively) 25 coexist among the same crystallites giving rise to non-periodic structures (I-Exp) 26 characterized by specific diffraction effects. Consistent with this model, reaction progress was characterized by the simultaneous increase in the illite content in I-Exp 27 28 and in their stacking order leading to the following mineralogical sequence: smectite \rightarrow 29 randomly interstratified I-Exp with high smectite contents (> 50% Exp layers) \rightarrow 30 ordered I-Exp with high illite contents (> 50% I layers) \rightarrow illite. Although reaction 31 mechanisms have been extensively debated, this structural characterization has not been 32 challenged, possibly due to a methodological bias. In the present study, X-ray diffraction 33 patterns typical of the diagenetic illitization of smectite are interpreted using modern 34 approaches involving profile fitting (multi-specimen method). Novel insights into the 35 structure of intermediate reaction products are thus obtained. In particular, original 36 clay parageneses are described including the systematic presence of illite, kaolinite, 37 chlorite and a mixed layer containing kaolinite and expandable layers (K-Exp). 38 In contrast to previous descriptions, the early stages of smectite illitization are 39 characterized by the coexistence of discrete smectite and of a randomly interstratified I-40 Exp with a high content of illite layers (>50% I layers). Both the smectite and the I-Exp 41 are authigenic and form under shallow burial, that is at low temperature conditions. 42 With increasing burial depth, the relative proportion of I-Exp increases, essentially at 43 the expense of discrete smectite, and the composition of I-Exp becomes slightly more

44 illitic. In the second stage of smectite illitization, two illite-containing mixed layers are 45 observed. They result from two parallel reaction mechanisms affecting the randomly interstratified I-Exp present in the shallow section of the series. The first reaction 46 47 implies the dissolution of this randomly interstratified I-Exp and leads to the 48 crystallization of an ordered I-Exp without significant illitization, possibly because of the 49 low K-availability. The second reaction affecting the randomly interstratified I-Exp 50 implies the growth of trioctahedral (Mg, Al) hydroxide sheets in Exp interlayers, thus 51 developing di-trioctahedral chlorite layers (Ch layers) in the initial I-Exp to form an I-52 Exp-Ch. A layer-by-layer mechanism is hypothesized for this reaction. In this scheme, 53 Mg cations released by the dissolution-recrystallization reaction of I-Exp likely 54 represent the source of Mg for the formation of brucite-like sheets in expandable 55 interlayers, and thus of the I-Exp-Ch. 56 The reported structural characterization of smectite illitization intermediate products

57 contradicts the conventional wisdom of a homogeneous reaction through a series of pure 58 mixed layers of variable composition. In contrast, the coexistence of different phases 59 implies a heterogeneous reaction via a sequence of intermediate phases and requires reassessing the reaction mechanisms proposed in the literature. The compositional range 60 61 (relative proportion of the different layer types) of these phases is limited and smectite 62 illitization proceeds essentially as relative proportions of the different phases vary. In addition, reaction kinetics and stability of the different intermediate products also need 63 64 to be reconsidered.

INTRODUCTION

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For about half a century, smectite illitization has been extensively described in different 67 68 geological contexts: burial diagenesis of clay-rich sediments (Burst, 1957, 1969; Weaver, 69 1957, 1959; Perry and Hower, 1970; Hower and others, 1976; Srodon, 1978, 1984a; Boles 70 and Francks, 1979; Velde and others, 1986; among many others), hydrothermal alteration of 71 volcanic tuffs (Inoue and others, 1978, 1988, 2005; Inoue and Utada, 1983; Altaner and 72 others, 2003), metasomatic alteration of bentonites (Hoffman and Hower, 1979; Velde and 73 Brusewitz, 1982, 1986; Inoue and others, 1990; Sucha and others, 1993; Li and others, 1997), 74 and contact metamorphism (Nadeau and Reynolds, 1981; Pytte and Reynolds, 1989; Drits and 75 others, 2007). Although different reaction mechanisms have been inferred (see Altaner and 76 Ylagan, 1997, for a review; Srodon and others, 2000), this mineralogical transition has been 77 systematically described to occur through mixed layers. In these intermediate structures, illite 78 and smectite, or more generally expandable, layers (I and Exp layers, respectively) coexist 79 among the same crystallites giving rise to non-periodic structures, hereafter referred to as I-80 Exp. The structural characterization of I-Exp, essential for the reconstruction of thermal and 81 chemical paleoconditions, requires determining the nature of interstratified layers, their 82 relative proportions and their stacking sequences through analysis of their specific diffraction 83 effects (see Reynolds, 1980, Drits and Tchoubar, 1990, Moore and Reynolds, 1997, for 84 details). Such analysis has revealed that smectite illitization is a continuous two-stage reaction 85 characterized by a steady increase of the illite content in I-Exp and by the simultaneous 86 increase of stacking order: illite and expandable layers are interstratified at random when 87 expandable layers dominate ("R0 zone" - early diagenesis), whereas interstratification is 88 ordered when illite prevails (" $R \ge 1$ zone" – late-stage diagenesis; Shutov and others, 1969;

Perry and Hower, 1970, 1972; Hower and others, 1976; Bethke and others, 1986; Srodon,
1999).

91 Following these pioneering works, simplified methods have been proposed for the 92 structural characterization of I-Exp from X-ray diffraction (XRD) data (Srodon, 1980, 1981, 93 1984b; Watanabe, 1981, 1988; Velde and others, 1986; Inoue and others, 1989; Moore and 94 Reynolds, 1997). These methods essentially rely on peak migration curves which link the 95 position of a given reflection (or of a set of reflections) to the composition (relative proportion 96 of the different layer types) of the mixed layers and to their stacking order. Peak migration 97 curves were obtained mostly from XRD patterns calculated using programs implemented 98 from Reynolds (1967, 1980) or Watanabe (1981) algorithms. These calculations were 99 essentially restricted to I-Exp composition and ordering that were described in the early works 100 reported above, thus confining the simplified identification methods to these specific mixed 101 layers. Logically, the early description of smectite illitization was not challenged by the 102 numerous subsequent case studies. The lack of direct comparison between experimental and 103 calculated XRD patterns concealed possible incomplete or erroneous identifications. A 104 significant proportion of the studies devoted to smectite illitization thus focused on the 105 definition of reaction mechanisms and on the possible use of this mineralogical 106 transformation as a paleogeothermometer. For the latter purpose, the influence of time and 107 temperature (Hower and others, 1976; Velde and Vasseur, 1992), K availability (Huang, 108 1993; Bauer and Velde, 1999), and water/rock ratio (Whitney, 1990) on reaction progress was 109 estimated.

However, a more appropriate crystallography-based approach has been developed over the last decade. In particular, direct comparison between calculated and experimental diffraction patterns has been favored and has allowed reproduction of not only the positions of the reflections but also of their profiles, both of which are strongly influenced by

114 interstratification. In addition to the frequent occurrence of multi-component mixed layers in 115 nature, the multi-specimen method proposed initially by Drits and others (1997), and by 116 Sakharov and others (1999a, 1999b) uncovered the existence of mixed layers exhibiting 117 "unusual" composition and/or stacking order (Drits and others, 1997, 2002a, 2002b, 2004, 118 2007; Sakharov and others, 1999b, 2004; Lindgreen and others, 2000, 2002; Claret and 119 others, 2004; McCarty and others, 2004). This new approach thus challenges the commonly 120 accepted description of smectite illitization in diagenetic series by invalidating hypotheses 121 sustaining usual I-Exp identification criteria such as homogeneity of the swelling behavior, 122 random interstratification restricted to smectite-dominated mixed layers, absence of 123 segregation and of partial ordering, et cetera (see Lanson, 2005, for further discussion). 124 The present study thus aims at obtaining an accurate structural characterization of 125 samples characteristic of diagenetic smectite illitization in clay-rich sediments from modeling 126 of their XRD patterns. The proposed models are shown to be consistent with the coexistence 127 of discrete smectite with I-Exp, as has been observed on similar samples with transmission 128 electron microscopy. In addition, the definition of structure models at various stages of the 129 reaction constrains the possible reaction mechanisms of this transformation. In particular, 130 analysis of stacking parameters refutes the solid-state transformation hypothesis for illitization 131 of I-Exp over the "R0 zone", and for the transition from randomly interstratified I-Exp to 132 ordered varieties, consistent with crystal growth features reported during smectite illitization. 133 It is shown also that part of the I-Exp formed early in the "R0 zone" transforms, possibly 134 through solid-state processes, into a complex mixed layer present in the deeper samples.

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136	MATERIALS AND METHODS
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138	Samples
139	Samples were collected in two different onshore wells in the Texas Gulf Coast (Carter -
140	Tyler County in central Gulf Coast Texas, and Mustang Island – Nueces County in south Gulf
141	Coast Texas). These wells have been described previously by Velde and Espitalié (1989), and
142	Velde and Vasseur (1992), and the stratigraphic age of the samples ranges from Cretaceous to
143	Eocene (Carter well) and from Eocene to Pleistocene (Mustang Island). In the two wells, little
144	or no erosion has occurred and present depths are approximately maximum burial depths. The
145	temperature gradient is similar in both wells (32.7°C/km and 35°C/km, in Mustang Island and
146	Carter, respectively), and they both extend through most of the smectite-to-illite transition
147	(fig. 1).
148	
149	Experimental
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 149 150 151 152 153 154 155 156 157 158 	<i>Experimental</i> Carbonates were removed from all samples using the acetic acid-acetate buffer method described in Moore and Reynolds (1997). Then, organic matter was removed at 50°C by adding small aliquots of hydrogen peroxide (H ₂ O ₂ – 30%) to the suspension until gaseous emission ceased. The <2 µm size fraction was extracted by centrifugation for a set of samples selected from -2170 to -5500 m in Carter and Mustang Island boreholes. From preliminary XRD results, 6 of the initial samples were selected as representative of the complete transition between "smectite-rich" and "illite-rich" samples in Gulf Coast series. All samples were selected in the Carter well at 2170, 3660, 4000, 4640, 5010, and 5180 m (samples A-F). To minimize the contributions from mica, kaolinite, chlorite and quartz, the <0.2 µm
 149 150 151 152 153 154 155 156 157 158 159 	Experimental Carbonates were removed from all samples using the acetic acid-acetate buffer method described in Moore and Reynolds (1997). Then, organic matter was removed at 50°C by adding small aliquots of hydrogen peroxide (H ₂ O ₂ – 30%) to the suspension until gaseous emission ceased. The <2 µm size fraction was extracted by centrifugation for a set of samples

161	temperature to ensure a complete cation exchange. After three replications of this procedure,
162	the excess chloride was rinsed with distilled water (Milli-Q – $18.2 \text{ M}\Omega.\text{cm}^{-1}$).
163	Oriented preparations were obtained by pipetting a slurry of the Ca-saturated
164	suspensions on a glass side and drying this suspension at 40°C for a few hours to obtain an
165	air-dried (AD) preparation. Ethylene-glycol (EG) solvation of the slides was achieved by
166	exposing them to EG vapor at 70°C for a minimum of 12 hours. XRD patterns were recorded
167	with a Bruker D5000 powder diffractometer equipped with a Kevex Si(Li) solid state detector
168	using CuK α_{1+2} radiation. Intensities were recorded at 0.04° 20 step intervals from 2 to 50°,
169	using a 6 sec counting time per step except for sample D (40 sec/step). Sizes of the divergence
170	slit, the two Soller slits, the antiscatter, and resolution slits were 0.5°, 2.3°, 2.3°, 0.5° and
171	0.06°, respectively. Humidity was controlled at 40% RH for AD measurements.
172	
173	XRD Profile Modeling
174	Structure models were determined using the multi-specimen method described by Drits
175	and others (1997), and Sakharov and others (1999a, 1999b). In contrast to usual identification
176	methods of mixed layers, the multi-specimen method requires recording XRD patterns after
177	different treatments for each sample. For a given sample, these patterns usually differ
178	significantly because of the contrasting hydration/expansion behavior of expandable
179	interlayers in response to these treatments. The method itself relies on the direct comparison
180	of experimental profiles with those calculated for a structure model, the optimum agreement
181	between data and calculated patterns being obtained by a trial-and-error procedure.
182	The different treatments can affect the thickness and scattering power (nature, amount,
183	and position of interlayer species) of the expandable interlayers, but not the layer sequences
	and position of interfayer species) of the expandable interfayers, but not the fayer sequences
184	within the crystallites. As a consequence, a consistent structure model is obtained for a given

are nearly identical. XRD pattern modeling provides also a quantitative phase analysis of the
samples. One essential requirement for structure model soundness is that the relative weight
contributions of periodic and interstratified phases to the different XRD patterns of a given
sample must be similar (Sakharov and others, 1999b; Claret, 2001; Lindgreen and others,
2002; McCarty and others, 2004, 2005).

