Clays and Clay Minerals, Vol. 61, No. 6, 551–565, 2013.

MINERALOGY OF EGYPTIAN BENTONITIC CLAYS II: GEOLOGIC ORIGIN

MOHAMED A. AGHA[1,*], RAY E. FERRELL[2], GEORGE F. HART[2], MOHAMED S. ABU EL GHAR[1], AND A. ABDEL-MOTELIB[3]

[1] Department of Geology, Faculty of Science, Fayoum University, Egypt
[2] Department of Geology & Geophysics, Louisiana State University, Baton Rouge, LA 70803, USA
[3] Department of Geology, Faculty of Science, Cairo University, Egypt

Abstract—Reconstructing the origin of bentonitic clays is often a challenging and rather complicated undertaking, but the analysis of certain predictor clay minerals is proving to be an excellent method to simplify this process. The goal of the present investigation was to use abundance changes of five X-ray diffraction (XRD) predictor minerals to determine the relative contributions of weathering and parent-rock changes to the origin of clay minerals in Egyptian bentonitic clays as the test case. The XRD predictor minerals, selected in an earlier discriminant function analysis of quantitative abundances of 14 minerals, provided a simpler approach to the interpretation of clay-mineral origins because they are the minerals that were most responsible for statistically significant differences among the samples. Changes in mineral composition were basically a function of parent-rock lithology, drainage, and climate interactions. A Paleo-Climate Index (CI; the ratio of coarsely crystalline kaolinite to Fe-rich smectite), and a Parent-Rock Index (PI; the ratio of the illitic phases and quartz abundances to pure smectite) were established to track the paleo-climate and parent-rock changes, respectively. Low CI values indicated that a long, seasonally dry climate prevailed during the Middle Eocene, uppermost Eocene, Lower Miocene, and Upper Pliocene bentonitic clay deposition. Lowermost Upper Eocene and the Middle Miocene bentonitic clays were produced when a wet climate prevailed throughout the year. Moderate to high PI values suggested derivation of the clays from the acidic basement crystalline rocks at Uweinat-Bir Safsaf uplift and Lower Paleogene shales during the Middle Eocene and lowermost Upper Eocene. The youngest Upper Eocene and Lower Miocene materials contained abundant Fe-smectite and low PIs indicating derivation from tholeiitic basalts. Diagenetic and sedimentary segregation modifications were not apparent. Direct evidence for *in situ* derivation from volcanic precursor materials was lacking in general, but volcanic eruptions were common in the region. The minerals in the Egyptian bentonitic clays formed as weathering products on land and have been transported by north-flowing streams and rivers to the sites of accumulation.

Key Words—Bentonitic Clays, Climate, Egypt, Origin, Parent Rock.

INTRODUCTION

Clay minerals have diverse origins that make them useful for purposes such as paleoclimatic reconstructions, interpretation of tectonic history, determination of provenance, definition of the timing and nature of diagenetic reactions, evaluation of industrial use, and many others. Mineral assemblages and textures may be inherited from the parent rocks or soils and then evolve by adding or subtracting elements from exchangeable and structural positions, or the precipitation of new phases. Reviews of clay-mineral genesis were provided by Chamley (1989), Weaver (1989), Meunier (2005), Ferrell (2006), Galán (2006), Velde and Meunier (2008), and Galán and Ferrell (2013).

Some generalizations useful for interpreting the origin of specific clay minerals include: Fe-rich smectite develops preferentially under poor leaching conditions, low-lying topography, and abundant Fe and Mg from basic rocks. Its formation is enhanced in a seasonally contrasting climate with an average annual rainfall of <100 cm/y (Weaver, 1989), where precipitation is followed by evaporation and concentration (Velde, 1985; Hayden, 1988; Chamley, 1989; Boulet *et al.*, 1997; Galán, 2006). Basic volcanics accelerate the pedogenic processes (Chamley, 1989; Weaver, 1989; Meunier, 2005). In contrast to smectite, kaolinite is most often produced in wet tropical continental areas, where moderate to high rainfall in excess of 100 cm/y (Weaver, 1989) and steep relief leads to the strong leaching of soluble mono- and divalent cations and their removal in runoff (Hayden, 1988; Chamley, 1989; Galán, 2006). Kaolinites are typically formed from acidic parent rocks, but can also be the main weathered product formed from basic rocks under wet tropical climate (Galán, 2006). Randomly mixed-layer illite-smectite clays originate in temperate seasonal climates with pronounced dry seasons (Gibson *et al.*, 2000; Ernst *et al.*, 2006; Galán, 2006) and require K-bearing precursor minerals such as K-feldspar and muscovite common in granites (Millot, 1970; Chamley, 1989; Galán, 2006). A series of illite-smectite mixed layers can be developed from the progressive destruction of magmatic or metamorphic micas by mechanical weathering (Meunier, 2005). Illite

* E-mail address of corresponding author:
aliomaragha@yahoo.com
DOI: 10.1346/CCMN.2013.0610608

https://doi.org/10.1346/CCMN.2013.0610608 Published online by Cambridge University Press

can be inherited directly due to mechanical erosion of K-rich minerals during the weathering of acidic or metamorphosed pelitic rocks under cool or desert climates (Righi and Meunier, 1995; Galán, 2006; Velde and Meunier, 2008). In addition, I-S mixed layers and illite can form in a smectitic-rich soil at the soil and prairie-grass cover interface where plant/silicate interaction increases the availability of K and promotes the formation of illite-smectite and illite (Madsen and Nornberg, 1995; Velde *et al*., 2003; Velde and Meunier, 2008; Velde and Barré, 2010).

Smectite forms most commonly from the hydrothermal leaching or diagenetic alteration of volcanic glass in tuffs or other ashfall deposits (Christidis and Huff, 2009; Güven, 2009). The major processes affecting smectite formation in general are: (1) chemical precipitation (neoformation); (2) erosion of soil clays or previously deposited sediments; (3) transformation reactions in the water column of the sedimentary basin; (4) submarine alteration of volcanic debris; and (5) deposition directly from erosion of pre-existing crystalline rocks (Chamley, 1989). The (Fe+Al)/Mg content of the smectite formed may vary considerably depending on the climatic conditions, the tectonic setting, the type of material being altered, or the composition of the interstitial fluids.

The modern-day study of Egyptian bentonite began with the description of an occurrence near El Fayoum City (Al Alfi, 1946). Four provinces in the northern Western Desert (Agha *et al*., 2012) contain commercial deposits ranging in age from Middle Eocene to Late Pliocene. Some deposits have high kaolinite contents, and whether all the Egyptian deposits have volcanic precursors is unclear. Mineralogical studies of Egyptian bentonitic clays are not common and often report conflicting compositions ranging from trioctahedral Ca-Mg-smectite to Na-montmorillonite and kaolinite with or without mixed-layered illite-smectite, illite, quartz, feldspars, calcite, and gypsum (EGSMA, 1992; Abu El Ezz *et al*., 1993; El Hefnawi *et al*., 1994; Ibrahim *et al*., 1994; El Shabiny *et al*., 1996; Basta *et al*., 1970; El Anbaawy *et al*., 1990; Rashed, 1991; Attia *et al*., 1985). In the present study, the term 'bentonitic clay' will be used instead of bentonite for any soft, plastic, smectite-rich clay regardless of its origin, following the recommendations for industrial materials by Grim and Güven (1978) and Murray (2007).

The most frequently invoked origins for the Egyptian bentonitic clays are detrital. The Qasr El Sagha delta clays of the Fayoum area were derived from the African metamorphic-igneous complex (El Hefnawi *et al*., 1994). In the Fayoum and Alamein areas, the smectites of the Late Eocene and Middle Miocene bentonitic clays formed from weathered Tertiary basalts at slightly alkaline pHs, while kaolinites formed diagenetically at the expense of smectite (Abu El Ezz *et al*., 1993). Heavy-mineral investigations (El Shahat *et al*., 1997) indicate that the Upper Pliocene clastics of Qaret El Muluk Formation were derived directly from the Red Sea Hills and recycling of the Miocene and older sediments. Investigations supporting the direct derivation of the Egyptian clays from the alteration of volcanic ashes and tuffs, or the temporal and spatial variability of the deposits are rare.

The simplest approach in geological interpretations is to describe unique mineral assemblages or lateral and/or vertical variations in the XRD-determined abundances of major clay-mineral groups, often without any statistical assessment of analytical uncertainties, covariance, or knowledge of whether the sample differences are statistically significant (Środoń *et al*., 2006; McCarty *et al*., 2008; Huggett *et al*., 2010: Cuadros *et al*., 2011; Kadir *et al*., 2011). In other instances, various forms of cluster analysis such as principal component analysis have been employed to identify variables representing stratigraphic and environmental classes of genetic significance that could not be specified beforehand (Sanchez and Galán, 1995; Prudencio *et al*., 2006; Ekosse and Mwitondi, 2009; Cravero *et al*., 2010; Montero-Serrano *et al*., 2010). When the classes are known, discriminant function analysis (DFA) identifies the mean mineral content and the important mineralogical differences that distinguish one group from another (Hart *et al*., 1989; Huff and Kolata, 1990; Hart, 1994; Shane and Froggatt, 1994; Kolata *et al*., 1996; Ferrell *et al*., 1998; Christidis, 2001; Eden *et al*., 2001). These important mineralogical variables are referred to as XRD predictor minerals (Agha *et al*., 2012). Both of the statistical approaches facilitate an objective assessment of mineralogical associations within complex datasets that reflect the geologic origins of the deposits. The DFA approach is particularly useful when classes can be established in advance, based on field or other geologic data.

The purpose of this study was to use the diversity in the Egyptian XRD mineral predictors' abundances to reconstruct local geologic conditions during the Middle Eocene to Late Pliocene. The smaller dataset derived from a DFA shows variability at the epoch-level (Agha *et al*., 2012) which is based on the inclusion of specific structural and crystallite-size models in the XRD analysis and represents a unique approach that will facilitate the recognition of significant differences through time. The results should add to general knowledge of bentonitic clay origins by improving the ability to interpret conditions in the source area, potential changes occurring during transportation and deposition, and any post-depositional alteration that may occur, especially for bentonitic clays that contain large quantities of kaolinite and other clay minerals, and generally lack direct evidence of their volcanic precursors.

