Authigenic kaolin and illitic minerals during burial diagenesis of sandstones: a review

B. LANSON[1],*, D. BEAUFORT[2], G. BERGER[3], A. BAUER[4],
A. CASSAGNABÈRE[5] AND A. MEUNIER[2]

[1]*Environmental Geochemistry Group, LGIT-IRIGM, CNRS - University of Grenoble, 38041 Grenoble Cedex 9,
France,* [2]*HydrASA, University of Poitiers - CNRS, 40 av. Recteur Pineau, 86022 Poitiers Cedex, France,*
[3]*Geochemistry Lab., CNRS - University Paul Sabatier, 38 rue des Trente-Six Ponts, 31400 Toulouse, France,*
[4]*Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgungstechnik, PO Box 3640, 76021 Karlsruhe, Germany,*
and [5]*Etudes Recherches Matériaux, Espace 10 - République 2, Rue A. Haller, 86000 Poitiers, France*

ABSTRACT: The diagenetic evolution of kaolin and illitic minerals in sandstones is described here. The structural characterization of these minerals, the possible reaction pathways leading to their crystallization, and the origin of the fluids involved are discussed specifically.

While early precipitation of kaolinite is in general related to flushing by meteoric waters, subsequent diagenetic kaolinite-to-dickite transformation probably results from invasion by acidic fluids of organic origin. Dickite is the stable polytype in most sandstone formations and the kaolinite-to-dickite conversion is kinetically controlled.

The conventional model of kaolin illitization, assuming a thermodynamic control in a closed system, is discussed and compared to an alternative model in which illitization of kaolin is not coupled to dissolution of K-feldspar (Berger *et al.*, 1997). In the latter model, illite crystallization at the expense of kaolin implies that an energy barrier is overcome either by an increased K^+/H^+ activity ratio in solution or by a considerable temperature increase.

Together with quartz and carbonate cementations, clay cementation is among the most damaging diagenetic processes for petrophysical properties of sandstones. Apart from locally important occurrences of chlorite, kaolin and illitic minerals are the most abundant authigenic clays. However, despite the enormous wealth of literature on clay diagenesis in sandstones there is no general agreement on the reaction pathways leading to crystallization of these minerals and on the fluids responsible for the observed mineral reactions.

The occurrence of different kaolin polytypes (kaolinite and dickite) has been reported in early mineralogical studies of sandstones (Hemingway & Brindley, 1948; Smithson, 1954, 1957; Kossovskaya & Shutov, 1963; Ferrero & Kübler, 1964; Bayliss *et al.*, 1965; Cassan & Lucas, 1966; Chukhrov, 1968; Shutov *et al.*, 1970). More recently, textural characterization, facilitated by the increased availability of electron microscopy, has been preferred over structural determination in petrographic studies of sedimentary formations (Kantorowicz, 1984; Thomas, 1986; Osborne *et al.*, 1994). Over the last decade, Burley & MacQuaker (1992), Ehrenberg *et al.* (1993), Macaulay *et al.* (1993), Lanson *et al.* (1995, 1996) and Beaufort *et al.* (1998) have linked both

structural and textural evolutions. Furthermore, these authors have shown the decisive influence of temperature on the occurrence of either polytype. Recently, a similar temperature-related effect has been shown in shales (Ruiz Cruz & Reyes, 1998). All these studies consistently show that morphological and structural modifications of kaolin are continuous and temperature-, or depth-related and not the result of different crystallization events as proposed earlier (Hancock & Taylor, 1978; Sommer, 1978; Kantorowicz, 1984; Bath *et al.*, 1987; Lee *et al.*, 1989; Bjørlykke & Aagaard, 1992; Haszeldine *et al.*, 1992; McAulay *et al.*, 1994; Purvis, 1995). However, there is no agreement on whether these structural and morphological transitions correspond to an isograd, as proposed by Ehrenberg *et al.* (1993), or if the processes are kinetically controlled (Lanson *et al.*, 1996; Beaufort *et al.*, 1998).

In deeply buried sandstones, kaolin is most often illitized. This reaction is different from the continuous reaction leading to illite formation from a smectitic precursor via intermediate mixed-layer illite-smectite (I-S) described in shales (e.g. Perry & Hower, 1972; Hower *et al.*, 1976; Boles & Francks, 1979) (Fig. 1). Rather, a metastable kaolin + K-feldspar + quartz assemblage frequently persists to ~120°C, corresponding to burial depths of ~3.5–4.0 km in North Sea sandstones (Bjørlykke *et al.*, 1986; Ehrenberg & Nadeau, 1989; Scotchman *et al.*, 1989; Ehrenberg, 1991; Bjørlykke & Aagaard, 1992; Ehrenberg *et al.*, 1993). Conversely, direct precipitation of illitic minerals from a kaolin precursor has been described in shallow-buried
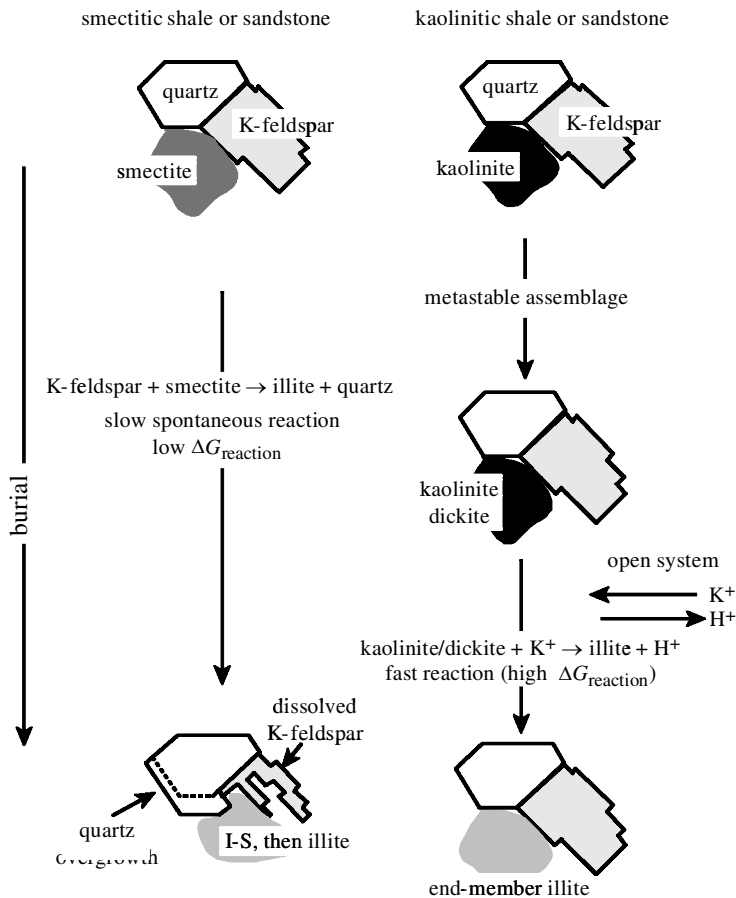

FIG. 1. Idealized schemes of the illitization process in sandstones as a function of the initial clay mineralogy (modified from Berger *et al.*, 1997).

sandstone units from the Norwegian Continental Shelf (Ehrenberg *et al.*, 1993; Cassagnabère, 1998; De Almeida Martins, 1999) at temperatures ranging from 90−95°C. These observations raise the question of the thermokinetic control of illitization, and of the exact nature of this reaction. In particular, the spontaneous reaction of the kaolin + K-feldspar (+ quartz) assemblage to form illite and quartz needs to be discussed (Berger *et al.*, 1995, 1997). In addition, contrasting stabilities of kaolinite and dickite with respect to illitization have to be considered as their thermodynamic stabilities are similar.

The present article provides an overview of the diagenetic evolution of kaolin and illitic minerals in sandstones with special emphasis on their structural and textural characterization. Because kaolin usually predates illite, its diagenetic evolution is described first, and special attention is paid to the origin of fluids responsible for kaolin crystallization at the expense of K-feldspars, or other Al-rich silicates. The reaction pathways leading to their illitization are detailed, and the conventional model assuming a thermodynamic control by the K-feldspar + kaolin + quartz assemblage is discussed in the light of data which suggest otherwise. An alternative model is proposed in which an energy barrier has to be overcome by an abrupt increase of either K^+/H^+ activity ratio in solution or temperature.

KAOLIN IN SANDSTONE DIAGENESIS

Descriptions of kaolinite and dickite structures can be found in Bailey (1980), Bookin *et al.* (1989), and Drits & Tchoubar (1990). As recommended by Guggenheim *et al.* (1997), these two terms are used hereafter as mineral names even though both species are in fact polytypes. Kaolin is used hereafter as a mineral group name to describe the subgroup of dioctahedral 1:1 phyllosilicates.

Recent works (Burley & MacQuaker, 1992; Ehrenberg *et al.*, 1993; Macaulay *et al.*, 1993; McAulay *et al.*, 1993; Osborne *et al.*, 1994; Lanson *et al.*, 1995, 1996; Beaufort *et al.*, 1998) indicate that the presence of both kaolinite and dickite in sandstones results from a diagenetic evolution, the two polytypes coexisting over a depth interval until the onset of illitization. The techniques used to follow this transformation are described in the next section.

