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K–Ar AGES OF 2:1 CLAY MINERALS, MACKENZIE DELTA – BEAUFORT SEA REGION, ARCTIC CANADA: SIGNIFICANCE OF *n*-ALKYLAMMONIUM EXCHANGE

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ABSTRACT

K–Ar ages of untreated 2:1 clay minerals of the <0.05 μm size-fraction separated from argillaceous rocks of the Reindeer D–27 well, Mackenzie Delta – Beaufort Sea region, Arctic Canada, generally increase with increasing depth of burial, from 19 ± 3 at *ca.* 1935 m to 65 ± 1 Ma at *ca.* 3832 m. Although the ages are lower than the stratigraphic ages, XRD patterns and TEM images of the same material suggest that the K–Ar ages are mixed ages. These result from a mixture of detrital and diagenetic illite. The K–Ar ages of the 0.05–0.1 μm fraction generally decrease with increasing burial, but are older than the stratigraphic ages. K–Ar ages of the <0.05 and 0.05–0.1 μm size fractions after intercalating octadecylammonium cations ($n_C = 18$) also vary with burial depth. The ages of the 0.05–0.1 μm fraction decreased slightly from 120 ± 2 to 115 ± 3 Ma at shallow depth (*ca.* 1935 m), and decreased from 95 ± 2 to 55 ± 3 Ma at slightly greater depth (*ca.* 2065 m). A decrease in age may be due to the exchange of K and Ar by the intercalation of $n_C = 18$ cations into the interlayers of an illitic phase of detrital origin. At maximum depth (*ca.*3832 m), the age of the 0.05–0.1 μm fraction increased slightly from 100 ± 2 to 106 ± 3 Ma after treatment with $n_C = 18$. The increase in K–Ar age with treatment is more evident in the <0.05 μm fraction, which increased from 19 ± 3 to 92 ± 4 Ma at *ca.* 1935 m and from 65 ± 3 to 97 ± 3 Ma at *ca.* 3832 m. This suggests that exchange of interlayer K and radiogenic Ar by $n_C = 18$ has occurred in a "young" illitic phase of diagenetic origin. The change in age is less significant in the deeper sample because it is dominated by an authigenic illitic phase, and the removal of K and Ar by $n_C = 18$ is incomplete. The K–Ar dating of IS and illite from argillaceous rocks of a burial-diagenetic sequence after treatment with long-chain alkylammonium cations may help to better constrain the timing of post-depositional events in the diagenetic history. It is possible to distinguish between diagenetic and detrital illitic subpopulations in shales with small amounts of detrital illite, as well as constraining the age of the detrital illitic component.

Keywords: K–Ar dating, illite, "alkylammonium illite", smectite, octadecylammonium cations, TEM, Pt–C replica, Reindeer D–27 well, Mackenzie Delta – Beaufort Sea region, Arctic Canada.

SOMMAIRE

Les âges K–Ar d'argiles 2:1 non traitées de la fraction <0.05 μm séparées de roches du puit de forage Reindeer D–27, région du delta de Mackenzie et de la mer de Beaufort, dans l'Arctique canadien, augmentent en général avec la profondeur d'enfouissement, de 19 ± 3 Ma à environ 1935 m à 65 ± 1 Ma à environ 3832 m. Quoique les âges sont inférieurs à l'âge

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stratigraphique, les spectres de diffraction X et les images en microscopie électronique par transmission des mêmes matériaux font penser que les âges K–Ar sont des âges mixtes dus à la présence d'argiles détritiques et d'illite diagénétique. Les âges K–Ar de la fraction 0.05–0.1 μm diminuent en général avec la profondeur de l'enfouissement, mais dépassent l'âge stratigraphique. Les âges K–Ar des fractions <0.05 et 0.05–0.1 μm après un échange avec cations octadécylammoniaque ($n_C = 18$) varient aussi avec la profondeur de l'enfouissement. L'âge de la fraction 0.05–0.1 μm diminue légèrement de 120 ± 2 à 115 ± 3 Ma à faible profondeur (*ca.* 1935 m), et diminue de 95 ± 2 à 55 ± 3 Ma à une profondeur légèrement plus grande (*ca.* 2065 m). Une diminution de l'âge pourrait résulter de l'échange de K et Ar par l'intercalation des cations $n_C = 18$ dans les interfeuillets d'une phase illitique d'origine détritique. A profondeur maximum, (*ca.*3832 m), l'âge de la fraction 0.05–0.1 μm augmente légèrement de 100 ± 2 to 106 ± 3 Ma après traitement au $n_C = 18$. L'augmentation de l'âge K–Ar suite au traitement est davantage évident dans la fraction <0.05 μm, qui va de 19 ± 3 à 92 ± 4 Ma à environ *ca.* 1935 m et de 65 ± 3 à 97 ± 3 Ma à environ *ca.* 3832 m. Ce résultat fait penser que l'échange de K et d'Ar radiogénique de l'interfeuillet par $n_C = 18$ a affecté une phase illitique "jeune", d'origine diagénétique. Le décalage dans l'âge est moins important dans l'échantillon le plus profond parce qu'il contient surtout une illite authigène, et le remplacement du K et Ar par le $n_C = 18$ serait incomplet. La datation au K–Ar d'illite–smectite et d'illite dans les roches argileuses d'une séquence diagénétique enfouie suite à un tel traitement avec des cations alkylammoniaque à chaînes longues pourrait bien éclaircir dans le temps les événements post-dépositionnels dans l'évolution diagénétique. Il semble possible de distinguer les sous-populations d'illite, diagénétique ou détritique, dans des shales ayant une faible proportion d'illite détritique, et de préciser l'âge de cette illite.

(Traduit par la Rédaction)

Mot-clés: datation K–Ar, illite, "illite à alkylammoniaque", smectite, cations octadécylammoniaques, microscopie électronique en transmission, réplication Pt–C, forage Reindeer D–27, delta de Mackenzie, mer de Beaufort, Arctique canadien.

INTRODUCTION

Interstratified illite–smectite (hereafter IS) and illite separated from argillaceous rocks buried at passive margins and foreland basins are commonly dated by the K–Ar method to determine the time-integrated age of illite diagenesis and the mean age of detrital illite derived from the weathering and erosion of rocks of the source terrane (*e.g.*, Glasmann *et al.* 1989, Elliott *et al.* 1991, Pevear 1992, Matthews *et al.* 1994, Clauer & Chaudhuri 1995, Clauer *et al.* 1997a, Zhao *et al.* 1997). The acquired K–Ar ages of IS and illite, however, are commonly recognized as mixed ages owing to the presence of both detrital and diagenetic components. As such, they are very difficult to interpret without applying techniques such as Illite Age Analysis (Pevear 1992). The errors in many of these methods are potentially large, and also include uncertainty in assuming that the ages can be modeled in terms of a two-component system consisting of diagenetic and detrital clay minerals, compositional heterogeneity of the detrital and diagenetic components (*e.g.*, IS, illite, mica) in various clay-size fractions, some of which may have their K–Ar clock reset by heating above 150°C, the accuracy of mineral abundances determined from X-ray diffraction (XRD), and the accuracy of K–Ar ages. Procedures to purify and separate diagenetic and detrital clay-mineral subpopulations have had limited success (*e.g.*, Liewig *et al.* 1987).

Concern for preferential loss of Ar from the structure of 2:1 layer silicates has been allayed, as recent K–Ar studies have shown that illitic phases do not lose argon at ambient temperatures, at least up to 150°C and perhaps higher, or if unperturbed by thermal, tectonic or fluid-circulation processes (Pevear 1992, Clauer *et al.* 1997a, Hassanipak & Wampler 1997).

Long-chain alkylammonium cations ($12 \leq n_C \leq 18$, where n_C is the number of carbon atoms per alkyl chain with the general formula $C_{n_C}H_{2n_C+1}NH_3^+$) have the capability to selectively replace K and other interlayer cations from weathered, degraded, altered or poorly crystallized phyllosilicates, and from higher charged 2:1 clay minerals such as illite and glauconite (Mackintosh & Lewis 1968, Mackintosh *et al.* 1971, 1972, Lagaly 1979, Vali & Köster 1986, Laird *et al.* 1987, Ghabru *et al.* 1989, Vali & Hesse 1990, Vali *et al.* 1991, 1994, Cetin & Huff 1995a, b, Sears *et al.* 1998). XRD and transmission electron microscopy (TEM) analyses have shown that dioctahedral illite treated with long-chain alkylammonium cations may be exchanged of its interlayer K, but it still retains the high-charge characteristic of illite (*i.e.*, "expandable illite", hereafter "*n*-alkylammonium illite" and its variations) (Laird *et al.* 1987, Vali *et al.* 1991, 1994).