191 Structure models for each mixed layer include the number of the different layer types 192 (not limited to 2), their nature and relative proportions. Markovian statistics are used to 193 describe possible layer stacking sequences and the relative abundance thereof. An important 194 parameter of this statistical description is the Reichweit parameter R (Jagodzinski, 1949) 195 which characterizes the extent of ordering as the number of adjacent layers influencing the 196 nature of a given layer. For R = 0, layer types are thus randomly interstratified, whereas for 197 R = 1 the occurrence probability of a given layer type depends on the nature of its nearest 198 predecessor. For a given value of the R parameter, a set of probability parameters is needed to 199 completely describe layer stacking. The relative content of the different layer types (W_i) is 200 systematically needed together with junction probability parameters (P_{ii}). P_{ii} parameters 201 define the probability for a j-type layer to follow an i-type layer (i,j = I or Exp for I-Exp). W_i 202 and Pii parameters are related, and only two parameters are necessary to describe a two-203 component mixed layer with R = 1, W_I and P_{ExpExp} being commonly used for I-Exp. In this 204 case, specific layer stacking modes for R = 1 include maximum possible degree of ordering 205 (MPDO), which is obtained when pairs of the least abundant layers are prohibited in the 206 stacking, that is when $P_{ExpExp} = 0$ assuming $W_I > W_{Exp}$. Random interstratification occurs 207 when $P_{ExpExp} = P_{IExp} = W_{Exp} = 1 - W_I$, and physical mixture of I and Exp layers when $P_{ExpExp} =$ 208 1 whatever the W_{Exp} value. In addition, a tendency to segregation of i-type layers is 209 characterized by $W_i < P_{ii}$ (i = I, Exp), whereas partial ordering occurs when $W_{Exp} > P_{ExpExp} > 0$

assuming $W_I > W_{Exp}$ (see Bethke and Altaner, 1986, Drits and Tchoubar, 1990, and Moore and Reynolds, 1997, for details).

212 The algorithm developed initially by Drits and Sakharov (1976) and used recently by 213 Drits and others (1997) and Sakharov and others (1999b) was used to fit experimental XRD 214 profiles over the 2–50° 20 range. Instrumental and experimental factors such as horizontal 215 and vertical beam divergences, goniometer radius, length and thickness of the oriented slides 216 were measured and introduced without further adjustment. Sigmastar (see Reynolds, 1986, for details) was set to 12 and the mass absorption coefficient (μ^*) to 45, as recommended by 217 218 Moore and Reynolds (1997). In the profile fitting process, it was necessary to define different 219 types of Exp layers as a function of their hydration or swelling behavior in AD and EG states, 220 respectively (Drits and others, 2002a). Irrespective of the hydration/swelling behavior of Exp 221 layers, the relative contents of I and Exp layers and their stacking sequences should be the 222 same in both AD and EG states. The hydration/swelling behavior of Exp layers is likely 223 related to the amount and location of the layer charge deficit, although this behavior may 224 differ for a given layer from AD to EG states. In the following I, K, Ch, and Exp denote illite, 225 kaolinite, di-trioctahedral chlorite, and expandable layers, respectively. For all layer types z 226 atomic coordinates proposed by Moore and Reynolds (1997) were used after modification to 227 fit the layer thickness values used for simulation; thermal motion parameters (B) were also set 228 as proposed by Moore and Reynolds (1997). The position and amount of interlayer species 229 (H₂O and EG molecules in particular) were considered as variable parameters and varied 230 about the values proposed by Moore and Reynolds (1997) during the fitting process. In bi-231 hydrated Exp layers (2W), a single plane of H₂O molecules was assumed to be present on 232 each side of the interlayer mid-plane as proposed by Ferrage and others (2005a, 2005b). 233 Finally, distributions of coherent scattering domain sizes (CSDSs) were assumed to be 234 lognormal and characterized by their mean value (Drits and others, 1997b). Quality of fit was assessed over the 4-50°2 θ (22.0-1.85 Å) range with the R_{wp} and R_{exp} factors (Howard and Preston, 1989).

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Qualitative Description of the Experimental XRD Patterns.

RESULTS

241 Evolution of sample structure with depth is best seen on XRD patterns obtained after 242 EG solvation (fig. 2A). The XRD pattern of sample A (2170 m) exhibits a strong peak at ~16.9 Å, well resolved on its low-angle side, and weaker peaks at 8.6, 5.54, 3.331, 2.781, and 243 244 2.023 Å that form a non-rational series. In addition, peaks at 7.21, 3.58 and 2.38 Å and weak 245 modulations at ~10.0 and 5.0 Å correspond to finely dispersed kaolinite and to discrete illite, 246 respectively. The peak at ~17.0 Å is still intense for sample B (3660 m) but its resolution is 247 significantly reduced on its low-angle side. Compared to sample A, the reflections at 5.54 Å and 2.781 Å are shifted to higher and lower angles, respectively, in the XRD pattern of 248 249 sample B. The reflection at 8.6 Å (sample A) is shifted also to lower angles and appears as a 250 high-angle shoulder of the 10.0 Å reflection (sample B). XRD patterns of samples B and C 251 are alike, except that the low-angle resolution of the ~17.0 Å peak is reduced for sample C 252 compared to sample B. Samples B and C also contain significant amounts of discrete illite and 253 kaolinite, and a small amount of chlorite.

254 XRD patterns of samples taken from depths > 4500 m (D, E, and F) are all akin and 255 their profiles strongly differ from those of samples A, B and C. Over the low-angle region, 256 there is no peak at ~17.0 Å, but broad maxima between ~13.5-15.0 Å (fig. 2). These patterns 257 also contain a super-reflection at ~30 Å, best seen for sample E, and additional broad maxima 258 at ~9.25-9.30 Å, and 5.20-5.25 Å. The low resolution of the latter reflections results to some extent from their partial overlap with illite peaks at 10.0 Å and 5.0 Å. Finally, sharp kaolinite
and chlorite reflections are visible at 3.579 Å and 3.528 Å.

261 To summarize the above observations, the six samples can be divided in two groups.

262 XRD patterns of group I (samples A, B, and C) exhibit a ~17.0 Å reflection (EG state) whose

263 low-angle resolution decreases with increasing depth. XRD patterns of group II (samples D,

E, and F) exhibit a broad maximum at ~13.5-15.0 Å and a super-reflection at ~30 Å. XRD

265 patterns collected in AD conditions are shown in the Appendix (fig. A-1).

The described evolution of XRD patterns with depth is typical for smectite illitization
resulting from the burial diagenesis of clay-rich rocks. For example, XRD patterns presented

by Perry and Hower (1970) for samples E-2131 m, E-2554 m, and E-2667 m are almost

superimposed (except for the kaolinite reflections) to those of samples A, B and C,

270 respectively (fig. 3). Similarly, the XRD pattern presented by Perry and Hower (1970) for

sample E-3658 m resembles that of samples D and E, except for the low-angle intensity.

272 According to Hower and others (1976) the observed evolution is evidence for a continuous

273 smectite-to-illite reaction series occurring through intermediate mixed layers. However in

both the Perry and Hower (1970) and Hower and others (1976) studies, XRD pattern

interpretation was restricted to a qualitative comparison with patterns calculated for two-

276 component I-Exp (EG) models. The relative proportions of I and Exp layer types (W_i), and

their ordering (P_{ij} parameters) were the two essential parameters refined.

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Quantitative Description of Experimental XRD Profiles

Group I samples: single-phase segregated I-Exp model.– According to this model, the non-rational series of basal reflections corresponds to a unique I-Exp in which I and Exp layers tend to segregate. XRD data are compared to calculated patterns in figure 4. Structural parameters used to calculate these patterns are listed in tables 1 and 2. Along with the main I-

284	Exp contribution, samples contain kaolinite, illite (an illite-rich mixed layer with $\sim 5\%$ of
285	expandable layers), minor chlorite, and a randomly interstratified K-Exp containing 75%
286	kaolinite and 25% expandable layers. Although K-Exp have attracted considerably less
287	attention than I-Exp, natural K-Exp covering the whole compositional range have been
288	reported in the literature (see for example Sakharov and Drits, 1973; Sudo and Shimoda,
289	1977; Brindley and others, 1983). Consistent with these reports, K-Exp whose composition is
290	dominated by kaolinite layers exhibit broad diffraction maxima shifted from the ideal
291	kaolinite maxima towards the nearest smectite peaks as predicted by Méring (1949).
292	Transition from sample A to sample C corresponds to an increase in illite and K-Exp
293	content (from 5 to ~21%, and from 5 to ~15%, respectively – table 2) and to a decrease of I-
294	Exp (from 79 to \sim 53%). The kaolinite and chlorite content is about constant. With increasing
295	depth, I-Exp expandability decreases from 55% in sample A to 35% in samples B and C
296	(table 1A). Under AD conditions, three types of expandable layers (15.0, 12.5 and 14.0 Å $$
297	layers) are found in I-Exp from sample A, whereas only 2W and 1W layers (15.0 and 12.5 Å,
298	respectively) are encountered in samples B and C. After EG solvation all Exp layers in I-Exp
299	from sample A swell to 16.76 Å with two planes of EG molecules in their interlayers (2EG
300	layers). Swelling behavior is more heterogeneous in samples B and C (table 1A). In all three
301	samples, $W_I < P_{II}$ (table 1B) for I-Exp and illite layers are thus slightly segregated, as
302	estimated by the S _q parameter (Drits and Tchoubar, 1990):

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To determine S_q , it is convenient to use P_{II} and W_I values so as to disregard the actual distribution of Exp layers. With increasing depth, the S_q parameter decreases from 0.27 to 0.19 and 0.10 (samples A, B and C, respectively), indicating that interstratification of I and

 $S_q = (P_{ii} - W_i)/(1 - W_i)$

(1)

Exp layers tends to become random with increasing burial depth and illite content (table 1A).
The CSDS of I-Exp increases with burial depth from 7 (sample A) to 15 layers (samples B
and C – table 1A). For a given sample, the P_{ij} parameters refined for the I-Exp are different
for AD and EG states (table 1B). This apparent inconsistency arises from the contrasting
expansion behavior of Exp layers in AD and EG states, and vanishes if the hydration/swelling
behavior of Exp layers is carefully analyzed (see Appendix for details).

315 Single-phase segregated I-Exp model: Intrinsic inconsistency of the model.- If I-Exp in 316 group I samples represent a series of diagenetically altered mixed layers, the occurrence 317 probabilities of I and Exp layers, and those of the different layer pairs and triplets (W_i , W_{ij} = $W_i \times P_{ij}$ and $W_{ijk} = W_i \times P_{ij} \times P_{jk}$, respectively – table 3) should evolve logically in the context 318 319 of illitization. For the sake of simplicity, all expandable layers will be considered together in 320 the following discussion. From these occurrence probabilities, transition from sample A to 321 sample B appears logical as the illite enrichment (from 45% to 65% at 2170 and 3660 m, 322 respectively) is associated with the decrease of occurrence probability for layer pairs, and 323 layer triplets (not shown), containing Exp layers (table 3). At the same time, the segregation 324 degree in I-Exp decreases from 0.27 (sample A) to 0.19 (sample B) because ExpExp pairs 325 disappear faster than II pairs form $[(W_{ExpExp})_B - (W_{ExpExp})_A = -0.205, and (W_{II})_B - (W_{II})_A =$ 326 0.194 – table 3].

In the general illitization scheme, the steady evolution of a segregated I-Exp towards random interstratification is a priori consistent with a solid-state transformation. The observed decrease of the S_q parameter between samples B (0.19) and C (0.10) follows the same logic although illite contents are similar in the two samples (table 3). However, when looking at the different W_{ij} probabilities, the I-Exp evolution between samples B and C cannot be interpreted reasonably in the illitization context. This evolution implies indeed the formation of IExp and ExpI pairs at the expense of both II and ExpExp pairs [(W_{II})_B > (W_{II})_C – table 3].