Techniques for kaolin polytype determination

In complex sandstone parageneses, qualitative and quantitative studies of kaolin polytypes are best achieved by the combined use of scanning electron microscopy (SEM), X-ray diffraction (XRD) on randomly oriented powders, Fourier transform infrared spectroscopy (FTIR) and differential thermal analysis (DTA).

The textural (size and morphology) characterization of kaolin polytypes is based on SEM observations. Observation of kaolin dissolution features may also provide information on the relative stability of the different morphologies/ polytypes during illitization.

Discrimination between kaolinite and dickite was originally based on XRD data. However, this method is not the most suitable as basal reflections of kaolinite and dickite are similar. All descriptions of kaolin polytypes without collection of XRD patterns on randomly oriented powders are meaningless, and dickite is likely to have been often misidentified as kaolinite on this simplified basis. On XRD patterns collected from randomly oriented samples, *hkl* reflections of kaolinite and dickite are distinct and may be used for their identification (Bailey, 1980). However, several problems may impede this identification. First, *hkl* reflections are often overlapped by reflections from minerals such as illite, quartz or feldspar. These reflections may also be weakened considerably as stacking disorder increases in either polytype. Furthermore, the possible interstratification of the two polytypes may induce additional uncertainty on their differentiation, as, in this case, identification is based on subtle peak shifts (Drits & Tchoubar, 1990). Finally, if identification of the kaolin polytype is performed on randomly oriented powders of the usual <2 µm size fraction, there is a question of how representative the XRD trace is. Indeed, such size fractionation may preclude the identification of coarse-grained kaolin, especially dickite the average particle size of which often exceeds 10 µm.

In contrast, in the hydroxyl-stretching band region (3500−3800 cm^{-1}), FTIR spectra of kaolinite and dickite are characterized by a strong absorbance and contrasting peak positions at 3695, 3668, 3652 and 3621 cm^{-1} for kaolinite and 3710, 3655 and 3620 cm^{-1} for dickite (Brindley *et al.*, 1986). The FTIR spectra are not affected by anhydrous silicates (i.e. quartz and feldspars) in this frequency range and are only slightly
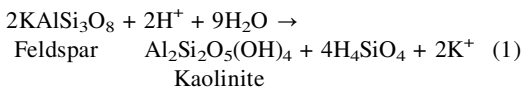
influenced by other phyllosilicates, such as illite or chlorite, because of their much lower absorbance. The IR spectroscopy may also be used to quantify kaolinite and dickite proportions as shown by Cassagnabère (1998). This method is based on the least-squares fitting, in the hydroxyl-stretching band region, of experimental FTIR spectra using two reference spectra of well-ordered kaolinite and dickite.

The DTA curves of kaolinite and dickite also differ considerably as their dehydroxylation temperatures are $525°C$ and $680°C$, respectively (Mackenzie, 1970). When coupled with thermogravimetric analysis, DTA may be used for a semi-quantitative determination of relative proportions of kaolin polytype. However, routine use of DTA is hampered by its sensitivity to morphological (size) and structural parameters. For example, increasing grain-size shifts the endotherm towards higher dehydroxylation temperatures, whereas increasing disorder in kaolin tends to lower the endotherm temperature (Brindley & Porter, 1978).

Occurrence and origin of diagenetic kaolin

In sandstones, three major types of diagenetic kaolin are recognized: kaolin replacing detrital mica, vermiform kaolin and blocky kaolin. Crystallization at the expense of detrital mica is obvious for the first kaolin type, because of petrographic relations between "expanded" mica flakes and authigenic kaolin growing in-between (Nedkvitne & Bjørlykke, 1992; Ehrenberg et al., 1993; Macaulay et al., 1993; Osborne et al., 1994). In contrast, the crystallization conditions of the latter two morphological types are controversial.

Two hypotheses have been suggested for the composition of fluids responsible for kaolin massive crystallization at the expense of both plagioclases and K-feldspars. According to the first hypothesis, kaolin crystallization is promoted at shallow burial depth by fluids of meteoric origin (Hancock, 1978; Hancock & Taylor, 1978; Sommer, 1978) that flush the formation either during early diagenesis or after structural inversion. As a consequence of feldspar dissolution, kaolin precipitates according to:

$$2KAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow$$
$$\text{Feldspar} \quad Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2K^+ \quad (1)$$
$$\text{Kaolinite}$$

If meteoric fluids are responsible for this reaction, a constant supply of protons and removal of K^+ cations require the system to be open to precipitate significant amounts of kaolin. The "meteoric-water flushing" model is supported by the presence of vermiform kaolinite in onshore basin margins, by its ubiquitous presence in shallow-buried sandstones (<2000 m; Lønøy et al., 1986; Burley & MacQuaker, 1992; De Ros, 1998), and by textural evidence of early kaolinite crystallization. Indeed, vermiform kaolinite usually predates calcite cementation. This interpretation has long been supported by geochemical models of mineral diagenesis which indicate that, in arkosic sandstones, the kaolin stability domain is restricted to low temperature and shallow burial depths. At temperatures of ~120−140°C, kaolin is supposed to react with the remaining K-feldspar to precipitate illite (Bjørkum & Gjelsvik, 1988; Ehrenberg & Nadeau, 1989; Bjørlykke & Aagaard, 1992). According to the "meteoric-water flushing" model, several crystallization episodes must be invoked to account for the different kaolin morphologies observed in sandstones (Kantorowicz, 1984; Bath et al., 1987; Lee et al., 1989; Bjørlykke & Aagaard, 1992; Haszeldine et al., 1992; McAulay et al., 1994; Purvis, 1995). The different episodes are possibly induced by successive flushings (Hancock & Taylor, 1978; Sommer, 1978).

According to the second hypothesis, CO_2-rich or organic acid-rich fluids may be, together with meteoric fluids, responsible for feldspar alteration and subsequent precipitation of kaolinite according to reaction 1 (Rossel, 1982; Blackbourn, 1984; Goodchild & Whitaker, 1986; Pye & Krinsley, 1986; Ehrenberg, 1991; Gaupp et al., 1993; Platt, 1993). These fluids result from maturation of organic matter in shales and coal beds adjacent to sandstones. One may note that temperature corresponding to CO_2-rich fluid peak expulsion (~100°C; Hunt, 1979; Platt, 1993) is compatible with the precipitation temperature of kaolin, and more especially dickite. Migration of such acidic fluids, and subsequent crystallization of kaolin at the expense of K-feldspars has been demonstrated by Ehrenberg (1991) in sandstones (Garn formation − Norwegian Continental Shelf). In this case study, K-feldspar alteration and kaolinite formation occur specifically at the top and basal contacts of the formation with adjacent shales. Similar observations were made by Gaupp et al. (1993), and Platt (1993) in the Rotliegend sandstones at their contact with the Carboniferous Coal Measures
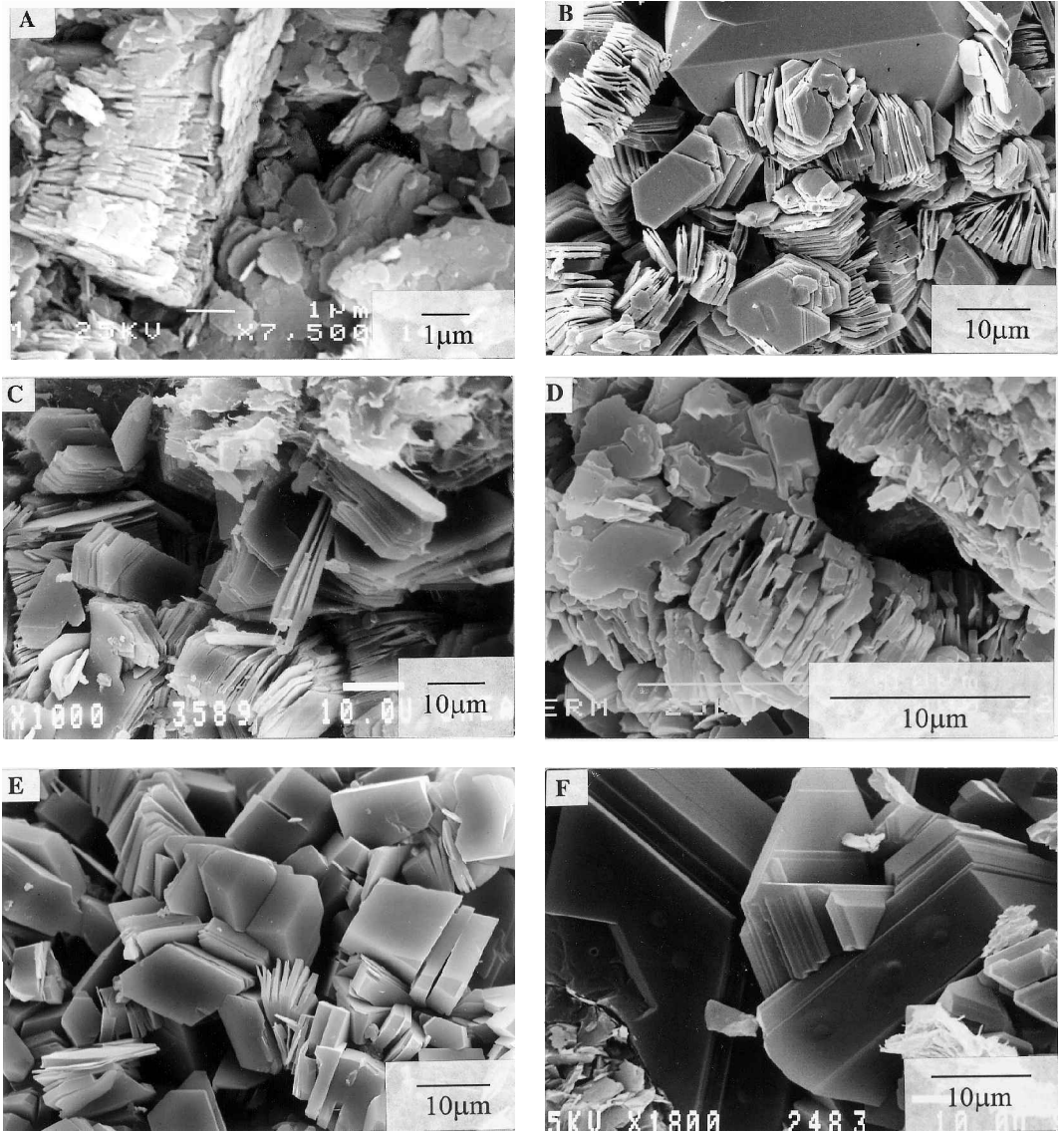
FIG. 2. Evolution of the habit of kaolin minerals as a function of burial depth. (A) <1000 m, mixture of authigenic vermiform crystals and of anhedral crystals. (B) 3000 m, vermiform kaolinite. (C) 3000 m, elongation within the *ab* plane of the crystals building up kaolin booklets and thickening of stacks along the *c* axis. (D) 3500 m, intercalation of blocky crystals between stacks of partly dissolved pseudohexagonal plates. (E) 4500 m, blocky dickite crystals whose spatial organization seems inherited from pre-existing booklets. (F) 5000 m, aggregates of large dickite crystals showing no traces of inherited booklet organization.

