Clay minerals of Pliocene deposits and their potential use for the purification of polluted wastewater in the Sohag area, Egypt

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Clay minerals of Pliocene deposits and their potential use for the purification of polluted wastewater in the Sohag area, Egypt.

Yasser Refaey\textsuperscript{a,b,*}, Boris Jansen\textsuperscript{a}, Abdel-Hamid El-Shater\textsuperscript{b}, Abdel-Aziz El-Haddad\textsuperscript{b}, and Karsten Kalbitz\textsuperscript{c}

\textsuperscript{a} Institute for Biodiversity and Ecosystem Dynamics (IBED), University of Amsterdam, P.O. Box 94240, 1090GE, Amsterdam, The Netherlands.

\textsuperscript{b} Geology Department, Faculty of Science, Sohag University, P.O. Box 82524, Sohag, Egypt.

\textsuperscript{c} Soil Resources and Land Use, Institute of Soil Science and Site Ecology, Faculty of Environmental Sciences, Technical University Dresden, Pienner Strasse 19, 01737 Tharandt, Germany.

\textsuperscript{*} Corresponding author e-mail address: (y.b.refaey@uva.nl).

Abstract

In our study we investigated the clay fraction composition of Pliocene clay deposits in the Sohag area, Egypt. Our goal was to obtain insights into the origin of the deposits, and to assess their potential for use in inexpensive wastewater purification. Rationale for the latter was that in Egypt both industrial wastewater and irrigation water are often polluted with heavy metals (HMs), the load of which can be significantly reduced using the Pliocene clay.

We combined physico-chemical analyses with detailed X-ray diffraction (XRD) mineralogical investigations and Specific Surface Area (SSA) measurements of samples from 16 locations in four areas containing Pliocene clay deposits. The grain size distribution of the studied samples was dominated by silt (75-89 \%) with lower quantities of clay (6-20 \%) and sand (2-15\%). Neither grain size distribution nor the distribution of individual clay minerals varied between the tested samples, suggesting they all originate from a single source area. The effect of differential cation saturation (K\textsuperscript{+} and Mg\textsuperscript{2+}) and differential heat treatments
(25°C, 300°C, and 550°C) on the XRD patterns of oriented aggregates of the clay-sized fractions revealed 4 different clay mineral groups in the tested samples. The relative abundances of the clay minerals were semi-quantified and revealed a dominance of smectite (69-91% on average) with relatively low contents of kaolinite (9-29% on average) and minor amounts of illite (1-7% on average) and chlorite (0-<1%). This mineral assemblage suggests chemical weathering and indicates warm climatic conditions of the source area during the period of deposition. The higher CEC values of the Pliocene clay deposits (32.3-65.4 cmol/kg) also pointed to the occurrence of smectite in the soils. The SSA of the Pliocene clay fractions (26.25-128.97 m²/g) correlated well with their exchangeable cation contents (K⁺ and Ca²⁺, R² = 0.96 and 1.0 respectively) and micropore volumes (R² = 1.0). Micropore volumes and SSA of the studied samples increased with the size of the exchanged cation: K⁺ > Ca²⁺ > Na⁺. The mineralogical composition suggests that Pliocene smectite-rich deposits in the studied area have great potential to be used as raw material for inexpensive, local purification of wastewater polluted with HMs.

1. Introduction

Clay materials (<2 μm size) are an important, abundant and inexpensive natural resource for many applications such as the process industries, agriculture, environmental remediation and construction (Pedro, 1994; Murray, 1999; Murray, 2000; Sanfeliu et al., 2002; Gomes & Silva, 2007). The main properties that make clay materials such an important resource are, inter alia, their high specific surface area, adsorptive capacity, rheological properties, chemical inertness and, depending on their chemical composition, absence of toxicity (Dixon and Weed, 1989; Lin et al., 2002; Carretero et al., 2006).
Given their high adsorptive capacity, a very interesting application of clay materials is as a low cost agent to remove heavy metals (HMs) from wastewaters, particularly in developing countries such as Egypt, where more sophisticated techniques are often not widely available (e.g., Srivastava et al., 1989; Ikhsan et al., 2005; Gu, et al., 2010; Refaey et al., 2014). In the Egyptian Sohag area a large reserve of Pliocene clay deposits is present. In a recent pilot study we showed that clay materials from several locations in this area offer great potential for removal of HMs from polluted waters, both in the presence and absence of naturally-occurring organic matter that might interfere with such an application (Refaey et al., 2014). A next step towards application of clay materials from the Sohag area for wastewater treatment is a thorough characterization of their clay mineral assemblage.

