HIGH-GRADE DIAGENETIC DICKITE AND 2M₁ ILLITE FROM THE MIDDLE PROTEROZOIC KOMBOLGIE FORMATION (NORTHERN TERRITORY, AUSTRALIA)

PATRICIA PATRIER¹,*, DANIEL BEAUFORT¹, EMMANUEL LAVERRÉT¹ AND PATRICE BRUNETON²

¹ University of Poitiers, HydrASA, CNRS UMR 6532, 40 Avenue du Recteur Pineau, 86022 Poitiers cédex, France
² COGEMA-BUM-DEX, 2 Rue Paul Dautier, 78141 Velizy cédex, France

Abstract—The aim of this paper was to define the nature and the relative chronology of the diagenetic clay bearing assemblages within sandstones of the Middle Proterozoic Kombolgie formation (Northern Territory, Australia). The detrital minerals of these rocks comprise quartz, accessory zircon, tourmaline, rutile and rare phengitic white micas. Diagenetic features consist of pore-sealing secondary quartz overgrowths, strong compaction shown by interlocked structures and stylolith joints, local hematization and the occurrence of two distinct clay parageneses. Blocky crystals of dickite constitute the earliest diagenetic clays. Their FTIR spectra and their DTA curves, with a sharp dehydroxylation endothermic peak near 680°C, are characteristic of the well-ordered dickite already encountered in many deeply-buried sandstones. Quartz overgrowth may be contemporaneous with the crystallization of dickite. Illite occurred during a subsequent stage as grain coatings and as pseudomorphs of dickite in the residual pores of the sandstones. Illite seems to be contemporaneous with the major deformation features associated with compaction phenomena at the maximal burial conditions experienced by the sandstone formation. These illites are essentially of 2M₁ polytype. They display pseudohexagonal platy crystals with average diameters ranging from 2 to 10 µm. Their chemical composition is Al-rich (Ca₀.₀₁Na₀.₀₂K₁.₇₂)(⁶⁺V₁Al₃.₈₂Fe³⁺₀.₁₃Mg₀.₀₅Ti₀.₀₀Mn₀.₀₁)(Si₆.₂₇Al₁.₇₃)O₂₀(OH)₄. These Proterozoic rocks provide a natural reference for the illite end-member occurring as a replacement of kaolin subgroup minerals during burial diagenesis of sandstones. The textural properties of the Kombolgie sandstones (absence of fracture network, low porosity, well-developed macroscopic stylolith joints...) and the crystal structure of both the diagenetic dickite and illite would tend to indicate that the Kombolgie sandstones were buried at a depth exceeding 5 km.

Key Words—Crystal Form, Crystal Structure, Diagenesis, Dickite, DTA Data, FTIR, Illite, Kombolgie, Proterozoic Sandstone, XRD.

INTRODUCTION

Although Proterozoic basins cover a large portion of the continental crust, knowledge of their diagenetic history is limited by the paucity of data published in the literature. The best described are those on the North American and Australian continents (the Athabasca and McArthur basins, respectively) because of numerous ore deposits. The Alligator Rivers Uranium Field (Northern Territory, Australia) contains ~15% of the world’s low-cost uranium resources and comprises the Jabiluka, Nabarlek, Ranger and Koongarra uranium deposits. Nevertheless only a few data are available on clay paragenesis and fluid evolution in the McArthur Basin and in the sandstones from the Kombolgie formation which directly overlie the mineralized metamorphic basement (Gustafson and Curtis, 1983; Wilde et al., 1989; Kyser et al., 2000). Some confusion still persists between clays resulting strictly from diagenetic processes and clays related to hydrothermal fluid circulations along the unconformity with the metamorphic basement. One goal of this paper was to define the nature and the relative chronology of the diagenetic clay assemblages within the Middle Proterozoic rocks of the Kombolgie sandstones by studying areas far away from the unconformity-related uranium deposits of the region and not affected by the hydrothermal alterations associated with the deposition of uranium.

Generally, as seen in younger sedimentary basins, the diagenesis of sediments like sandstones and shales results in characteristic sequences of phyllosilicates as a function of burial depth which involve trioctahedral clays (transformation of 7 Å layer minerals to chlorite or saponite to chlorite) (Reynolds, 1988; Ryan and Reynolds, 1996) and dioctahedral clays. The latter is expressed in siliciclastic sediments by (1) the kaolinite-to-dickite transformation and (2) the illitization of kaolin subgroup minerals and/or direct precipitation of illite from pore-waters (Środoni and Eberl, 1984; Ehrenberg et al., 1993; Lanson et al., 1996; Beaufort et al., 1998, among others). At the same time, in more argillaceous sediments, a significant reaction involves the progressive change of smectite through interstratified illite-smectite to illite (Eberl and Hower, 1976; Nadeau and Reynolds, 1981; Jennings and Thompson, 1986; Velde and Vasseur, 1992; Altaner and Ylagan, 1997, among others). Concomitantly, chlorite may increase in abun-
dance with depth and is inferred to be a direct byproduct of the smectite-to-illite reaction (Boles and Franks, 1979; Jennings and Thompson, 1986; Whitney, 1990). The evolution of the structural properties of these clay minerals (interlayering, polytypism) as a result of increasing temperature and pressure during burial diagenesis has been well documented for >30 y. Another goal of this paper was to compare the textural and crystal-chemical properties of Proterozoic authigenic clays with diagenetic clays from other younger basins in relation to their paleoburial conditions. Morphology, crystallinity and polytypism of authigenic phyllosilicates will be discussed, not ignoring the influence of kinetic factors (water/rock ratio, petrophysical properties).