formation. Similarly, McAulay *et al.* (1993) and Van Keer *et al.* (1998) reported a greater amount of kaolin close to the sandstone-coal and to the sandstone-shale contacts of the sandstone formations they studied.

Evidence for a diagenetic kaolinite-to-dickite conversion

In several recent studies, textural, isotopic and crystal-chemical analyses were used to describe

kaolin evolution as a function of temperature or parameters such as porosity or timing of reservoir invasion by hydrocarbons (Ehrenberg *et al.*, 1993; Macaulay *et al.*, 1993; McAulay *et al.*, 1993; Lanson *et al.*, 1995, 1996; Beaufort *et al.*, 1998; Cassagnabère, 1998; Cassagnabère *et al.*, 1999; Hassouta, 1999; Hassouta *et al.*, 1999). These studies have consistently shown that blocky dickite results from the diagenetic evolution of early vermiform kaolinite with increasing temperature rather than from a direct precipitation event induced by a late flush by meteoric fluids. In contrast with the hypothesis of successive flushings, the parental link between vermiform kaolinite and blocky dickite explains why the two polytypes have been widely recognized in sandstones with much different tectonic histories. However, if the temperature-dependence of kaolinite-to-dickite transition is indisputable, the concept of a kaolinite-dickite isograd developed by Ehrenberg *et al.* (1993) is more controversial. This concept was initially deduced from the seldom described coexistence of kaolinite and dickite (Ehrenberg *et al.*, 1993; McAulay *et al.*, 1994), and because kaolin crystallinity was not documented. Investigation of samples from comparable medium- to coarse-grained sandstones which experienced a large range of burial conditions (600–5000 m) in water zones allowed a better understanding of the temperature-related 'dickitization' in sandstones (Lanson *et al.*, 1995, 1996; Beaufort *et al.*, 1998; Cassagnabère, 1998; Cassagnabère *et al.*, 1999).

Temperature dependence of the kaolinite-to-dickite transition. Kaolinite is observed in shallow-buried sandstones (<2000 m; Fig. 2A) as a mixture of authigenic vermiform and anhedral crystals, the latter being described as "transported detrital clays" (Burley & MacQuaker, 1992). At greater depth, only vermiform kaolinite persists (Fig. 2B) and detrital aluminous silicates (feldspar, mica) show traces of dissolution. Dickite gradually replaces kaolinite within a 2500–5000 m range of burial depth (in the following description, burial depths are only
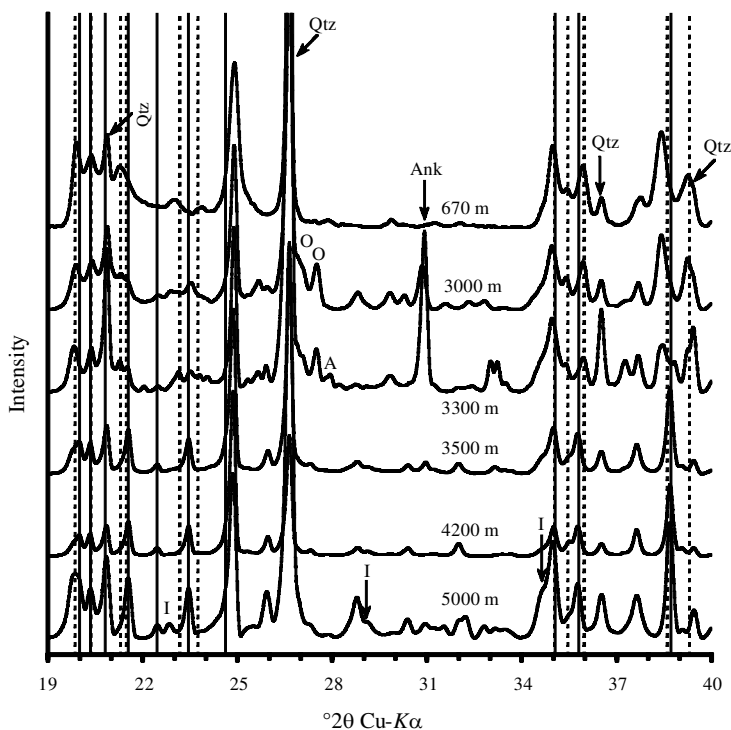

FIG. 3. XRD patterns of kaolin group minerals as a function of their maximum burial depth. Diagnostic peaks of kaolinite and dickite are shown as dashed and solid lines, respectively (modified from Beaufort *et al.*, 1998). A = albite, O = orthoclase, Qtz = quartz, Ank = ankerite, I = illite.

indicative values based on the observations made in the water zone of well sorted sandstones from southern North Sea (Lanson *et al.*, 1996; Beaufort *et al.*, 1998), and from the Norwegian Continental Shelf (Cassagnabère, 1998). The kaolinite-to-dickite transition proceeds by continuous structural changes concomitant with crystal coarsening and evolution from booklet to blocky morphology. Between 2500 and 3500 m, the presence of dickite coincides with the following morphological characters: (1) elongation within the *ab* plane of the crystals building up kaolin booklets and thickening along the *c* axis of stacks which become more regular (Fig. 2C), and (2) intercalation of blocky crystals between stacks of partly dissolved plates. The latter is more frequent as burial depth reaches ~3500 m (Fig. 2D). Aggregates of blocky crystals predominate within the 4000–5000 m range. At burial depth near 4000 m, the organization of blocky kaolin seems inherited from pre-existing booklets (Fig. 2E), but no traces of inherited organization persist at 5000 m (Fig. 2F).

Combined XRD, FTIR and DTA analyses of kaolin in North Sea sandstones indicate that its structural properties depend on both crystal size and temperature. The gradual changes presented by XRD patterns (Fig. 3), and IR spectra (Fig. 4 – broadening of the band at 3695 cm^{-1}, intensity weakening of the bands at 3668 and 3695 cm^{-1}) of kaolin from the 3000–5000 m depth range are characteristic of the increased dickite/(kaolinite + dickite) ratio (*D*%) with increasing temperature. However, DTA curves of these diagenetic kaolins are not compatible with a weighted sum of reference DTA curves of kaolinite and dickite (Fig. 5). Such thermal behaviour is consistent with that of dickite exhibiting a wide order-disorder range (Beaufort *et al.*, 1998). As temperature increases, *D*% increases simultaneously with dickite structural order and crystal size, the occurrence of well-ordered dickite being restricted to the deepest samples (~5000 m).