Geologic setting

The Paleogene and Neogene deposits of the northern Western Desert (Figure 1) are part of two shallowing-

https://doi.org/10.1346/CCMN.2013.0610608 Published online by Cambridge University Press

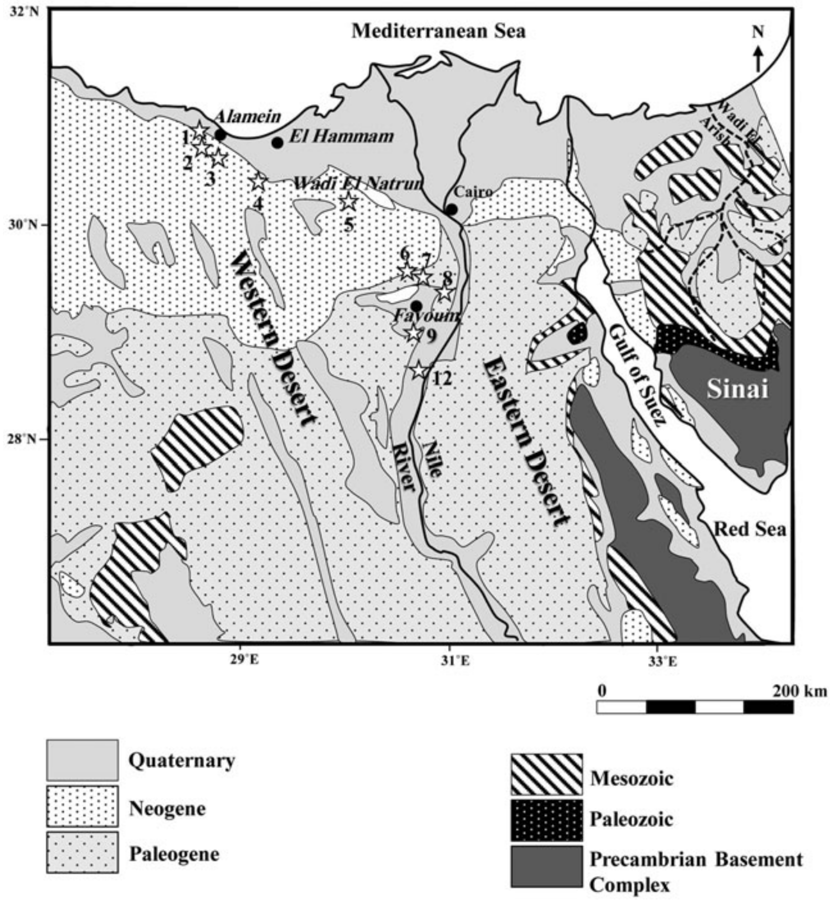

Figure 1. Approximate locations of quarries (stars) in the northern part of the Western Desert of Egypt. The numbered stars represent the quarry numbers, *e.g.* star No.1 refers to Q1.

upward allocycles, or megasequences, produced by extrabasinal forces including global sea-level fall, climate change, and tectonic activity (Tawadros, 2001). The Middle and Upper Eocene units, the upper boundary of which with the Oligocene is commonly marked by a regional unconformity associated with a period of maximum emergence and volcanic activity, are part of a Paleogene sequence produced by a northward-retreating sea. The Lower and Middle Miocene strata form part of a southward-advancing transgressive systems tract (TST). The Early Pliocene sediments represent an abrupt continental transgression following the extreme sea-level and salinity fluctuations of the Upper Miocene. The most recent retreat of the shoreline was marked by Quaternary deposits of the Nile Delta complex. From Upper Eocene to Holocene, magmatic activity was widespread regionally and extensive basaltic and silica-poor volcanic centers formed in the eastern Mediterranean and North Africa. The volcanism reflects the change in the plate tectonic regime induced by Alpine collision, domal uplifts of the basement, and rifting of the Red Sea and Gulf of Suez (Tawadros, 2001). The bentonitic clays are generally found in near-shore and fluvial environmental settings rather than in the deep marine.

The bentonitic clay sequences are underlain and flanked to the east by Mesozoic carbonates, Paleozoic materials, and a Precambrian Basement Complex. The Paleozoic is marked by Middle Cambrian to lower Permian clastic-dominated units punctuated by five main phases of mostly alkaline intrusives and granites. The Basement Complex is represented by an older series of gneissic domes and a younger Pan-African sequence containing a basal ophiolite overlain by metasediments, volcanoclastics, and intermediate volcanics and intrusives.

MATERIALS AND METHODS

Samples

Sixty-two side-by-side duplicates (124 total) of Middle Eocene to Upper Pliocene bentonitic clays were collected from 12 quarries in the NWD. The thicknesses of bentonitic clay units and some of the associated sediments were measured and their characteristics described. Representative, fresh samples of the clay-rich intervals were obtained. Table 1 provides the

https://doi.org/10.1346/CCMN.2013.0610608 Published online by Cambridge University Press

Table 2. Characteristics of 'bentonitic' clay samples from sites in the Western Desert of Egypt.

General location	Quarry	Period	Epoch	Formation	Environment
P3, Wadi El Natrun Valley	Q5, Deir El Baramous	NEOGENE	Upper Pliocene	Qaret El Muluk	Low-energy lagoonal/deltaic conditions (El Shahat *et al.*, 1997)
P1, south of Alamein City	Q1, Deir El Moreir Q2, Deir Abul Hegif Q3, Deir El Harrah		Middle Miocene	Marmarica	Low-energy shallow marine environment (El Hedeny, 2007)
P2, south of El Hammam City	Q4, El Barkan		Lower Miocene	Moghra	Coastal lagoon/deltaic environments (El Khoriby, 2005)
P4, El Fayoum Depression	Q6, Qasr El Sagha Q12, Reigha Q7, Kom Oshim	PALEOGENE	Upper Eocene	Qasr El Sagha unknown Birket Qarun	Low-energy shallow lagoon/bay settings (Abdel Fattah *et al.*, 2010)
	Q8, Girza Q9, Qalamshah		Middle Eocene	Gehannem 'Ravine beds'	

quarry location and name, age, formation, and general environment of deposition. More detailed descriptions of the samples and their stratigraphy are available from the senior author. Samples from two quarries, Q10 and Q11, were excluded from this analysis because of uncertainties in the reliability of the XRD results revealed by DFA analysis at the epoch level (Agha *et al*., 2012).

A typical section of the Middle Eocene Gehannem Formation in the Qalamshah quarry (Q9) is represented by a lower, 2–3 m thick, banded gray bentonitic clay that is overlain unconformably by >3 m of buff to tan, interbedded clayey silt and sand (Figure 2a). A gypsum bed occurs near the top of the bentonite. Horizontal bedding averaging ~10 cm thick is typical of the Egyptian bentonitic clays. Approximately 7 m of banded tan to buff clay (Figure 2b) of the Middle Miocene Marmarica Formation from the Deir El Moreir quarry, exhibits horizontal beds that are occasionally interrupted by small lenticular zones. The generally massive nature of the claystone beds and the sedimentary structures of the associated coarser beds suggest accumulation in the low-energy environments of lagoons, bays, and lakes. Only the clay beds were sampled.

Laboratory procedures

X-ray diffraction patterns of whole-sample, randomly oriented powders and oriented clay aggregates were quantified with selected peak mineral intensity factor ratios (Ferrell *et al.*, 1998) and whole-pattern fitting methods (Ferrell and Dypvik, 2009), respectively. The methods provided a wt.% estimate of mineral abundances that is semi-quantitative, with an estimated precision of ±10% at the 10–20 wt.% level. A table of all XRD results has been deposited with the Editor-in-

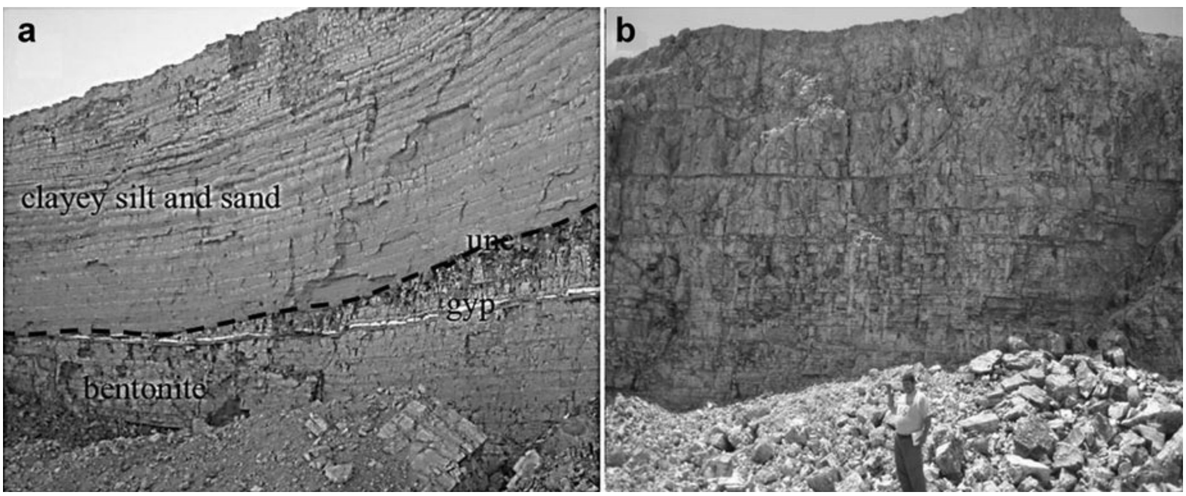

Figure 2. (a) Exposure of the middle Eocene Ravine Formation in Q9 gypsum (gyp); unconformity (unc). (b) Bentonitic clay section of the Middle Miocene Formation in Deir El Moreir quarry (Q1).

https://doi.org/10.1346/CCMN.2013.0610608 Published online by Cambridge University Press

Chief and is available from www.clays.org/JOURNAL/JournalDeposits.html

A JEOL JSM 840A scanning electron microscope was used for examination of clay microfabric. Freshly broken samples (⩽5 mm thick) were coated with gold and viewed perpendicular to bedding in the secondary electron imaging mode (SEI). Images were acquired at 15 kV accelerating voltage and working distances ranging from 10 to 20 mm and magnifications ranging from 50 to 10,000×.

Discriminant function analysis (DFA)

A DFA of the log-transformed mineral wt.%/feldspar wt.% ratio determined the mean mineral composition of samples belonging to each epoch and identified XRD predictor minerals based on the coefficients of discrimination (Agha *et al*., 2012). Fe-rich dioctahedral smectite, a randomly interlayered illite-smectite with 60% smectite layers (Fe-poor I-S), coarsely crystalline kaolinite, illite, and quartz were the important determinants for recognizing statistically significant differences among the samples at the epoch level. S-moderate I-S (random with 70% S), S-rich I-S (random with 80% S), two varieties of finely crystalline kaolinite, feldspar, and amorphous matter also were present, but were not included in this presentation because their abundance was correlated with one of the predictor minerals, or their distributions were highly skewed. Calcite and gypsum were excluded because they were only present in a small number of samples. More details regarding the use of DFA to recognize clay mineral differences at the epoch level as well as due to geographic province and quarry were presented by Agha *et al*. (2012).