GEOLGY

The Paleoproterozoic to Mesoproterozoic McArthur Basin (Northern Territory, Australia) which covers an area of ~180,000 km$^2$, is a 5–15 km thick platform cover sequence deposited on the North Australian Craton (Plumb, 1979a,b). The basin is a multiphase composite basin system formed in a dynamic tectonic environment over a period of 350 million years. Five distinct packages (sub-basins) have been regionally separated, each characterized by a unique association of igneous and sedimentary lithofacies (Rawlings, 1999). The newly-defined Kombolgie Subgroup forms the basal part of the Katherine River Group and is the oldest preserved component of the northwest McArthur Basin. It is limited in age between 1822 Ma and probably 1730 Ma (Sweet et al., 1999).

The Kombolgie Subgroup is ~1500 m thick. It is essentially composed of unmetamorphosed conglomerates and quartz sandstones with a basaltic intercalation (Nungbalgarri volcanics) separating the lower Mamadawerre Sandstone member from the upper Gumarrirbang Sandstone. The lower parts were deposited in a mainly braided stream environment punctuated by brief intervals of marine deposition. It covers large portions of Arnhem Land (300 × 200 km) where it forms rugged topographic highs.

The Kombolgie Formation directly overlies the early Proterozoic metamorphic basement which contains the unconformity-related uranium deposits of the Alligator Rivers field (Jabiluka, Naborlek, Ranger and Koongarra – Figure 1). However, due to very difficult logistical conditions, it has so far been poorly drilled.

In this study, we analyzed core samples of fine- to medium-grained sandstones from the lowermost Kombolgie units overlying the unconformity in a drill hole, U 65-3, located 10 km ESE of the Naborlek uranium deposit. This drill hole was selected because the 151 m thick sandstones drilled in this area are far away from any known uranium showings of the region and are not affected by the hydrothermal alterations associated with the deposition of uranium. Twelve core samples collected at depths between 20 and 150 m (Table 1) were analyzed using the methods detailed below.

ANALYTICAL METHODS

Microscopy

Petrographic data, including morphological and textural relationships, were recorded from the observation of polished thin-sections using an Olympus BH2 polarizing microscope and from the examination of rock slabs, previously coated with gold, with a Jeol JSM6400 scanning electron microscope (SEM). This microscope was equipped with an energy dispersive X-ray analyzer (EDS, Si(Li) semi-conductor). Analytical conditions were as follows: accelerating voltage 15 kV, probe current 60 nA, working distance 25 mm, counting time 100 s. The standards used for EDS consisted of albite, forsterite, orthoclase, wollastonite, manganese metal, titanium metal and pyrite.

X-ray diffraction

Acquisition of X-ray diffraction (XRD) patterns was performed with a Siemens D501 diffractometer (CuK$\alpha$ radiation) equipped with a Si(Li) detector cooled by Peltier effect. Diffraction patterns were recorded using a DACO MP acquisition device. Background stripping, indexing of the diffraction peaks and mineral identifications by comparison with ICDD files were carried out using Diffrac-AT software (SOCABIM). For this study, all the diffraction patterns are of the c<4 μm fraction separated by sedimentation.

Oriented clay aggregates were analyzed by XRD in air-dried (AD) conditions and after ethylene glycol (EG) solvation. The diffraction patterns were recorded using a step-scanning mode from 2.5 to 33°2θ (40–3 Å) with a step size of 0.02°2θ and a counting time of 5 s per step. Oriented clay aggregates were prepared by filter peel (pore diameter of 0.08 μm). This method produces mounts that have reasonable crystallite orientation and gives accurate intensity (Bish and Reynolds, 1989).

Illite polytypes were identified by XRD on randomly oriented separates using the step scanning mode from 19 to 34°2θ (4.67–2.64 Å) with a step size of 0.02°2θ and a counting time of 20 s per step. The clay separates were randomly oriented using a back-loading method as described and recommended by Moore and Reynolds (1989). For this identification, six samples were disintegrated by freezing-heating cycles. This methodology was preferred to classical grinding to prevent, as far as possible, contamination of the clay fraction by fine-grained particles of quartz created by grinding. The identification of illite polytypes was based on comparison with data given in Bailey (1980) and Brindley (1980) for 1M (previous name for 1Mt) and 2M$_1$ polytypes and in Drits and Tchoubar (1990) and Drits et al. (1993) for 1Mt and 1Mc (previously described as
In the literature, polytypes 1\textit{Mt} and 1\textit{Mc} correspond to the 1\textit{M} illite polytype with \textit{trans}-vacant octahedral sites and \textit{cis}-vacant octahedral sites, respectively. The standard form of the Scherrer equation has been used to calculate the mean thickness of the coherent scattering domain (CSD) of illite crystals employing a constant $k$ of 0.89. For comparison, values obtained from the Scherrer equation modified by Drits et al. (1997) have also been reported. Their adjustment of the $k$ value is realized to integrate a lognormal thickness distribution for clay particles. “$N$”, which represents the number of layers in the CSD, has been calculated from the 001 reflection.
Microprobe analyses

Microprobe analyses were performed with a CAMECA SX50 apparatus using a wavelength-dispersive spectrometer (WDS). The analyzed elements were Na, Mg, Al, Si, K, Ca, Ti, Mn and Fe. This microprobe was calibrated using synthetic and natural oxides and silicates (MnTiO$_3$, hematite, albite, orthoclase and diopside) and corrections were made with a ZAF program. The analytical conditions were as follows: current intensity of 4 nA; accelerating voltage of 15 kV; spot size of 2 μm; counting time of 10 s per element. The relative error is <1.5%. Total Fe is presented as Fe$_2$O$_3$.