In an effort to better understand the diagenetic changes of 2:1 clay minerals that constitute the smectite to illite (S → I) reaction, and the significance of K–Ar ages of diagenetic illite during progressive burial of the Brooks – Yukon Basin (BYB) and Beaufort – Mackenzie Basin (BMB) in the passive continental setting of the Mackenzie Delta – Beaufort Sea (MDBS) region, Arctic Canada, TEM imaging of Pt–C replicas was used to characterize the evolving morphology of the 2:1 clay mineral separates with depth of burial, and K–Ar dating was applied to the samples before and after treatment with long-chain alkylammonium cations (*i.e.*, octadecylammonium cations). Our emphasis in this study was to clarify the origin of "octadecylammonium illite",

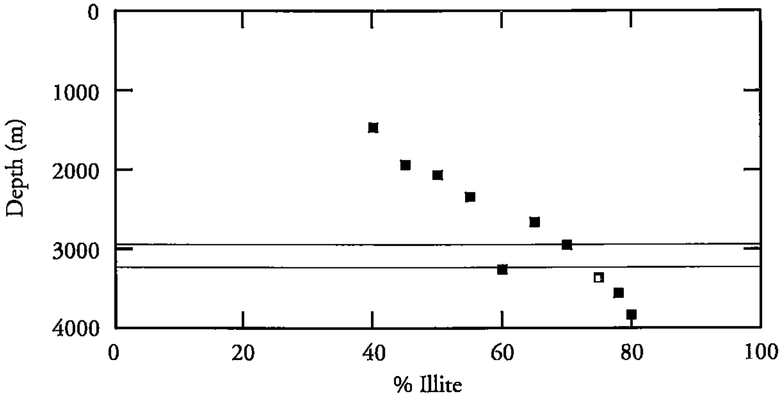


FIG. 1. A plot of the proportion of illite layers in interstratified IS, as determined from conventional XRD analysis, with depth along the Reindeer D–27 well. Some of the values are slightly different from those given in Sears *et al.* (1995a). The solid lines delineate the zone of the mineralogical discontinuity (Ko *et al.* 1995).

account for its contribution to the K–Ar ages of untreated samples, and assess the presence of detrital illitic or micaceous phases in fine clay-size separates.

PREVIOUS STUDY

The 2:1 clay mineral separates investigated in this study were characterized in detail by Sears *et al.* (1998), and the following is a brief summary. Conventional X-ray-diffraction analysis of the Mg-saturated and ethylene-glycol-solvated <0.05 μm fraction separated from argillaceous rocks of the Reindeer D–27 well, MDS region, suggests that the dominant clay mineral is IS, with the proportion of illite layers progressively increasing with depth of burial (Sears 1993, Sears *et al.* 1998) (Fig. 1). XRD analysis and high-resolution transmission electron microscopy (HRTEM) imaging of the same size fraction after treatment with *n*-alkylammonium cations reveals a complex diagenetic evolution characterized by multiphase assemblages of 2:1 layer silicates (Sears *et al.* 1998). These results contrast with the notion of the gradual and progressive conversion of S → I with increasing burial depth through a series of intermediate IS interstratified structures, as characterized by numerous conventional XRD studies (*e.g.*, Hower *et al.* 1976). Rather, the evolution of S → I is characterized as a prograde sequence of multiple phases: (1) low- and high-charge expandable 2:1 clay minerals, (2) a rectorite-like R1 ordered phase, (3) "*n*-alkylammonium illite", and (4) illite, whose patterns of distribution overlap with depth. Low- and high-charge expandable 2:1 clay minerals dominate at shallow depths, a rectorite-like R1 ordered phase is dominant at intermediate depths, whereas apparently coherent sequences (packets) of illite with three to seven layers (R3 ordered) are dominant at maximum depths in the well. The rectorite-like R1 ordered phase has compositional and structural properties that are unique, and cannot be considered as the interlayering of smectite and illite layers (Vali *et al.* 1994). Illitic and micaceous phases exist in the fine fractions throughout the entire depth of the well, but it is difficult to distinguish between detrital and diagenetic illitic components in XRD patterns and HRTEM images (Sears *et al.* 1998). "Alkylammonium illite" is only recognized in HRTEM images of samples at maximum depth in the well.

MATERIALS AND ANALYTICAL TECHNIQUES

Samples of drill-core and well cuttings of argillaceous rocks of the B.A. – Shell – I.O.E. Reindeer D–27 well of the MDBS region, Arctic Canada, were collected from the Early to Middle Eocene Taglu and the Late Paleocene to Early Eocene Aklak sequences (Reindeer supersequence) of the BMB, and the informally named Early to Middle Albian flysch formation of the BYB (Jeletzky 1971, Young *et al.* 1976, Dixon 1990, Dixon *et al.* 1992a, b, McNeil 1997, pers. commun., 1998) (Fig. 2). More detailed information about location, geological setting, and sample-preparation methods are available in Sears *et al.* (1998).

Pt–C replicas

A detailed investigation of surface microtopography and morphology of individual crystals and mineral fragments was possible through the Pt–C replication technique. TEM imaging of replicas obtained by the dispersion of heavy metals such as Au, Ag, and Pt onto surfaces of 2:1 layer silicates allowed us (i) to distinguish between detrital and diagenetic particles, and (ii) to investigate the dissolution and growth character-

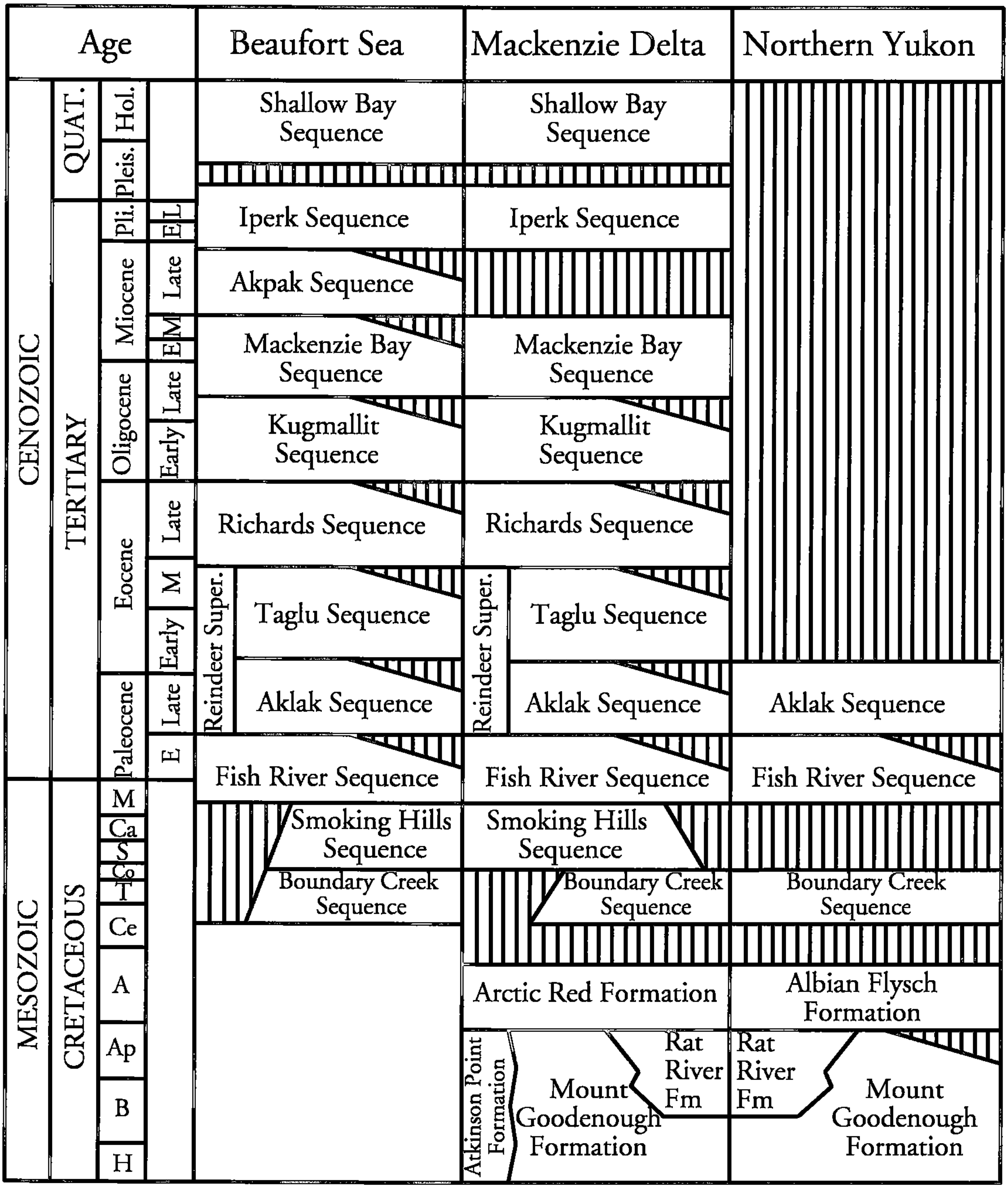


FIG. 2. Stratigraphic column of of the Mackenzie Delta – Beaufort Sea region, Arctic Canada (after Dietrich & Dixon 1997).

istics of ultrafine 2:1 layer silicates at a resolution close to 1 nm (Vali & Bachmann 1988). Freeze-dried clay-mineral separates were dispersed on a freshly cleaved mica surface, shadowed with a Pt–C film ~1.5 nm thick consisting of 95% platinum and 5% carbon, and coated with a supporting C film 10–15 nm thick. This procedure was performed rapidly using a Balzers High-Vacuum Freeze–Etch unit, Model 301, to minimize dissolution of mineral surfaces. The Pt–C film (replica) was carefully peeled from the mica substrate, and any mineral particles adhering to the replica were dissolved in a 6% HF solution, rinsed with de-ionized water and transferred onto 300 mesh TEM grids covered with a supporting film of formvar and carbon. TEM investigation was performed with a JEOL JEM–2000 FX TEM at an accelerating voltage of 100 kV. Correlation can be made between the morphological features of individual 2:1 clay-mineral particles observed in the Pt–C replica images and microstructural information provided by lattice-fringe images of microtomed thin sections treated with $n_C = 18$, as presented in Sears *et al.* (1998).