RESULTS

Previous work

At the epoch level the XRD predictor mineral medians, derived from Agha *et al*. (2012), exhibited major variations (Figure 3). Their sum accounted for 50−70 wt.% of the total mineral assemblage. Fe-rich smectite varied from <10 wt.% in the Middle Miocene samples to almost 40 wt.% in the Lower Miocene. Upper Pliocene had the largest Fe-poor I-S median value and Upper Eocene had the lowest. Coarsely crystalline kaolinite was lowest in samples from Lower Miocene and Upper Pliocene, where the sums of Fe-rich smectite and Fe-poor I-S medians were highest. Kaolinite was greater than either of the expandable clay minerals in

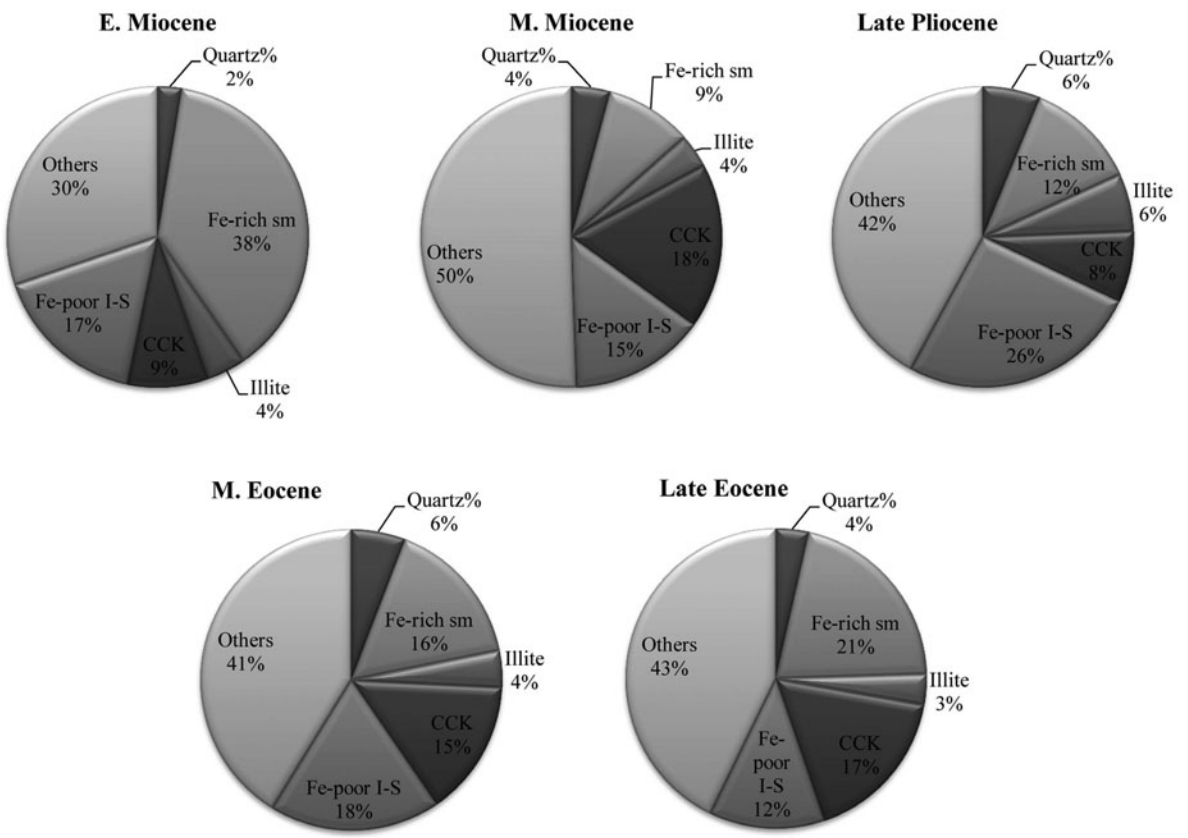

Figure 3. Pie charts illustrating the median abundances of the XRD predictor minerals in Egyptian clays from different epochs. CCK = coarsely crystalline kaolinite.

https://doi.org/10.1346/CCMN.2013.0610608 Published online by Cambridge University Press

Middle Miocene. Illite median values were greatest in Upper Pliocene, whereas the other epochs had almost constant median values (~4 wt.%). Median values for quartz were consistently low, representing just 2–6 wt.% of the whole-rock samples. Changes in the relative abundance of Fe-rich smectite with respect to coarsely crystalline kaolinite and the other minerals were most notable. Somewhat abrupt changes in mineral-abundance means between the Upper Eocene and the Lower Miocene, and the Middle Miocene and the Upper Pliocene were produced by two regional unconformities. Variations in the XRD predictor minerals at the epoch level were those most likely to reflect different environments of clay-mineral formation discussed below. I-S and kaolinite varieties, and other minerals comprising 30–50 wt.% of the sample may be important with respect to industrial use of the bentonitic clays from a particular age, but they did not contribute significantly to the recognition of differences among the epochs.

Microfabric

The microfabric (Figure 4) of representative bentonitic clays was highly variable, ranging from highly oriented flakes to more randomly oriented masses containing coarser grains and hollow spheres. A laminated mass of wavy clay flakes (Figure 4a) was presented in a sample from the Upper Eocene Qasr El Sagha Formation exposed near the top of Q6. Individual flakes of >6 μm long were a composite mosaic of smaller flakes lacking distinctive crystal forms. Orientation due to fissility, indicated by the white line, can be observed at lower magnification in samples from the Lower Miocene Moghra Formation (Figure 4b). Zones of silty (S) grains (mostly quartz) >40 μm in diameter were interlaminated with bands of clay (C) flakes. Randomly oriented swirls of wavy (W) clay flakes were very abundant in another sample from the Lower Miocene Moghra Formation (Figure 4c). Two circular regions were obvious in the left central and right central portions of the figure. Both appeared to be cavities in the rock. That on the right represented a plucked silt grain similar to those illustrated in Figure 4b. Clay flakes surrounding the small feature on the right appear to encircle the cavity and may have been a rim (R) on the grain that was removed. Good examples of clay bundles (W) swirling around coarser features were provided in a sample from the Upper Eocene Qasr El Sagha Formation where an embedded sand grain (G) was wrapped by clay flakes (Figure 4d). Several hollow spheres (H) with clay linings appeared in the upper section of the same figure. Most

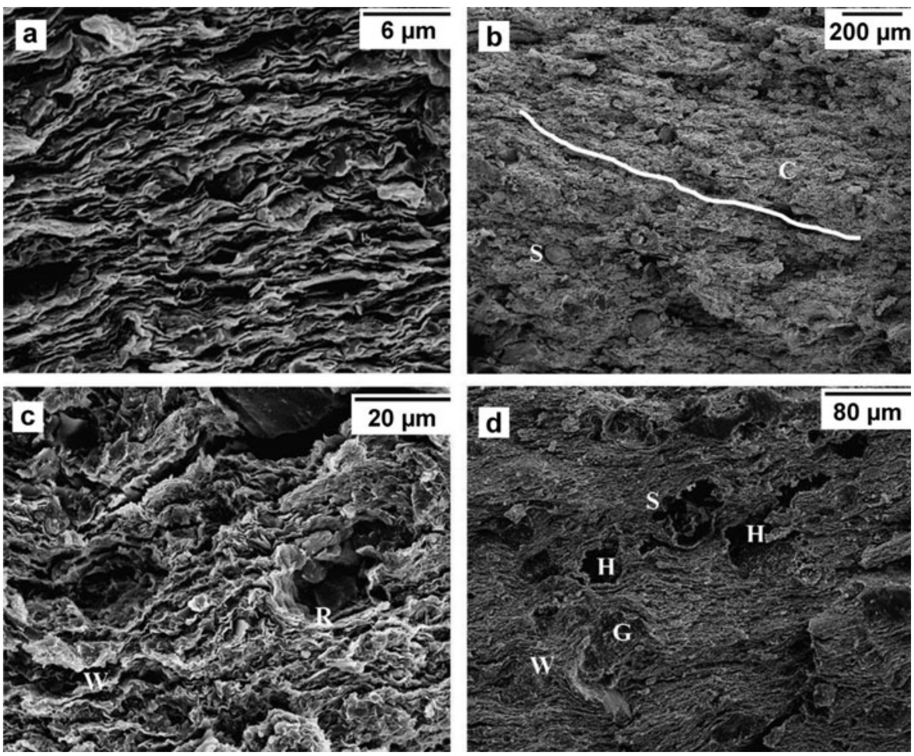

Figure 4. Electron micrographs of typical clay microfabrics: (a) Mostly parallel clay flakes in sample S53 from Q6. (b) Thin interlaminated silt (S) and clay (C) in S21 from Q4; approximate orientation of bedding indicated by white line. (c) Spherical depressions enclosed in regions of wavy flakes (W) in sample S15. The depression on the left appears to be a result of plucking. That on the right has a rim (R) suggesting that a grain may have been dissolved. (d) Silt-sized grains (G) and hollow microspheres (H) enclosed by wavy bundles of clay minerals (W) in S60 from Q6.

https://doi.org/10.1346/CCMN.2013.0610608 Published online by Cambridge University Press

were compound, made of a larger sphere surrounded by multiple smaller spheres (S). The hollow features may have formed by the replacement of volcanic glass spheres or tests of foraminifera.

Vertical variation in XRD predictor mineral abundances

A composite section illustrating vertical variations in the proportions of the discriminator minerals revealed changes that can be linked to climate and parent-rock types (Figure 5). A continuous moving trend line had been drawn through the data for illustrative purposes although two regional unconformities are present at the top of Upper Eocene and Middle Miocene. The samples were arranged in order of decreasing age, starting with the oldest at the bottom.

Fe-rich smectite abundance in the Middle Eocene sediments was ~25 wt.% in Q9 and decreased to almost 15 wt.% in Q8 (Figure 5). In the Upper Eocene, a decline to 10 wt.% in Q7 was followed by an increase to 17 wt.% in Q12. Samples from the uppermost Eocene (Q6) and those from the Lower Miocene exhibited broad maxima of ~30 and 40 wt.%, respectively. In the Middle Miocene sediments, Fe-rich smectite was 10 wt.% and increased to an average of ~20 wt.% near the middle of the Upper Pliocene. The largest differences in Fe-rich smectite occurred between the Upper Eocene and Lower Miocene, the Lower Miocene and Middle Miocene, and the Middle Miocene and the Upper Pliocene bentonitic clays.

Coarsely crystalline kaolinite distribution (Figure 5) was generally the mirror image of Fe-rich smectite with broad maxima in the base of the Upper Eocene samples (Q7) and in the Middle Miocene. Two minima were apparent in the Lower Miocene and the Upper Pliocene bentonitic clays.