Infrared spectroscopy

Fourier transform infrared (FTIR) spectra were recorded, in transmission mode, with a Nicolet 510 FTIR spectrometer. The resolution was 4 cm$^{-1}$ in the 400–4000 cm$^{-1}$ analyzed range. This spectrometer was flushed continuously with dry air containing substantially less CO$_2$ than normal air. Spectra were obtained at room temperature from KBr pressed pellets prepared by mixing 1.5 mg of sample with 150 mg of KBr.

Differential thermal analysis

Differential thermal analysis (DTA) curves were obtained from 20 mg samples in a Pt crucible on a Netzsch STA 409 EP differential thermal analyzer. The instrument was calibrated with standard substances at 20°C/min. Typical DTA curves for kaolinite are characterized by a dehydroxylation endotherm ranging from 500 to 580°C, while dickites have endotherms ranging from broad peaks at 500–680°C to a sharp peak near 680°C (Mackenzie, 1970). Differences in the temperature of these dehydroxylation peaks are attributed to variations in the degree of structural order but could also be the result of kaolinite/dickite interstratifications (Brindley and Porter, 1978).

RESULTS

Sandstone petrography

The Kombolgie sandstones studied in the U 65-3 drill hole may be classified as orthoquartzitic sandstones. The detrital mineralogy is dominated by monocrystalline quartz, as well as minor amounts of polycrystalline quartz, accessory minerals (zircon, apatite, tourmaline and rutile) and rare white mica. These sandstones appear poorly sorted and range from fine- to medium-grained for the most part with variable grain morphologies (subrounded in medium-grained sandstone and subangular in fine-grained sandstone). The amount of matrix is generally small and variable (from <1% to 6%) consistent with their SiO$_2$ content (>97%) (Table 1). No feldspar has been observed in these sandstones. However on the basis of textural evidence, Gustafson and Curtis (1983) suggest that most of the clay material was formed by alteration of detrital feldspars during the burial history of the Kombolgie basin.

Several diagenetic processes affected these sandstones. Field observations clearly showed the occurrence of well-expressed stylolith joints in sandstone formations, also recognized on core samples (Figure 2a), suggesting a compaction process. In thin-sections, microstyloliths, interlocked structures with indentations of the mutual contacts between detrital quartz grains, impingement of secondary quartz overgrowths and triple-point quartz junctions confirm the strong compaction of these sandstones and coincide with a strong decrease in pore size (Figure 2b). The porosity of the

Table 1. Sampling: bulk-rock chemical compositions and clay contents of the unaltered Kombolgie sandstones, drill hole U 65-3. The unconformity is located at 156 m.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Core depths (m)</th>
<th>Bulk rock chemical composition (%)</th>
<th>Clay content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SiO$_2$</td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>8445-1</td>
<td>20.10</td>
<td>98.34</td>
<td>0.72</td>
</tr>
<tr>
<td>8445-2</td>
<td>34.70</td>
<td>99.29</td>
<td>0.27</td>
</tr>
<tr>
<td>8445-3</td>
<td>41.00</td>
<td>97.96</td>
<td>0.78</td>
</tr>
<tr>
<td>8445-4</td>
<td>74.80</td>
<td>97.17</td>
<td>1.52</td>
</tr>
<tr>
<td>8445-5</td>
<td>91.00</td>
<td>98.47</td>
<td>0.46</td>
</tr>
<tr>
<td>8445-6</td>
<td>102.00</td>
<td>97.21</td>
<td>1.55</td>
</tr>
<tr>
<td>8445-7</td>
<td>107.00</td>
<td>98.26</td>
<td>0.36</td>
</tr>
<tr>
<td>8445-8</td>
<td>116.60</td>
<td>98.74</td>
<td>0.95</td>
</tr>
<tr>
<td>8445-9</td>
<td>121.10</td>
<td>97.68</td>
<td>1.55</td>
</tr>
<tr>
<td>8445-10</td>
<td>131.10</td>
<td>97.74</td>
<td>1.24</td>
</tr>
<tr>
<td>8445-11</td>
<td>139.30</td>
<td>98.51</td>
<td>0.97</td>
</tr>
<tr>
<td>8445-12</td>
<td>150.90</td>
<td>97.76</td>
<td>1.34</td>
</tr>
</tbody>
</table>

Clay contents were estimated from chemical data (K$_2$O and Al$_2$O$_3$ contents)
<d.l.: below detection limit (i.e. 0.1% for MgO and Fe$_2$O$_3$ and 0.05% for K$_2$O). CaO amounts are <0.1%. TiO$_2$ and Na$_2$O are <0.05% and MnO <0.03% (CRPG Nancy analysis)
Kaol-dick: kaolin subgroup minerals
sandstones studied (determined by Hg-porosimetry) varies from 2 to 9% and appears to be the lowest in silicified sandstones observed at core depths of 34.7, 91 and 107 m. Indeed, quartz overgrowths sometimes sealed the overall porosity producing a dense quartzite (Figure 2b). This growth of authigenic quartz is a widespread phenomenon. Its abundance is particularly marked in sandstones with very little matrix material (≤ 1%). The principal impact of these silicified zones is the creation of an impermeable level preventing vertical