K–Ar analysis

Freeze-dried clay-mineral separates intended for K–Ar dating were treated with a 0.05 N solution of octadecylamine hydrochloride ($n_C = 18$) for 5 days at 65°C. During this period, the solution was replaced three times. At the end of the exchange process, the samples were washed by centrifugation with a solution of distilled H_2O and 90% ethanol (1:1) followed by 12 to 14 washes in 90% ethanol to remove excess alkylammonium salts and alkylamines (Lagaly 1994).

The Ar isotopic composition of the untreated clay-mineral samples and of those treated with $n_C = 18$ was measured on ~50 mg samples. Argon and reactive gases were liberated by heating with a radio-frequency induction furnace. The untreated samples were relatively clean, allowing standard methods of sample analysis, whereas the samples treated with $n_C = 18$ produced significant quantities of reactive gases, which resulted in higher background pressures than typical for Ar measurements and longer cleanup times (<1 hour). The gases were extracted and then cleaned with heated Ti. The hydrocarbons used in the exchange treatments were cleaned by the Ti furnaces as Ti cooled to room temperature (30 minutes). Final cleanup of the extracted gases was performed using a SAE getter heated to 5 amperes with a Variac controller for 5 minutes. A calibrated spike of ^{38}Ar was added as the gases were extracted from the sample during the final heating step. Argon isotopes 36, 38 and 40 were measured on-line. The ratios ^{40}Ar/^{38}Ar and ^{40}Ar/^{36}Ar were calculated with a computer interface on-line with the AEI MS–10 mass spectrometer. The concentration of potassium was measured using flame photometry with a lithium internal standard (Ingamells 1970). The K decay constants recommended by the IUGS Subcommission on Geochronology were used in the calculation of K–Ar age (Steiger & Jäger 1977).

RESULTS

K–Ar age of untreated 2:1 clay-mineral separates

The K–Ar age of untreated 2:1 clay minerals in the two size-fractions, <0.05 and 0.05–0.1 μm, were determined from eleven samples of argillaceous rock: two core samples from a burial depth of 896.6 and 1463.0 m, a composite core sample from 1920.3–1950.7 m, and eight composite well-cuttings samples at ~300-m stratigraphic intervals from 2057.4.2–2072.6 to 3825.2–3840.5 m. To simplify discussion, composite samples are labeled according to their median depth.

In general, the K–Ar age trend of the 0.05–0.1 μm fraction over the present depth-interval of 896–3840 m, deposited over a >75 Ma period (McNeil 1997), is similar to that found for whole-rock and coarse clay size-fractions (1–2 μm to 2–5 μm) from samples of mudrock and shale in the majority of sedimentary basins (*e.g.*, Aronson & Hower 1976, Velde & Renac 1996). The K–Ar age decreases with increasing age of deposition or burial depth (Fig. 3a). Nearly all K–Ar ages of the 0.05–0.1 μm fraction are older than the inferred ages of

TABLE 1. K-Ar AGES OF UNTREATED 2:1 LAYER SILICATES IN THE <0.05 μm SIZE FRACTION FROM MUDROCKS OF THE REINDEER D-27 WELL, MACKENZIE DELTA – BEAUFORT SEA REGION

Sample Depth (m)	Type	Sequence[1, 2]	Stratigraphic Age[2]	Lithology[3]	K_2O (wt %)	^{40}Ar* (10^{-10} mol g^{-1})	K-Ar Age (Ma)
896.6	core	Taglu	Middle Eocene	mst, sltst	2.5	5.990	159 ± 5
1463.0	core	Taglu	Middle Eocene	mst, sltst	1.136	1.035	62 ± 4
1935.4 (1920.2-1950.7)	core	Taglu	Middle Eocene	mst, sltst	2.175	1.588	19 ± 3
2065.0 (2057.4-2072.6)	cuttings	Taglu	Early Eocene	mst, sltst	1.586	0.638	27 ± 7
2339.4 (2331.7-2347.0)	cuttings	Taglu	Early Eocene	mst, sltst	1.82	1.154	44 ± 3
2659.4 (2651.8-2667.0)	cuttings	Taglu	Early Eocene	mst, clyst	2.321	1.862	55 ± 4
2948.9 (2941.3-2956.6)	cuttings	Aklak	Late Paleocene	mst, clyst	2.866	1.280	31 ± 1
3253.7 (3246.1-3261.4)	cuttings	Aklak	Late Paleocene	mst, clyst	2.996	1.383	31 ± 2
3360.4 (3352.8-3368.0)	cuttings	Albian flysch fm	Early - Mid-Albian	mst	1.246	1.048	58 ± 3
3558.5 (3550.9-3566.2)	cuttings	Albian flysch fm	Early - Mid-Albian	mst	2.853	2.493	60 ± 2
3832.8 (3825.2-3840.5)	cuttings	Albian flysch fm	Early - Mid-Albian	mst	3.479	3.329	65 ± 1

[1] Dixon (1990). [2] McNeil (1997). [3] Symbols: mst: mudstone, sltst: siltstone, clyst: claystone.

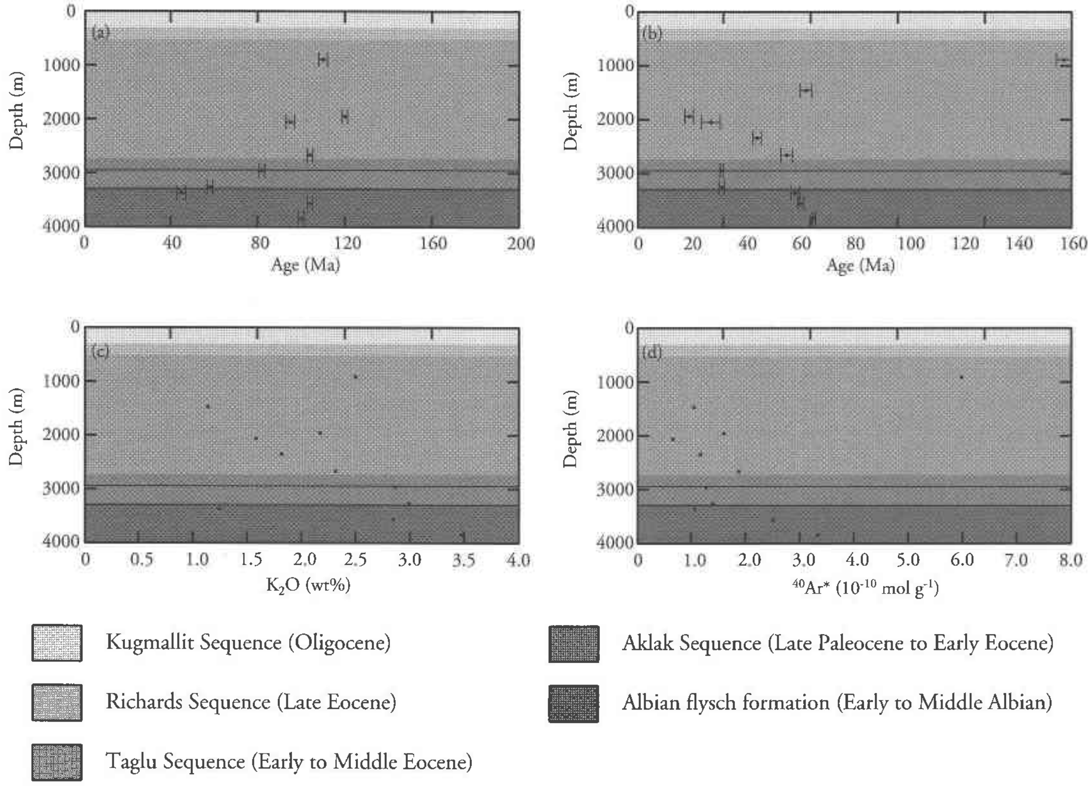


FIG. 3. (a) Plot of K–Ar ages *versus* depth for the untreated 0.05–0.1 μm size fraction. (b) Plot of K–Ar ages *versus* depth for the untreated <0.05 μm size fraction. (c) Plot of K_2O content *versus* depth for the untreated <0.05 μm size fraction. (d) Plot of $^{40}Ar^*$ content *versus* depth for the untreated <0.05 μm size fraction. The solid lines delineate the zone of the mineralogical discontinuity (Ko *et al.* 1995).

deposition and suggest mixed ages, resulting from variable mixtures of detrital and diagenetic components of illitic and micaceous phases.