The single-phase segregated I-Exp model is thus inadequate to describe the structuralevolution of group I samples, and should be rejected.

336 Group I samples: The mixture model. – According to this model, the ~17 Å peak of 337 group I samples corresponds to discrete smectite coexisting with a randomly interstratified I-338 Exp with a high content of illite layers ($W_1 > 50\%$ – Claret, 2001; Drits and others, 2002b; 339 Claret and others, 2004; Lanson and others, 2005; McCarty, 2005; Aplin and others, 2006; 340 McCarty and others, 2008). Data are compared in figure 5 to XRD patterns calculated for this 341 model. Table 4A contains the structural and probability parameters for the I-Exp contribution, 342 whereas relative proportions of the different contributions to the diffraction patterns are 343 reported in table 5. In all group I samples, the major contribution is I-Exp whose relative 344 proportion increases with increasing burial depth from 44% to 50% and 57% (samples A, B 345 and C, respectively). Simultaneously, the content of discrete smectite decreases dramatically 346 from 27% to 5% and ~2% in samples A, B and C, respectively. As for the single-phase 347 segregated I-Exp model the content of discrete illite increases significantly with depth from 348 5% to ~17% and 21% in samples A, B and C. I-Exp is randomly interstratified despite its high 349 illite content that ranges from 57% to 62 and 67% (samples A, B and C, respectively). I-Exp 350 has the same mean (12 layers) and maximum (50 layers) CSDS in all group I samples (table 351 4A). A randomly interstratified K-Exp with 75% kaolinite layers completes the clay 352 paragenesis. K-Exp exhibits broad diffraction maxima at ~6.8-7.0 and 3.4-3.5 Å both in AD 353 state and after EG solvation (fig. A-2A, B).

Group II samples.– Along with 4-5% of chlorite, 5-10% of illite (with 5% Exp layers),
6-12% of kaolinite, all group II samples contain I-Exp, I-Exp-Ch and K-Exp mixed layers.
The structural and probability parameters providing the best fit to XRD data (fig. 5) are
reported in table 4C. The major phases are I-Exp and I-Exp-Ch. The relative proportion of IExp decreases slightly with burial depth from 40% (sample D) to 33 and 34% (samples E and

F, respectively) whereas that of I-Exp-Ch steadily increases from 27% to 31% and 42%
(samples D, E and F, respectively).

361 Parallel to this phase composition change, transition from sample D to sample F is 362 characterized by a slight increase of the illite content in I-Exp (from 70 to 75%). In sample D, interstratification of I and Exp layers is ordered (R = 1) with MPDO ($P_{Exp1Exp1} = P_{Exp1Exp2} =$ 363 364 $P_{Exp2Exp1} = P_{Exp2Exp2} = 0$). Longer-range ordering (R = 2 - table 4C) is observed for samples E 365 and F. In the latter samples P_{ii} parameters are similar to sample D, and longer-range ordering 366 is characterized by a slight segregation of IExpIExp sequences as $P_{ExpIExp} > W_{Exp} / W_I$ (see 367 Drits and Tchoubar, 1990, for details). Compared to I-Exp in group I samples, the size of I-368 Exp CSDs is significantly increased for group II samples (mean and maximum values are 15 369 and 100 layers compared to 12 and 50, respectively, for group I samples - tables 4A, 4C). In all group II samples, I-Exp-Ch contains 70% of illite layers interstratified with Exp and di-370 371 trioctahedral chlorite layers, the proportion of Ch layers increasing from 15% in samples D 372 and E, to 20% in sample F. In contrast to the ordered I-Exp, I-Exp-Ch CSDSs are similar to 373 those determined for the I-Exp in group I samples (tables 4A, 4C). Finally, K-Exp (R = 0)374 consists of 75% kaolinite and 25% Exp layers as in group I samples. 375 376 DISCUSSION 377 378 Reliability of Structure Models 379 The results obtained in the present work demonstrate the ability of the multi-specimen 380 approach to provide good quality fit to experimental data obtained on natural polyphasic 381 samples, in agreement with previous studies (Drits and others, 1997a, 2002a, 2002b, 2004; 382 Sakharov and others, 1999a, 1999b; Lindgreen and others, 2000, 2002; Claret and others,

383 2004; McCarty and others, 2004, 2008). This approach can thus be used to determine accurate

384 structural parameters for the phases present in a given sample. In the present work,

385 satisfactory fit to experimental positions, intensities and profiles of basal XRD reflections was

386 obtained using up to three mixed layers, each incorporating from two to four layer types, in

387 addition to discrete phases.

Obviously, the more discrete and mixed-layer phases that coexist in a sample, the more independent structural parameters that are needed for simulation. As a result, the reliability and accuracy in determining these parameters may decrease as more phases are introduced, although constraints are provided by the required uniqueness of structure models used to fit different patterns of a given sample (AD and EG patterns of Ca-saturated samples in the present case).

394 *Evidence for the actual phase composition.*– As the optimum fits to XRD data were 395 obtained using a trial-and-error approach, the actual sensitivity of XRD simulations to key 396 structural parameters needs to be assessed. The presence of the different contributions is the 397 first of these parameters, and samples B and E will be used as typical for group I and II, 398 respectively. Elementary contributions to the intensity diffracted by these two samples are 399 shown in the Appendix (fig. A-2, A-3). Figure 6 compares the XRD pattern of sample B with 400 those calculated for models similar to the optimal one (fig. 5) after subtraction of the 401 contributions of discrete smectite or of K-Exp. Logically, the absence of the minor smectite 402 contribution leads to the absence of the 17 Å peak in the calculated EG pattern (fig. $6A - R_{wp}$ 403 = 17.56%). Similarly, the absence of the K-Exp contribution leads to significant misfits at $\sim 11.5^{\circ}$ and $\sim 26^{\circ}2\theta$ (fig. 6B – R_{wp} = 16.00%). 404

For group II samples, exclusion of either I-Exp or I-Exp-Ch contributions in the
calculated XRD pattern decreases dramatically the agreement with the data. For example,
calculated intensity is reduced in the low-angle region if the I-Exp contribution is subtracted
from the optimal fit (fig. 7A). Additional significant misfits are observed at 16-19° 2θ and 26-

409 $36^{\circ} 2\theta$ in both EG and AD XRD patterns (fig. 7A – $R_{wp} = 23.04\%$, and fig. 7B – $R_{wp} =$

410 27.73%, respectively). Figure 7C ($R_{wp} = 20.62\%$) shows that the I-Exp-Ch contribution is 411 essential to fit the AD pattern in the 18-20 and 26-31° 20 ranges. In the present work, mixed 412 layers are introduced only if they allowed fitting specific angular ranges without significant 413 overlap with other phases.

414 Evidence for the presence of chlorite layers in I-Exp-Ch.– The actual nature of the 415 mixed layer coexisting with the ordered I-Exp was determined after testing numerous illite-416 containing structure models with contrasting amounts, and distributions, of Exp layers: in 417 addition to I and Exp layers the optimum mixed layer (I-Exp-Ch) contains di-trioctahedral 418 layers consisting of dioctahedral 2:1 layers and of trioctahedral brucite-like interlayer sheets. 419 Despite a similar basal spacing, the 14.0 Å Ch layers can be differentiated from 14.0 Å Exp 420 layers because of their contrasting scattering factors. If Ch layers (with 3.0 Mg and 6.0 OH 421 per half unit-cell in their interlayers) are replaced by Exp layers (with 0.25 Mg and 2.0 H₂O per half unit-cell in their interlayers), significant misfits are visible at $17-18^{\circ}$ and $26-31^{\circ} 2\theta$ 422 for sample E (fig. $8A - R_{wp} = 17.41\%$). XRD patterns calculated for the optimum I-Exp-Ch 423 424 contribution and for the contribution in which Ch layers are replaced by Exp layers are shown in figure A-4. The strong intensity increase at $17-18^{\circ} 2\theta$ induced by the presence of Ch layers 425 426 is related to the specific intensity distribution observed for sudoite (di-trioctahedral chlorite), 427 whose 4.7 Å reflection is most intense (Lin and Bailey, 1985; Billault and others, 2002; 428 Kameda and others, 2007).

Heterogeneous hydration/swelling of Exp layers.- In both AD and EG states, Exp layers present in mixed layers often exhibit various interlayer configurations and *d*-spacings as reported for reference smectite samples (Ferrage and others, 2005b, 2007). For example, in the AD state I-Exp from group I samples systematically contains 15.0, 14.0 and 12.5 Å layers (table 4). Sensitivity of XRD to such heterogeneous behavior may be assessed by replacing, for example, 14.0 Å Exp layers (8% of the layers in I-Exp from sample B) either by 15.0 Å or
by 12.5 Å layers (fig. 8B and C, respectively). In both cases, significant misfits are visible at
28-30° 20.

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Diagenetic Illitization of Clay-rich Sediments: A Two-Stage Process

439 Undoubtedly, illitization of clay-rich sediments during burial diagenesis of mudstones 440 and shales ranks among the most important and most documented mineral reactions. In the 441 present work, the innovative interpretation of XRD patterns provides detailed information on 442 the different phases present in the sediments and on their evolution. As a result, a structural 443 mechanism can be proposed which contrasts with the usual description of a continuous 444 transformation described by Perry and Hower (1970), Hower and others (1976) and many 445 other authors (see Srodon, 1999, for a review). According to this commonly accepted model, 446 diagenetic illitization of clay-rich sediments consists of two main stages whose existence is 447 not challenged in the present study. The evolution of the mineralogical composition, and the 448 structural evolution of individual phases will thus be described separately for group I and 449 group II samples.

450 Smectite illitization in the upper part of the series (group I samples). – The commonly 451 accepted model assumes the steady illitization of a unique randomly interstratified I-Exp. By 452 contrast two phases, a discrete smectite and a randomly interstratified I-Exp with high illite 453 content, coexist in group I samples in addition to discrete illite, kaolinite, K-Exp and chlorite 454 (except for sample A). When burial depth increases the relative proportion of discrete 455 smectite decreases sharply from 27% at 2170 m to 2-3% at 4000 m and the illite content in I-Exp increases (from 57% to 67% at the same depths). Except for a few early reports (Perry 456 457 and Hower, 1970, 1972; Reynolds and Hower, 1970; Bethke and others, 1986), randomly 458 interstratified I-Exp with such high illite contents have seldom been described in diagenetic

environments, interstratification of I and Exp layers being usually described as ordered (R = 1and MPDO) when illite layers prevail. However, the coexistence of discrete smectite with randomly interstratified I-Exp with high illite content is possibly widespread at shallow depth in sedimentary basins, the absence of significant maximum in the low-angle region being responsible for their scarce description. The steady decrease of the 17.0 Å peak intensity and of its low-angle resolution observed with depth for group I samples is indeed characteristic of the early stage of the diagenetic smectite-to-illite transition (fig. 3).

466 A similar mineralogical composition was described in the Callovo-Oxfordian 467 sedimentary formation (Paris Basin - Claret, 2001; Claret and others, 2004). Using the same 468 methodological approach McCarty (2005), and McCarty and others (2008) also demonstrated 469 that discrete smectite and randomly interstratified I-Exp with high illite content coexist in 470 shallow samples from the off-shore Gulf Coast. The similarities between the XRD patterns 471 recorded for group I samples and those obtained from Gulf Coast wells B and E by Perry and 472 Hower (1970, 1972) support such a coexistence in the latter samples. TEM observations 473 performed on shallow samples from various sedimentary basins also support the ubiquity of 474 such a clay paragenesis (Dong and others, 1997; Dong, 2005; Freed and Peacor, 1992).