Figure 2. (a) Example of a stylolith joint observed in sandstone samples. (b) Highly silicified sandstone completely cemented by quartz overgrowths with interlocked structures (Q Over.). Transmitted polarized light observations (sample 8845-6). (c) View of pore filling by dickite aggregates (D). Illite (I) pore lining along quartz grains (Q). Illite filled the overall pore space locally. Transmitted polarized light observations (sample 8845-6). (d) Blocky crystal of dickite (D) disseminated in the coarse-grained illitic matrix (I). SEM secondary electron mode (sample 8845-10). (e) Euhedral crystals of illite, identified by SEM analysis, with subhexagonal morphology in coarse-grained illitic material. SEM secondary electron mode (sample 8845-12). (f) Pseudomorphs of dickite aggregates by coarse-grained illites. The morphological characters of the blocky crystals of dickite have been preserved. Transmitted polarized light observations (sample 8845-9).
fluid flow and focusing the fluid flow into higher permeable rocks (without quartz cement) where compaction is then inhibited. Dissolution of detrital quartz occurred in response to pressure-solution mechanisms created by the compaction and contributed to the redistribution of silica in secondary quartz overgrowths.

Authigenic clays have been studied in more detail. The greatest amounts of clay matrix (close to 6%) were observed in samples at 74.80, 102.00, 121.10 and above the unconformity (150.90 m). The texture, morphology and mineral paragenesis of the authigenic clay minerals are summarized in Table 2 and some representative examples are shown in Figure 2. Two distinct groups of authigenic clay minerals have been found: illite and kaolin subgroup minerals.

Illite represents by far the predominant diagenetic clay mineral observed in all samples. It has various morphologies according to the site of crystallization. It is essentially observed coating grains in highly silicified sandstones, whereas it appears lining pores and bridging pores in more porous sandstones. Pore lining is particularly developed in sandstones in which pores were also occupied by kaolin aggregates (Figure 2c). More frequently, illite filled the overall pore spaces in which only a few relict kaolin crystals were observed. Detrital white micas were also partly replaced by diagenetic coarse-grained illites. Illite is seen as a boxwork texture essentially composed of relatively coarse-grained pseudo-hexagonal platy crystals (average diameters ranging from 2 to 10 μm, Figure 2d,e) with rare lath-shaped crystals. Hematite, occurring as small grains, was locally disseminated in the illitic matrix.

In most samples, only very small amounts of kaolin minerals have been observed by microscopy, in agreement with XRD analyses. In the less silicified sandstones, kaolin minerals occur as aggregates of coarse-grained euhedral crystals (average diameter >10 μm) which occupy most of the residual space between subrounded grains of detrital quartz (Figure 2c). The blocky habits of these coarse-grained kaolin minerals (Figure 2d) are typical of dickite observed in deeply buried sandstone reservoirs (Ehrenberg et al., 1993; McAulay et al., 1994; Beaufort et al., 1998). The spatial organization of these blocky particles sometimes suggests pre-existing booklet morphologies. Rare dolomite and/or ankerite may be associated with authigenic dickite. Observations by SEM also indicate that these kaolin minerals occur as disseminated and partly dissolved blocky crystals embedded in the illite material. Detailed observations indicate that authigenic illite postdates authigenic kaolins which were partly or totally replaced by illite (Figure 2f).

Finally, it should be noted that fine-grained flaky crystals of kaolinite replace or pseudomorph authigenic illites in the sample collected just below the lateritic weathering profile (20.15 m). Indeed, from the beginning of the Cretaceous to the present, there have been only minor modifications of the landscape except the geomorphological changes related to the initiation of weathering processes in tropical climates.

**X-ray diffraction**

**Identification of clay minerals.** The air-dried oriented samples are presented in Figure 3. In spite of a grain size <4 μm, the amount of quartz is still significant; it was probably produced by the mechanical crushing of the rock. However, it was greatly reduced by the powder preparation created by heating-freezing cycles.

As observed by microscopy, illite is the major or even the only clay mineral in all the studied samples. It is characterized by 00l reflections near 10.0, 5.0 and 3.34 Å. No expandable components, such as illite-smectite mixed-layers, have been identified as indicated by the absence of peak shifts on XRD patterns of ethylene-glycol solvated preparations (Figure 4).

Smaller amounts of minerals from the kaolin subgroup (kaolinite or dickite) have also been identified. These minerals are best seen at 102 and 121.10 m but can be found at 74.85, 116.60, 131.10, 139.35 and 150.90 m in decreasing order of abundance. Their relative abundance is probably underestimated because of the <4 μm fraction studied. Their grain sizes, as shown by SEM observations, frequently exceed 10 μm. This is the case for sample 8845-10 (131.10 m), as suggested by the bulk rock chemical analysis. The full width at half maximum intensity (FWHM) of the 001 peak of these kaolin minerals is close to 0.10° except in the shallowest sample where this value is totally

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Texture</th>
<th>Morphology</th>
<th>Paragenesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dickite</td>
<td>Pore-filling; replacement after feldspars?</td>
<td>Blocky, euhedral crystals, partly dissolved (mean size &gt;15 μm). Pseudohexagonal platy crystals (euhedral) (2 μm &lt; mean size &lt;5 μm). Rare lath-shaped crystals. Rare flaky-shaped crystals.</td>
<td>Early diagenetic clay mineral associated with rare dolomite and/or ankerite.</td>
</tr>
<tr>
<td>Illite</td>
<td>Grain-coating, pore-lining, pore-bridging, pseudomorph of altered dickite, partial replacement of detrital white micas.</td>
<td></td>
<td>Postdates and replaces early authigenic dickite; associated with variable amounts of hematite.</td>
</tr>
</tbody>
</table>
different (0.25°2θ). Apart from this last sample, the diffraction patterns of the randomly oriented powders clearly prove the occurrence of $2M_1$ dickite (Figure 5) with typical reflections (Bailey, 1980).