In contrast to the 0.05–0.1 μm fractions, the K–Ar ages of the untreated <0.05 μm fraction generally increase, from 19 ± 3 Ma at 1935.4 m to 65 ± 1 Ma at 3832.8 m, with increasing depth of burial (Fig. 3b, Table 1). The K–Ar ages of the <0.05 μm fractions are younger than the ages of deposition, with the exception of the two shallow samples, and younger than the corresponding ages of the 0.05–0.1 μm fractions. Samples from 896.6 and 1463.0 m gave ages of 159 ± 5 and 62 ± 4 Ma, respectively, both older than the age of deposition (Middle Eocene, (37–49 Ma; Berggren *et al.* 1995, McNeil 1997). These latter two ages are interpreted to reflect a mixture of detrital and diagenetic illitic and micaceous phases. In addition, the trend of decreasing age of these two samples with depth suggests the loss of a dominant, metastable detrital component, possibly due to dissolution at shallow depth, and the possible addition of an authigenic illitic component, albeit minor (Sears *et al.* 1998). The trends for K_2O (Fig. 3c) and $\%^{40}Ar^*$, as a consequence of the radioactive decay of ^{40}K to Ar (Fig. 3d), increase with depth for the <0.05 μm fraction, generally paralleling the trends in IS composition inferred from XRD (Fig. 1) and the K–Ar age (Fig. 3b) observed for this fraction.

K–Ar age of 2:1 clay minerals after treatment with octadecylammonium cations

In the lattice-fringe images of the <0.05 μm clay-mineral separates from the Reindeer D–27 well after treatment with $n_C = 18$, Sears *et al.* (1998) identified, in addition to expandable 2:1 clay minerals, a rectorite-like R1 ordered phase, illite and "octadecylammonium illite". To evaluate the contribution of the "octadecylammonium illite" to the K–Ar age of untreated samples and ascertain its origin, selected 0.05–0.1 and <0.05 μm fractions were dated after treatment with $n_C = 18$. Shifts in K–Ar ages were observed in comparison to the original untreated samples (Table 2). After treatment with

n_C = 18, the age of the 0.05–0.1 μm fraction at 2065.0 m decreased from 95 ± 2 to 55 ± 3 Ma as the $^{40}Ar^*$ decreased from 3.901 to 2.429 × 10^{-10} mol g^{-1}. The 0.05–0.1 μm size fraction at a slightly shallower depth, 1935.4 m, however, showed a much smaller decrease after treatment with n_C = 18, possibly within the analytical uncertainty (120 ± 2 to 115 ± 3 Ma) as the $^{40}Ar^*$ decreased from 4.792 to 3.555 × 10^{-10} mol g^{-1}. The apparent ages of both treated samples are still greater than the inferred age of deposition (Middle Eocene, 49–37 Ma; Berggren *et al.* 1995, McNeil 1997), which suggests that there is still a significant residue of a detrital component in this size fraction.

The fact that the K–Ar ages become younger after treatment with n_C = 18 suggests that the cation-exchange reaction removes K and $^{40}Ar^*$ from the interlayers of "older" illitic or micaceous phases of detrital origin. Lattice-fringe images of the 0.05–0.1 μm fractions at shallow depths show illitic or micaceous phases having a core of contracted interlayers with a spacing of 1.0 nm and outer layers with intercalated n_C = 18 interlayers, the spacing being ~2.4–2.5 nm. Also present are apparently coherent sequences of layers (packets) with complete interlayer expansion after intercalation with n_C = 18, *i.e.*, "octadecylammonium illite" (Figs. 4a, b). Some particles or packets have layers with a frayed and wispy appearance suggestive of dissolution (Vali & Köster 1986). Fanning *et al.* (1989) also proposed that K released from interlayers or edges of interlayers during weathering results in wedges around a mica core and frayed edges. Thick packets of illite or mica with more than six to eight layers are unlikely to have precipitated as authigenic phases at this shallow depth, whereas thinner packets of illite with two to six contracted interlayers were observed as the dominant structures at maximum depth in the well (Sears *et al.* 1998). We believe that the thicker packets are detrital in origin, whereas the thinner ones are diagenetic or authigenic.

In contrast to the shallow samples, the K–Ar age of the 0.05–0.1 μm fraction after treatment with n_C = 18 at the maximum depth of 3832.8 m increased slightly from 100 ± 2 to 106 ± 3 Ma. The $^{40}Ar^*$ decreased from 8.531 to 7.160 × 10^{-10} mol g^{-1} (Table 2). Although the magnitude of the apparent increase in age is not much greater than the limits of analytical uncertainty, the fact that the age increased after treatment suggests some selective removal of interlayer K and $^{40}Ar^*$ by n_C = 18 cation exchange from a "younger" n_C = 18 illite of diagenetic origin (see below). Conventional XRD analysis of untreated, Mg-saturated, EG-solvated samples clearly attests to the increase in proportion of illite layers in IS with burial depth (Fig. 1), whereas lattice-

TABLE 2. K–Ar AGES OF UNTREATED 2:1 CLAY MINERAL SEPARATES, EITHER UNTREATED OR TREATED BY OCTADECYLAMMONIUM (n_c = 18) CATION EXCHANGE

Sample	Size Fraction (μm)	Treatment	K_2O (wt %)	ΔK_2O (%)	$^{40}Ar^*$ (10^{-10} mol g^{-1})	$\Delta ^{40}Ar^*$ (%)	K-Ar Age (Ma)	ΔK-Ar Age (Ma)
1935.4 (1920.2-1950.7)[1]	<0.05	none	2.175		1.588		19 ± 3	
1935.4 (1920.2-1950.7)[1]	<0.05	n_C = 18	0.849		1.152		92 ± 4	
				-61.0		-27.5		+73 ± 7
1935.4 (1920.2-1950.7)[1]	0.05-0.1	none	2.694		4.792		120 ± 2	
1935.4 (1920.2-1950.7)[1]	0.05-0.1	n_C = 18	2.075		3.555		115 ± 3	
				-23.0		-25.8		-5 ± 5
2065.0 (2057.4-2072.6)[1]	<0.05	none	1.586		0.638		27 ± 7	
2065.0 (2057.4-2072.6)[1]	<0.05	n_C = 18	1.173		n/a		n/a	n/a
				-26.0				
2065.0 (2057.4-2072.6)[1]	0.05-0.1	none	2.762		3.901		95 ± 2	
2065.0 (2057.4-2072.6)[1]	0.05-0.1	n_C = 18	3.045		2.429		55 ± 3	- 40 ± 5
				+10.1		-37.7		
3832.8 (3825.2-3840.5)[1]	<0.05	none	3.479		3.329		65 ± 1	
3832.8 (3825.2-3840.5)[1]	<0.05	n_C = 18	2.250		3.149		97 ± 4	
				-35.3		-5.4		+32 ± 5
3832.8 (3825.2-3840.5)[1]	0.05-0.1	none	5.730		8.531		100 ± 2	
3832.8 (3825.2-3840.5)[1]	0.05-0.1	n_C = 18	4.568		7.160		106 ± 3	
				-20.3		-16.1		+6 ± 5
K-bentonite (R0-I[0.57]/EG-S)[2]	0.5-1.0	none	1.65		0.1485		60 ± 3	
K-bentonite (R0-I[0.57]/EG-S)[2]	0.5-1.0	n_C = 18	0.94		0.0945		69 ± 3	
				-43.0		-36.4		+9 ± 6
K-bentonite (R3-I[0.91]/EG-S)[3]	<0.1	none	6.85		2.967		293 ± 13	
K-bentonite (R3-I[0.91]/EG-S)[3]	<0.1	n_C = 18	5.13		2.334		291 ± 13	
				-25.1		-21.3		-2 ± 26

[1] Reindeer D–27 well, with depth expressed in meters. [2] Lykin's Gulch, Boulder, Colorado (Elliott *et al.* 1991). [3] Gadsden, Alabama (Elliott & Aronson 1987).