475 I-Exp in group I samples are characterized also by heterogeneous hydration/swelling behavior of Exp layers. In the AD state, 1W ($d_{001} \sim 12.5$ Å) and 2W ($d_{001} \sim 15.0$ Å) layers 476 477 systematically coexist in I-Exp (table 4), most likely as a consequence of the heterogeneous 478 distribution of the amount and/or location of the layer-charge deficit. However, layer-charge 479 heterogeneity is likely not considerable as both layer types swell to 16.7-16.9 Å following EG solvation (table 4). In addition, I-Exp includes 14.0 Å layers present in similar proportions 480 481 under AD and EG conditions. These layers cannot be considered as smectite layers as their 482 basal spacing remains constant upon EG solvation, and their actual nature is unclear. Their 483 basal spacing and swelling behavior are consistent with hydroxy-interlayered vermiculite

layers that are often found in soils as a separate phase (Douglas, 1989; Moore and Reynolds,
1997; Chen and others, 2001; Marques and others, 2002). The observed hydration/swelling
heterogeneity of Exp layers is most likely common in natural samples, thus impairing the
potential of most usual identification methods for I-Exp as discussed in more detail by
McCarty and others (2008).

489 *Group I samples: origin of the randomly interstratified I-Exp with high illite content* 490 $(\sim 65\% I)$. – It is commonly assumed that the smectite-to-illite reaction starts from a pure 491 smectite precursor. However, Hower and others (1976) pointed out that in young sedimentary 492 basins the pure smectite stage may be concealed by the high variability of smectite contents in 493 randomly interstratified I-Exp from surface samples. According to Jennings and Thompson 494 (1986) and Velde and Vasseur (1992), the compositional homogenization of I-Exp, likely 495 through its recrystallization and formation of pure smectite, occurs at burial depths ranging 496 typically from several hundred meters in older rocks to 1-2 km in younger ones. Smectite then 497 acts as a precursor for the diagenetic smectite-to-illite conversion (Velde and Iijima, 1988). In 498 the Carter well, the presence of pure smectite was inferred at 683 m from XRD analysis 499 (Berger and others, 1999). In the present study, no XRD data were collected over the 683-500 2150 m depth interval. It is however reasonable to assume that steady smectite-to-illite 501 conversion occurs over this depth interval, and that both smectite and I-Exp are authigenic in 502 group I samples. Additional support for the authigenic origin of I-Exp comes from the similar 503 XRD patterns obtained in this study and from other Gulf Coast samples (Perry and Hower, 504 1970, 1972). The diagenetic smectite-to-illite sequences described by the latter authors start 505 from very smectitic material and subsequently evolve to form parageneses having XRD 506 patterns very similar to those of group I samples (fig. 3).

507 *Group I samples: new description of smectite illitization during the first stage.* – From
508 the present interpretation of XRD patterns, the shallow part of the diagenetic smectite-to-illite

509 sequence thus corresponds to the formation of a randomly interstratified I-Exp with prevailing 510 illite layers ($W_1 > 50\%$) at the expense of smectite which is present as a pure phase in the 511 shallowest samples. At burial depths lower than 4000 m, the overall smectite-to-illite 512 conversion thus results i) from the dissolution of pure smectite, and ii) from the formation of 513 the randomly interstratified I-Exp with $W_I > W_{Exp}$. The latter process is likely fed by smectite 514 dissolution and favored by K-availability. The overall (I-Exp + smectite) content decreases 515 with increasing burial depth (from \sim 70% in sample A to \sim 60% in sample C) possibly because 516 smectite dissolution does not only feed I-Exp formation. Several important conclusions derive 517 from these results.

518 The first stage of smectite illitization is heterogeneous, with the simultaneous progress 519 of smectite dissolution and of I-Exp illitization, in agreement with electron microscopy 520 observation of Gulf Coast shales (Dong and others, 1997; Dong, 2005; Freed and Peacor, 521 1992). As a consequence, pure smectite is present at significant burial depth, indicating a 522 much higher stability than commonly accepted. In the Carter well for example, pure smectite 523 which accounts for most of the clay fraction at 683 m (Berger and others, 1999) persists down 524 to ~4000 m depth where it still represents 2% of the clay fraction (table 5). Although in the 525 investigated samples smectite illitization proceeds simultaneously with partial smectite 526 dissolution, the two reactions do not appear to be systematically linked. For example, Claret 527 and others (2004) presented evidence that I-Exp composition is constant while smectite is 528 steadily dissolving over a narrow depth interval in the Callovo-Oxfordian formation (eastern 529 Paris basin). Similarly, McCarty (2005) and McCarty and others (2008) describe important 530 variations of discrete smectite relative proportion without any compositional evolution of the 531 coexisting I-Exp.

532 The new description also raises the need to reconsider the kinetics of smectite533 illitization. According to the usual identification criteria (for example Srodon, 1981; Inoue

534 and others, 1989), XRD data obtained from the Carter samples correspond to an I-Exp with \sim 535 20% illite layers (R = 0) down to ~2000 m depth (Velde and Vasseur, 1992; Berger and 536 others, 1999). Similarly, shallow samples from Gulf Coast wells are dominated by randomly 537 interstratified I-Exp with ~25% illite layers according to Perry and Hower (sample E-1829 m 538 - 1970, 1972). By contrast, XRD profile modeling shows that I-Exp contains 57% illite layers 539 at similar depth (sample A). Illitization is thus faster than commonly assumed as randomly 540 interstratified I-Exp with $W_I > W_{Exp}$ likely forms under shallow burial conditions consistent 541 with the TEM observations of Freed and Peacor (1992). The formation of a randomly 542 interstratified I-Exp having a given composition thus occurs at much lower temperature than 543 assumed from the commonly accepted model of smectite illitization for similar conditions of 544 burial diagenesis (temperature, pressure, K activity, water-rock ratio, et cetera). The illite 545 content in I-Exp obtained from both approaches may however be partially reconciled by 546 taking into account the contribution of pure smectite. When this contribution is minimum (2% 547 - sample C), similar compositions are determined for I-Exp (~65%I) using either the usual 548 identification criteria (3500-4000 m deep samples in Carter well, fig. 1 - Velde and Vasseur, 549 1992; Berger and others, 1999) or the present modeling approach.

550 In any case, the rate of smectite illitization strongly decreases with increasing burial 551 depth, in contrast with the commonly accepted model (see for example Srodon and Eberl, 552 1984). According to the present data, the illite content in I-Exp increases at a minimum rate of 553 40%I/km from 683 to 2170 m depth. By contrast, from 2170 m to 4000 m the increase of illite 554 content in I-Exp is limited to $\sim 10\%$ (table 4), at a rate of $\sim 5\%$ I/km. In agreement with Berger 555 and others (1999), this rate decrease is likely due to the low amount of available K, in relation 556 with the dissolution of K-feldspars and micas. In the studied samples, the maximum 557 illitization rate coincides with the dissolution of K-feldspars which disappear at ~ 2000 m in 558 the Carter well (Berger and others, 1999).

559 Structural evolution of clay minerals during deep burial diagenesis (group II samples).-560 The presence of a unique illite-rich ordered ($R \ge 1$) I-Exp is characteristic of deep burial 561 diagenesis in the commonly accepted model for smectite illitization. According to the present 562 modeling results, such a phase is actually present in group II samples coexisting with another 563 illite-containing mixed layer. In addition to illite and Exp layers, the latter structure includes 564 di-trioctahedral chlorite layers, whose formation is consistent with the low K-availability 565 (Whitney and Northrop, 1988) and whose relative proportion increases slightly with 566 increasing burial depth (table 4). Interstratification of the different layer types is almost 567 random in I-Exp-Ch, with only a slight tendency to segregation of Ch layers. By contrast, the 568 slight increase of the illite content in I-Exp is associated with a steady increase of layer 569 ordering. Specifically, the succession of dominant illite layers is favored and the extent of this 570 ordering (quantified by the Reichweit R parameter – Jagodzinski, 1949; Reynolds, 1980) 571 tends to increase beyond the nearest neighbor with increasing burial depth (table 4). 572 Transition from group I to group II samples: structural evolution of I-Exp from group I 573 to group II samples.- The illite content in I-Exp increases only slightly from sample C to 574 sample D, whereas the layer distribution is dramatically modified between the two samples, 575 interstratification being random in sample C and ordered (R =1 with MPDO) in sample D. In 576 the context of smectite illitization, II pairs should be preserved and solid-state transformation 577 can be hypothesized only if the relative proportion of IExp and ExpI pairs increases at the 578 expense of the sole ExpExp pairs. On the contrary, it is clear from table 6 that ExpExp pairs 579 originally present in sample C are not abundant enough (0.109) to account for the increase of 580 IExp and ExpI pairs from sample C to sample D $[(W_{IExp} + W_{ExpI})_D - (W_{IExp} + W_{ExpI})_C =$ 581 0.158]. The transition from sample C to sample D can thus only result from a dissolution-582 recrystallization process. Indirect support for the proposed mechanism comes from the 583 extremely low intensity scattered by sample D which required a seven-fold increase of the

584 collection time to obtain a similar signal-to-noise ratio for a given amount of material. The 585 low amplitude of the XRD signal is likely due to the presence of XRD-amorphous material 586 whose presence is expected for a major dissolution-reprecipitation process. Additional 587 indirect support arises from the significant CSDS increase observed for the I-Exp from 588 sample C to sample D (table 5). No K-Ar ages are available for the samples investigated in 589 the present study. However, Aronson and Hower (1976) reported significantly younger ages 590 for deep Gulf Coast samples (typical of group II samples) than for shallower samples (typical 591 of group I samples). The gap between the two groups of samples also supports a major 592 dissolution-recrystallization process leading to the crystallization of an ordered I-Exp at the 593 expense of a randomly interstratified I-Exp of similar composition.

594 Transition from group I to group II samples: possible solid-state formation of I-Exp-Ch 595 at the expense of I-Exp. – The illite contents in I-Exp from sample C and in I-Exp-Ch from 596 sample D are similar (67 and 70%I, respectively). Their junction probability parameters 597 exhibit also strong similarities, interstratification being random in I-Exp from sample C, and 598 showing only slight tendency to segregation in I-Exp-Ch from sample D (table 4C). In 599 addition, I-Exp from sample C and I-Exp-Ch from sample D have similar CSDSs. It is thus 600 possible to hypothesize a solid-state mechanism, involving Mg polymerization in former Exp 601 interlayers, for the transition between the two mixed layers. In this case, a series of mixed 602 layers with compositions intermediate between those of the two end members can be 603 envisaged. In I-Exp from sample C and in I-Exp-Ch from sample D, Exp layers are randomly 604 distributed within crystallites ($P_{Expi} = W_i$), whereas I and Ch layers are slightly segregated in 605 sample D ($W_I < P_{II}$, and $W_{Ch} < P_{ChCh}$). The degree of segregation of I and Ch layers in I-Exp-606 Ch from sample D is 0.083 and 0.135, respectively (Eq. 1 – table 4C). To propose 607 compositional and structural parameters for intermediate phases, one may thus hypothesize 608 that the increase of I and Ch contents from sample C to sample D is accompanied by the

609	increase of their tendency to segregation. Probability parameters describing such theoretical
610	intermediate phases (phases I and II) are reported in table 7. In particular, the relative
611	proportions of I and Ch layers in these phases are equal to 68% and 5% (phase I) and 69%
612	and 10% (phase II), respectively, to account for the compositional change from sample C
613	(67%I and 0%Ch) to sample D (70%I and 15%Ch). In addition, the degrees of segregation of
614	I and Ch layers increase steadily from sample C (0.000 and 0.000, random interstratification)
615	to phase I (0.027 and 0.045), to phase II (0.054 and 0.090), and finally to sample D (0.083 and
616	0.135, respectively). Exp layers are randomly distributed in both intermediate phases so that
617	$P_{ExpExp} = W_{Exp}$, $P_{ExpI} = W_I$ and $P_{ExpCh} = W_{Ch}$ as in I-Exp from sample C and in I-Exp-Ch from
618	sample D. Possible mechanisms of the hypothesized solid-state transformation of I-Exp from
619	sample C to I-Exp-Ch from sample D through intermediate I-Exp-Ch phases are detailed in
620	the Appendix.
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622	CONCLUDINGS REMARKS
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624	A General Pattern for Diagenetic Smectite-to-Illite Transition in Shales
625	The XRD patterns obtained from the Carter well samples are typical for the diagenetic
626	smectite-to-illite transition (fig. 3). The multi-specimen method led however to an unusual
627	description of the data. In particular, an original clay paragenesis is reported and a novel
628	diagenetic evolution of this paragenesis proposed which includes two stages of smectite
629	illitization.
630	In the first stage, the clay paragenesis corresponds to the physical mixture of discrete
631	smectite and of a randomly interstratified I-Exp with a high content of illite layers ($W_I > 50\%$)
632	in addition to illite, kaolinite, chlorite and K-Exp. With increasing burial depth, the relative
633	proportion of I-Exp increases, essentially at the expense of discrete smectite, and its

634 composition becomes slightly more illitic. Several conclusions in this study contradict the

635 conventional wisdom of smectite-to-illite transition:

636 - Smectite illitization is a heterogeneous reaction involving the physical mixture of pure

637 smectite and I-Exp.