**Illite crystallinity.** The illite crystallinity is classically estimated by the Kükler index (Kükler, 1964, 1968) which corresponds to the FWHM of the reflection located around 10 Å. According to the standard form of the Scherrer equation, “$N$”, which represents the number of layers in the CSD, ranges from 29 to 30 in the upper samples to 37 to 42 in the lower ones (Table 3). For comparison, values obtained from the Scherrer equation modified by Drits et al. (1997) have also been reported. These values are lower (between 19 and 28) than values obtained by the Scherrer equation.

Figure 3. XRD patterns of air-dried oriented clay-aggregate samples (granulometric clay fraction <4 μm). Illite is by far the major clay mineral identified by XRD.

Figure 4. XRD patterns of air-dried (a) and ethylene-glycol solvated (g) oriented clay-aggregate samples (samples 8845-1 and 8845-6, granulometric clay fraction, <4 μm). No peak shift is observable after ethylene-glycol solvation, suggesting the absence of expandable components (i.e. mixed-layered illite-smectite).
Determination of illite polytypes. The XRD patterns of random powder mounts are presented in Figure 6. For a better interpretation of these diffraction patterns, the diagnostic reflections of $2M_1$, $1M_t$ and $1M_c$ illite have been superimposed and listed in Table 4. These XRD patterns show that, in all the samples, the polytype of illite is mostly $2M_1$. Only very small amounts of $1M_t$ illite, in which $1M_t$ illite predominates over $1M_c$ illite, may be suspected at shallow depths. No polytypic differences were noted between illite crystallized in highly silicified sandstones as grain coatings, and illite developed as pore bridges in more porous levels.
Fourier transform infrared

The FTIR spectra are better than XRD patterns for identification of dickite associated with kaolinite. The distinction between the kaolin minerals, kaolinite and dickite, is made on the basis of the position and relative intensities of the absorption bands in the OH-stretching region (3800–3500 cm$^{-1}$). Infrared spectra for kaolinite show four bands at 3695, 3668, 3652 and 3620 cm$^{-1}$ (Farmer, 1974). The IR spectra of the >20 μm clay fraction, chosen to eliminate the illitic components, clearly prove the occurrence of dickite as illustrated in Figure 7a (characteristic Al$_2$OH vibration bands near 3705, 3654 and 3622 cm$^{-1}$).

Differential thermal analysis

The DTA curve of kaolin minerals presents a dehydroxylation peak at ~670º C and an exothermic peak at ~997º C (Figure 8a). This is in agreement with a typical curve of dickite (Mackenzie, 1970). However, the position of the dehydroxylation peak towards the high-temperature limit (dehydroxylation peak generally found in the region 500–700ºC), as well as its sharpness, are in accord with a well-ordered dickite structure (Bish and Duffy, 1990).

Table 5. Average chemical composition and standard deviation of illites from the Kombolgie sandstones (drill hole U 65-3).

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Al</th>
<th>$^{IV}$Al</th>
<th>$^{VI}$Al</th>
<th>Fe$^{3+}$</th>
<th>Mg</th>
<th>Ti</th>
<th>Mn</th>
<th>Oct</th>
<th>Ca</th>
<th>Na</th>
<th>K</th>
<th>Int</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg</td>
<td>6.27</td>
<td>5.55</td>
<td>1.73</td>
<td>3.82</td>
<td>0.13</td>
<td>0.05</td>
<td>0.00</td>
<td>0.00</td>
<td>4.00</td>
<td>0.01</td>
<td>0.02</td>
<td>1.72</td>
<td>1.75</td>
</tr>
<tr>
<td>Std. dev.</td>
<td>0.06</td>
<td>0.08</td>
<td>0.05</td>
<td>0.05</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.06</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Structural formula is calculated per O$_{26}$(OH)$_4$

Number of measurements: 65

Figure 6. XRD patterns of random powder mounts (clay fraction <4 μm). The diagnostic reflections of 2$M_1$, 1$Mt$ and 1$Mc$ illites are represented by vertical lines. Hem: hematite impurities, Qtz: quartz. The illite polytype is mostly 2$M_1$. Only very small amounts of 1$Mt$ may be suspected at shallow depth.
Microprobe analyses

The detrital micas have a chemical composition close to phengite. A representative structural formula of these minerals is: \((\text{Na}_{0.10} \text{K}_{1.92})(\text{VI}_{\text{Al}}\text{Al}_{3.06}\text{Fe}_{0.56}\text{Mg}_{0.36}\text{Ti}_{0.06}\text{Mn}_{0.03})(\text{Si}_{6.68}\text{Al}_{1.32})\text{O}_{20}(\text{OH})_{4}\). These minerals are characterized by an interlayer charge typical of mica (near 2 per \(\text{O}_{20}(\text{OH})_{4}\)) and high negative charges of the octahedral sheet which are due to the Tschermak substitution \((\text{Si} + R^{2+} = \text{Al}^{IV} + \text{Al}^{VI})\). Iron is the major divalent component within the octahedral sheet, \(i.e.\) \(\text{Fe}/(\text{Fe} + \text{Mg})(X_{\text{Fe}})\) varies between 0.53 and 0.62.