Fe-poor I-S (Figure 5) maxima were apparent in the Middle Eocene and Upper Pliocene samples. Values in the Upper Pliocene sediments were among the highest recorded. Fe-poor I-S and Fe-rich smectite abundances were not directly related. The illite content was small in all samples (Figure 5) except for a greater abundance in the Upper Pliocene sediments and very small quantities, <2 wt.%, from the uppermost Eocene samples (Q6). The quartz content was small in all samples (Figure 5). The smallest values, ~2 wt.%, occurred in the Upper Eocene of Q12 samples and the Lower Miocene. Maximum values were present at the Middle Eocene and in the middle of the Upper Eocene Q6 deposits.

DISCUSSION

Origin of clay mineral assemblages

Clay-mineral assemblages in sedimentary materials are a product of physical and chemical weathering in the source terrane, physical sorting and chemical modification during transport and deposition, and post-depositional changes associated with diagenesis or hydrothermal alteration. Changes in the magnitude of these processes influence directly the amounts and varieties of clay minerals occurring in sedimentary rocks (Galán, 2006). Weathering and source-terrane variability are the most important variables in the origin of differences in the Egyptian bentonitic clays at the epoch level.

Paleo-climate index (CI). A CI derived from the ratio of clay mineral abundances is a useful tool for visualizing the changes produced by climatic processes. Assuming that Fe-rich smectite and coarsely crystalline kaolinite in the bentonitic clays were a result of soil weathering under different climatic conditions, the ratio of coarsely crystalline kaolinite to Fe-rich smectite (K/Sm) can be useful for climatic interpretation (Figure 6a). Large CI values reflect the prevalence of a wet tropical climate with rainfall of >100 cm/y. Small ratios point to a

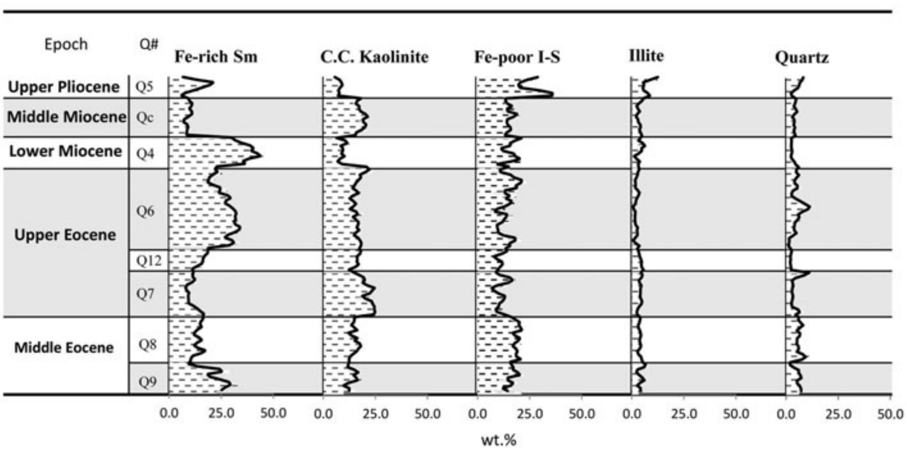

Figure 5. Composite sections illustrating vertical variations in the abundances (wt.% of the total rock) of the five most important discriminator minerals. C.C. kaolinite = coarsely crystalline kaolinite (data obtained from Agha *et al*., 2012).

https://doi.org/10.1346/CCMN.2013.0610608 Published online by Cambridge University Press

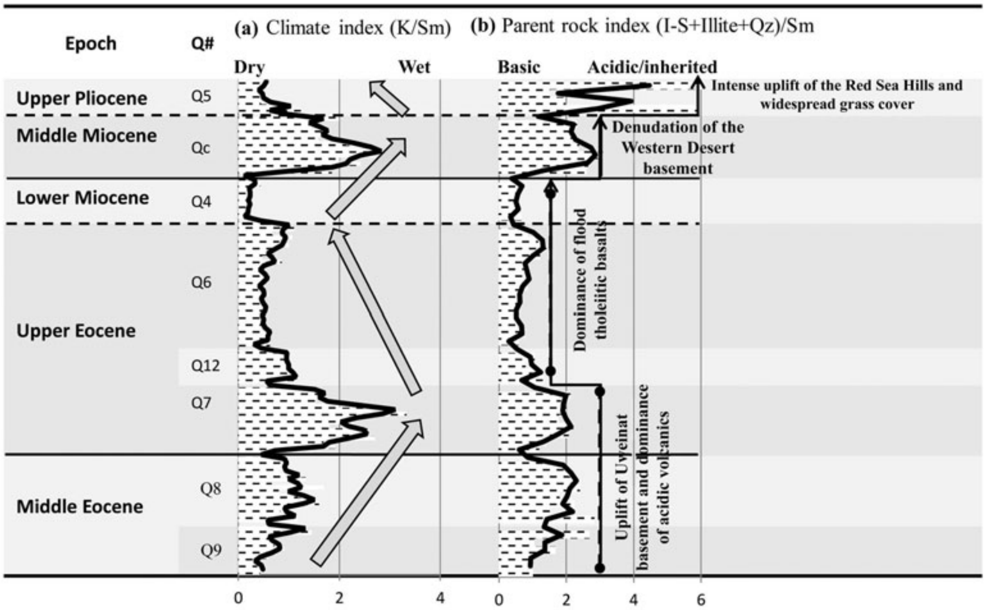

Figure 6. (a) Climate index, the ratio of coarsely crystalline kaolinite (K) to Fe-rich smectite (Sm), varies with stratigraphic position. (b) Parent-rock index, (I-S+Illite+Qz)/Sm, identifies effects due to source-terrane changes.

seasonally contrasting climate (alternating wet and well marked dry seasons) with annual rainfall of <100 cm/y. Limited flushing and leaching of pre-existing crystalline rock in weakly drained landscapes favors the formation of smectite-rich soil. Fe-poor I-S and illite were excluded from the CI because these illitic components could be partly inherited from older sedimentary rocks (see the 'Source Area' section). The XRD indicator quartz has limited usefulness because of its resistance to weathering.

Two contrasting climate cycles were recognized in Figure 6a. The Middle Eocene had a relatively small CI suggesting the predominance of a seasonally dry climate. The CI values became greater and more indicative of wetter conditions and higher rainfall (more than 100 cm/y) through the base of the Upper Eocene deposits (Q7). A shift to semi-arid climate with an average annual rainfall of <100 cm/y was suggested by the smaller average CIs of the uppermost Eocene and the Lower Miocene clays. Pronounced dry seasons and relatively low annual rainfall were consistent with the presence of small nanophyll leaf sizes (2.5–22.5 mm^2) (Figure 7) that grow in relatively dry savanna environments in the uppermost Late Eocene clays (Jacobs, 2004). The Middle Miocene patterns indicated a return to wet climate and strong leaching conditions. The Upper Pliocene clays indicated that seasonal contrast in precipitation was less pronounced than in the Middle Miocene. The wettest source-area conditions were indicated from the base of the Late Eocene and the Middle Miocene bentonitic clays. The most pronounced seasonally dry period was observed in the Early Miocene.

The CI results were well correlated with the paleoclimate literature from North Africa and Egypt based mostly on flora, fauna, and isotope records. The Middle Eocene was characterized by pronounced dry seasons that led to relatively moderate rainfalls (<100 cm/y) and the development of woodland communities in Africa, except for the western coast (Jacobs, 2004). In Egypt, the prevailing climate of the Middle Eocene was characterized by well marked dry seasons (Millar, 1993; Maley, 1996; Herendeen and Jacobs, 2000; Jacobs and Herendeen, 2004; Swezey, 2009). By the beginning of the Late Eocene, the climate was humid (Maley, 1996; Egyptian National Commission for

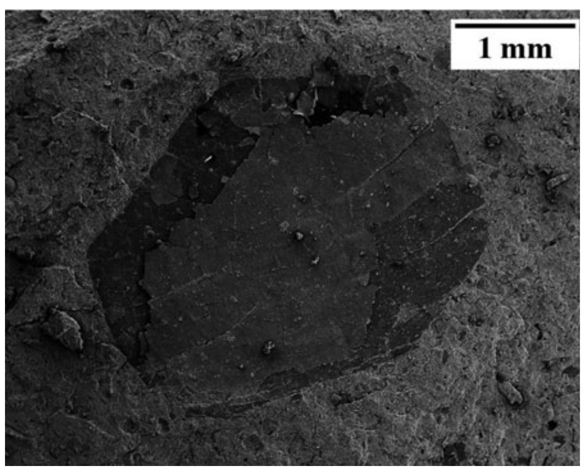

Figure 7. Electron micrograph showing a leaflet, within nanophyll leaf size (~8 mm^2) in Q6.

UNESCO, 2004) favoring an increase in kaolinite production. The prevailing seasonally dry conditions lasted until the end of Eocene and during the Early Miocene (Cachel, 1979; Maley, 1996; Mess *et al*., 2001; Herendeen and Jacobs, 2000; Jacobs, 2004; Swezey, 2009; Abdel Fattah *et al*., 2010). Wet and warm climatic conditions and rain forest prevailed during the Middle Miocene (Maley, 1996; Swezey, 2009). Based on the carbon isotopic signature of fossil herbivore tooth enamel and the prevalence of C4 grasses (characteristic of seasonal, arid, and warm environments and more tolerant of lower atmospheric CO_2 (< 400 ppmv) than C3 plants), East Africa was characterized by seasonal, arid, and warm environments during the Pliocene (Jacobs *et al*., 1999). The Late Pliocene climate, specifically in Egypt, was arid to semi-arid with seasonal runoff that resulted in a prevalence of grasslands (Chapman, 1971; Said *et al*., 1975; Saad *et al*., 1987; Griffin, 2002; Mannion, 2008; Swezey, 2009; Talbot and Williams, 2009; Lahr, 2010).

Parent-rock index (PI). Variations in the clay minerals developed under similar paleo-climatic conditions from different epochs suggested other genetic factors. For instance, Fe-rich smectite was more abundant in the uppermost Eocene bentonitic clays than in Upper Pliocene clays, while the latter was richer in Fe-poor I-S and illite (Figure 5). The Middle Eocene had more Fe-poor I-S, and less Fe-rich smectite than the Early Miocene, in spite of deposition during semi-arid conditions. In one setting the more predominant smectite was Fe-rich and in the other the smectite component was Fe-poor (although both of these expandable minerals develop under dry climate and poor leaching conditions), suggesting changes in parent rocks. The Fe-poor I-S and illite require K-bearing precursor minerals such as muscovite and K-feldspars that are abundant in granitoids, while basic rocks foster the formation of Fe-rich smectite. In addition, quartz is an important indicator for acidic and gneissic rocks. Thus the ratio of the illitic phases and quartz abundances to pure smectite ([I-S + illite + Qz]/Sm) can be used as a PI to trace the changes of parent-rock lithology and topography through time (Figure 6b). The use of Fe-rich smectite and Fe-poor I-S values in the index can be justified because their abundances were not covariant. Kaolinite was avoided in this index as it could have been developed from either acidic or basic rocks as long as strong leaching conditions existed.