From these observations, Beaufort *et al.* (1998) proposed a model for the kaolinite-to-dickite transition. In this model (Fig. 6), the crystallization and growth process by which dickite replaces kaolinite consists not just of redistribution of material from dissolved kaolin. Rather, within the 2500–4000 m depth range, this process is also fed by detrital feldspar and mica dissolution. However, K-feldspar dissolution also occurs in sandstones preserved from illitization (Lønøy *et al.*, 1986 –
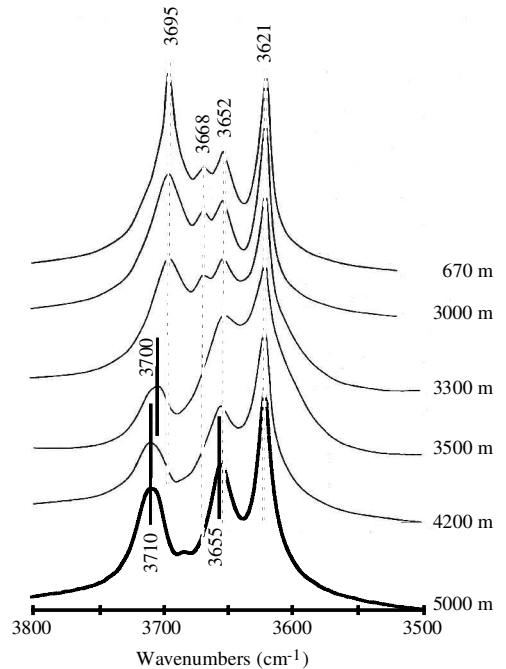

FIG. 4. Infrared spectra of kaolin group minerals in the hydroxyl-stretching band region as a function of their maximum burial depth (modified from Beaufort *et al.*, 1998).

block K/5; Lacharpagne, pers. comm.). This supports a reaction scheme in which dissolution of K-feldspars and kaolin illitization are uncoupled, in either space or time. At higher temperature, and if detrital Al-bearing minerals are absent, the morphological evolution of kaolin (essentially dickite) is isochemical and involves only recrystallization of kaolin material.

In this model, dickite is the stable polytype over the 2500–5000 m depth interval, and the kaolinite-to-dickite transition rate is kinetically controlled, in agreement with Zotov *et al.* (1998).

Influence of the water/rock ratio on the kaolinite-to-dickite conversion in sandstones. Significant differences in diagenetic reaction progress are commonly observed between sandstones and shales with similar burial history (Howard, 1981) suggesting the influence of porosity or water/rock ratio (W/R). Hydrothermal experiments also demonstrate that reaction rate increases with increasing W/R (Whitney, 1990). In sandstones, W/R are difficult to assess through the different diagenetic stages because they vary significantly on a local
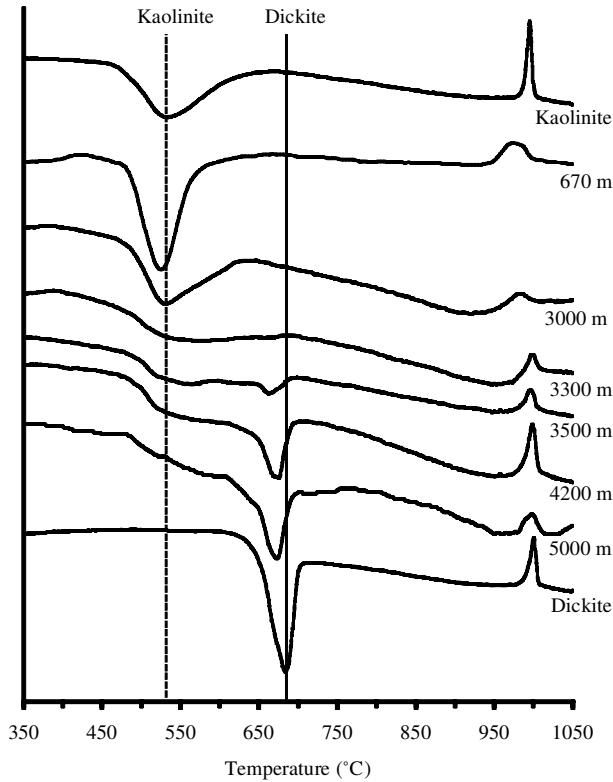
Fig. 5. DTA curves of kaolin group minerals as a function of their maximum burial depth (modified from Beaufort *et al.*, 1998).

scale as a function of compaction, cementation, partial mineral dissolution, or hydrocarbon invasion. However, information from core logging, porosity measurements, petrology, identification of diagenetic cements, or evaluation of oil/water ratio in fluids allow a rough estimation of W/R variation within the formations. Several studies have suggested that high porosity and permeability favour dickite precipitation (Ferrero & Kübler, 1964; Cassan & Lucas, 1966; Kisch, 1983; Zimmerle & Rösch, 1991). Similarly, these studies have suggested that persistence of kaolinite through late-stage diagenesis and incipient metamorphism is enhanced in low-permeability rocks, in the absence of K⁺.

Cassagnabère (1998) and Cassagnabère *et al.* (1999) investigated the influence of W/R on the kaolinite-to-dickite reaction rate in the Frøy and Rind oil fields (Brent formation, North Sea). In rock types varying from shales to medium-grained sandstones, kaolin exhibits an extreme textural and crystal-chemical variability. In the two oil fields,

variability over a 300 m depth range (2900–3200 m and 3300–3600 m for Frøy and Rind, respectively) is similar to that described by Beaufort *et al.* (1998) for a 1500 m thick sequence. However, the latter study focused on medium- to coarse-grained sandstones that experienced diagenesis in the water zone exclusively.

Cassagnabère (1998) and Cassagnabère *et al.* (1999) showed that the relative proportion of dickite is highly variable, even on a metric scale (Fig. 7). This observation supports the dependence of kaolinite-to-dickite reaction rate not only on temperature (or burial depth) but also on other parameters. Porosity, for example, wields a major control as shown by the positive correlation between $D\%$ and present-day porosity (Fig. 8). Similarly, $D\%$ is low (from 0 to 30%) in shales and sandstones cemented by early carbonates or quartz. In addition, hydrocarbon invasion probably inhibits kaolinite-to-dickite reaction as noticeable differences exist between hydrocarbon and water zones in the Frøy reservoir, for example. In fine- to

Kaolinite pseudomorphs
of detrital micas

Feldspar dissolution

600 m — Disordered kaolinite

3000 m

Ordered kaolinite
–
disordered dickite

Ordered dickite?

Disordered dickite
–
ordered dickite

Ordered dickite?

3500 m

Ordered dickite
–
disordered dickite

4000 m — Ordered dickite

20 μm
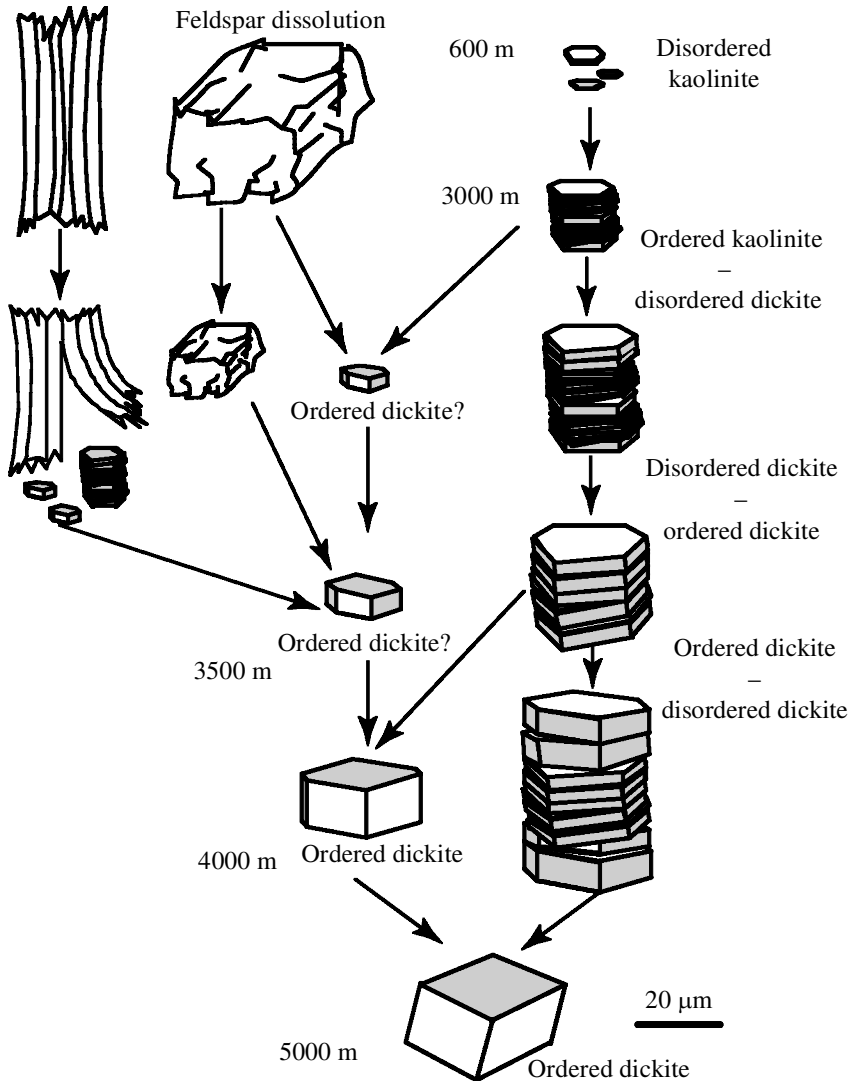
5000 m — Ordered dickite

FIG. 6. Idealized scheme of the kaolinite-to-dickite conversion involving both morphological and structural changes as a result of water-rock interaction in sandstone reservoirs (modified from Beaufort *et al.*, 1998; Cassagnabère, 1998).

medium-grained sandstones, pure dickite is present in the water zone only (Fig. 8). This suggests that hydrocarbon invasion occurred as dickite crystallization was in progress and that mineral reactions feeding dickite precipitation were inhibited because of the reduced amount of pore water. In the Ellon Field (Alwyn, North Sea), Hassouta (1999) and Hassouta *et al.* (1999) documented a similar inhibition of 'dickitization' as early calcite cementation significantly decreased porosity.