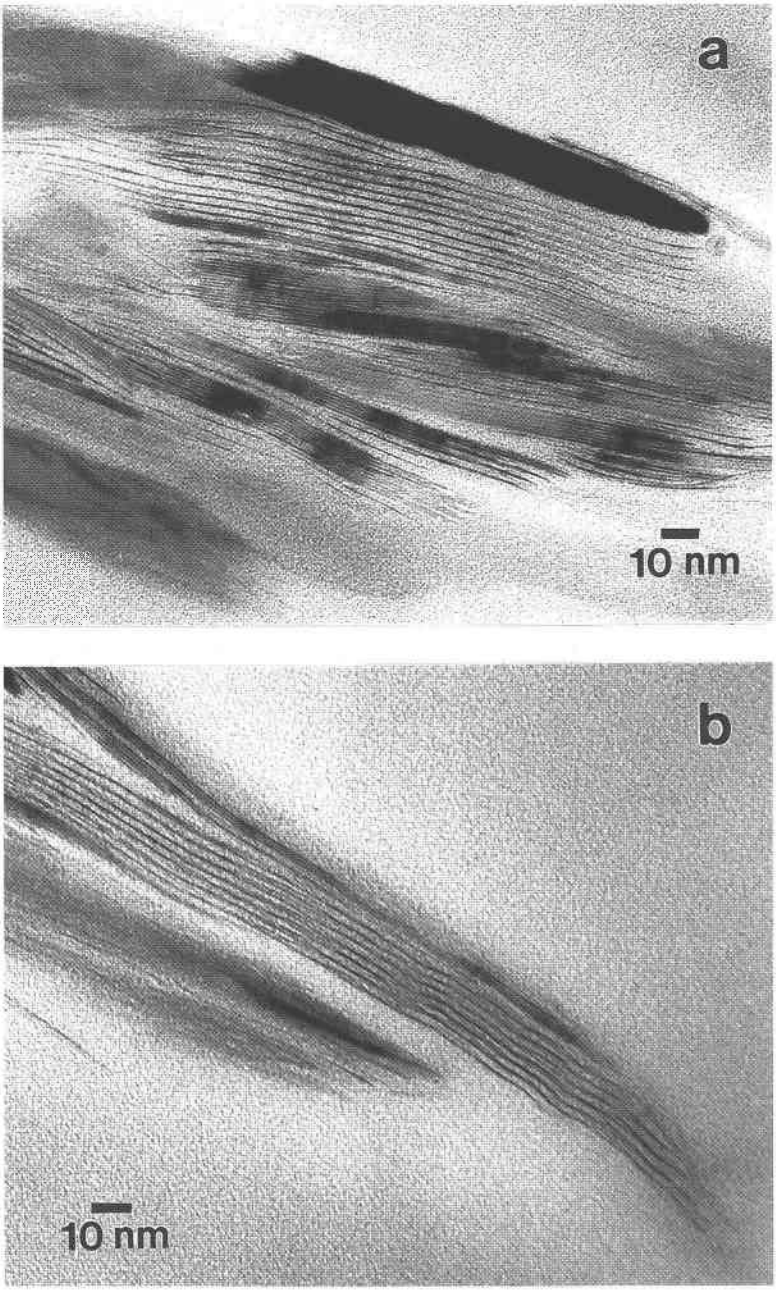


FIG. 4. HRTEM images of the 0.05–0.1 μm size fraction after treatment with $n_C = 18$. (a) Discrete packets of 2:1 layer silicates have a core of layers having non-expanded interlayers with spacings of 1.0 nm surrounded by layers with interlayers expanded with $n_C = 18$ having spacings of ~2.4–2.5 nm. (b) Packet of illite with apparently coherent sequences of interlayers expanded with $n_C = 18$ and with spacings of ~2.4–2.5 nm.

fringe images show that intercalation of $n_C = 18$ has occurred in the interlayers of an illitic or micaceous phase (Sears *et al.* 1998). The K–Ar ages suggest, therefore, that the 0.05–0.1 μm size-fraction at this depth is still principally detrital or, at least, the detrital fraction dominates the total mixed age.

The <0.05 μm fraction from 1935.4 m after treatment with $n_C = 18$ shows an age increase from 19 ± 3 to 92 ± 4 Ma, as the ^{40}Ar* decreased from 1.588 to 1.152 × 10^{-10} mol g^{-1} (Table 2). The age of the untreated sample is much younger than the inferred age of deposition (Middle Eocene, 49–37 Ma; Berggren *et al.* 1995, McNeil 1997), whereas the age of the sample treated with $n_C = 18$ is significantly greater. Again, the fact that the apparent age has increased after treatment suggests the selective extraction of K and ^{40}Ar* by cation exchange with $n_C = 18$ from the interlayers of a "younger" illitic phase, leaving an "older" residue of a contracted illite or mica. Lattice-fringe images of the sample treated with $n_C = 18$ showed this fraction to consist of a mixture of single layers and sequences of layers of low- and high-charge expandable 2:1 clay minerals and packets of illite (Sears *et al.* 1998). In these fine fractions, however, it is generally difficult to distinguish in HRTEM images between sequences of intercalated $n_C = 18$ smectite and packets of intercalated $n_C = 18$ illite, owing to the very fine size of the clay mineral particles and the infiltration of embedding resin into the interlayers of the expandable 2:1 clay minerals. It may be reasonable to assume that the removal of interlayer K has occurred from a K-bearing, high-charge expandable 2:1 clay mineral (Eberl 1993). A high-charge smectite-group phase can mimic illite in XRD by incorporating interlayer K, but may be unable to retain daughter ^{40}Ar* in hydrated interlayers at the increasing temperatures associated with increasing depth of burial (Gramann *et al.* 1975, Bell 1986).

Expandable 2:1 clay minerals of the <0.05 μm size fraction at 1935.4 m are observed in TEM images of Pt–C replicas as free particles, usually one layer (~1.0 nm) thick (Fig. 5a). They have the anhedral, flake-like morphology usually associated with smectite (Inoue *et al.* 1987). These particles correspond to the dispersed single layers of expandable 2:1 clay minerals observed in the lattice-fringe images of Sears *et al.* (1998). Thicker particles of illite are observed in Pt–C replicas of the same sample as predominantly euhedral to subhedral, lath-like particles indicative of diagenesis, or as irregularly shaped particles with embayments, suggestive of dissolution of detrital particles (Fig. 5b). The lath-like particles correspond to the apparently coherent sequences (packets) of illite observed in the lattice-fringe images (Sears *et al.* 1998). This observation, however, does not preclude smectite, both low- and high-charge, occurring as lath-like particles (Holtzapffel & Chamley 1986, Clauer *et al.* 1990, Lindgreen *et al.* 1991).

The K–Ar age of the <0.05 μm fraction at 3832.8 m in the subsurface after treatment with $n_C = 18$ showed an increase from 65 ± 3 to 97 ± 2 Ma as the ^{40}Ar* decreased from 3.329 to 3.149 × 10^{-10} mol g^{-1}. As with the <0.05 μm fraction at 1935.4 m, the exchange of interlayer K and ^{40}Ar* by treatment with $n_C = 18$ is assumed to have occurred in a "younger" "octadecylammonium illite" of diagenetic origin. In contrast to the <0.05 μm fraction at a depth of 1935.4 m, however, both the ages of the untreated samples and those treated with $n_C = 18$ are younger than the inferred age of deposition (Early Albian, 109–112 Ma; Bralower *et al.* 1995, McNeil 1997, pers. commun., 1998). The age difference is less striking in this sample (+32 ± 5 Ma) than in the shallow sample at 1935.4 m (+73 ± 5 Ma) because of the predominance of illite of diagenetic origin which is the more stable phase, in the deeper sample.

Lattice-fringe images of the 3832.8 m sample after treatment with $n_C = 18$ show predominantly (i) distinct packets of illite with between two and six non-expanded interlayers (R3 ordered), (ii) double layers and sequences of double layers of a rectorite-like R1 ordered phase, and (iii) apparently coherent sequences of an illitic phase with between two and four intercalated $n_C = 18$ interlayers ("octadecylammonium illite") (Sears *et al.* 1998). In this instance, treatment of the sample with a short-chain alkylammonium cation ($n_C = 8$) did not reveal any expansion of the interlayers of expandable 2:1 clay minerals. Thus a distinct, expandable 2:1 clay mineral is not present at maximum depth in the well. TEM images of Pt–C replicas of this sample show the illitic phases predominantly as equidimensional or pseudohexagonal plates, with lesser amounts of subhedral lath-like particles and irregularly shaped particles (Figs. 6a, b, c). The evolving morphology of the particles from shallow to maximum depth supports the dissolution–crystallization reaction; metastable 2:1 layer silicates (*i.e.*, low- and high-charge smectite, micaceous particles) dissolved with depth and more stable illitic phases crystallized.