Variations in the PI (Figure 6b) reflected the relative contributions of different parent rocks during the Middle Eocene to the Late Pliocene. The relatively high PI ratios of the Middle Eocene and the base of Upper Eocene (Q7) pointed to weathering of acidic parent rocks rather than basic rocks. The low PI values of the upper parts of the Upper Eocene and the Lower Miocene samples indicated that these clays were derived chiefly from tholeiitic basic rocks characterized by low-lying topography, with lesser contributions from acidic rocks. The Middle Miocene and Upper Pliocene samples had high PI ratios suggesting the predominance of acidic parent rocks.

Full reconstruction of the puzzle of the Egyptian bentonitic clays' origin requires consideration of the following questions: (1) Where were the possible source areas and what was their composition? (2) Could transportation of the weathering products from the source areas to the sites of accumulation have modified their composition? and (3) What was the likelihood of post-depositional modification by diagenesis or hydrothermal processes?

Source areas. Recent and Holocene clay assemblages deposited along the southeastern Mediterranean margin (from Gaza to Lebanon) were derived chiefly from the River Nile and the seasonal Wadi El Arish (Stanley *et al*., 1998). Further north, Pliocene smectite and kaolinite were also derived mainly from Egyptian rivers (Diester-Haass *et al*., 1998). The potential source areas for the Tertiary bentonitic clays were probably located within the Egyptian landscape, containing the Precambrian basement complex, younger crystalline rocks, and pre-Middle Eocene sediments.

The present, well exposed Egyptian basement complex crops out in the southwest corner of the Western Desert forming an uplifted system (Gabal Uweinat Bir Safsaf inliers) and the western bank of the Red Sea and Gulf of Suez (Red Sea hills). The Precambrian basement complex is composed of intertwined igneous (acidic to ultrabasic) and metamorphic rocks in which the granitoids are the most common (Gass, 1977; El Gaby *et al*., 1990; Richter and Schandelmeier, 1990; Said, 1990a). The complex occupies about one tenth of the total area of Egypt and is overlain by Cretaceous to Eocene sediments. The Gabal Uweinat and Bir Safsaf inliers (occupying ~37,500 km^2) were initially uplifted during Paleozoic times (Richter and Schandelmeier, 1990; Thurmond *et al*., 2004; Talbot and Williams, 2009) and deeply eroded by river incision in the Middle Eocene (Issawi and McCauley, 1993). The uplift and exposure of the basement rocks along the Red Sea Coast and Gulf of Suez was much younger, probably during Late Oligocene to Early Miocene (Kohn and Eyal, 1981; Steckler, 1985; Garfunkel, 1988; Bohannon *et al*., 1989; McGuire and Bohannon, 1989; Omar *et al*., 1989; Harms and Wray, 1990; Meshref, 1990; Morgan, 1990; Said, 1990a, 1990b; Issawi and McCauley, 1993; Kusky and El Baz, 2000; Nyblade *et al*., 2006; Mansour and Hasebe, 2010; Avni *et al*., 2012).

Tertiary volcanic activity (Meneisy, 1990; Richter and Schandelmeier, 1990) represented by isolated plugs of granites, syenites, and trachytes in the Uweinat-Bir and Safsaf areas began during the Middle Eocene (48–41 Ma). Younger Mid-Tertiary, mainly tholeiitic

https://doi.org/10.1346/CCMN.2013.0610608 Published online by Cambridge University Press

basalt sequences erupted within the Uweinat inlier at the end of Late Eocene (~37 Ma), and were followed by Late Oligocene–Early Miocene basalts extruded in the northeastern parts of Egypt during the opening of the Red Sea. The Oligocene–Miocene basalts occurred as numerous extensive lava flows averaging 30 m in thickness around the present Nile delta. They extend westward into the Western Desert where they are mainly covered by the Lower Miocene clastic sediments (Meneisy, 1990; Said, 1990b; Perrin *et al*., 2009). These basalts also extend to the east where they become up to 328 m thick.

Paleogene shales occurring south and east of the study area are potential sources of randomly interstratified illite-smectite minerals in the younger bentonitic clays. The Global Standard Stratotype section (GSSP) for the Paleocene/Eocene boundary has been established in the Dababiya Quarry, near Luxor, where the Tarawan Chalk, the Esna Shale, and the Thebes Limestone overlie the Dakhla Formation shales. Poorly crystalline illite-smectite is the most dominant clay mineral (up to 100% of the total clay minerals) in the uppermost Paleocene–Lower Eocene Esna Formation with minor kaolinite and chlorite (Ernst *et al*., 2006; Schulte *et al*., 2011). The Paleocene Dakhla Shale Formation in the Central Eastern Desert has clay mineral abundances similar to the Esna Formation (Schulte *et al*., 2007). The minor chlorite content of the Esna and Dakhla shales disappears east and west of the Nile Valley (Ghandour *et al*., 2004; Temraz, 2005). These lower-Tertiary shales formed cliffs in the southern parts of Egypt during the Tethys Sea regression (Said, 1990b; Issawi and McCauley, 1993).

Petrographic investigation of the Middle Eocene and lower part of the Upper Eocene rocks (Gehannem and Birket Qarun formations, respectively) suggested a granitic parent rock not far from the depocenters (Hamblin, 1987). Various geochemical indexes indicated that the Upper Eocene (Qasr El Sagha Formation) and the Lower Miocene mudstones originated essentially from the weathering of basic parent rocks, with minor contributions from acidic rocks and reworked sediments, especially in the Lower Miocene deposits that are unconformably overlying Oligocene–Miocene basalts (Abayazeed, 2012). Heavy-mineral studies revealed that the EBC along the Red Sea coast as well as recycling of Miocene and older sedimentary rocks are the main parent rocks for the Upper Pliocene sediments (El Shahat *et al.*, 1997). These petrographical and geochemical criteria agreed with the PI interpretations presented above.

Physical sorting. Clay minerals transported in suspension by streams may experience physical sorting due to size segregation of individual mineral grains or flocculated aggregates that may control their relative abundance in sedimentary basins (Chamley, 1989; Weaver, 1989; Meunier, 2005; Galán, 2006; Bican-Brişan and Hosu, 2006; Velde and Meunier, 2008). When this process is operative, the typical order of relative clay-mineral abundance from the coastline to the open sea is: kaolinite, illite, and then I-S mixed-layers and smectite. The data do not permit a rigorous evaluation of this process. However, the relative similarity of the depositional environments of the Egyptian bentonitic clays, low-energy shallow lagoon to deltaic settings in which chemical composition and current strength differences were not pronounced, should minimize the influence of the sorting process.

Burial diagenesis. Low overburden thicknesses, the tectonic setting, and the generally friable nature of the sediments suggested that deep burial diagenetic alteration is implausible. The continuous retreat of the sea northward since the Early Eocene, due to tectonic uplift, uncovered large parts of Egypt (Morgan, 1990; Said, 1990b; Tawadros, 2001) and provided little accommodation space for sediments. Deposition in transitional and shallow-marine environments resulted in bentonitic clays that were never buried deeply enough to attain the temperatures required for conversion of smectite to illite. The transformation of smectite into illite *via* burial diagenesis also involves the formation of ordered mixed-layered illite-smectite (Hower *et al*., 1976; Lindgreen and Hansen, 1991; Christidis, 1995) that was never detected in the samples. No evidence for hydrothermal alteration was observed during field sampling.

Alternative smectite origin. Alternative origins for smectite and mixed-layered illite-smectites in the region were presented by Shoval (2004a, 2004b). The clay minerals in Senomian to Eocene marine sediments, equivalent to Lower Paleogene shales in Egypt, on the Neo-Tethys margin, were produced by the marine argillization of volcanics and island-arc volcanism. Detrital illite and kaolinite were transported from the continent to the basin. Upwelling currents carried the smectite from open-marine conditions to the stratified higher-salinity water bodies in the synclinal basins of the Syrian arc deformation belt where they fixed K to create a smectite-rich illite-smectite. Relatively pure Ca- and Na-smectites in the Cretaceous of NE Turkey were attributed to hydrothermal alteration of volcanogenic materials *in situ*, or subaerial alteration and diagenesis in the sedimentary basin (Arslan *et al*., 2010; Karakaya *et al*., 2011). These conditions of smectite and mixed-layered illite-smectite development were not important during the formation of the Egyptian bentonitic clays, where all the deposits contain multiple clay minerals regardless of the sub-environment in which they accumulated, thus supporting the interpretation that they were mainly detrital products of weathering and erosion.

Lower Miocene sediments exhibited clay assemblages similar to those in the present-day Nile. The modern Nile sediments contain ~70% smectite, <25% kaolinite, and <10% illite derived primarily from

https://doi.org/10.1346/CCMN.2013.0610608 Published online by Cambridge University Press

Ethiopian Oligo-Miocene tholeiitic basalts (Stanley and Wingerath, 1996; Issar, 2003; Goudie, 2005; Woodward *et al.*, 2007) closely comparable to the Egyptian Oligo-Miocene basalts (Abdou, 1983; Ebinger and Sleep, 1998). The Ethiopian basalts are weathering in a seasonally contrasting climate. In the summer, due to monsoon conditions, rainstorms are common in the highlands from June until mid-September. The rest of the year, the climate is arid and many minor stream channels do not flow (Conway, 2000). However, the Ethiopian basalts cannot be a significant parent rock for the Lower Miocene sediments. The Egyptian paleo-drainage systems did not drain areas beyond the modern borders of Egypt until the Pleistocene (Said, 1993; Goudie, 2005; Van Damme and Van Bocxlaer, 2009; Lahr, 2010).

Importance of DFA. Extensive statistical tests were applied to the data prior to multivariate analysis to determine which mineral abundances could be used as XRD predictor variables determined by DFA (Agha *et al.*, 2012). The simplification of the database from 14 to 5 variables eliminated redundancies due to covariance, and focused attention on the minerals responsible for differences that are statistically significant. The predictor minerals represent a novel approach to distinguish climatic and source-terrane influences on the origin of the Egyptian bentonitic clays.