KAOLIN AND ILLITE IN SANDSTONES

Kaolin is an important precursor of illite in deeply buried sandstones (Bjørlykke *et al.*, 1986; Ehrenberg & Nadeau, 1989; Bjørlykke & Aagaard, 1992; Lanson *et al.*, 1996; Berger *et al.*, 1997), in contrast to shales where illite typically results from the diagenetic conversion of smectitic precursors via a series of I-S (Eslinger & Pevear, 1988).

Several morphologies were described for illite occurring in sandstones (Kantorowicz, 1984, 1990; Bjørlykke & Aagaard, 1992; Bjørlykke *et al.*, 1992; Lanson *et al.*, 1996). However, there is no general agreement on a possible relation between the morphology of these illitic minerals and their timing of precipitation, their chemistry or their crystal structure. Conversely, Small *et al.* (1992) related the morphology of illitic particles obtained experimentally from gels to their rate of precipitation, and to the presence of organic anions in solution. These authors described differences in illite chemical composition having contrasting morphology, the layer charge of lath-shaped and platy particles originating from octahedral and tetrahedral substitutions, respectively. Such distinct charge locations have not been reported in nature (Środoń *et al.*, 1986). In contrast, Lanson *et al.* (1995, 1996) showed a clear dependence of both morphological and structural characteristics of illite on its crystallization temperature.

Techniques for monitoring kaolin illitization

As for kaolin, the size and morphology of illitic minerals, as well as petrographic relationships between different authigenic minerals are characterized by SEM observations. However, one should be careful not to interpret intuitively SEM images as the present state of rock samples results from a complex diagenetic history. For example, it is possible to observe intergrowths of quartz with kaolinite (Fig. 9A), dickite (Fig. 9B), and illite
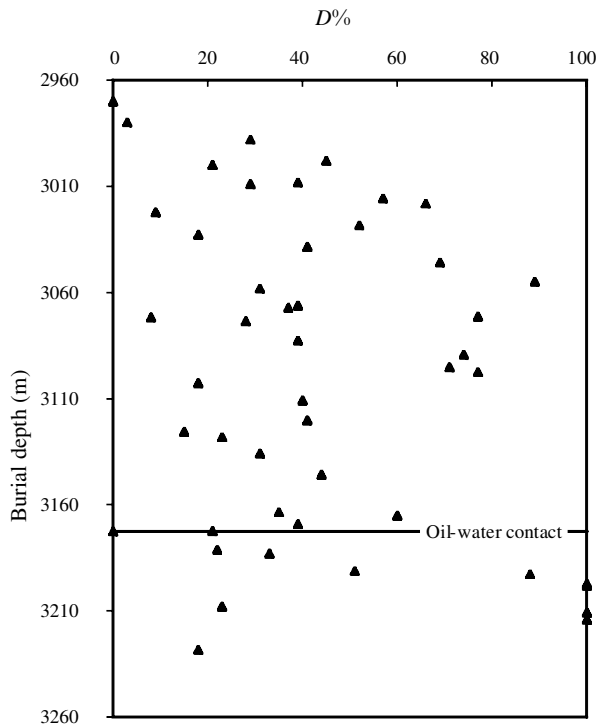

Fig. 7. Relative proportion of dickite (*D*%) as a function of burial depth in the Frøy reservoir (Norwegian sector North Sea − modified from Cassagnabère, 1998).
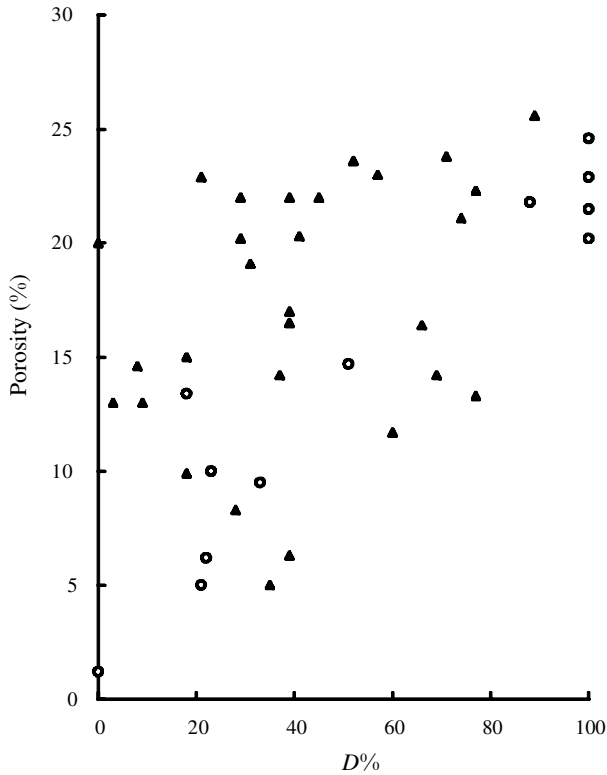
FIG. 8. Relative proportion of dickite ($D\%$) in the kaolin group minerals as a function of present-day porosity in the Frøy reservoir (Norwegian sector North Sea). Open circles: water-saturated zone; Solid triangles: oil-saturated zone.

(Fig. 9C) within the same sandstone unit. However, because dickite and illite may result from diagenetic alteration of kaolinite, their petrographic relation to quartz is unclear; it is possible that only kaolinite is cogenetic with quartz.

The XRD of oriented clay-size fraction is routinely used to determine the mineralogy of phyllosilicates. A detailed identification of illitic minerals may be performed by comparison with simulated profiles (Reynolds, 1980; Drits & Tchoubar, 1990). The illite-smectite identification diagrams derived from these simulations (Środoń, 1980, 1981, 1984; Watanabe, 1981, 1988; Velde *et al.*, 1986; Lanson *et al.*, 1995) may also be used. However, these methods are difficult to apply routinely, because either they require measurements on low-intensity higher-angle peaks or they necessitate the separation of diffraction effects from the coexisting clay phases (Lanson & Besson, 1992). Often, these phases are character-

ized globally by using the Kübler index (Kübler, 1964, 1968; Kisch, 1990), but in this case no detail is given on individual populations (e.g. I-S and illite relative proportions, I-S composition, illite crystallite size). To account for the heterogeneity of illitic material, XRD profiles may be processed numerically (Lanson, 1997).

The three-dimensional (3-D) structure of illitic minerals may be investigated using XRD data collected on randomly oriented clay-size samples. For example, polytype and distribution of octahedral cations between *trans* and *cis* sites may be determined (Drits *et al.*, 1993; Lanson *et al.*, 1996) by comparison with calculated distributions of intensity, and peak positions (Drits & Tchoubar, 1990; Drits *et al.*, 1993; Reynolds & Thomson, 1993). The latter information may also be obtained from DTA analysis of purified illitic fractions (Drits *et al.*, 1995, 1998). At present, the two documented evolutions of illite octahedral occupancy as a

Crystal chemistry and texture of illitic minerals as a function of temperature

The size and shape of illitic crystals vary significantly with temperature, as described by Lanson *et al.* (1996) in their study of the Rotliegend sandstones in offshore Netherlands. In the shallowest well (3000 m), illitic crystals are elongated, filamentous, almost one-dimensional (Fig. 10A). With increasing palaeo-burial depth, illitic minerals show first a more rigid lath morphology (Fig. 10B), the maximum width of these lath-shaped crystals increasing from 0.5 μm at 3500 m to ~2.0 μm at 3500 m, and 3.0–5.0 μm below 4000 m (Fig. 10C). Lath-shaped particles make up the dominant population of illitic minerals whatever the estimated maximum burial depth. However, isometric pseudo-hexagonal-shaped particles are present only below 4000 m (Fig. 10D), and their proportion increases with depth. Their maximum diameter reaches 3.0–5.0 μm at ~4500 m.

This morphological evolution occurs simultaneously with the usual increase of illite 'crystallinity' with increasing temperature (Figs 10, 11 and 12 in Lanson *et al.*, 1996). In addition, an evolution of illitic mineral 3-D structure from $1M$ with octahedral *trans* sites vacant ($1Mt$) to $1M$ with octahedral *cis* sites vacant ($1Mc$) is observed (Fig. 11). The relative intensities of $\bar{1}12$ and 112 peaks indicate that $1Mt$ prevails in shallower samples, whereas the proportion of $1Mc$ polytype increases with temperature as indicated by the increased intensity of $1Mc$ peaks (e.g. 111, $\bar{1}13$), and with the size fraction (Fig. 14 in Lanson *et al.*, 1996).

Differential illitization of kaolin polytypes in sandstones.