638 - Discrete smectite and I-Exp are authigenic.

639 - The apparent stability of smectite is higher than commonly assumed as this mineral persists
640 down to 4000 m, although its relative abundance decreases with increasing depth.

- Smectite illitization occurs very early and randomly interstratified I-Exp with $W_I > W_{Exp}$ is

642 formed at shallow burial depth, the temperature at which a I-Exp with a given composition is

643 formed being lower than commonly assumed.

- Smectite illitization rate decreases rapidly, most likely as the result of K-feldspar

645 dissolution.

646 In the second stage of smectite illitization (below 4000 m depth in the present case 647 study), clay paragenesis consists of two illite-containing mixed layers in addition to illite, 648 kaolinite, chlorite and K-Exp. These two illite-containing mixed layers result from two 649 parallel reaction mechanisms affecting the randomly interstratified I-Exp present in the upper 650 part of the series. The first reaction implies the dissolution of the I-Exp and the crystallization 651 of an ordered I-Exp with R = 1 (MPDO) without significant increase of the I layer content 652 (70% versus 67%, tables 4A, 4C), possibly as the result of low K-availability. With increasing 653 depth, ordering increases together with a marginal increase of the I layer content (up to 75% 654 in sample F – table 4C). The second reaction affects the remaining fraction of the randomly 655 interstratified I-Exp and implies the polymerization and growth of trioctahedral brucite-like 656 sheets in Exp interlayers, thus developing di-trioctahedral chlorite layers in the initial I-Exp to 657 form an I-Exp-Ch. A possible layer-by-layer mechanism is supported for this reaction by the 658 random layer distribution in the I-Exp-Ch, similar to that of the initial I-Exp. In this scheme,

659	Mg cations released by the dissolution-recrystallization of I-Exp likely represent the Mg
660	source for the formation of brucite-like sheets.
661	
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663	
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672	
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933

FIGURE CAPTIONS

934

Fig. 1. Age of the sediments as a function of depth in Carter and Mustang Island wells
(top – Velde and Vasseur, 1992). Smectite content in I-Exp as determined by Velde and
Vasseur (1992) as a function of depth in these two wells.

Fig. 2. Experimental XRD patterns obtained from Carter well samples selected as being representative of the complete smectite-to-illite diagenetic transition. Sampling depths are 2170 (A), 3660 (B), 4000 (C), 4640 (D), 5010 (E), and 5180 m (F). XRD patterns obtained on EG solvated samples. Dashed and dot-dashed lines indicate the positions of illite and smectite reflections. Solid and dot-dot-dashed lines indicate positions of some kaolinite and chlorite reflections. For all samples, the gray bar indicates a modified scale factor for the high-angle region.

Fig. 3. Comparison between experimental XRD patterns obtained from Carter well samples investigated in the present study and those obtained by Perry and Hower (1970) on selected samples from well E (Galveston county). The latter samples were used to establish the smectite-to-illite diagenetic transition in Gulf Coast clay-rich sediments. XRD patterns obtained on EG solvated samples.

Fig. 4. Comparison between experimental and calculated XRD patterns as a function of depth for group I samples (single-phase segregated I-Exp model). Experimental and calculated optimal XRD patterns are shown as crosses and as solid lines, respectively. Optimal structure models are described in tables 1 and 2. For all samples, the gray bar indicates a modified scale factor for the high-angle region. **A**. XRD patterns obtained on EG solvated samples. **B**. XRD patterns obtained on air-dried samples at 40% relative humidity.

Fig. 5. Comparison between experimental and calculated XRD patterns as a function ofdepth for all Carter well samples (mixture model). Experimental and calculated optimal XRD

patterns are shown as crosses and as solid lines, respectively. Optimal structure models are
described in tables 4 and 5. For all samples, the gray bar indicates a modified scale factor for
the high-angle region. A. XRD patterns obtained on EG solvated samples. B. XRD patterns
obtained on air-dried samples at 40% relative humidity.

Fig. 6. Sensitivity of calculated XRD patterns to the mineralogical composition.
Patterns as for figure 5. Arrows indicate significant misfit as compared to the optimum fits
shown in figure 5. The optimum mineralogical composition is given in table 5. A. Sample B –
3660 m Ca-saturated after EG solvation without the contribution of discrete smectite. B.
Sample B – 3660 m Ca-saturated after EG solvation without the contribution of K-Exp.

Fig. 7. Sensitivity of calculated XRD patterns to the mineralogical composition. Patterns as for figure 5. Arrows indicate significant misfit as compared to the optimum fits shown in figure 5. The optimum mineralogical composition is given in table 5. **A**. Sample E =5010 m Ca-saturated after EG solvation without the contribution of I-Exp. **B**. Sample E =5010 m Ca-saturated air-dried without the contribution of I-Exp. **C**. Sample E =5010 m Ca-saturated air-dried without the contribution of I-Exp. **C**. Sample E =5010 m Ca-saturated air-dried without the contribution of I-Exp. **C**. Sample E =5010 m Ca-saturated air-dried without the contribution of I-Exp. **C**. Sample E =5010 m Ca-saturated air-dried without the contribution of I-Exp. **C**. Sample E =5010 m Ca-saturated air-dried without the contribution of I-Exp. **C**. Sample E =5010 m Ca-saturated air-dried without the contribution of I-Exp. **C**. Sample E =5010 m Ca-saturated air-dried without the contribution of I-Exp. **C**. Sample E =5010 m Ca-saturated air-dried without the contribution of I-Exp. **C**. Sample E =5010 m Ca-saturated air-dried without the contribution of I-Exp. **C**. Sample E =5010 m Ca-saturated air-dried without the contribution of I-Exp. **C**.

973 Fig. 8. Sensitivity of calculated XRD patterns to structural parameters. Patterns as for 974 figure 5. Arrows indicate significant misfit as compared to the optimum fits shown in figure 975 5. The structural parameters for the optimal models are given in table 4. A. Sample E -976 5010 m Ca-saturated air-dried. In I-Exp-Ch, Ch layers (with 3.0 Mg and 6.0 OH per half unit-977 cell in their interlayers) are replaced by Exp layers (with 0.25 Mg and 2.0 OH per half unit-978 cell in their interlayers). **B**. Sample B – 3660 m Ca-saturated air-dried. In I-Exp, 14.0 Å Exp 979 layers (8% of the layers) are replaced by 15.0 Å Exp layers. C. Sample B – 3660 m Ca-980 saturated air-dried. In I-Exp, 14.0 Å Exp layers (8% of the layers) are replaced by 12.5 Å Exp 981 layers.

982

Table 1A. Single-phase segregated I-Exp model. Composition and structural parameters of the segregated I-Exp in group I samples	Table 1A	. Single-phase	segregated I	-Exp model.	Composition	and structural	parameters of	of the segreg	gated I-Exp	in group	I samples
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Sample	WI	W_{Exp1}	W_{Exp2}	W_{Exp3}	h _{Exp1}	h _{Exp2}	h _{Exp3}	R	N_{av}	N _{max}	S_q
A – EG	0.45	0.55	-	-	16.76	-	-	1	7	50	0.27
A – AD	0.45	0.30	0.15	0.10	15.00	12.50	14.00	1	7	50	0.27
B – EG	0.65	0.27	0.08	-	16.76	14.00	-	1	15	50	0.10
B – AD	0.65	0.21	0.14	-	15.00	12.50	-	1	15	50	0.19
C – EG	0.65	0.27	0.08	-	16.76	14.00	-	1	15	50	0.10
C – AD	0.65	0.15	0.20	-	14.90	12.50	-	1	15	50	0.10

Note: The basal *d*₀₀₁ distances of the different layer types (h_i) are given in Å. R is the Reichweit parameter (Jagodzinski, 1949) which characterizes the extent of ordering as the number of adjacent layers influencing the nature of a given layer. N_{av} and N_{max} are the average and maximum numbers of layers in coherent scattering domains (lognormal size distribution). S_q parameter is an estimator of the degree of segregation in I-Exp (eq 1).

Table 1B. Single-phase segregated I-Exp model. Junction probabilities of the segregated I-Exp in samples A, B, and C.

A-AD	l 9.98 Å	Exp1 15.00 Å	Exp2 12.50 Å	Exp3 14.00 Å
l (9.98 Å) 0.45	0.600	0.133	0.133	0.133
Exp1 (15.00 Å) 0.30	0.200	0.500	0.167	0.133
Exp2 (12.50 Å) 0.15	0.400	0.333	0.267	0.000
Exp3 (14.00 Å) 0.10	0.600	0.400	0.000	0.000

A-EG	ا 9.98 Å	Exp 16.76 Å
l (9.98 Å) 0.45	0.600	0.400
Exp (16.76 Å) 0.55	0.327	0.673

B-AD	l 9.98 Å	Exp1 15.00 Å	Exp2 12.50 Å
l (9.98 Å) 0.65	0.716	0.178	0.106
Exp1 (15.00 Å) 0.21	0.520	0.350	0.130
Exp2 (12.50 Å) 0.14	0.537	0.150	0.313

B-EG	l 9.98 Å	Exp1 16.76 Å	Exp2 14.00 Å
l (9.98 Å) 0.65	0.716	0.216	0.068
Exp1 (16.76 Å) 0.27	0.520	0.480	0
Exp2 (14.00 Å) 0.08	0.550	0	0.450

		Exp1	Exp2		
C-AD	9.98 Å	15.00 Å	12.50 Å		
I (9.98 Å) 0.65	0.684	0.138	0.178		
Exp1 (14.90 Å) 0.15	0.600	0.150	0.250		
Exp2 (12.50 Å) 0.20	0.580	0.240	0.180		

C-EG	l 9.98 Å	Exp1 16.76 Å	Exp2 14.00 Å
l (9.98 Å) 0.65	0.683	0.249	0.068
Exp1 (16.76 Å) 0.27	0.600	0.400	0
Exp2 (14.00 Å) 0.08	0.550	0	0.450

Sample	I-Exp	III	Kaol	Ch	K-Exp ^a	R_{wp}^{b}	R_{exp}^{b}
A – EG	79	5	11	-	5	11.42%	1.73%
A – AD	79	5	11	-	5	11.00%	1.64%
B – EG	64	10	9	1	16	11.60%	2.36%
B – AD	57	13	9	2	19	10.80%	2.05%
C – EG	55	18	8	1	18	11.31%	1.94%
C – AD	52	25	8	2	13	9.85%	1.85%

 Table 2. Single-phase segregated I-Exp model. Relative proportions (in wt%) of the different contributions to the diffracted intensity.

^a The composition of K-Exp is constant (75:25 K:Exp ratio).
 ^b Estimators of the fit quality (R_{wp}) and of the statistical error associated with measured intensities (R_{exp} – Howard and Preston, 1989)).

Layer	А	В	С
sequence	sample	sample	sample
I	0.45	0.65	0.65
Exp	0.55	0.35	0.35
II	0.270	0.465	0.444
IExp	0.180	0.184	0.206
Expl	0.180	0.184	0.206
ExpExp	0.370	0.166	0.144

Table 3. Single-phase segregated I-Exp model. Relative abundance of the different layers and layer pairs (W_i and W_{ij} parameters) for the segregated I-Exp in group I samples.

Sample	Phase	Wı	W_{Exp1}	W_{Exp2}	W_{Exp3}	h _{Exp1}	h _{Exp2}	h _{Exp3}	N _{av}	N _{max}	R	Junction probability parameters
A – EG	I-Exp	0.57	0.35	0.08	-	16.70	14.00	-	12	50	0	$R = 0 (P_{ij} = W_j)$
A – AD	I-Exp	0.57	0.20	0.08	0.15	15.00	14.00	12.50	12	50	0	-
B – EG	I-Exp	0.62	0.30	0.08	-	16.72	14.00	-	12	50	0	-
B – AD	I-Exp	0.62	0.15	0.08	0.15	15.00	14.00	12.50	12	50	0	-
C – EG	I-Exp	0.67	0.30	0.03	-	16.85	14.00	-	12	50	0	-
C – AD	I-Exp	0.67	0.17	0.03	0.13	15.00	14.00	12.50	12	50	0	-

Table 4A. Mixture model. Composition and structural parameters of I-Exp in group I samples.