The structural formula of diagenetic illites analyzed by microprobe are reported in Table 5 and in Figure 9. No distinction can be made between illite crystallized as grain coatings and illite observed as pore linings or pore bridges. Their chemical compositions are scattered between aluminous illite and muscovite. A representative structural formula of diagenetic illite is: \((\text{Ca}_{0.01}\text{Na}_{0.02}\text{K}_{1.72})(\text{VI}_{\text{Al}}\text{Al}_{3.82}\text{Fe}_{0.13}\text{Mg}_{0.05}\text{Ti}_{0.00}\text{Mn}_{0.01})(\text{Si}_{6.27}\text{Al}_{1.73})\text{O}_{20}(\text{OH})_{4}\). Diagenetic illite is characterized by lower interlayer charges compared to mica (most of them are between 1.7 and 1.8 for \(\text{O}_{20}(\text{OH})_{4}\)) and lower negative octahedral charges. \(\text{Fe}/(\text{Fe} + \text{Mg})(X_{\text{Fe}})\) varies between 0.5 and 0.9.

INTERPRETATION AND DISCUSSION

The diagenetic sequence

The diagenetic sequence of clay minerals in the Kombolgie sandstones can be summarized as follows:

1. Well-ordered dickite, clearly shown by XRD and FTIR results, was related to an earlier diagenetic stage, associated with quartz overgrowths and minor carbonate minerals (dolomite-ankerite).
2. Iilitization constituted a subsequent stage. Detailed SEM observations of dickite aggregates clearly
indicate that, in the presence of illite, relics of dickite present some evidence of dissolution and several features of pseudomorphs of blocky dickite by illite. Only one stage of illitization is inferred because no chemical, microstructural and textural distinctions exist between illite occurring in the different sites (grain coating, pore lining or bridging and pseudomorph of dickite in the most porous sandstones). This clay mineral seems contemporaneous with the major deformation features associated with compaction phenomena such as quartz indentations and/or pressure solution and so probably corresponds to the maximal burial conditions experienced by the sandstone formation.

Dickite + dolomite-ankerite + quartz is a mineralogical assemblage which is well known in the diagenesis of deeply-buried sandstone reservoirs (see compilation in Kisch, 1983; or Bjorlykke and Aagaard, 1992). According to Shutov et al. (1970), the kaolinite-to-dickite transition begins at a depth of ~2500 m. More recently, other authors (Ehrenberg et al., 1993; Ruiz Cruz and Moreno Real, 1993) have confirmed this transition depth. However, the occurrence of ordered dickite alone is not observed at burial depths <5000 m (Beaufort et al., 1998).

Illitization of kaolin minerals is a common process in sandstone reservoirs (Bjorlykke and Aagaard, 1992) and, even if direct precipitation of illite cannot be definitively discarded, it is clear that dickite is the best candidate as a source material for the authigenic illites analyzed in this study. Such temporal overlap in the nature of authigenic clay minerals (dickite then illites) was described in many deeply-buried sandstone reservoirs by Šrodón and Eberl (1984), Ehrenberg et al. (1993) and Lanson et al. (1995, 2002). Illitization of kaolin requires a source of K which is difficult to identify unambiguously. In their present state, the Kombolgie sandstones contain no K-bearing detrital minerals, excepted rare detrital white micas. However, it should be noted that the sediments which filled the intracratonic McArthur Basin were derived from Paleoproterozoic and Archean metamorphic and igneous rocks which contained K-feldspars and micas. So it seems probable that the source of the K (0.1–0.4% K$_2$O in bulk rock) incorporated in the illites of the Kombolgie sandstones must have originated in the small amounts of detrital feldspars and/or micas (1–3%) progressively dissolved during the burial diagenesis. The presence of detrital feldspars in the Kombolgie sediments has already been suggested by Gustafson and Curtis (1983).

This reaction contrasts with that observed in shales where illite results from the diagenetic conversion of mонтmorillonite to illite via illite-smectite mixed layers (with minor chlorite as a byproduct). Considering the very small amount of K contained in the Kombolgie sandstones (Table 1), it seems difficult to invoke montmorillonite as a source material for the observed authigenic illite.

**Textural and microstructural properties of the diagenetic clays**

Dickites from the Kombolgie sandstones appear better ordered than dickites crystallized in similar younger sandstone formations buried at 5000 m depth. This is particularly well illustrated by comparing our results with those given in Lanson et al. (2002) and obtained on the Rotliegend sandstone formation for which the estimated maximum paleoburial depth experienced before the Kimmerian uplift is ~5000 m.

The DTA curves of kaolinite minerals from the deepest Rotliegend sandstone samples always present a broad endothermic peak at temperatures close to 560–570°C in addition to a sharp one at 660°C (Figure 8b). This association suggests the simultaneous occurrence of dickites with a wide range of stacking order-disorder. Dickites observed in the Kombolgie sandstones display a DTA curve (Figure 8a) which is characterized by a dehydroxylation endothermic peak close to 680°C with a very sharp and symmetric profile characteristic of well-ordered structure. The same conclusion can be deduced from IR spectra. The Kombolgie sandstones spectrum is characterized by absorption bands typical of pure dickite with sharp profiles (Figure 7a) while the Rotliegend spectra show absorption bands characteristic of intermediate kaolinite-dickite structures (Figure 7b; Beaufort et al., 1998).