Most studies of diagenetic sequences in sandstones point out the precipitation of illite (or illitic I-S) during deep burial diagenesis. In the North Sea area, illite generally forms at depths >3500 m (i.e. temperature >120°C) at the expense of kaolin (Ehrenberg & Nadeau, 1989; Bjørlykke & Aagaard, 1992; Bjørlykke *et al.*, 1992). However, the relationship between illite and kaolin polytypes is still ambiguous. It is usually admitted that illite precipitates mostly at the expense of vermicular kaolinite, whereas blocky kaolin (dickite) is described as coexisting with illite at burial depth
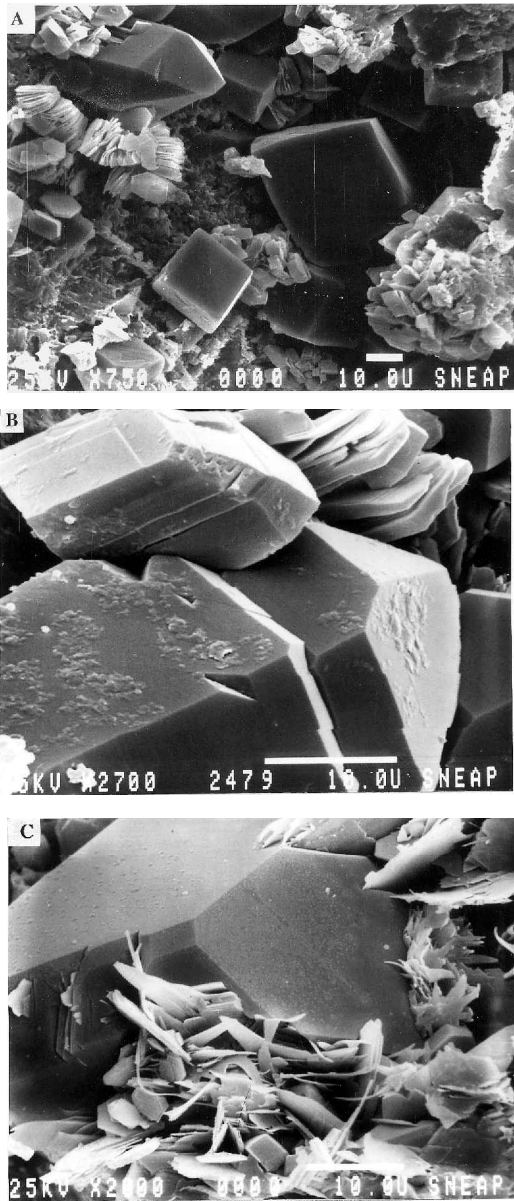
FIG. 9. (A) Simultaneous growth of kaolinite books and quartz inducing intergrowth features. (B) Cogenetic (?) dickite and quartz crystals showing mutual stopping of growth faces. (C) Apparent simultaneous growth of illite laths and quartz (adapted from Lanson *et al.*, 1996).

function of temperature (Drits *et al.*, 1993; Lanson *et al.*, 1996) seem controversial.
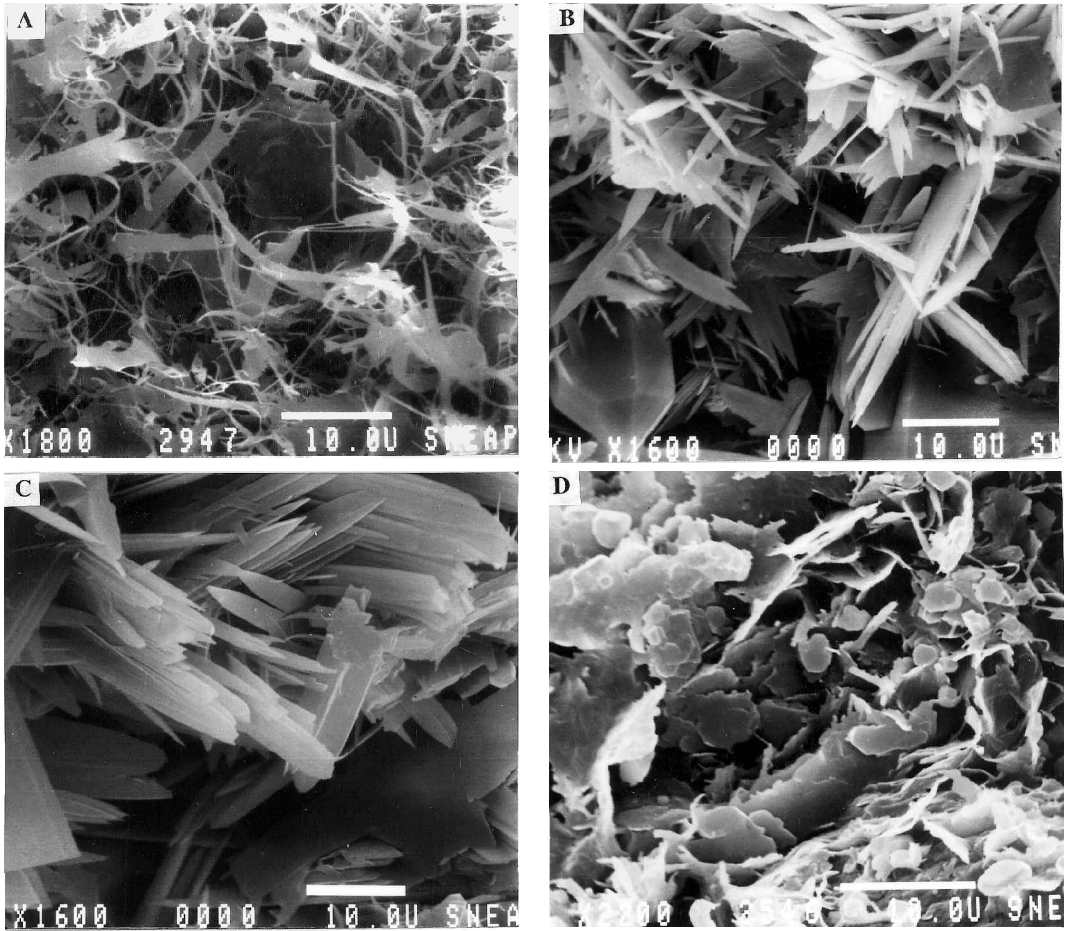
FIG. 10. Evolution of illitic minerals habit as a function of burial depth. (A) 3000 m, elongated, filamentous, almost one-dimensional illitic crystals. (B) 3500 m, lath-shaped illitic minerals. (C) 4200 m, lath-shaped illitic minerals showing an increased width. (D) 5000 m, isometric pseudo-hexagonal-shaped illitic crystals.

>3500 m. This assumption is often used to claim that blocky kaolin corresponds to a late diagenetic stage which postdates the illitization event (Hurst & Irwin, 1982; Hurst, 1985; Thomas, 1986; Lee *et al.*, 1989; Giles *et al.*, 1992; Haszeldine *et al.*, 1992).

However, petrographic examination of illite, kaolinite and dickite in deeply buried illitized sandstones (Fig. 12) may lead to an alternative interpretation of the observed dickite and illite coexistence, in agreement with the kaolinite-to-dickite transition mechanism proposed by Beaufort *et al.* (1998). In the water zone of North Sea sandstones, illite replaces vermicular kaolinite at burial depths of ~3000 m (Fig. 12A). The remaining kaolinite crystals show evidence of dissolution (Fig. 12B). From 3000–3500 m, illitization develops at the expense of kaolin crystals consisting of blocky dickite crystals intercalated within vermicular stacks of kaolinite (Fig. 12C). Kaolinite plates are strongly dissolved whereas blocky dickite crystals seem unaltered. However, dickite crystals show evidence of small-scale dissolution and associated incipient illitization (Fig. 12D). At greater burial depth (~5000 m) individual blocky crystals of dickite, which persist in the coarse-grained illitic matrix (Fig. 12E), often show evidence of partial dissolution (Fig. 12F).
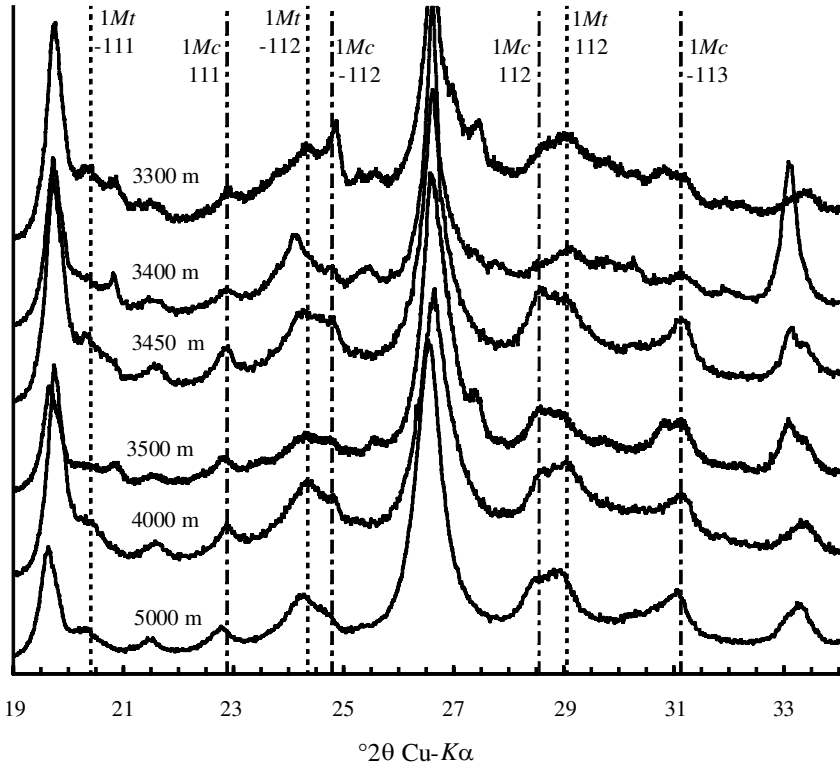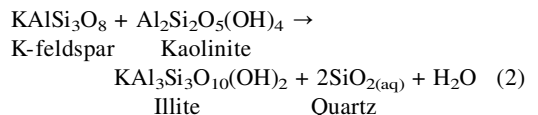
FIG. 11. Evolution of the 3-D crystallographic structure of illitic minerals as a function of burial depth (modified from Lanson *et al.*, 1996).