The basal *d*₀₀₁ distances of the different layer types (h_i) are given in Å. R is the Reichweit parameter (Jagodzinski, 1949) which characterizes the extent of ordering as the number of adjacent layers influencing the nature of a given layer. N_{av} and N_{max} are the average and maximum numbers of layers in coherent scattering domains (lognormal size distribution).

Sample	Phase	Wı	W _{Exp1}	W _{Exp2}	Ηĸ	h _{Exp1}	h _{Exp2}	N _{av}	N _{max}	R	Junction probability parameters
A – EG	K-Exp	0.75	0.10	0.15	7.156	16.90	12.90	12	50	0	$R = 0 (P_{ij} = W_j)$
A – AD	K-Exp	0.75	0.05	0.20	7.156	15.00	12.50	12	50	0	-
B – EG	K-Exp	0.75	0.00	0.25	7.156	16.90	12.90	12	50	0	-
B – AD	K-Exp	0.75	0.00	0.25	7.156	15.00	12.50	12	50	0	-
C – EG	K-Exp	0.75	0.10	0.15	7.156	16.90	12.90	12	50	0	-
C – AD	K-Exp	0.75	0.00	0.25	7.156	15.00	12.50	12	50	0	-
D – EG	K-Exp	0.75	0.15	0.10	7.156	16.90	12.90	12	50	0	-
D – AD	K-Exp	0.75	0.05	0.20	7.156	15.00	12.50	12	50	0	-
E – EG	K-Exp	0.75	0.15	0.10	7.156	16.90	12.90	12	50	0	-
E – AD	K-Exp	0.75	0.00	0.25	7.156	15.00	12.50	12	50	0	-
F – EG	K-Exp	0.75	0.10	0.15	7.156	16.90	12.90	12	50	0	-

Table 4B. Mixture model. Composition and structural parameters of K-Exp.

The basal *d*₀₀₁ distances of the different layer types (h_i) are given in Å. R is the Reichweit parameter (Jagodzinski, 1949) which characterizes the extent of ordering as the number of adjacent layers influencing the nature of a given layer. N_{av} and N_{max} are the average and maximum numbers of layers in coherent scattering domains (lognormal size distribution).

Sample	Phase	W	W_{Exp1}	W_{Exp2}	W_{Ch}	h _{Exp1}	h _{Exp2}	h _{Ch}	Nav	N _{max}	R	Junction probability parameters
D – EG	I-Exp	0.70	0.25	0.05		16.86	12.90		15	100	1	$R = 1 \text{ with MPDO}^{a}$ $P_{Exp1Exp1} = P_{Exp1Exp2} = 0$ $P_{Exp2Exp1} = P_{Exp2Exp2} = 0$
	I-Exp-Ch	0.70	0.15	-	0.15	16.86		14.00 ^b	12	50	1	$P_{Exp1Exp1} = P_{Exp1Ch} = P_{ChExp1} = 0.150$ $P_{ChCh} = 0.265$
D – AD	I-Exp	0.70	0.30			15.00			15	100	1	$R = 1 \text{ with MPDO}^{a}$ $P_{Exp1Exp1} = 0$
												$P_{Exp1Exp1} = P_{Exp2Exp1} = P_{ChExp1} = 0.050$
	I-Exp-Ch	0.70	0.05	0.10	0.15	15.00	12.50	14.00 ^b	12	50	1	$P_{Exp1Exp2} = P_{Exp2Exp2} = P_{ChExp2} = 0.100$ $P_{Exp1Exp2} = P_{Exp2Exp2} = 0.150$
												$P_{ChCh} = P_{ChCh} = 0.150$ $P_{ChCh} = 0.265$ $P_{ChCh} = P_{ChCh} = P_{ChCh} = P_{ChCh}$
E – EG	I-Exp	0.75	0.21	0.04		16.92	12.90		15	100	2	$P_{Exp1Exp1} = 0.350^{b}$
	I-Exp-Ch	0.70	0.15		0.15	16.86		14.00 ^b	12	50	1	$P_{Exp1Exp1} = P_{Exp1Ch} = P_{ChExp1} = 0.150$
												$P_{ChCh} = 0.265$ $P_{Exp1Exp1} = P_{Exp1Exp2} = P_{Exp2Exp1} =$
E – AD	I-Exp	0.75	0.21	0.04		15.00	12.50		15	100	2	$P_{Exp2Exp2} = 0$ $P_{Exp1IExp1} = 0.350^{b}$
	I-Exp-Ch	0.70		0.15	0.15		12.50	14.00 ^b	12	50	1	$P_{Exp1Exp1} = P_{Exp1Ch} = P_{ChExp1} = 0.150$
F – EG	I-Exp	0.75	0.20	0.05		16.86	12.90		15	100	2	$P_{ChCh} = 0.265$ $P_{Exp1Exp1} = P_{Exp1Exp2} = P_{Exp2Exp1} = P_{Exp2Exp2} = 0$

Table 4C. Mixture model. Composition and structural parameters of the mixed layers in group II samples.

										$P_{Exp1IExp1} = 0.300, P_{Exp1IExp2} = 0.050^{\circ}$
										$P_{Exp1Exp1} = P_{Exp1Ch} = P_{ChExp1} =$
I-Exp	o-Ch	0.70	0.10	0.20	16.86	14.00	^b 12	50	1	0.150
										$P_{ChCh} = 0.265$
^a Maximum pos	sible c	legree o	f ordering	which prohibits p	airs of th	he minor layers	: P _{ii} = 0	if W _i <0.5	. Refer t	to Reynolds (1980), Drits and
Tchoubar	Tchoubar (1990), and Moore and Revnolds (1997) for additional details.									
^b Other junction probability parameters needed to describe layer stacking are $P_{Exp1 Exp2} = P_{Exp2 Exp1} = P_{Exp2 Exp2} = 0$										
^c Other junction	proba	bility pa	rameters	needed to descril	be layer s	stacking are P	xp2lExp1	= P _{Exp2IExp}	₂ = 0	r

Sample	I-Exp	I-Exp- Ch	Sm	III	Kaol	Ch	K-Exp	R_{wp}^{a}	R_{exp}^{a}
A – EG	45	-	27	4	9	-	15	9.14%	1.73%
A – AD	43	-	26	6	11	-	14	8.06%	1.64%
B – EG	51	-	5	15	14	2	13	14.16%	2.36%
B – AD	50	-	5	19	12	2	12	9.30%	2.05%
C – EG	57	-	2	21	6	2	12	11.12%	1.94%
C – AD	58	-	3	22	7	2	8	9.72%	1.85%
D – EG	42	26	-	10	6	4	12	8.23%	2.28%
D – AD	39	28	-	9	5	4	15	8.99%	1.15%
E – EG	34	30	-	9	11	4	12	10.23%	2.11%
E – AD	31	32	-	6	12	5	14	11.94%	2.00%
F – EG	34	42	-	5	7	5	7	13.38%	3.07%

 Table 5. Mixture model. Relative proportions (in wt%) of the different contributions to the diffracted intensity.

^a Estimators of the fit quality (R_{wp}) and of the statistical error associated with measured intensities (R_{exp} – Howard and Preston, 1989).

Layer	С	D
sequence	sample	sample
I	0.670	0.700
Exp1	0.300	0.250
Exp2	0.030	0.050
П	0.449	0.400
IExp1	0.201	0.250
IExp2	0.020	0.050
Exp1I	0.201	0.250
Exp1Exp1	0.090	0.000
Exp1Exp2	0.009	0.000
Exp2I	0.020	0.050
Exp2Exp1	0.009	0.000
Exp2Exp2	0.001	0.000

Table 6. Mixture model. Relative abundance of the different layers and layer pairs (W_i and W_{ij} parameters) in the I-Exp of samples C and D.

Table 7. Mixture model. Junction probabilities of mixed layers occurring during the hypothesized solid-state transformation of I-Exp from sample C to I-Exp-Ch from sample D. The composition and structural parameters (segregation of I and Exp layers) of these mixed layers are thus theoretically intermediate between those of the two end members.

Layer	Sample	Inter.	Inter.	Sample					
sequence	С	Phase I	phase II	D					
W	0.670	0.680	0.690	0.700					
W_{Exp}	0.330	0.270	0.210	0.150					
W_{Ch}	0.000	0.050	0.100	0.150					
S _q - I	0.000	0.027	0.054	0.083					
S _q - Ch	0.000	0.045	0.090	0.135					
P _{II}	0.670	0.689	0.707	0.725					
P _{IExp}	0.330	0.264	0.205	0.150					
P_{ICh}	0.000	0.047	0.088	0.125					
P _{Expl}	0.670	0.680	0.690	0.700					
P _{ExpExp}	0.330	0.270	0.210	0.150					
P_{ExpCh}	0.000	0.050	0.100	0.150					
P_{Chl}	-	0.561	0.573	0.585					
P_{ChExp}	-	0.346	0.246	0.150					
P_{ChCh}	-	0.093	0.181	0.265					
Note: S _q is of I an	Note: S _q is an estimator of the degree of segregation of I and Ch lavers in I-Exp-Ch (eq 1).								

881

APPENDIX

882

883 Single-phase segregated I-Exp model: Self-consistency of the model. 884 For a given sample, junction probability parameters, P_{ii}, refined for the I-Exp 885 contribution are different for AD and EG states (table 1B). This apparent inconsistency arises 886 from the contrasting expansion behavior of Exp layers in AD and EG states. For example, the 887 hydration behavior of Exp layers is highly heterogeneous in sample A with three types of Exp 888 layers, whereas EG solvation results in the homogeneous swelling of all Exp layers to 889 16.76 Å (2EG). However, the distribution of illite and expandable layers in I-Exp should be 890 identical in both states. Therefore, the four-component I-Exp in sample A (AD state) must be 891 reduced to a two-component system following EG solvation if the 15.0, 14.0 and 12.5 Å 892 layers become 2EG layers. To ensure the consistency of the structure model for sample A the 893 sums $(W_{Exp1I} + W_{Exp2I} + W_{Exp3I})$, $(W_{IExp1} + W_{IExp2} + W_{IExp3})$, and $(W_{Exp1Exp1} + W_{Exp1Exp2} + W_{IExp3})$ 894 $W_{Exp1Exp3} + W_{Exp2Exp1} + W_{Exp2Exp2} + W_{Exp2Exp3} + W_{Exp3Exp1} + W_{Exp3Exp2} + W_{Exp3Exp3}$) obtained 895 for the four-component I-Exp (AD state) must be equal to the parameters W_{ExpI} , W_{IExp} and 896 W_{ExpExp}, respectively, determined for the two-component I-Exp following EG solvation (table 897 1B). Here, $W_{ii} = W_i P_{ii}$ is the occurrence probability for an ij layer pair (i, j = I, Exp, Exp₁, 898 Exp₂ and Exp₃ – Exp, Exp₁, Exp₂ and Exp₃ denote 16.76, 15.0, 12.5 and 14.0 Å layers). W_{ii} 899 parameters are reported in table A-1 for I-Exp in group I samples. For sample A, $W_{II} = 0.270$ 900 in both AD and EG states and the above relationships are valid. In samples B and C, two 901 types of expandable layers coexist in both AD and EG states. However, the relative amounts 902 of the two types differ in AD and EG states, thus leading to contrasting values of P_{ii} 903 parameters for the corresponding models (table 1B). To ensure the consistency of the 904 proposed models these parameters can be reconciled by considering that some of the

905 expandable layers (noted as Exp' layers in tables A-1B, C) behave as Exp2 layers in the AD
906 state and as Exp1 layers when EG solvated (tables A-1B, C).