DISCUSSION

Geological significance of K–Ar ages of untreated 2:1 clay-mineral separates

Several explanations have been proposed in the literature for the depth-dependent trend of increasing K–Ar ages of IS and illite separated from argillaceous rocks of progressive burial-diagenetic sequences, as observed in the <0.05 μm fraction of this study. Elliott *et al.* (1991) suggested that the increasing K–Ar ages of IS (separated from bentonite devoid of contamination by detrital illite) represent the true ages of illite formation during the progressive addition of illite layers with burial. In sediments not undergoing dissolution and precipitation, Zhao *et al.* (1997) stated that the K–Ar ages

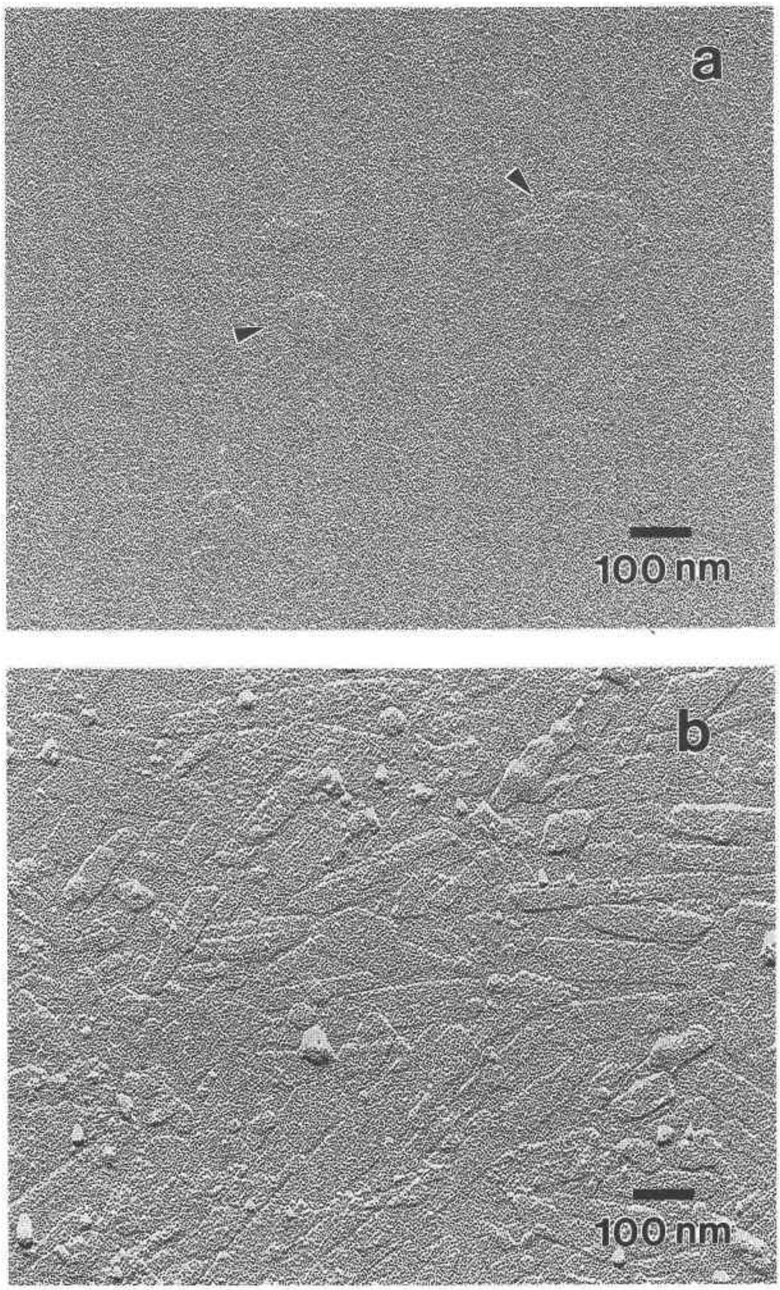


FIG. 5. CTEM images of Pt–C replicas of the <0.05 μm size fraction from 1935.5 m subsurface depth. (a) Expandable 2:1 clay minerals occur as anhedral, flake-like particles one layer thick (arrow). (b) Illitic phases occur as subhedral lath-like particles and irregularly shaped particles.

of IS should increase with increasing depth, as deeper regions of a subsiding basin have reached critical temperatures for the formation of illite earlier than shallow regions. If the supply of reactants is limited, illite growth will cease first in the deeper parts of the basin (Hamilton *et al.* 1992). On the other hand, Zhao *et al.* (1997) also contended that if clay-mineral separates from a sedimentary succession contain a detrital component, deeper samples should have more of an authigenic component and furnish K–Ar ages that are younger than samples from shallower depths, thus giving a decreasing age with increasing depth, as observed in the 0.05–0.1 μm fraction of this study.

In shales of low permeability, the systematic dissolution of detrital illite concomitant with the recrystallization or precipitation of authigenic illite may allow excess ^{40}Ar* to become trapped in 2:1 layer silicates during crystal growth (Hamilton *et al.* 1989, Clauer *et al.* 1997a). It is conceivable, however, that the incorporation of excess ^{40}Ar* would yield isotopic ages that are greater than the stratigraphic age, which is not the case in the <0.05 μm fraction of this study. In addition, if the incorporation of excess ^{40}Ar* was responsible for the trend of increasing K–Ar age with depth in the <0.05 μm fraction, it seems reasonable to presume that it would also affect the K–Ar age trend of the 0.05–0.1 μm fraction in the same way.

Awwiller (1994) suggested the contrary view that a K–Ar trend of increasing age with increasing depth may be an artifact of sample preparation, which enables the fine fractions to incorporate broken fragments of coarser detrital grains. The downhole increase in the amount of contamination by detrital illite in size-fractionated material enriched in diagenetic illite is a consequence of the progressively buried mudrocks being better lithified, and requiring more vigorous techniques of sample disaggregation. If this was the case in the clay-mineral separates studied, it would be expected that the trend of increasing age with depth observed in the <0.05 μm fraction also would be observed in the slightly coarser fraction (0.05–0.1 μm). In addition, the ages of the <0.05 μm size fraction for the deepest samples should approach or be older than the ages of deposition, which is not the case.

The trend of K–Ar ages of the untreated 0.05–0.1 μm fraction from Reindeer D–27 shows scattered values similar to the downwardly decreasing age commonly found in oil wells and attributed to the progressive increase of diagenetic IS and the decrease in the amount of detrital IS (Perry & Hower 1970, Aronson & Hower 1976, Burley & Flisch 1989, Velde & Renac 1996). In contrast, the K–Ar age trend of the <0.05 μm fraction indicates that illite diagenesis was coeval with the development and subsidence of the BMB. This basin formed as a result of the northward migration of sediment depocenters, from cratonic foredeeps and deep-water troughs in front of the rising Cordilleran fold belt in the Late Aptian – Early Albian to a subsiding passive continental margin of the Beaufort Sea in the Late Maastrichtian and throughout the Cenozoic (Dixon 1993, McNeil 1997, pers. commun., 1998). The K–Ar age profile of the untreated <0.05 μm size fraction suggests a real diagenetic trend wherein illite formation occurs rapidly after reaching critical threshold conditions of time, temperature, pressure, composition (*e.g.*, charge deficiency) or fluid chemistry; this illite was subsequently buried without further diagenetic change during the development of the BMB. The K–Ar ages of the 2:1 clay mineral of the <0.05 μm size fraction, however, must be reconciled with the XRD and TEM data for the same material. These data give structural, morphological and chemical evidence for illite neoformation continuing to the deepest sample (Sears 1993, Sears *et al.* 1998). As observed in lattice-fringe images, the packets of illite show regular thicknesses, implying particle homogeneity due either to simultaneous processes of dissolution and growth, or the nucleation and growth of particles at an earlier stage (Clauer *et al.* 1997a). The two samples of the <0.05 μm fraction, which after treatment with $n_C = 18$ become older, suggest that there is a residual component of detrital illite. The K–Ar apparent ages of the untreated <0.05 μm size fraction, therefore, must be interpreted as a mixture of detrital illite and micaceous minerals and dominantly diagenetic illite, with an increasing transfer of a detrital component with depth of burial to the finer fractions, due to partial dissolution in the subsurface, or perhaps, to an artifact of preparation. In addition, as illite continues to grow with depth, it grows larger than the <0.05 μm fraction, and so is incorporated into the coarser fractions (Eberl *et al.* 1990, Eberl 1993). Šucha *et al.* (1993) measured the size of illite particles, and reported that they continue to grow during the entire process of the smectite-to-illite transition. Thus, the proportion of detrital illite in the <0.05 μm fraction increases with depth for the possible reasons outlined above.