In the Kombolgie sandstones, illites of 2$M_1$ polytype predominate and systematically display hexagonal shapes as generally admitted for this polytype (Inoue et al., 1987), with diameters which can reach 10 μm. In the Rotliegend sandstones, the illitic material is of 1$M$ polytype (1$M_1$ and 1$M_2$) with hairy habits or lath shapes (Lanson et al., 1996). With increasing depths, these authors note more rigid lath morphology down to 4000 m and locally, from 4000 m and deeper, pseudo-hexagonal shaped particles with a maximum diameter of
3–5 μm. However, $2M_1$ illites were not observed in these samples. Illites from the Kombolgie formations also exhibit greater crystallinity. In the Rotliegend sandstones (Lanson et al., 1995), illites have a Kübler index between 0.5 and 0.75° (CuKα) in the deeper sample buried at 5000 m against 0.20°, CuKα for our studied sandstones (Table 3). Such a difference (at least 0.3°) exceeds the error analysis of the “illite crystallinity technique” as proposed by Robinson et al. (1990). The Kübler index of illites from the Kombolgie formation is also less than those generally admitted for illite of anchizone limits correspond to ~25 and 50 or more layers, respectively, of pure illite or to a Kübler index of 0.42º (CuKα) and 0.25º (S´rodon´ and Eberl, 1984; Jaboyedoff, 1999). However, in comparison with sandstones, pelitic formations are characterized by very low permeability and therefore by slower reaction progress (the other parameters being equivalent).

Chemical composition of illite

The chemical compositions of the diagenetic illites which result from a smectite-to-illite reaction (via I-S mixed layers) are quite variable because these minerals display variable interlayer charges resulting from a small but variable amount of smectitic material (the term illite is generally admitted for smectitic content ≤5%). In diagenetic context, the chemistry of the illite end-member was determined by extrapolation of the chemical compositions of I-S mixed layers with different numbers of smectite layers – $K_{1.80}(Al_{3.60}Fe_{0.10}Mg_{0.30})$ (Si$_{6.60}$Al$_{1.40}$)O$_{20}$OH$_4$ (Meunier and Velde, 1989); $K_{1.80}(Al_{3.50}Fe_{0.20}Mg_{0.30})$ (Si$_{6.50}$Al$_{1.50}$)O$_{20}$OH$_4$ (Lanson and Velde, 1992); $K_{1.80}(Al_{3.70}Fe_{0.10}Mg_{0.20})$ (Si$_{6.40}$Al$_{1.60}$)O$_{20}$OH$_4$ (S´rodon´ et al., 1992). The diagenetic illites from the Kombolgie formation do not contain any smectite layers and consequently can also be considered as an illite end-member. Their interlayer charge is close to those of the pure illites reported above and is totally satisfied by K ions. However they differ from the above reference analyses by a higher Al content (5.55 vs. 5.00–5.30 per O$_{20}$OH$_2$), a very small number of Tschermak substitutions ($Si + R^{2+} \rightarrow \frac{V}{4}Al^{4+}Al$) and a higher tetrahedral charge ($Si_{6.25}^{IV}Al_{1.75}$) relative to the octahedral one (Figure 10). These chemical differences could be explained by the nature of the source material (smectite for the reference illite in the literature, dickite for the Kombolgie samples) and thus by a different illitization process. Plotted in the $M^+-4Si-R^{2+}$ diagram, their microprobe analyses are very homogeneous and positioned on the kaolinite-muscovite line far from the montmorillonite-illite line determined for the montmorillonite-to-illite reaction (Figure 10). In conclusion, we suggest that the composition of the Kombolgie illite represents the end-member of the kaolin subgroup minerals to illite reaction.

Estimated paleoconditions recorded by the Proterozoic Kombolgie sandstones

These differences in crystallochemical and microstructural properties of the diagenetic clays from the Proterozoic Kombolgie formation and the much younger Rotliegend sandstones can be explained by the time span during which the diagenetic reactions operated, by different burial depths, or by different thermal gradients. Considering the low porosities of the Kombolgie formation, the permeability (or fluid/rock ratio), which is also an important parameter known to control the reaction progress, seems inoperative in this case. Therefore only the former points will be discussed below.

According to Kyser et al. (2000), the crystallization of diagenetic clays in the Kombolgie formation took place between approximately 1550 and 1650 Ma. After peak diagenesis, the overall cooling path model of the basin showed a slow decrease in temperature from 230 to 100°C until 400 My and a preservation of temperatures close to 200°C up to ~1100 Ma. The role of time in the progress of the following reactions, kaolinite $\rightarrow$ illite $1M_1 \rightarrow$ illite $2M_1$, is difficult to appreciate. However, a hydrothermal event associated with a major deposition of uranium led to the crystallization of secondary illites dated at ~1640 Ma (Kyser et al., 2000) in the same unit of Kombolgie sandstones located a few km around this area of interest. They have been superimposed on these diagenetic illites and are characterized by very different microstructural properties ($1M_1$ polytype) and preservation of small amounts of smectitic components in their structure (Patirier et al., 2000; Beaufort et al., 2003). This suggests that the clay structure was controlled by

![Figure 10. Projection in 4Si-$M^+-R^{2+}$ coordinates (Meunier and Velde, 1989) of the structural composition of illites from the Kombolgie sandstones. Cel: celadonite; Ill 0.9: high-charge illite end-member of the I-S series as proposed by Meunier and Velde (1989); K/D: kaolin subgroup minerals. Structural compositions are plotted along the kaolinite-muscovite line far from the I-S line proposed by Meunier and Velde (1989).]
the crystallization paleoconditions (mostly temperature) rather than by the duration of the reaction, even if it took over a billion years.