Geologic history and origin of the bentonitic clay deposits

The Middle Eocene to Late Pliocene geologic history of the Western Desert area was marked by a succession of fluvial off-lapping systems accompanying the general relative uplift of the region and the northward regression of the Tethys Sea (Said, 1981, 1993; Issawi, 1983; Issawi and McCauley, 1993; Goudie, 2005). Throughout this period the region was situated near the equator and experienced a warm, humid tropical climate marked by changes in the seasonality of the rainfall. The ubiquitous occurrences of mixtures of various clay species that generally form from different source rocks under diverse weathering conditions suggested a detrital origin for the Egyptian bentonitic clays.

From the Middle Eocene into the lower part of the Late Eocene, rocks relatively rich in illite-smectite mixed minerals, illite, and kaolinite were derived from the weathering of acidic sources (based on PIs) such as the Uweinat-Bir Safsaf crystalline rocks or the surrounding Lower Paleogene shales (Esna and Dakhla Shales). The Red Sea basement contribution was negligible as it was covered by Cretaceous sediments and the resistant Eocene Thebes limestone during the Eocene (*e.g.* Said, 1990a, 1990b; Issawi and McCauley, 1993). A general increase in the CI indicated that the annual wet periods became longer, thus accelerating severe leaching. Following the peak wet period, seasonal changes in aridity distribution became more pronounced by the end of the Eocene and the importance of acidic rock sources was overshadowed by Fe-smectite derived from basaltic sources similar to the Mid-Tertiary basaltic volcanic phases producing an age of ~37 Ma at the Uweinat-Bir Safsaf uplift. The Late Eocene was a time of pronounced regression and a regional unconformity formed.

When sedimentation resumed in the Early Miocene, the rainfall had been reduced to a minimum. The PI was also minimal, indicating the importance of basic rock weathering in the production of the bentonitic clays, where the Late Oligocene-Early Miocene basalts were common in the NWD. By the Middle Miocene, uniform distribution of annual precipitation resumed and well drained conditions had returned. The denudation of the Basement Complex contributed materials derived from acidic assemblages. Another regional unconformity closed the epoch.

Late Pliocene sediments had PI values that were much greater than in the underlying materials, indicating development of acidic parent rock. Seasonal contrasts in rainfall distribution returned as suggested from the CI. The notable abundance of Fe-poor I-S and illite within the Upper Pliocene samples could be attributed to the increased relative importance of mechanical weathering due to intense uplift of the Red Sea Hills, and the presence of a grassland dominated environment that prevailed in East Africa during the Late Pliocene (Lahr, 2010).

SUMMARY OF ORIGIN

The ubiquitous occurrences of several clay species in most samples, which generally develop under diverse weathering conditions, suggest a primarily detrital origin for the Egyptian bentonitic clays. The clay minerals developed on varied source rocks in different topographic and climatic conditions. The abundant Fe-rich smectite recorded from the close of the Eocene and during the Early Miocene was derived from the weathering of Mid-Tertiary tholeiitic basalts in a poorly drained, low-lying landscape. Abundant kaolinite was produced in source-area soils in a humid tropical environment with intense weathering conditions from acidic or basic rocks. Illite abundance is linked to inheritance or enhanced formation in the organic horizon of grassland soils near the end of the Neogene. The weathered products of the crystalline rocks and other sediments were carried to the northern parts of the Western Desert by north-flowing streams and river systems and mixed prior to deposition in deltaic complexes.

CONCLUSIONS

Variations in the abundances of five XRD predictor clay minerals: Fe-rich smectite, coarsely crystalline kaolinite, Fe-poor I-S, illite, and quartz revealed the

https://doi.org/10.1346/CCMN.2013.0610608 Published online by Cambridge University Press

origins of the Middle Eocene to Upper Pliocene bentonitic clays in the northern Western Desert of Egypt. The abundance variations of XRD predictor clay minerals selected by DFA pointed to the importance of weathering as the major process producing variations in the detrital Tertiary clay mineral abundances in the bentonitic clays from the northern parts of Egypt. A climate index (CI) based on the ratio of coarsely crystalline kaolinite, produced in tropical humid environments, to Fe-rich smectite, favored by well marked dry season climatic conditions, provided a reasonable estimate of relative climate change. The parent rock index ratio (PI) of Fe-poor I-S, illite, and quartz developed from acidic igneous rock, to Fe-rich smectite originating from tholeiitic basic parent rock, can be used to evaluate changes in the source areas. The pedogenetic origin of the clay minerals, especially coarsely crystalline kaolinite, distinguished these bentonitic clays from 'true' bentonites formed from the alteration of volcanic materials in shallow-marine environments.

ACKNOWLEDGMENTS

This study was funded by the Egyptian Cultural Affairs and Missions Sector. Assistance with fieldwork was provided by Dr Sobhi Helal (of Fayoum University). The authors are grateful to Wanda LeBlanc for her able assistance in all phases of XRD work at Louisiana State University (LSU). Many thanks to Dr Xiagong Xie for his advice with the SEM analyses. The LSU Department of Geology & Geophysics provided support for the project.

REFERENCES

Abayazeed, S.D. (2012) The geochemistry of some Egyptian smectitic clays. *Australian Journal of Basic and Applied Sciences*, **6(3)**, 589–599.

Abdel Fattah, Z.A., Gingras, M.K., Caldwell, M.W., and Pemberton, S.G. (2010) Sedimentary environments and depositional characteristics of the Middle to Upper Eocene whale-bearing succession in the Fayum depression, Egypt. *Sedimentology*, **57**, 446–476.

Abdou, M.I. (1983) Geological studies of some volcanic rocks in northern Egypt. *M.Sc. thesis, Cairo University*.

Abu El Ezz, A.R., Kholeif, M.M., and Abdo, A.A. (1993) Contribution to mineralogy and geochemistry of some bentonite deposits in Egypt. *El-Minia Science Bulletin*, **6**, 79–88.

Agha, M.A., Ferrell, R.E., and Hart, G.F. (2012) Mineralogy of Egyptian bentonitic clays I: Discriminant function analysis. *Clays and Clay Minerals*, **60**, 387–404.

Al Alfi, E.M. (1946) The mineral resources of Egypt. *Mining and Petroleum Association of Egypt*, **1**, 3–47.

Arslan, M., Abdioglu, E., and Kadir, S. (2010) Mineralogy, geochemistry, and origin of bentonite in Upper Cretaceous pyroclastic units of the Tirebolu Area, Giresun, Northeast Turkey. *Clays and Clay Minerals*, **58**, 120–141.

Attia, A.K., Murray, H.H., Azim, A.A., and Boulis, S.N. (1985) Chapter 10. Mineralogy of some Egyptian bentonitic-clay deposits. Pp. 157–184 in: *Mineralogy – Applications to the Minerals Industry, Paul F. Kerr Symposium* (O. Kopp, editor). Society of Mining Engineers, New York.

Avni, Y., Segevl, A., and Ginat H. (2012) Oligocene regional denudation of the northern Afar dome: Pre- and syn-breakup stages of the Afro-Arabian plate. *Geological Society of America Bulletin*, **124**, 1871–1897.

Basta, E.Z., El-Kadi, M.B., and Abdel Maksoud, M. (1970) Mineralogy of some bentonitic clays from Fayoum, U.A.R. and Aldress, Shropshire, England. *Bulletin of the Faculty of Science, Cairo University*, **43**, 271–284.

Bican-Brişan, N. and Hosu, A. (2006) Clay mineral association in the salt formation of the Transylvanian basin and its paleoenvironmental significance. *Studia Universitatis Babeş-Bolyai, Geologia*, **51**, 35–41.

Bohannon, R.G., Naeser, C.W., Schmidt, D.L., and Zimmermann, R.A. (1989) The timing of uplift, volcanism, and rifting peripheral to the Red Sea: a case for passive rifting? *Journal of Geophysical Research*, **94** (B4), 1683–1701.

Boulet, R., Lucas, Y., Fritsch, E., and Paquet, H. (1997) Geochemical processes in tropical landscapes: role of the soil covers. Pp. 67– 96 in: *Soils and Sediments: Mineralogy and Geochemistry* (H. Paquet and N. Clauer, editors). Springer, Berlin.

Cachel, S. (1979) A paleoecological model for the origin of higher primates. *Journal of Human Evolution*, **8**, 351–359.

Chamley, H. (1989) *Clay Sedimentology*. Springer-Verlag, Berlin, Heidelberg, 623 pp.

Chapman, R.W. (1971) Climatic changes and the evolution of landforms in the Eastern Province of Saudi Arabia. *Geological Society of America Bulletin*, **82**, 2713–2728.

Christidis, G.E. (1995) Mechanism of illitization of bentonites in the geothermal field of Milos Island, Greece. Evidence based on mineralogy, chemistry, particle thickness and morphology. *Clays and Clay Minerals*, **43**, 569–585.

Christidis, G.E. (2001) Geochemical correlation of bentonites from Milos Island, Aegean, Greece. *Clay Minerals*, **36**, 295–306.

Christidis, G.E. and Huff, W.D. (2009) Geological aspects and genesis of bentonite. *Elements*, **5**, 93–98.

Conway, D. (2000) The climate and hydrology of the Upper Blue Nile River. *The Geographical Journal*, **166**(1), 49–62.

Cravero, F., Marfil, S.A., and Maiza, P.J. (2010) Statistical analysis of geochemical data: a tool for discriminating between kaolin deposits of hypogene and supergene origin, Patagonia, Argentina. *Clay Minerals*, **45**, 183–196.

Cuadros, J., Dekov, V.M., Arroya, X., and Nieto, F. (2011) Smectite formation in submarine hydrothermal sediments: Samples from the HMS Challenger Expedition (1872–1876*). Clays and Clay Minerals*, **59**, 147–167.

Diester-Haass, L., Robert, C., and Chamley, H. (1998) Paleoproductivity and climate variations during Sapropel deposition in the Eastern Mediterranean Sea. Pp. 227–248 in: *Proceedings of the Ocean Drilling Program, Scientific Results,* **160** (A.H.F. Robertson, K.C. Emeis, C. Richter, and A. Camerlenghi, editors). College Station, Texas, USA.

Ebinger, C.J., and Sleep, N.H. (1998) Cenozoic magmatism throughout east Africa resulting from impact of a single plume. *Nature*, **395**, 788–791.

Eden, D.N., Palmer, A.S., and Cronin, S.J. (2001) Dating the culmination of river aggradation at the end of the last glaciation using distal tephra compositions, eastern North Island, New Zealand. *Geomorphology*, **38**, 133–151.

EGSMA (1992) Report on the Egyptian bentonite deposits. *Egyptian Geological Survey and Mining Authority (internal report, in Arabic)*, 36 pp.

Egyptian National Commission for UNESCO (2004) Nomination File for the Inscription of Wadi Al-Hitan (Whale Valley), the Western Desert of Egypt. *The World Heritage List*, **1186**. [Contains a bibliography of 30 references].