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908 *Possible solid-state formation of I-Exp-Ch (sample D) at the expense of I-Exp (sample C)*

909 As described in the main text, the contents of illite layers in I-Exp from sample C and in 910 I-Exp-Ch from sample D are similar (67 and 70%I, respectively). Junction probability 911 parameters exhibit also strong similarities, interstratification being random in I-Exp from 912 sample C, and showing only slight tendency to segregation in I-Exp-Ch from sample D (table 913 4). In addition, I-Exp from sample C and I-Exp-Ch from sample D have similar CSD sizes. 914 As a consequence, a solid-state mechanism can be hypothesized for the transition between the 915 two mixed layers, and a series of mixed layers with compositions and structural features (for 916 example the segregation degree of I and Ch Layers, and the random interstratification of Exp 917 layers) intermediate between those of the two end members can be envisaged (table 7). The 918 scope of this section is to describe in detail this hypothesized solid-state transformation and to 919 assess its robustness from the analysis of the relative abundance of layer pairs and triplets $(W_{ij}, and W_{ijk}, respectively - i, j, k = I, Exp, Ch)$ and of their evolution during the 920 921 transformation. This evolution should follow logically from that of the relative proportion of 922 the different layer types and of their layer stacking.

For this purpose, relative abundances of layer pairs and triplets deduced from structure models (W_{XRD} in table A-2) serve as the basis for this analysis. The first step is thus to calculate the occurrence probabilities for layer pairs and triplets in I-Exp from sample C, in I-Exp-Ch from sample D, and in the two intermediate phases. These occurrence probabilities can be calculated from the junction probabilities listed in table 7 ($W_{ij} = W_i P_{ij}$, and $W_{ijk} =$ $W_{ij}P_{jk}$) and are reported in table A-2 (columns W_{XRD}). The second step is to identify layer pairs whose occurrence probability deduced from structure models (columns W_{XRD}) is

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930 decreasing along the reaction pathway (from I-Exp in sample C to phase I to phase II and 931 finally to I-Exp-Ch in sample D). For example, from I-Exp in sample C to phase I, the 932 occurrence probabilities of IExp, ExpI and ExpExp pairs (W_{IExp}, W_{ExpExp}) are 933 decreasing. In table A-2 such pairs are identified with an arrow following their occurrence 934 probability. The third step is to distribute these layer pairs so as to match the occurrence 935 probabilities of layer pairs in the next phase (phase I in our example) as shown in table A-3A. In our example, 0.1798 out of the initial 0.2211 IExp pairs are preserved whereas 0.0319 pairs 936 937 are transformed to ICh pair, as required for intermediate phase I, the remaining 0.0094 pairs 938 being transformed to II pairs. The same procedure can be applied to ExpI and ExpExp pairs. 939 As a result, theoretical occurrence probabilities can be calculated for all layer pairs in phase I, 940 phase II, and in the I-Exp-Ch from sample D. These values are reported in the W_{Cal} columns 941 of table A-2, and they systematically coincide with W_{XRD} values. The fourth step is to 942 calculate occurrence probabilities for all layer triplets. Again, this starts with the identification 943 of the layer triplets whose occurrence probability deduced from structure models (columns 944 W_{XRD}) is decreasing along the reaction pathway (from I-Exp in sample C to phase I to phase 945 II and finally to I-Exp-Ch in sample D). For example, from I-Exp in sample C to phase I, the 946 occurrence probabilities of IIExp, IExpI, IExpExp, ExpII, ExpIExp, ExpExpI, and 947 ExpExpExp triplets (W_{IIExp}, W_{IExpI}, W_{IExpExp}, W_{ExpI}, W_{ExpIExp}, W_{ExpExpI}, and W_{ExpExpExp}) are 948 decreasing. In table A-2 such triplets are identified with an arrow following their occurrence 949 probability. To distribute these "disappearing" layer triplets among newly formed ones, the 950 R = 1 Reichweit parameter implies that the transition probability from one layer pair to 951 another does not depend on the preceding or following layer. As an illustration, one may 952 consider the transformation of the 0.1481 IIExp triplets present in I-Exp from sample C. As 953 IExp pairs may be transformed to II, IExp, and ICh pairs (table A-3A) IIExp triplets are 954 transformed to III, IIExp, and IICh triplets $(0.0063 = 0.1481 \times 0.0094 \div 0.2211, 0.1204 =$

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955	$0.1481 \times 0.1798 \div 0.2211$, and $0.0214 = 0.1481 \times 0.0319 \div 0.2211$, respectively). In this case,
956	the initial layer pair (II) is not modified during transformation from I-Exp in sample C to
957	intermediate phase I. If both the initial and final layer pairs of a triplet are modified (such as
958	for IExpI triplets from sample C), the two modifications have to be considered separately.
959	Transformation of the first layer pair (IExp) leads to the formation of III, IExpI, and IChI
960	triplets, whereas that of the second layer pair (ExpI) leads to III, IExpI, and IExpCh triplets.
961	Relative proportions of the newly formed layer triplets are calculated as described above
962	$(0.0031 = 0.1481 \times 0.0094 \div (0.2211 + 0.2211), 0.0602 = 0.1481 \times 0.1798 \div (0.2211 + 0.2211))$
963	0.2211), $0.0214 = 0.1481 \times 0.0319 \div (0.2211 + 0.2211)$, $0.0032 = 0.1481 \times 0.0095 \div$
964	(0.2211 + 0.2211), et cetera). These values are reported in table A-3B for all layer triplets and
965	for the different transitions. They can be summed up to calculate theoretical occurrence
966	probabilities for all layer triplets in phase I, phase II, and in the I-Exp-Ch from sample D that
967	are reported in the W_{Cal} columns of table A-2. These values are very similar to those
968	calculated from the XRD structure models determined for I-Exp from sample C and for I-
969	Exp-Ch from sample D, and hypothesized for intermediate phases I and II. Following the
970	transition from I-Exp (sample C) to phase I, differences between W_{Cal} and W_{XRD} are
971	maximum for ExpIExp (0.0115), ChExpI (-0.0080), IExpExp (0.0074), and ExpExpI (0.0069)
972	triplets. For the phase I to phase II transition, these differences are most substantial for
973	ExpIExp (0.0085) and ExpExpI (0.0061) triplets. For the transition from phase II to I-Exp-Ch
974	(sample D), only IChCh and ChChI layer triplets present non-negligible differences between
975	the W_{Cal} and W_{XRD} (-0.0079, and -0.0065, respectively). Overall, the observed agreement
976	between calculated W_{ijk} values and those derived from structure models is excellent and
977	supports the hypothesized solid-state reaction mechanism as it is strongly influenced by the
978	choice of junction probability parameters. In particular, if the $P_{SS} = W_S$ is not maintained for
979	intermediate phases, calculated W_{ijk} values differ significantly from those derived from

- 980 structure models. However, I-Exp-Ch structure models hypothesized for intermediate phases I
- and II and layer pair transitions are to be considered only as an approximation to the actual
- 982 mechanism of I-Exp-Ch formation at the expense of I-Exp.

FIGURE CAPTIONS

Fig. A-1. Experimental XRD patterns obtained from Carter well samples selected as being representative of the complete smectite-to-illite diagenetic transition. Sampling depths are 2170 (A), 3660 (B), 4000 (C), 4640 (D), 5010 (E), and 5180 m (F). Data collected on air-dried samples at 40% relative humidity. Patterns as in figure 1.

Fig. A-2. Elementary contributions to the intensity diffracted by sample B (3660 m). Patterns as for figure 5. The structural parameters for the optimal models are given in table 4A. A. Air-dried sample. **B**. EG solvated sample.

Fig. A-3. Elementary contributions to the intensity diffracted by sample E (5010 m). Patterns as for figure 5. The structural parameters for the optimal models are given in table 4C. A. Air-dried sample. **B**. EG solvated sample.

Fig. A-4. Sensitivity of calculated XRD patterns to structural parameters. Patterns as for figure 5. **A**. Sample E - 5010 m Ca-saturated air-dried. Elementary contribution of the optimum I-Exp-Ch (table 4C). **B**. Sample E - 5010 m Ca-saturated air-dried. 14.0 Å Ch layers (with 3.0 Mg and 6.0 OH per half unit-cell in their interlayers) of the optimum I-Exp-Ch are replaced by 14.0 Å Exp layers (with 0.25 Mg and 2.0 OH per half unit-cell in their interlayers).

A-AD		Exp1	Exp2	Exp3				
	9.98 A	15.00 A	12.50 A	14.00 A				
ا 9.98 Å	0.270	0.060	0.060	0.060				
Exp1 15.00 Å	0.060	0.150	0.050	0.040				
Exp2 12.50 Å	0.060	0.050	0.040	0.000				
Exp3 14.00 Å	0.060	0.040	0.000	0.000				
A-EG	l 9.98 Å	Exp 16.76 Å						
ا 9.98 Å	0.270	0.180						
Exp 16.76 Å	0.180	0.370						
Note: The W _{ii} r	Note: The W _{ii} matrices obtained for							
AD and E								
equivaler								
Exp1 _{AD} +	Exp2 _{AD} +	Exp3 _{AD} .						

Table A-1A. Single-phase segregated I-Exp model. Relative abundance of the different layer pairs (W_{ij} parameters) calculated for the segregated I-Exp from sample A.

	B-AD	l 9.98 Å	Exp 15.0	o1 0 Å	Ex 12.5	p2 50 Å		
	ا 9.98 Å	0.465	0.1	16	0.0	69		
	Exp1 15.00 Å	0.109	0.0	74	0.0)27		
_	Exp2 12.50 Å	0.075	0.02	21	0.0)44		
	B-EG	l 9.98 Å	Exp 16.7	o1 6 Å	Ex 14.(p2)0 Å		
	ا 9.98 Å	0.465	0.14	40	0.0)44		
	Exp1 16.76 Å	0.140	0.1	30	0.0	000		
-	Exp2 14.00 Å	0.044	0.0	00	0.0)36		
							,	
	В			EX	p1	Exp)`	Exp2
	I	0.4	165	0.1	16	0.02	5	0.044
	Exp1	0.1	109	0.0)74	0.02	7	0.000
	Exp'	0.0	031	0.0)21	0.00	8	0.000
	Exp2	0.0)44	0.0	000	0.00	0	0.036
	Note: The W _{ij} matrices obtained for AD and EG states are equivalent if Exp layers from the present table are combined as follows: $Exp1_{AD} = Exp1$, $Exp2_{AD} =$ $Exp' + Exp2$, $Exp1_{EG} = Exp1 + Exp'$, and $Exp2_{EG} =$ Exp2.							

Table A-1B. Single-phase segregated I-Exp model. Relative abundance of the different layer pairs (W_{ij} parameters) calculated for the segregated I-Exp from sample B.

C-AD	ا 9.98 Å	Exp 15.0	o1 0 Å	Ex 12.5	o2 0 Å		
ا 9.98 Å	0.445	0.0	90	0.1	16		
Exp1 14.90 Å	0.090	0.0	23	0.0	38		
Exp2 12.50 Å	0.116	0.0	48	0.0	36		
			. 4		- 0		
C-EG	ا 9.98 Å	Exp 16.7	6 Å	Ex 14.0	0 Å		
ا 9.98 Å	0.444	0.1	62	0.0	44		
Exp1 16.76 Å	0.162	0.1	80	0.0	00		
Exp2 14.00 Å	0.044	0.0	00	0.0	36		
С		I	Ex	p1	Exp	,	Exp2
I	0.4	145	0.0	90	0.07	2	0.044
Exp1	0.0	090	0.0	23	0.03	8	0.000
Exp'	0.0)72	0.0	48	0.00	0	0.000
Exp2	0.0)44	0.0	000	0.00	0	0.036
Note: The W_{ij} matrices obtained for AD and EG states are equivalent if Exp layers from the present table are combined as follows: Exp1 _{AD} = Exp1, Exp2 _{AD} = Exp' + Exp2, Exp1 _{EG} = Exp1 + Exp', and Exp2 _{EG} =							

Exp2.

Table A-1C. Single-phase segregated I-Exp model. Relative abundance of the different layer pairs (W_{ij} parameters) calculated for the segregated I-Exp from sample C.

Table A-2. Relative abundance of layers, layer pairs and triplets determined for the hypothesized solid-state transformation transition between the I-

Exp phase from sample C and the I-Exp-Ch phase from sample D.