K–Ar ages of untreated 2:1 clay minerals in the zone of the mineralogical discontinuity

Ko *et al.* (1995) recognized a distinct discontinuity in the IS mineralogy between 2987.0 m and 3291.8 m, on the basis of XRD analysis of the <0.1 μm fraction. The base of this mineralogical discontinuity coincides with a regional unconformity at 3270.5 m that may have resulted from a break in sedimentation attributed to a major pulse of uplift and erosion in the Late Albian – Early Cenomanian. As the K–Ar age of the untreated <0.05 μm size fractions increases with depth, the inferred age of deposition (Early Eocene, 55–49 Ma) is approached near the top of the mineralogical discontinuity at 2987.0 m, but the illitic material is significantly younger than the inferred age of deposition (Early to Middle Albian, 112–104 Ma) below the discontinuity. Young ages for the two samples from the Aklak Sequence at 2948.9 and 3253.7 m may reflect the age of

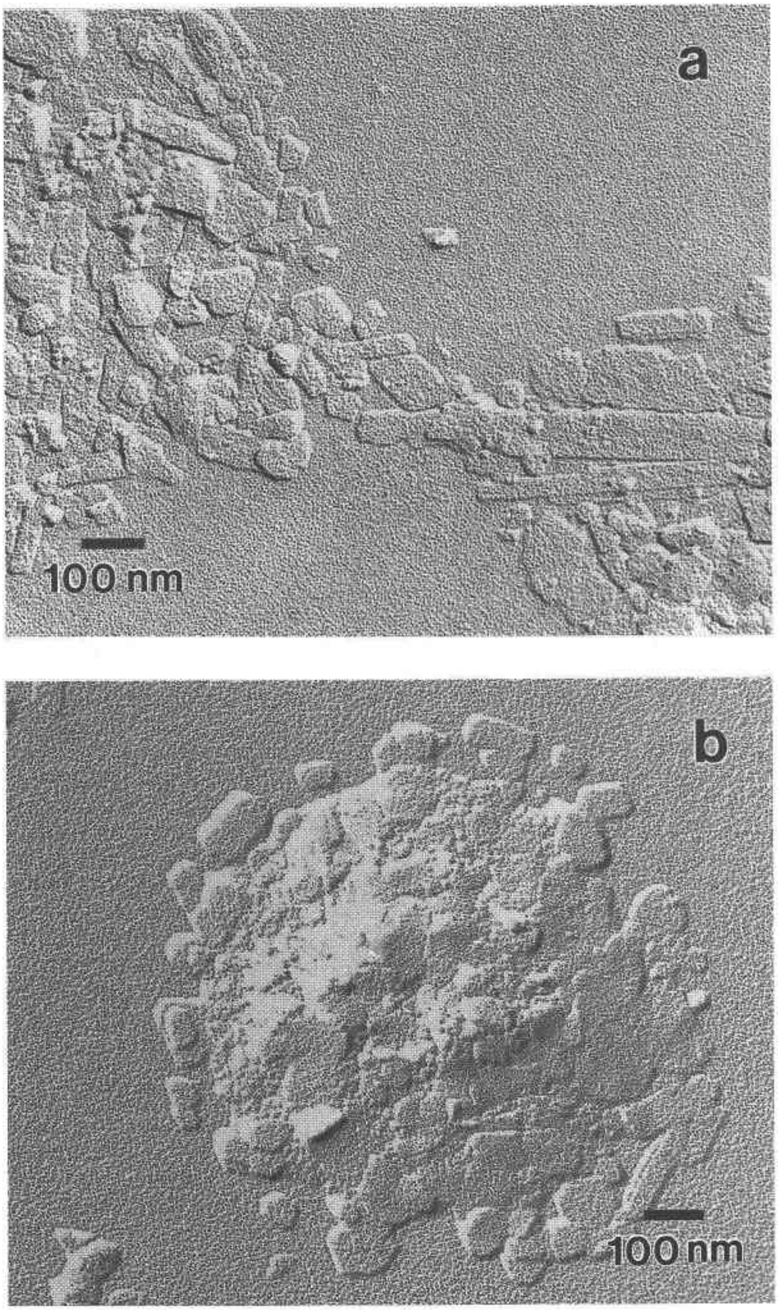
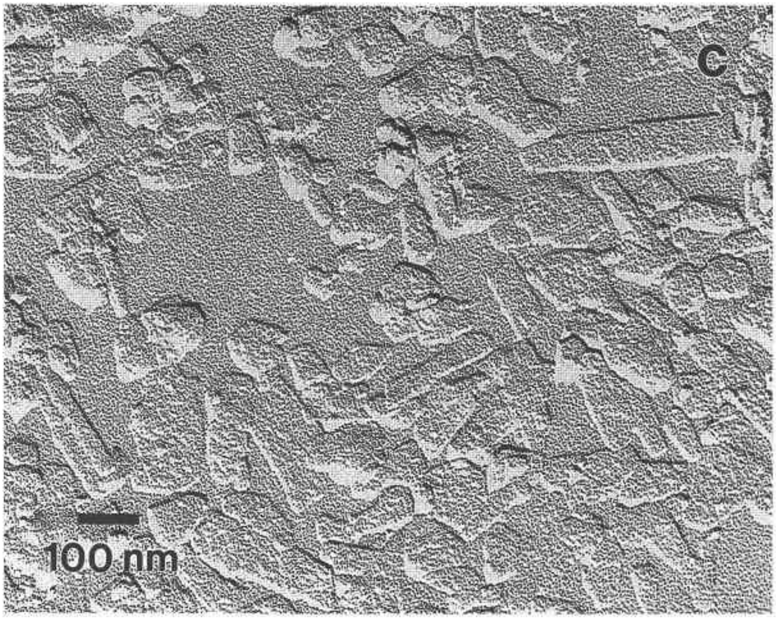


FIG. 6. CTEM images (a–c) of Pt–C replicas of the <0.05 μm size fraction at a depth of 3832.8 m in the subsurface. Illitic phases occur primarily as equidimensional or pseudohexagonal particles.



diagenetic illite, as they correspond to anomalously low contents of illite in IS, as determined from XRD, and anomalous O-isotope values in IS of the <0.1 μm fraction (Ko *et al.* 1995). The ages may reflect retardation of the S → I reaction in a normal environment with regard to pressure, as opposed to accelerated rates of reaction in suspected zones of former geopressure above and below (Ko & Hesse 1992). Issler (1992), however, reported that porosity of a shale increases sharply at ~2000 m and again at ~3710 m. This increase is attributed to zones of strong overpressure that may have been in existence since the Tertiary (Lane & Dietrich 1995).

As K–Ar age is dependent on ^{40}Ar* content, young radiometric ages from this anomalous zone are the result of a major decrease in the interlayer ^{40}Ar* content from the trend above and below this zone, as the K content continues to increase with burial depth (Figs. 3c, d). It is difficult to find an explanation for the apparent loss of ^{40}Ar* from such a tightly bound mineral structure; such loss may reflect the geochemical and isotopic changes induced during a retrograde stage of diagenesis, perhaps due to a major pulse of uplift during the Eocene (Criss *et al.* 1982, Lane & Dietrich 1995). Other factors that may perturb the ^{40}Ar* in 2:1 layer silicate structures include processes of fluid circulation and thermal events (Maluski 1978, Solé *et al.* 1998). Clauer *et al.* (1997b) reported a similar disturbance in the trend of K–Ar ages of illite across a fault zone, which was attributed to either mixing of multiple generations of illite during shearing or limited isotopic homogenization during late migration of fluid.

Significance of K–Ar ages of 2:1 clay mineral separates treated with octadecylammonium cations ($n_C = 18$)

Studies of the radiometric dating of 2:1 clay minerals after treatment with *n*-alkylammonium cations have shown that K–Ar ages may increase, decrease or remain invariant in comparison to untreated samples (Chaudhuri *et al.* 1994, 1997, Sears *et al.* 1995a, b, 1997). Comparison of the amount of K and ^{40}Ar* depleted from the interlayers of 2:1 clay minerals in the two size fractions of this study after treatment with $n_C = 18$ would seem to suggest the preferential depletion of K (ΔK_2O) relative to ^{40}Ar* (Δ^{40}Ar*) (Table 2). From experiments on two reference samples of biotite (one igneous and one metamorphic) and a 1–2 μm size fraction from intermediate depths of the Reindeer D–27 well, Sears *et al.* (1997) reported that K–Ar ages remained constant, within the limits of analytical uncertainty, with treatment with $n_C = 18$ for two, five and seven days. This finding suggests that no preferential depletion of interlayer K relative to ^{40}Ar* had occurred in well-crystallized layer silicates. The two reference samples of biotite had K–Ar ages that increased with treatment in comparison with the untreated sample, whereas the K–Ar age of the diagenetic sample became younger (Sears *et al.*, in prep).