Ekosse, G-I.E., and Mwitondi, K.S. (2009) Multiple data clustering algorithms applied in search of patterns of clay minerals in soils close to an abandoned manganese oxide

https://doi.org/10.1346/CCMN.2013.0610608 Published online by Cambridge University Press

mine. *Applied Clay Science*, **46**, 1–6.

El Anbaawy, M.I.H., Dardir, A.A., and Meabed, E.E. (1990) Liability of bentonitic clays from eastern part of El-Fayoum Governorate in Foundry sands. *Annals of the Geological Survey of Egypt*, **XVI**, 45–49.

El Gaby, S., List, F.K., and Tehrani, R. (1990) The basement complex of the Eastern Desert and Sinai. Pp. 175–184 in: *The Geology of Egypt* (R. Said, editor). A.A. Balkema, Rotterdam.

El Hedeny, M. (2007) Encrustation and bioerosion on Middle Miocene bivalve shells and echinoid skeletons: paleoenvironmental implications. *Revue de Paléobiologie, Genève*, **26**, 381–389.

El Hefnawi, M.A., Loukina, S.M., and Abayzeed, S.D. (1994) Mineralogy and geochemistry of smectitic clays from Fayoum region, Egypt. *The Mineralogical Society of Egypt, Proceedings of the 1st International Symposium on Industrial Applications of Clays*, Cairo, pp. 128–150.

El Khoriby, E.M. (2005) Origin of the gypsum-rich silica nodules, Moghra Formation, Northwest Qattara depression, Western Desert, Egypt. *Sedimentary Geology*, **177**, 41–55.

El Shabiny, A.M., Hammad, S.M., Ibrahim, I.A., and Ismail, A.k. (1996) Combined thermal and structural study of some Egyptian bentonitic clays. *Journal of Thermal Analysis*, **46**, 1421–1435.

El Shahat, A., Ayyad, S.N., and Abdalla, M.A. (1997) Pliocene facies and fossil contents of Qaret El-Muluk Formation at Wadi El Natrun Depression, Western Desert, Egypt. *Facies*, **37**, 211–224.

Ernst, S.R., Guasti, E., Dupuis, C., and Speijer, R.P. (2006) Environmental perturbation in the southern Tethys across the Paleocene/Eocene boundary (Dababiya, Egypt): Foraminiferal and clay mineral records. *Marine Micropaleontology*, **60**, 89–111.

Ferrell, R.E. (2006) *Clay Mineralogy – An Introductory Course*, CD Series 1. The Clay Minerals Society, Chantilly, Virginia, USA.

Ferrell, R.E. and Dypvik, H. (2009) The mineralogy of the Exmore beds – Chickahominy Formation boundary section of the Chesapeake Bay impact structure revealed in the Eyreville core. *Geological Society of America Special Paper* **458**, 723–746.

Ferrell, R.E., Hart, G.F., Swamy, S., and Murthy, B. (1998) X-ray mineralogy discrimination of depositional environments of the Krishna Delta, Peninsular India. *Journal of Sedimentary Research*, **68**, 148–154.

Galán, E. (2006) Genesis of clay minerals. Pp. 1129–1162 in: *Handbook of Clay Science* (F. Bergaya, B.K.G. Theng, and G. Lagaly, editors). Elsevier, Oxford, UK.

Galán, E. and Ferrell, R.E. (2013) Genesis of clay minerals. Pp. 83–126 in: *Handbook of Clay Science, 2nd edition, Part A* (F. Bergaya and G. Lagaly, editors). Elsevier, Oxford, UK.

Garfunkel, Z. (1988) Relation between continental rifting and uplifting: evidence from the Suez Rift and northern Red Sea. *Tectonophysics*, **150**, 33–49.

Gass, I.G. (1977) The evolution of the Pan-African crystalline basement in NE Africa and south Arabia. *Journal of Geological Society of London*, **134**, 129–138.

Ghandour, I.M., Abd El-Hameed, A.T., Faris, M., Marzouk, A., and Maejima, W. (2004) Textural, mineralogical and microfacies characteristics of the Lower Paleogene succession at the Nile Valley and Kharga Oasis regions, Central Egypt. *Journal of Geosciences, Osaka City University*, **47**, 39–53.

Gibson, T.G., Bybell, L.M., and Mason, D.B. (2000) Stratigraphic and climatic implications of clay mineral changes around the Paleocene/Eocene boundary of the northeastern US margin. *Sedimentary Geology*, **134**, 65–92.

Goudie, A.S. (2005) The drainage of Africa since the Cretaceous. *Geomorphology*, **67**, 437–456.

Griffin, D.L. (2002) Aridity and humidity: two aspects of the late Miocene climate of North Africa and the Mediterranean. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **182**, 65–91.

Grim, R.E., and Güven, N. (1978) *Bentonites: Geology, Mineralogy, Properties and Uses*. Developments in Sedimentology, **24**, Elsevier North-Holland, Amsterdam, 256 pp.

Güven, N. (2009) Bentonites – Clays for molecular engineering. *Elements*, **5**, 89–92.

Hamblin, R.D. (1987) Stratigraphy and Depositional Environments of the Gebel-Rus Area, Eastern Faiyum, Egypt. *Brigham Young University, Geology studies*, **34**, 61–84.

Harms, J.C. and Wray, J.L. (1990) Nile Delta. Pp. 329–344 in: *The Geology of Egypt* (R. Said, editor). A.A. Balkema, Rotterdam.

Hart, G.F. (1994) Maceral palynofacies of the Louisiana deltaic plain in terms of organic constituents and hydrocarbon potential. Pp. 141–176 in: *Sedimentation of Organic Particles* (A. Traverse, editor). Cambridge University Press, UK.

Hart, G.F., Ferrell, R.E., Lowe, D.R., and Lenoir, A.E. (1989) Shelf sandstones of the Robulus L zone, offshore Louisiana. Pp. 117–141 in: *Shelf Sedimentation, Shelf Sequences and Related Hydrocarbon Accumulation* (R.A. Morton and D. Nummedal, editors). Proceedings of the Seventh Annual Gulf Coast Section SEPM Research Conference.

Hayden, C.C. (1988) Clay mineral origin and alteration in fluvial facies of the Lebo Member, Fort Union Formation (Paleocene), Custer County, Southeastern Montana. *Keck Geology Consortium*, **1**, 57–60.

Herendeen, P.S. and Jacobs, B.F. (2000) Fossil Legumes from the Middle Eocene (46.0 MA) Mahenge Flora of Singida, Tanzania. *American Journal of Botany*, **87**(9), 1358–1366.

Hower, Z., Eslinger, E.V., Hower, M.E., and Perry, E.A. (1976) Mechanism of burial metamorphism of argillaceous sediment – Mineralogical and chemical evidence. *Bulletin of Geological Society of America*, **87**, 725–737.

Huff, W.D. and Kolata, D.R., (1990) Correlation of K-bentonite beds by chemical fingerprinting using multivariate statistics. Pp. 567–577 in: *Quantitative Dynamic Stratigraphy* (T.A. Cross, editor). Prentice Hall, New Jersey, USA.

Huggett, J.M., Gale, A.S., and McCarty, D. (2010) Petrology and palaeoenvironmental significance of authigenic iron-rich clays, carbonates and apatite in the Claiborne Group, Middle Eocene, NE Texas. *Sedimentary Geology*, **228**, 119–139.

Ibrahim, I.A., Felix, N.S., Ismail, A.K., and Abdul Azim, F. (1994) Improvement of the rheological properties of Egyptian bentonitic clay through alkali activation. *The Mineralogical Society of Egypt, Proceedings of the 1st International Symposium on industrial applications of clays*, Cairo, pp. 174–180.

Issar, A. (2003) *Climate Changes during the Holocene and their Impact on Hydrological Systems*. The Press Syndicate of the University of Cambridge, Cambridge, UK, 129 pp.

Issawi, B. (1983) Ancient Rivers of the Eastern Egyptian Desert. *Episodes*, **2**, 3–6.

Issawi, B. and McCauley, J.F. (1993) The Cenozoic landscape of Egypt and its river system. *Annals of the Geological Survey of Egypt*, **XIX**, 357–384.

Jacobs, B.F. (2004) Palaeobotanical studies from tropical Africa – relevance to the evolution of forest, woodland and savannah biomes. *Philosophical Transactions of Royal Society, London*, **359**, 1573–1583.

https://doi.org/10.1346/CCMN.2013.0610608 Published online by Cambridge University Press

Jacobs, B.F. and Herendeen, P.S. (2004) Eocene dry climate and woodland vegetation in tropical Africa reconstructed from fossil leaves from northern Tanzania. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **213**, 115–123.

Jacobs, B.F., Kingston, J.D., and Jacobs, L.L. (1999) The origin of grass-dominated ecosystems. *Annals of the Missouri Botanical Garden*, **86(2)**, 590–643.

Kadir, S., Erman, H., and Erkoyun, H. (2011) Characteristics and genesis of hydrothermal kaolinite deposits within Neogene volcanites, Kutahya (Western Anatolia), Turkey. *Clays and Clay Minerals*, **59**, 250–276.

Karakaya, M.C., Karakaya, N., and Kupeli, S. (2011) Mineralogical and geochemical properties of the Na- and Ca-bentonites of Ordu (NE Turkey). *Clays and Clay Minerals*, **59**, 75–94.

Kohn, B.P. and Eyal. M. (1981) History of uplift of the crystalline basement and its relation to opening of the Red Sea as revealed by fission track dating of apatites. *Earth and Planetary Science Letters*, **52**, 129–141.

Kolata, D.R., Huff, W.D., and Bergstrom, S.M. (1996) Ordovician K-bentonites of Eastern North America. *Geological Society of America Special Paper*, **313**, 84 pp.

Kusky, T. and El Baz, F. (2000) Neotectonics and fluvial geomorphology of the northern Sinai Peninsula. *Journal of African Earth Sciences*, **31**, 213–235.

Lahr, M.M. (2010) Saharan corridors and their role in the evolutionary geography of "Out of Africa I". Pp. 27–46 in: *Out of Africa I: The First Hominin Colonization of Eurasia* (J.G. Fleagle, J.J. Shea, F.E. Grine, A.L. Baden, and R.E. Leakey, editors). Springer, Dordrecht, The Netherlands.

Lindgreen, H. and Hansen, P.L. (1991) Ordering of illite/smectite in Upper Jurassic claystones from the North Sea. *Clay Minerals*, **26**, 105–125.

Madsen, H.B., and Nornberg, P. (1995) Mineralogy of four sandy soils developed under heather, spruce and grass in the same fluvioglacial deposit in Denmark. *Geoderma*, **64**, 233–256.

Maley, J. (1996) The African rain forest – main characteristics of changes in vegetation and climate from the Upper Cretaceous to the Quaternary. *Proceedings of the Royal Society of Edinburgh*, **104**, 31–73.