The above observations suggest that kaolinite dissolves faster than dickite during illitization. Because dickite is thermodynamically more stable than kaolinite in the temperature range of burial diagenesis (Zotov *et al.*, 1998), the chemical force which drives kaolin illitization (i.e. the deviation from equilibrium) is greater for kaolinite than for dickite. Therefore, kaolinite reacts at a higher rate than dickite for the same temperature and fluid composition. The rate of dissolution of kaolinite may also be increased by the large reaction surfaces of thin individual kaolinite plates. These contrasting dissolution rates preferentially preserve dickite blocky crystals, and $D\%$ is increased by the partial illitization of kaolin. The persistence of partly dissolved dickite blocky crystals in the presence of $2M_1$ illites in deeply buried and illitized Kombolgie sandstones (Northern Territory, Australia − 1850−1730 Ma range), which experienced incipient anchizonal metamorphism, confirms the low dissolution rate of dickite (Beaufort, pers. comm.).

Possible reaction pathways for kaolin illitization

It is commonly assumed that a minimum temperature of ~120°C, which corresponds to an average burial depth of 3.5−4.0 km in the North Sea, is required before extensive illitization of kaolin begins (Bjørlykke *et al.*, 1986; Ehrenberg & Nadeau, 1989; Scotchman *et al.*, 1989; Bjørlykke & Aagaard, 1992). According to Bjørlykke (1984), Bjørkum & Gjelsvik (1988), Ehrenberg & Nadeau (1989), and Bjørlykke & Aagaard (1992) this temperature threshold corresponds to the thermodynamical de-stabilization temperature of the kaolin + K-feldspar (+ quartz) assemblage according to the reaction

$$KAlSi_3O_8 + Al_2Si_2O_5(OH)_4 \rightarrow$$
K-feldspar   Kaolinite
$$KAl_3Si_3O_{10}(OH)_2 + 2SiO_{2(aq)} + H_2O \quad (2)$$
Illite   Quartz

In this case, two stages of feldspar dissolution are inferred: (1) an early stage, during which feldspars
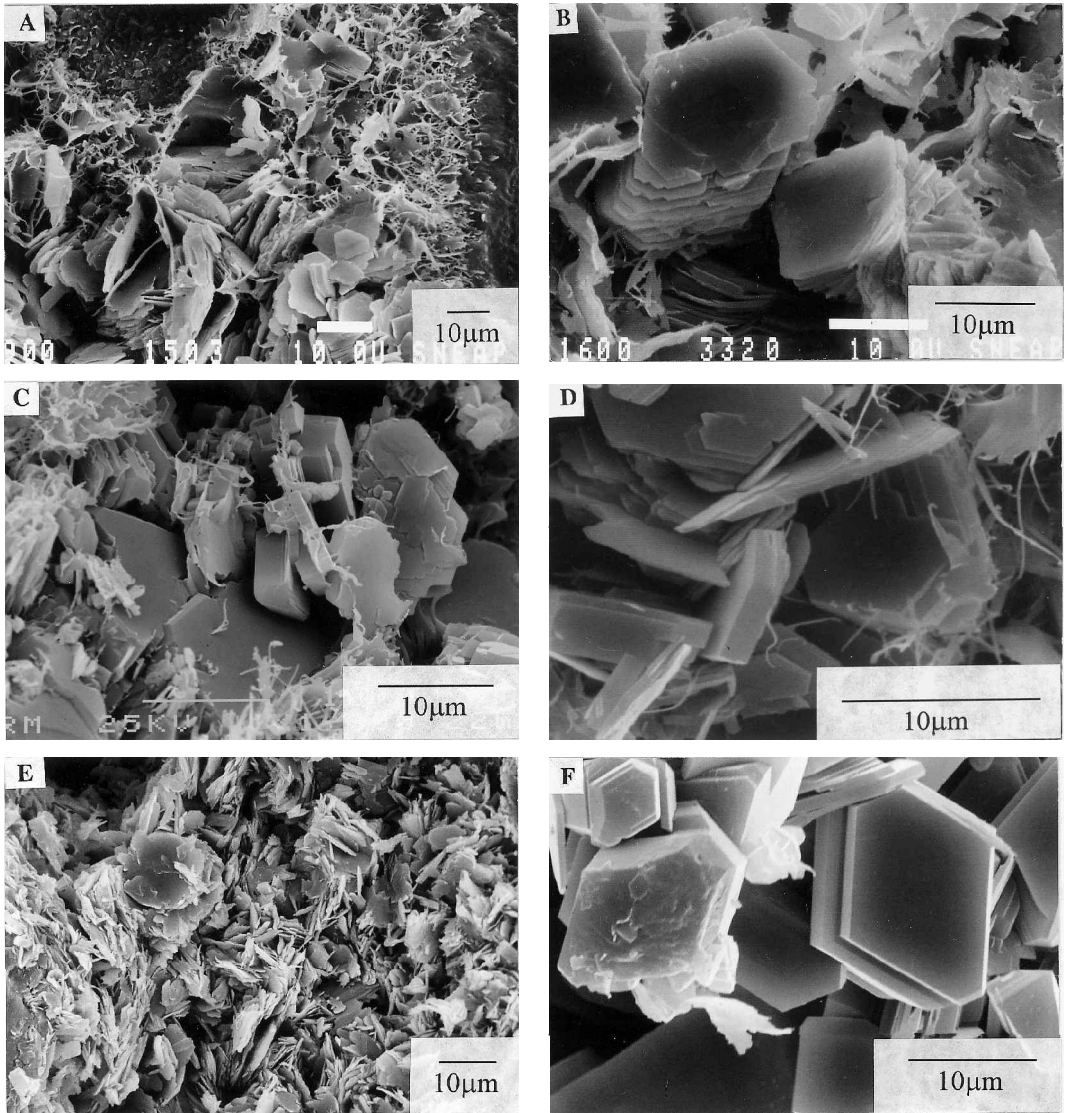
FIG. 12. Impact of illitization on the different habits of kaolin minerals encountered as a function of burial depth. (A) 3000 m, illite replacing vermicular kaolinite. (B) 3000 m, kaolinite crystals showing evidence of dissolution. (C) 3500 m, illite growing at the expense of blocky dickite crystals intercalated within vermicular stacks of kaolinite. (D) 3500 m, incipient illitization of blocky dickite crystals. (E) 5000 m, blocky dickite crystals in a coarse-grained illitic matrix. (F) 5000 m, blocky dickite crystals showing evidence of dissolution.

are altered to kaolinite, possibly in response to meteoric water influx; and (2) a late-stage dissolution according to reaction 2, in response to temperature increase.

However, illitization of kaolin, although frequent, is not always observed in deeply buried sandstones and there seems to be no systematic relationship between temperature and intensity of kaolin illitization. In Jurassic sandstones from the northern North Sea, for instance, significant amounts of kaolin coexisting with K-feldspar have been reported in partly illitized sandstones at burial depths ranging from 3000–4000 m (Ehrenberg, 1991; Ehrenberg *et al.*, 1993). On the other hand,

the thermodynamic conditions existing in these boreholes indicate that reaction 2 should have taken place leading to exhaustion of either kaolinite or K-feldspar. Furthermore, kaolin replacement by illitic minerals occurs in several shallow-buried (<3000 m) sandstones from the Norwegian Continental Shelf (Ehrenberg et al., 1993; De Almeida Martins, 1999). The estimated maximum temperature of ~90–95°C experienced by these formations (Ehrenberg et al., 1993; Cassagnabère, 1998), is much less than that calculated for destabilization of the kaolin + K-feldspar (+ quartz) assemblage. Similar low precipitation temperatures of illitic minerals are reported by Lee et al. (1989) and Bjørlykke & Aagaard (1992) in the Leman and Indefatigable gas fields and by De Ros (1998) in the Paraná basin (Brazil).

These observations led Berger et al. (1995) to propose a model in which kaolin conversion to end-member illite is promoted by a high K^+/H^+ activity ratio which allows the kinetic barrier to illite crystallization to be overcome. These conditions are not met in a closed system in which K^+/H^+ activity ratio is controlled by K-feldspar solubility. To reach the critical K^+/H^+ activity ratio and overcome this energy barrier, the fluid should be highly oversaturated with respect to illite. In this case, the fluid is also oversaturated with respect to K-feldspar which cannot be the source of K^+, and either an external source of K^+ or a pH increase is needed to reach this critical K^+/H^+ activity ratio. According to this model, illitization of kaolin is not coupled to the dissolution of K-feldspar, as frequently described, but results from the non-isochemical reaction

$$3Al_2Si_2O_5(OH)_4 + 2K^+ \rightarrow$$

Kaolinite $2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O$ (3)
                                Illite
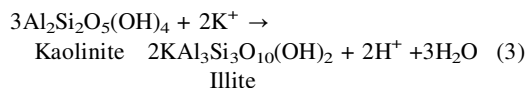
It is likely that the kinetic barrier to illite crystallization decreases with increasing temperature, and that reaction 2 may be predominant at high temperature, as shown by the frequent illitization of kaolin in deeply buried sandstones (>4000 m).