Samples								
Layer	Sample C	Inter.	phase I	Inter	. phase II	Sample D		
Sequence	W _{XRD}	W_{Cal}	W _{XRD}	W_{Cal}	W _{XRD}	W_{Cal}	W _{XRD}	
I	0.67	0.68	0.68	0.69	0.69	0.70	0.70	
Exp	0.33 →	0.27	0.27 →	0.21	0.21 →	0.15	0.15	
Ch	0.00	0.05	0.05	0.10	0.10	0.15	0.15	
II	0.4489	0.4684	0.4684	0.4879	0.4878	0.5072	0.5072	
IExp	0.2211 →	0.1798	0.1798 →	0.1413	0.1413 →	0.1050	0.1050	
ICh	0.0000	0.0319	0.0319	0.0609	0.0609	0.0878	0.0878	
Expl	0.2211 →	0.1836	0.1836 →	0.1449	0.1449 →	0.1050	0.1050	
ExpExp	0.1089 →	0.0729	0.0729 →	0.0441	0.0441 →	0.0225	0.0225	
ExpCh	0.0000	0.0135	0.0135	0.0210	0.0210	0.0225	0.0225	
Chl	0.000	0.0280	0.0280	0.0573	0.0573	0.0878	0.0878	
ChExp	0.000	0.0173	0.0173	0.0246	0.0246 →	0.0225	0.0225	
ChCh	0.000	0.0046	0.0046	0.0181	0.0181	0.0397	0.0398	
III	0.3008	0.3200	0.3226	0.3424	0.3449	0.3647	0.3676	
llExp	0.1481 →	0.1241	0.1238 →	0.1007	0.0999 →	0.0768	0.0761	
llCh	0.0000	0.0214	0.0219	0.0419	0.0430	0.0621	0.0636	
IExpl	0.1481 →	0.1217	0.1223 →	0.0958	0.0975 →	0.0716	0.0735	
IExpExp	0.0730 →	0.0559	0.0485 →	0.0356	0.0297 →	0.0204	0.0158	
IExpC	0.0000	0.0030	0.0090	0.0104	0.0141	0.0143	0.0158	
IChl	0.0000	0.0201	0.0179	0.0374	0.0349	0.0545	0.0513	
IChExp	0.0000	0.0109	0.0110	0.0180	0.0150 →	0.0180	0.0132	
IChCh	0.0000	0.0010	0.0030	0.0056	0.0110	0.0154	0.0233	
Expll	0.1481 →	0.1267	0.1265 →	0.1032	0.1024 →	0.0768	0.0761	
ExplExp	0.0730 →	0.0600	0.0485 →	0.0382	0.0297 →	0.0218	0.0158	
ExplCh	0.0000	0.0053	0.0086	0.0125	0.0128	0.0156	0.0132	
ExpExpI	0.0730 →	0.0567	0.0496 →	0.0365	0.0304 →	0.0205	0.0158	
ExpExpExp	0.0359 →	0.0240	0.0197 →	0.0120	0.0093 →	0.0048	0.0034	
ExpExpCh	0.0000	0.0022	0.0036	0.0046	0.0044 →	0.0024	0.0034	
ExpChl	0.0000	0.0091	0.0076	0.0147	0.0120	0.0169	0.0132	
ExpChExp	0.0000	0.0051	0.0047	0.0067	0.0052 →	0.0050	0.0034	
ExpChCh	0.0000	0.0008	0.0013	0.0031	0.0038	0.0064	0.0060	
Chll	0.0000	0.0188	0.0193	0.0395	0.0405	0.0630	0.0636	
ChIExp	0.0000	0.0046	0.0074	0.0113	0.0117	0.0149	0.0132	
ChICh	0.0000	0.0000	0.0013	0.0013	0.0051	0.0051	0.0110	
ChExpl	0.0000	0.0038	0.0118	0.0132	0.0170 →	0.0130	0.0158	
ChExpExp	0.0000	0.0029	0.0047	0.0057	0.0052 →	0.0034	0.0034	
ChExpCh	0.0000	0.0000	0.0009	0.0009	0.0025	0.0026	0.0034	
ChĊhI	0.0000	0.0010	0.0026	0.0052	0.0104	0.0168	0.0233	
ChChExp	0.0000	0.0008	0.0016	0.0034	0.0045	0.0068	0.0060	
ChChCh	0.0000	0.0000	0.0004	0.0004	0.0033	0.0068	0.0105	

Note: W_{XRD} values are deduced directly from the structure model determined from I-Exp in sample C and for I-Exp-Ch in sample D. For the theoretical phase I and II, W_{XRD} values are deduced from the hypothesized structure models intermediate between the two end-members (see text for details). W_{Cal} values are calculated assuming the redistribution of layers, layer pairs and triplets whose relative proportion is decreasing from one step to the next one. These layers, layer pairs and triplets are indicated by arrows in the present table. Redistribution of these layers, layer pairs and triplets is described in table A-3.

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Table A-3A. Redistribution of layer pairs whose relative proportion is decreasing from one step to the next one during the hypothesized solid-state transformation transition between the I-Exp phase in sample C and the I-Exp-Ch phase in sample D.

I-Exp in s	sample C	$\square \rangle$	Phase I
		II	0.0094
0.2211	IExp	IExp	0.1798
		ICh	0.0319
		II	0.0095
0.2211	Expl	Expl	0.1836
		Chl	0.0280
		II	0.0006
		ExpCh	0.0135
0.1089	ExpExp	ExpExp	0.0729
		ChExp	0.0173
		ChCh	0.0046

Note: Layer pairs whose proportion is stable or increasing during any of the three steps are not reported in the present table. Their relative abundances, reported in table A-2, are calculated as the sum of their relative abundance in the previous reaction step and of the present redistribution.

	Phase I	$\square \rangle$	Phase II
			0.0095
0.1798	IExp	IExp	0.1413
		ICh	0.0290
		II	0.0095
0.1836	Expl	Expl	0.1449
		Chl	0.0292
		II	0.0005
		ExpCh	0.0075
0.0729	ExpExp	ExpExp	0.0441
		ChExp	0.0073
		ChCh	0.0135

Phase II		I-Exp-Ch in sample D	
		II	0.0094
0.1413	IExp	IExp	0.1050
		lCh	0.0269
		II	0.0094
0.1449	Expl	Expl	0.1050
		Chl	0.0305
0.0441	ExpExp	II	0.0006
		ExpCh	0.0015
		ExpExp	0.0225
		ChCh	0.0195
0.0246	ChEvp	ChExp	0.0225
0.0240	CIIExp	 ChCh	0.0021

Table A-3B. Redistribution of layer triplets whose relative proportion is decreasing from one step to the next one during the hypothesized solid-state transformation transition between the I-Exp phase in sample C and the I-Exp-Ch phase in sample D.

I-Exp in	sample C		Phase I
			0.0063
0.1481	llExp	llExp	0.1204
		llCh	0.0214
			0.0031
		IExpl	0.0602
0 1/81	IEvol	IChl	0.0107
0.1401	іслрі		0.0032
		IExpl	0.0615
		IChl	0.0094
		llExp	0.0021
		IExpExp	0.0398
		IChExp	0.0071
0 0730	IEvnEvn		0.0001
0.0730	ιεχρεχρ	IExpCh	0.0030
		IExpExp	0.0161
		IChExp	0.0038
		IChCh	0.0010
			0.0064
0.1481	Expll	Expll	0.1230
		Chll	0.0188
		llExp	0.0016
		ExplExp	0.0303
0.0730	ExplExp	ChIExp	0.0046
0.0700	Слріслр	Expll	0.0016
		ExplExp	0.0297
		ExplCh	0.0053
		III	0.0001
		ExpChl	0.0029
		ExpExpl	0.0161
0 0730	ExpExpl	ChExpl	0.0038
	Схрсхрі	ChChl	0.0010
		Expli	0.0021
		ExpExpl	0.0406
		ExpChl	0.0062
0.0359	ExpExpExp	ExpChExp	0.0022
		ExpExpEx	p 0.0120
		ChExpExp	0.0029
		ChChExp	0.0008
		ExpExpCl	n 0.0022
		ExpExpEx	p 0.0120
		ExpChExp	0.0029

	ExpChCh	0.0008
Note: The redistribution of layer triplets amo	ng newly formed one	s is done assuming
that the transition probability from one	layer pair to another	does not depend on
the preceding or following layer as R =	1 (see text for detail	s). Layer triplets
whose proportion is stable or increasing	ig during any of the th	nree steps are not
reported in the present table. Their rela	ative abundances, rep	ported in table A-2,
are calculated as the sum of their relat	ive abundance in the	previous reaction
step and of the present redistribution.		

	Phase I	$\square \rangle$		Phase II	
				0.0066	
0.1241	llExp		llExp	0.0975	
			llCh	0.0200	
				0.0032	
			IExpl	0.0473	
0 1017	IEvol		IChI	0.0097	
0.1217	ТЕхрі			0.0032	
			IExpl	0.0485	
			IChl	0.0098	
			llExp	0.0018	
			IExpExp	0.0271	
			IChExp	0.0056	
0.0495	IEvnEvn		III	0.0001	
0.0405	техрехр		IExpCh	0.0014	
			IExpExp	0.0085	
			IChExp	0.0014	
			IChCh	0.0026	
				0.0066	
0.1267	Expll		Expll	0.1000	
			Chll	0.0202	
			llExp	0.0013	
			ExplExp	0.0189	
0.0495	EvolEvo		ChIExp	0.0039	
0.0485 ExplExp	Exhiexh		Expli	0.0013	
			ExplExp	0.0193	
		ExplCh	0.0039		
				0.0001	
			ExpChI	0.0015	
0.0406			ExpExpl	0.0085	
	EvnEvnl		ChExpl	0.0014	
0.0490	стрстрі		ChChl	0.0026	
			Expll	0.0018	
			ExpExpl	0.0280	
			ExpChI	0.0056	
			llExp	0.0001	
			ExpChExp	0.0010	
			ExpExpExp	0.0060	
			ChExpExp	0.0010	
0 0107	FvnFvnFvn	·	ChChExp	0.0018	
0.0137			Expll	0.0001	
			ExpExpCh	0.0010	
			ExpExpExp	0.0060	
			ExpChExp	0.0010	
			ExpChCh	0.0018	

Table A-3B continued

	Phase II	I-Exp-C	h in sample D
			0.0066
0.0999	llExp	llExp	0.0742
		llCh	0.0190
			0.0032
		IExpl	0.0358
0.0075	IEvol	 IChl	0.0092
0.0975	ι⊏хрі		0.0032
		IExpl	0.0358
		IChl	0.0104
		llExp	0.0015
		IExpExp	0.0168
		 IChExp	0.0043
0.0297	IExpExp	111	0.0001
		IExpCh	0.0002
		IExpExp	0.0036
		IChCh	0.0031
0.0150	IChExp	IChExp	0.0137
0.0100) IChExp	IChCh	0.0013
			0.0066
0.1024	Expll	Expll	0.0742
		Chll	0.0216
		llExp	0.0010
		ExplExp	0.0109
0.0297	ExplExp	 ChIExp	0.0032
0.0201		Expll	0.0010
		ExplExp	0.0109
	ExplCh	0.0028	
		111	0.0001
		ExpExpl	0.0036
		ChExpl	0.0002
0.0304	ExpExpI	 ChChl	0.0031
		Expll	0.0015
		ExpExpl	0.0169
		ExpChl	0.0049
		llExp	0.0001
		ExpChExp	0.0002
		ExpExpExp	0.0024
0.0093	axBaxBaxB		0.0021
	1. — 1. — 1 .		0.0001
		ExpExpCh	0.0002
		ExpExpExp	0.0024
		 ExpChCh	0.0021

Table A-3B continued

	Phase II	I-Exp-C	Ch in sample D
	EveEveCh	llCh	0.0001
0.0150		ExpExpCh	0.0022
0.0150	Ехрехрон	ExpChCh	0.0001
		ChChCh	0.0020
0.0052	ExpChExp	ExpChExp	0.0048
0.0032	схропсхр	ExpChCh	0.0004
		ChExpl	0.0023
		ChChI	0.0002
0.0170	ChExpl	Chll	0.0009
		ChExpl	0.0105
	0.0170 ChExpl	ChChI	0.0031
0.0052	ChExpExp	ChExpExp	0.0017
		ChChExp	0.0002
		Chll	0.0000
		ChExpExp	0.0017
		ChExpCh	0.0001
		ChChCh	0.0015

Table A-3B continued






