Illitization of kaolin minerals, although very frequent, is not always observed in deeply buried sandstone reservoirs and so is not systematically related to burial depth. This mechanism of illitization usually occurs within a restricted time and often coincides with tectonically active periods inducing increased heat flow and intense fracturing and faulting (Lanson et al., 2002). No fracturing is seen in the studied area (at the time of illitization) and the low porosity of the Kombolgie sandstones does not favor introduction of significant hot fluid flow of external origin. According to Berger et al. (1997), if external sources of K or pH variations (i.e., high K⁺/H⁺ activity ratio) are necessary to overcome the kinetic barrier to the kaolinite-illite conversion for a burial depth below 4000 m, temperature could be the most likely driving force in such reactions for greater burial depths. Indeed, the kinetic barrier to illite crystallization decreases with increasing temperature and the reaction kaolin mineral + K-feldspar $\rightarrow$ illite may be predominant at high temperature as shown by the frequent illitization of kaolin in deeply buried sandstones (Šrodon and Eberl, 1984; Ehrenberg et al., 1993; Lanson et al., 1995). The temperature threshold is estimated at ~120–140º C (Lanson et al., 2002) which generally corresponds to an average burial depth of 3500–4000 m. If we refer to fluid inclusion data published for the Kombolgie basin, the hypothesis that temperature is the main controlling factor could be realistic. Derome et al. (2003) studied fluid inclusions trapped in secondary quartz (overgrowths or drusy quartz) and estimated a trapping temperature close to 170º C. High-temperature fluid inclusions ($T_h$ between 140 and 200º C) were also examined by Durak et al. (1983) and Wilde et al. (1989) in quartz overgrowth and quartz veins. In this thermodynamic context, illitization would last as long as the temperature and/or K activity of the diageneric solutions were high enough.

The petrographic evidence for a strong compaction of the Kombolgie sandstones (stylolith joints, interlocked structures with indentations of contacts between detrital quartz grains, impingements of secondary quartz overgrowths, triple-point quartz junctions and very low porosity) and the absence of fracture-controlled illitization, suggest that deep-burial rather than high thermal gradient explains the evolution of the microstructural properties of the illitic material. Indeed, as stylolites occur most readily in carbonate rocks, their development in siliciclastic sandstones implies deep diagenesis. As an example, sandstones with similar structures to those of the Kombolgie sandstones have been described in the Natal Group (South Africa) for estimated burial depths between 4800 and 7200 m (Liu, 2002). Such a hypothesis is also supported by the results of Derome et al. (2003) which suggest paleoburial depth of at least 4000–5000 m.

The differences in properties of illitic material, i.e. (1) increasing sizes, (2) more isometric shapes, and (3) $1M$ to $2M_1$ polytype transition, are often interpreted as the result of increasing burial depths (Inoue et al., 1987; Lanson and Champion, 1991; Reynolds, 1993). The $2M_1$ illite polytype is typical of pure illite (Inoue et al., 1987) that crystallized in high-grade diagenetic or metamorphic terrains (temperatures >200º C). If we consider that the geothermal gradient in a post-Archean sedimentary basin is between 25 and 35º C, the occurrence of illite of $2M_1$ polytype suggests a burial depth of >5000 m.

The increase of dickite ordering can also be interpreted in terms of increasing burial depth. Indeed, with an advancing degree of burial diagenesis, the kaolinite to dickite reaction proceeds by gradual structural modifications concomitant with crystal coarsening and morphological changes (Beaufort et al., 1998; Ehrenberg et al., 1993). The reactions proceed through dissolution, solute transport and crystallization mechanism in agreement with the Ostwald step rule irreversible process and are underlined by the occurrence of intermediate structures (Lanson et al., 1996), with varying degrees of order/disorder.

CONCLUSIONS

The results reported here on the diageneric material of the Kombolgie sandstones can be considered as a reference for the regional diageneric background. The occurrence of well-ordered dickite and illite, both of the $2M_1$ polytype, in these Proterozoic rocks confirms the stability of these clay minerals during sandstone diagenesis. These Proterozoic rocks provide a natural reference for the illite end-member occurring as replacement of kaolin subgroup mineral during burial diagenesis of sandstones. Its chemistry is different from the illite compositional pole deduced from the I-S series. The chemistry of diageneric illites was controlled by the chemical (and physical) environment in which they precipitated (pore-fluid chemistry or mineral precursor). The kinetic control of the crystallochemical and microstructural properties of the authigenic clays is difficult to appreciate in this context even for such long geological periods. Their textural and microstructural properties seem rather related to paleoconditions associated with burial depths. The occurrence of well-ordered dickite and illite of $2M_1$ polytype, in agreement with the existence of macroscopic stylolith joints and fluid inclusion data, demonstrate that the Kombolgie sandstones have experienced a burial depth >5000 m and not necessarily a high thermal gradient.

ACKNOWLEDGMENTS

The research for this paper was supported financially by COGEMA exploration division and AFMEX. We thank J. Mondy and F. Brisset for sharing their knowledge about
the geological background of the Kombolgie Basin and for their assistance with sampling.

REFERENCES


(Received 18 January 2001; revised 5 August 2002; Ms. 559; A.E. W. Crawford-Elliott)