At shallower depth, two observations are difficult to reconcile with the hypothesis that illite originates only from reaction 2. First, Lanson et al. (1996) showed that in the Rotliegend sandstones the intensity of illitization (abundance of illitic minerals in the clay size-fraction) varies independently of burial depth, even though crystal size, morphology

and structure are temperature-related. Similar observations were made by Ehrenberg et al. (1993) who observed significant illitization in shallow units of a few wells whereas most wells with intermediate burial depths (3000–3800 m) did not undergo kaolin illitization. Illitization also occurs regardless of burial depth or temperature in the Village Fields area (Robinson et al., 1993), and in Rotliegend sandstones (Lee et al., 1989).

In addition, kaolin illitization usually occurs within a restricted span of time, as indicated by the narrow range of K/Ar datings in a specific formation (Lee et al., 1985, 1989; Platt, 1993; Robinson et al., 1993; Matthews et al., 1994; Lanson et al., 1996). If thermodynamic stability of the K-feldspar + kaolinite (+ quartz) assemblage was the sole controlling factor, illitization would last as long as temperature is high enough or as long as neither K-feldspar nor kaolinite is depleted. This would lead to radiogenic ages scattered as a function of the analysed size fraction. Conversely, illite radiogenic ages usually scatter within a narrow range, often consistent with a tectonically active period.

According to this model, Lanson et al. (1996) interpreted kaolin illitization in the Dutch sector of the Rotliegend sandstones as a consequence of reservoir invasion by K^+-rich fluids from the overlying Zechstein. In this case, the K^+/H^+ activity ratio is dramatically increased by the flow of K-rich fluids evidenced in previous studies (Rossel, 1982; Goodchild & Whitaker, 1986; Pye & Krinsley, 1986). The fluid circulation is purportedly induced by the intense faulting associated with the late Cimmerian orogeny, which permits lateral contacts between the Zechstein and Rotliegend formations. This timing is similar to that determined by Platt (1993) and Gaupp et al. (1993) in the North German Basin, or by Robinson et al. (1993), Turner et al. (1993), and Ziegler et al. (1994) in the British sector of the Rotliegend sandstones.

The same model may account for the observations of Gaupp et al. (1993) and Platt (1993), who related illitization to invasion of Rotliegend sandstones by acidic fluids of organic origin. In this case study, kaolin precipitates close to the faults, whereas illitic minerals precipitate further away. The sequence of diagenetic reactions leading to illite precipitation (K-feldspar dissolution, kaolin precipitation, and kaolin illitization) may be explained by the change of K^+/H^+ activity ratio in solution as a result of water-rock interactions. This

ratio increases progressively as protons are consumed by alteration of rock-forming minerals and as K^+ is released by K-feldspar hydrolysis. However, the increase in the K^+/H^+ activity ratio is limited by K-feldspar solubility except if additional proton-consuming reactions (e.g. carbonate dissolution) are operative further from the acidic front. In this case, the K^+/H^+ activity ratio continues to increase and a chemical gradient exists from fault to more distant zones, where illitic minerals precipitate from kaolin precursors. Similarly, Furlan *et al.* (1996) describe a more intense kaolin illitization further away from underlying shale formation in the Mahakam Delta Basin (Indonesia). Feldspar dissolution, and subsequent kaolin precipitation, prevails in the deeper part, closer to the source rock.

The above reaction pathway assumes that fluid chemistry is controlled by the combined solubility of quartz, K-feldspar and kaolinite, when porewater equilibrates with mineral matrix from undersaturated conditions. However, the basic assumption that minerals buffer fluid chemistry deserves some discussion. Specifically, the application of the Law of Mass Action to complex aluminosilicates close to equilibrium is questioned by the experimental results of Berger *et al.* (1998). To assess consequences of partial equilibrium between porewater and mineral matrix, the saturation index of illite-mica (Q/K muscovite) in a closed-system sandstone was calculated as a function of pH for

several assumptions (Fig. 13). Calculations were performed using the EQ3/6 package (Wolery, 1983) and the SUPCRT92 database (Johnson *et al.*, 1992) at 100°C. When quartz, K-feldspar and kaolinite control concentrations of aqueous silica, K^+ and aluminium (global equilibrium), supersaturation of illite does not depend on pH but increases with temperature. When K^+ concentration is set constant, and aqueous aluminium constrained by kaolinite solubility, illite precipitation is favoured at high pH, in agreement with the experimental studies of Huang (1993) and Bauer *et al.* (1998). If the aqueous aluminium concentration is controlled by K-feldspar, illite supersaturation decreases as pH increases, precipitation of illite being then favoured at low pH. These calculations suggest that the K^+/H^+ activity ratio may not be the only chemical parameter controlling illite precipitation. Unfortunately, the compositions of fluids responsible for kaolin illitization are not readily available, and these theoretical considerations remain speculative. To further constrain any thermokinetic model, it is therefore essential to identify unambiguously the mechanism and the phases controlling aqueous aluminium concentration in the system.

CONCLUSIONS

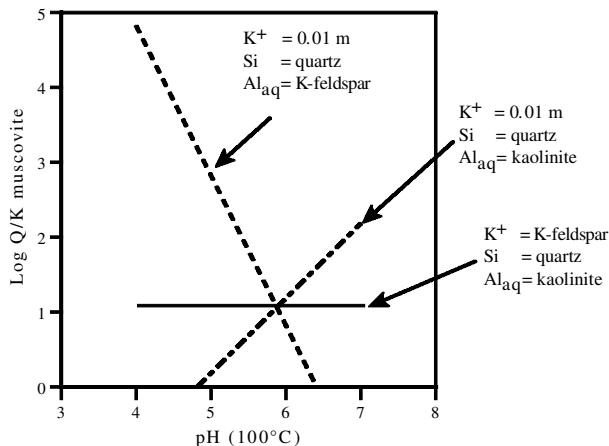In sandstones, the occurrence, evolution and structure of clay minerals reflect diagenetic

FIG. 13. Chemical force driving the precipitation of muscovite/illite in a kaolinite-rich sandstone at 100°C. Calculations are performed using the EQ3/6 software (Wolery, 1983) and the SUPCRT92 database (Johnson *et al.*, 1992). In all cases [Si] is controlled by quartz. Solid line: $[Al_{aq}]$, and $[K^+]$ are controlled by the quartz + K-feldspar + kaolinite assemblage; dashed line: $[K^+]$ is set to 0.01m, $[Al_{aq}]$ is controlled by K-feldspar; irregular dashed line: $[K^+]$ is set to 0.01 m, $[Al_{aq}]$ is controlled by kaolinite.

history. The two groups of clay minerals most often encountered are kaolin and illitic minerals. Although there is no general agreement on the factors controlling precipitation and growth of authigenic minerals or more specifically about the fluids involved, an overall sketch may be drawn for the sequence of mineral reactions.

Kaolinite and dickite are genetically linked to each other. Kaolinite occurs alone only at shallow depth, and its formation is probably related to interaction of meteoric waters with detrital Al-rich silicates. As temperature increases, the formation of kaolin continues to be favoured thermodynamically, due to the invasion of the formation by organic acids. As a consequence, vermiform kaolinite converts progressively to coarse and blocky dickite. Dickite is the stable kaolin polytype in deeply buried sandstones, kaolinite being meta-stable in the thermal range related to burial diagenesis (Zotov *et al.*, 1998). Dickite does not result exclusively from kaolinite diagenetic trans-formation, but also from dissolution of K-feldspar and other Al-rich silicates with increasing tempera-ture, probably because of the evoked presence of organic acids. The relative proportion of dickite, which is best estimated from FTIR analysis, is representative of the overall 'dickitization' reaction, which is the integration of the two processes above.

Kaolinite-to-dickite conversion is slower than dickite formation from K-feldspar decay (Beaufort *et al.*, 1998). The coexistence of both polytypes over a large temperature range implies a kinetic control on this structural transformation. The influence of porosity and timing of hydrocarbon invasion on 'dickitization' also supports this kinetic control.

Subsequent illitization of kaolin may be consid-ered as a consequence of the thermodynamic destabilization of K-feldspar and kaolinite in a closed system within a $120-140°C$ temperature interval. However, numerous conflicting examples have been described in sedimentary basins world-wide. Furthermore, illitization often coincides with tectonically active periods inducing increased heat flows, intense fracturing and faulting, and possible cross-formational fluid flow. In the model proposed by Berger *et al.* (1997), the crystallization of illite at the expense of kaolin suggests that an energy barrier has to be overcome. This energy barrier is likely to be overcome by an increase of the K^+/H^+ activity ratio induced either by an important tectonic event (e.g. invasion by K^+-rich fluids), or by progressive buffering of initially acidic pore-

fluids by mineral reactions (e.g. dissolution of K-feldspar, and subsequent carbonate dissolution) Conversely, illitization of kaolin is inhibited in closed systems where K-feldspar is the unique source of K^+, and illitization of kaolin is not coupled to K-feldspar dissolution. However, in this latter case the energy barrier may be overcome by a temperature increase.

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