The incorporation of alkylammonium cations into the interlayer space of 2:1 layer silicates proceeds by a cation-exchange reaction whereby naturally occurring interlayer inorganic cations are replaced by organic alkyl chains (Lagaly & Weiss 1969, 1970). Lattice-fringe images of the <0.05 μm fraction after treatment with $n_C = 18$ generally showed complete expansion of the interlayers, *i.e.*, no partial expansion of the interlayer (Sears *et al.* 1998). Differences in the type or amount of cation exchanged from the interlayers during alkylammonium exchange could be expected if the cations are not distributed uniformly or if they tend to segregate into various interlayers or parts thereof. As $^{40}Ar^*$ is the daughter product of the radioactive decay of ^{40}K, it is unlikely to have migrated to a site very far from where it evolved. Assuming no gain or loss of K and $^{40}Ar^*$ other than through the decay process, for samples that show greater depletion of interlayer K relative to $^{40}Ar^*$ after treatment with $n_C = 18$, an explanation other than preferential depletion, must be proposed. If we assume a relative uniform distribution of K and $^{40}Ar^*$ in the interlayer space of the 2:1 clay minerals at each sample depth, then the percentage change in depletion for each cation after treatment should be similar. Therefore, the differences in interlayer K and $^{40}Ar^*$ after treatment with $n_C = 18$ as shown in Table 2 could reflect the variance in mineralogical composition, *i.e.*, detrital or diagenetic illite, or differences in the rate of interlayer cation-exchange in 2:1 clay minerals of detrital and diagenetic origin. On the other hand, the different response of the illitic phases to treatment with *n*-alkylammonium cations may be controlled by growth characteristics, *e.g.*, polytypism, structural defects. This is evident in the K–Ar ages of IS from K-saturated bentonite (devoid of contamination from detrital illite) and treated with $n_C = 18$. The 0.5–1.0 μm fraction from Lykin's Gulch, Colorado (Elliott *et al.* 1991) showed an increase in K–Ar age from 61 ± 2 to 69 ± 2 (Table 2). The shift in the K–Ar age of a second IS sample from K-saturated bentonite (<1.0 μm, Gadsden, Alabama, Elliott & Aronson 1987) after treatment with $n_C = 18$ was inconclusive owing to a conservative estimate of age (Table 2). Muscovite is generally more resistant to weathering than biotite, and Clauer (1981) concluded that K–Ar ages of muscovite do not change with weathering. In a diagenetic zone, it is to be expected that loss of $^{40}Ar^*$ by diffusion should occur in K-bearing interlayers in phyllosilicates that were altered, degraded or poorly crystallized (Clauer *et al.* 1997a). Hames (1994), for example, proposed the possible loss of Ar from the outer layers of mica particles. Removing the K from these altered interlayers using the alkylammonium cation-exchange method would result in a more appropriate K–Ar age. Some of the illite (or micaceous) particles shown in Figures 4a, b have outer interlayers or packets of illite that are expanded with $n_C = 18$ cations, which may help to explain why a "younger" age component is removed after alkylammonium exchange. Altaner & Ylagen (1997) noted that in the Ostwald ripening model of crystal growth, large crystals of illite may consist of an authigenic core with a set of progressively younger epitactic overgrowths. Overgrowths may crystallize in both the c^* (thickness) and a^* and b^* (lateral) directions. Depletion of interlayer cations from the young epitactic overgrowths after treatment with $n_C = 18$ would result in increased K–Ar ages.

Detrital illite

Sears *et al.* (1995b) advocated the potential of the *n*-alkylammonium cation-exchange technique in conjunction with Pt–C replicas to differentiate between detrital and diagenetic populations in illite from burial diagenetic settings. This notion was based on the observations of Vali & Köster (1986) and Vali *et al.* (1991) in HRTEM images of the selective expansion of illite and IS from various geological and pedogenic settings after treatment with *n*-alkylammonium cations. It is difficult, however, to distinguish between detrital and diagenetic 2:1 clay minerals in XRD patterns and lattice-fringe images alone. Increases in K–Ar ages of illitic phases after treatment with $n_C = 18$ offers compelling evidence for the presence of a detrital illitic component, even where the untreated K–Ar ages are significantly younger than the inferred ages of deposition and appear to contain diagenetic illite. For example, the K–Ar age of the untreated <0.05 μm size fraction at a depth of 1935.4 m is younger than the age of deposition, whereas the same sample treated with $n_C = 18$ gives an age significantly older than the age of deposition (Table 2). The trend is not quite as clear in the <0.05 μm size fraction at a depth of 3832.8 m. The sample treated with $n_C = 18$ gives a synsedimentary K–Ar age that is slightly younger than the inferred age of deposition (Early Albian, 109–112 Ma). K–Ar ages that are synchronous with the time of deposition imply a terrigenous, authigenic K-bearing 2:1 layer silicate component, synsedimentary authigenesis, or both (Steinitz *et al.* 1995), or a coincidental mixture of diagenetic and detrital components. What is evident about both <0.05 μm samples after treatment with $n_C = 18$, however, considering the analytical uncertainty, is the similarity in age, 92 ± 4 and 97 ± 4 Ma. This similarity may reflect a mean age of a detrital illitic or micaceous phase in this size fraction. The K–Ar ages of the 0.05–0.1 μm fractions after treatment with $n_C = 18$ suggest a mean age of the detrital material of 106–115 Ma. On the basis of Illite Age Analysis (IAA: Pevear 1992), Glasmann (1996, pers. commun., 1996) proposed a possible metamorphic source-terrane for the detrital illite found in Tertiary sedimentary basins of Alaska, which records a K–Ar age of illite of about 130 Ma.

Implications for Illite Age Analysis (IAA)

The results presented in this study also suggest that there can be no single component of detrital illite (or diagenetic illite) in an argillaceous rock. This inference is important, for example, in the application of Illite Age Analysis to extrapolate end-member ages of diagenetic and detrital illite (Pevear 1992). There cannot be a "true" end-member detrital illite giving one radiometric age, if the detrital fraction is a complex and heterogeneous mixture of K-bearing 2:1 clay minerals, *i.e.*, K- bearing smectite-group phases, rectorite-like R1 ordered phase, illite, and mica, having differing origin and stability, and existing in varying size-fractions. Simple quantification of the abundance of each component will not allow for extrapolation of known age-relationships. It follows that meaningful geological interpretation of K–Ar ages of 2:1 clay minerals from argillaceous rocks may well always be hampered by the complex nature of the detrital fraction.

SUMMARY AND CONCLUSIONS

The analytical approach (XRD, TEM and K–Ar analysis after *n*-alkylammonium-cation exchange) applied in this study and in Sears *et al.* (1998) facilitates the distinction among different types of expandable and non-expandable 2:1 clay minerals in argillaceous rocks, (*e.g.*, low-charge smectite, high-charge smectite or vermiculite), and between distinct illitic phases, (*e.g.*, rectorite-like R1 ordered phase, "*n*-alkylammonium illite", and illite). Application of long-chain alkylammonium cations to 2:1 clay minerals for the purpose of K–Ar dating does not result in the preferential removal of K or ^{40}Ar* from the interlayers in all 2:1 clay minerals, but rather selective removal of K and Ar from metastable 2:1 clay minerals, such as weathered, altered, and poorly crystallized 2:1 layer silicates.

The most significant findings of this study can be summarized as follows:

1. Although the K–Ar ages of the untreated <0.05 μm size-fraction from argillaceous rocks of the Reindeer D–27 well are younger than the stratigraphic ages, and the trend of increasing age coincides with the development and subsidence of the BYB and BMB of the MDBS region, the radiometric ages are considered to be mixed ages that result from concurrent processes of dissolution and growth of detrital and diagenetic subpopulations of illitic materials with increasing depth of burial.
2. Results of the K–Ar dating and TEM imaging of the 2:1 layer silicates in the fine fractions after octadecylammonium ($n_C = 18$) cation exchange offer evidence for the presence of illitic phases with a heterogeneous layer-charge, and enable the identification and distinction of subpopulations of detrital and diagenetic illitic phases.
3. It is apparent that regardless of size fraction, it is not possible to separate diagenetic and detrital illitic phases from an argillaceous rock solely on the basis of size, if the simultaneous processes of dissolution and growth of metastable 2:1 clay minerals are occurring.
4. The alkylammonium cation-exchange method removes exchangeable K and Ar from interlayer, edge and surface sites of expandable 2:1 clay minerals. Short-chain alkylammonium cations ($6 \leq n_C \leq 11$) are capable of replacing K and other interlayer cations from high-charge smectite-group and vermiculite phases, not easily replaceable by the usual cation-exchange reaction (Brindley 1980). As short-chain alkylammonium cations are not capable of removing K from the interlayers of more highly charged 2:1 layer silicates such as illite and mica, it is possible to isolate the potential contribution of a K-bearing smectite-group phase to the untreated K–Ar age, *i.e.*, subtracting the K–Ar age after treating the sample with $n_C = 8$ from the age of the untreated sample (or the opposite, depending on which age was older), giving the age contribution of the K-bearing smectitic component.
5. Given the nature of the *n*-alkylammonium cation-exchange reaction, the potential exists to completely replace the inorganic cations from the interlayer space of 2:1 clay minerals. Thus, it may be possible to identify the various components in a size-fractionated sample from argillaceous rock by treating the samples with alkylammonium cations of differing chain-lengths and for varying periods of exchange.

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