Mannion, A.M. (2008) The Tertiary–Quaternary environmental history of the Mediterranean Basin – the background to Mediterranean Island environments. Pp. 15–35 in: *Mediterranean Island Landscapes: Natural and Cultural Approaches* (I.N. Vogiatzakis, G. Pungetti, and A.M. Mannion, editors). Springer, Dordrecht, The Netherlands.

Mansour, S. and Hasebe, N. (2010) Evolution and thermo-tectonic development of the basement complex, west-central Sinai, Egypt: Constraints from uranium-lead dating and apatite fission track low-temperature thermochronology. *Fission-track Newsletter*, **23**, 8–9.

McCarty, D.K., Sakharov, B.A., and Drits, V.A. (2008) Early clay diagenesis in Gulf Coast sediments: new insights from XRD profile modeling. *Clays and Clay Minerals*, **56**, 359–379.

McGuire, A.V. and Bohannon, R.G. (1989) Timing of mantle upwelling: Evidence for a passive origin for the Red Sea rift. *Journal of Geophysical Research*, **94**, 1677–1682.

Meneisy, M.Y. (1990) Vulcanicity. Pp. 157–174 in: *The Geology of Egypt* (R. Said, editor). A.A. Balkema, Rotterdam, The Netherlands.

Meshref, W.M. (1990) Tectonic framework. Pp. 113–156 in: *The Geology of Egypt* (R. Said, editor). A.A. Balkema, Rotterdam, The Netherlands.

Mess, A., Mohr, B., and Martin, T. (2001) Evolutionary transformations of hystricognath Rodentia and the climatic change in the Eocene to Late Oligocene time interval. *Mitteilungen aus dem Museum für Naturkunde in Berlin Zoologische Reihe*, **77**, 193–206.

Meunier, A. (2005) *Clays*. Springer-Verlag, Berlin, 472 pp.

Millar, I. (1993) Impact of the Eocene on the evolution of Pinusl. *Annals of the Missouri Botanical Garden*, **80**, 471–498.

Millot, G. (1970) *Geology of Clays*. Springer-Verlag, New York, 429 pp.

Montero-Serrano, J.C., Pararea-Albaladejo, J., Martin-Fernandez, J.A., Martinez-Santana, M., and Gutierrez-Martin, J.V. (2010) Sedimentary chemofacies characterization by means of multivariate analysis. *Sedimentary Geology*, **228**, 218–228.

Morgan, P. (1990) Egypt in the framework of global tectonic. Pp. 91–112 in: *The Geology of Egypt* (R. Said, editor). A.A. Balkema, Rotterdam, The Netherlands.

Murray, H.H. (2007) *Applied Clay Mineralogy: Occurrences, Processing and Applications of Kaolins, Bentonites, Palygorskite-Sepiolite, and Common Clays*. Developments in Clay Science, **2**, Elsevier, Amsterdam, 188 pp.

Nyblade, A., Park, Y., Rodgers, A., and Al-Amri, A. (2006) Seismic structure of the Arabian Shield lithosphere and Red Sea margin. *Margins Newsletter*, **17**, 13–15.

Omar, G.I., Steckler, M.S., Buck, W.R., and Kohn, B.P. (1989) Fission-track analysis of basement apatites at the western margin of the Gulf of Suez rift, Egypt: evidence for synchroneity of uplift and subsidence. *Earth and Planetary Science Letters*, **94**, 316–328.

Perrin, M., Saleh, A., and Alva-Valdivia, L. (2009) Cenozoic and Mesozoic basalts from Egypt: a preliminary survey with a view to paleointensity. *Earth Planets Space*, **61**, 51–60.

Prudencio, M.I., Sequeira Braga, M.A., Oliviera, F., Dias, M.I., Delgado, M., and Martins, M. (2006) Raw material sources for the Roman Bracarense ceramics (NW Iberian Peninsula). *Clays and Clay Minerals*, **54**, 638–649.

Rashed, M.A. (1991) Engineering-geological properties of Pliocene argillaceous sediments of the Wadi El Natrun area, Egypt. *Bulletin of the International Association of Engineering Geology*, **44**, 69–77.

Richter, A. and Schandelmeier, H. (1990) Precambrian basement inliers of Western Desert: geology, petrology and structural evolution. Pp. 185–200 in: *The Geology of Egypt* (R. Said, editor). A.A. Balkema, Rotterdam, The Netherlands.

Righi, D. and Meunier, A. (1995) Origin of clays by rock weathering and soil formation. Pp. 43–161 in: *Origin and Mineralogy of Clays: Clays and the Environment* (B. Velde, editor). Springer-Verlag, Berlin, Heidelberg.

Saad, S.I., Zaghloul, Z.M., and El Beialy, S.Y. (1987) Late Tertiary-Quaternary palynomorphs from the northern coast of the Nile Delta. *Neues Jahrbuch für Geologie und Paläontologie Monatshefte*, **5**, 314–320.

Said, R. (1981) The geological evolution of the River Nile. Spring-Verlag, New York, 151 pp.

Said, R. (1990a) Red Sea coastal plain. Pp. 345–360 in: *The Geology of Egypt* (R. Said, editor). A.A. Balkema, Rotterdam, The Netherlands.

Said, R. (1990b) Cenozoic. Pp. 451–486 in: *The Geology of Egypt* (R. Said, editor). A.A. Balkema, Rotterdam, The Netherlands.

Said, R. (1993) *The River Nile: Geology, Hydrology and Utilization*. Pergamon Press, Oxford, UK, 320 pp.

Said, R., Wendorf, F., and Schild, R. (1975) The geology and prehistory of the Nile Valley in Upper Egypt. *Archaeologia Polona*, **12**, 43–60.

Sanchez, C. and Galán, E. (1995) An approach to the genesis of palygorskite in a Neogene-Quaternary continental basin using principal factor analysis. *Clay Minerals*, **30**, 225–238.

Schulte, P., Sprong, J., Speijer, R.P., Ali, M.Y., and Krumm, S.

https://doi.org/10.1346/CCMN.2013.0610608 Published online by Cambridge University Press

(2007) Sedimentology and quantitative mineralogy of the Danian-Selandian (D-S) transition on the southern Tethyan margin in Egypt: Implications for sequence stratigraphy and eustatic sea-level changes. *Geophysical Research Abstracts*, **9**, 07338.

Schulte, P., Scheibner, C., and Speijer, R.P. (2011) Fluvial discharge and sea-level changes controlling black shale deposition during the Paleocene–Eocene thermal maximum in the Dababiya Quarry section, Egypt. *Chemical Geology*, **285**, 167–183.

Shane, P.A.R. and Froggatt, P.C. (1994) Discriminant function analysis of glass chemistry of New Zealand and North American tephra deposits. *Quaternary Research*, **41**, 70–81.

Shoval, S. (2004a) Deposition of volcanogenic smectite along the southeastern Neo-Tethys margin during the oceanic convergence stage. *Applied Clay Science*, **24**, 299–311.

Shoval, S. (2004b) Clay sedimentation along the southeastern Neo-Tethys margin during the oceanic convergence stage. *Applied Clay Science*, **24**, 287–298.

Środoń, J., Kotarba, M., Biron, A., Such, P., Clauer, N., and Wojtowicz, A. (2006) Diagenetic history of the Podhale-Orava Basin and the underlying Tatra sedimentary structural units (Western Carpathians): evidence from XRD and K-Ar of illite-smectite. *Clay Minerals*, **41**, 751–774.

Stanley, D.J. and Wingerath, J.G. (1996) Letter Section-Nile sediment dispersal altered by the Aswan High Dam – the kaolinite trace. *Marine Geology*, **133**, 1–9.

Stanley, D.J., Nir, Y., and Galili, E. (1998) Clay mineral distributions to interpret Nile Cell provenance and dispersal: III. Offshore margin between Nile Delta and northern Israel. *Journal of Coastal Research*, **14**, 196–217.

Steckler, M.S. (1985) Uplift and extension at the Gulf of Suez: Indication of induced mantle convection. *Nature*, **317**, 135–139.

Swezey, C.S. (2009) Cenozoic stratigraphy of the Sahara, northern Africa. *Journal of African Earth Sciences*, **53**, 89–121.

Talbot, M.R. and Williams, M.A.J. (2009) Cenozoic evolution of the Nile Basin. Pp. 37–60 in: *The Nile: Origin, Environments, Limnology and Human Use* (H.J. Dumont, editor). Springer, Berlin.

Tawadros, E. (2001) *Geology of Egypt and Libya*. A.A. Balkema, Rotterdam, The Netherlands, 468 pp.

Temraz, M.G.M.A. (2005) Mineralogical and geochemical studies of carbonaceous shale deposits from Egypt. PhD thesis, Technischen Universität Berlin, 124 pp.

Thurmond, A.K., Stern, R.J., Abdelsalam, M.G., Nielsen, K.C., Abdeen, M.M., and Hinz, E. (2004) The Nubian Swell. *Journal of African Earth Sciences*, **39**, 401–407.

Van Damme, D. and Van Bocxlaer, B. (2009) Freshwater molluscs of the Nile Basin, past and present. Pp. 585–629 in: *The Nile: Origin, Environments, Limnology and Human Use* (H.J. Dumont, editor). Springer, Berlin.

Velde, B. (1985) *Clay Minerals – A Physico-Chemical Explanation of their Occurrence*. Developments in Sedimentology, **40**, Elsevier, Amsterdam, 427 pp.

Velde, B. and Barré, B. (2010) *Soil, Plants, and Clay Minerals – Mineral and Biologic Interaction*. Springer-Verlag, Berlin, Heidelberg, 349 pp.

Velde, B. and Meunier, M. (2008) *The Origin of Clay Minerals in Soils and Weathered Rocks*. Springer-Verlag, Berlin, Heidelberg, 406 pp.

Velde, B., Goffe, B., and Hoellard, A. (2003) Evolution of clay minerals in a chronosequence of poldered sediments under the influence of natural pasture development. *Clays and Clay Minerals*, **51**, 205–217.

Weaver, C.E. (1989) *Clays, Muds and Shales.* Developments in Sedimentology, **44**, Elsevier, Amsterdam, 819 pp.

Woodward, J.C., Macklin, M.G., Krom, M.D., and Williams, M.A.J. (2007) The Nile – Evolution, Quaternary river environments and material fluxes. Pp. 261–292 in: *Large Rivers – Geomorphology and Management* (A. Gupta, editor). John Wiley & Sons, Chichester, UK.

(*Received 11 July 2013; revised 23 November 2013; Ms. 790; AE: S. Kadir*)

https://doi.org/10.1346/CCMN.2013.0610608 Published online by Cambridge University Press