The clay mineral assemblage determines properties related to the retention of HMs, such as cation exchange capacity (CEC) and specific surface area (SSA), but also properties like swelling ability and plasticity that are crucial for the technical applicability of the clays in wastewater cleanup. With respect to CEC, the clay mineral composition determines the amount of permanent negative charge, and contributes to a larger or smaller extent to the amount of variable charged sites present (McBride 1994). For instance, kaolins have only a modest amount of permanent negative charge due to limited isomorphic substitution and only a modest amount of residual charge at their edges and from exposed basal hydroxyls (Grim 1968; Bolland et al., 1976; Murray, 1999). On the other hand, due to extensive isomorphic substitution, smectites and vermiculites have high permanent negative charge and thus are responsible for most of the high CECs generally found in soils (Aparicio et al., 2010). The SSA is mainly influenced by the grain size distribution, CEC, geotechnical characteristics and types and amounts of clay minerals and is considered one of the most important parameters that quantify interaction processes at the liquid-solid interface (e.g., Yukselen-Aksoy & Kaya, 2010; Heister, 2014).
Clay mineral distribution in parent material of marine origin, like in the Sohag region in Egypt, generally reflects varying climatic zones in the clastic source areas in addition to means of transport (Biscaye, 1965; Griffi et al., 1968; Rateev et al., 1969). It therefore has also been used for paleoclimatic reconstructions (Singer, 1984; Chamley, 1989). Characterization of Sohag region clay minerals therefore not only is important to assess their technical applicability in local wastewater treatment, but will also shed light on the climatic and environmental records of the sediments, yielding valuable insights in the history and genesis of the region (El-Shahat et al., 1997).

Therefore, the main objectives of this study were: (i) discriminating the Pliocene deposits from several locations in the Egyptian Sohag area on the basis of their textural and mineralogical attributes, (ii) identifying and characterizing the different clay mineral types in the context of their application in local wastewater treatment, and (iii) shedding light on the paleoclimatic conditions that prevailed during formation of the sediments and their influence on the sediment’s composition. To this end, X-ray diffraction (XRD) analyses were applied on air-dried, heated and glycerol-saturated oriented preparations with prior saturation with $K^+$ and $Mg^{2+}$.

2. Materials and methods

2.1. Area of study and sedimentary successions

The study area is presented in Fig. 1 and is referred to as the Sohag area given the central location of this town in the study area. The area is bordered from both the east and west by a higher relief Eocene limestone plateau. Fig. 1 presents a simplified geological map of the area.
The Sohag area is located at East and West Sohag governorate, Egypt, in the middle part of the Nile Valley that is situated south of Cairo (460 km), represented by the Nile basin stretch extending between 26° 19’ 87” to 26° 33’ 08” N lat; 31° 39’ 04” to 32° 03’ 62” E long. The study area comprises various sediments ranging in age from Lower Eocene to Recent (Said, 1990; Omer, 1996; Omer and Issawi, 1998; Hassan et al., 2005) as shown in Fig. 1. The studied samples were collected from The Muneiha Formation (Pliocene) deposits that are characterized by their high fine earth fraction and smectite contents.

Fig. 1. Simplified geological map of Sohag area (TEGPC and CONOCO 1987) with indication of clay mineral assemblages at each sampling area.
The Muneiha Formation forms a single lithostratigraphic unit (Omer, 1996; Omer and Issawi, 1998; Hassan et al., 2005), that is equivalent to the Madmoud Formation of Said (1981). The Muneiha Formation includes estuarine fine clastic sediments formed as a result of the rising and invasion of the Mediterranean Sea through a long gulf extending from Cairo to Aswan in the Pliocene (Issawi et al. 1978; Hassan et al., 2005). This Formation was divided into two main divisions (lower and upper members) based on its deposition environment and facies (Omer, 1996). Fig. 2 represents the deposit. The lower part is composed mainly of bedded to massive dark brown (chocolate) clay to dark grey marine clay with thin interbeds of fine sand and silt (Fig. 2). The upper part is dominated by fluvial sediments consisting of fining upward cycles. The sediments are sloped toward the cultivated flood plain covered with the younger sediments and widespread in both the surface and subsurface in the study area.

2.2. Sampling

Sixteen samples were selected from the larger suite of twenty seven soils sampled from the Muneiha formation in the Egyptian Sohag region.

The samples were collected from outcrops of this Pliocene deposit at the east and west bank of the Nile River. The Pliocene clay deposits constitute the main outcrops in the studied area. They lack diagnostic soil horizons and are capped by poorly consolidated sand, gravel, and clay of Quaternary age. The wadi deposits, including the Pliocene deposits, in the Sohag area are infertile and generally classify as Calcaric Fluvisols according to the FAO World Reference Base for Soil Resources 2006 (Jones et al., 2013).

Selection of the sixteen samples was based on analyses of grain size distribution, texture and clay mineral composition such that the samples represented a variation in physico-
chemical characteristics linked to potential use for large scale application purposes revolving around treatment of wastewater. Specifically, multiple spatially distributed samples were taken from the Al-Kwamel (KW; 5 samples), Al-Kola (KO; 3 samples), Al-Ahaywa (AH; 2 samples) and Wadi Qasab (WQ; 6 samples) areas. The samples from KW, KO, AH, and WQ were collected along the surface of vertical exposures, i.e. both artificial and natural outcrops in the field at heights of 1 to up to 10 m (see Fig. 2 for an example). The geographic distribution of the sampling sites is displayed in Fig. 1. The samples were transported from Egypt to The Netherlands in sealed plastic bags and stored at 4°C until analyzed.

Fig. 2. Outcrop field photograph of the Al-Kola area showing an alternation of Pliocene clay-rich beds with thin interbeds of fine sand and silt laminae.

2.3. Physico-chemical characteristics of the Pliocene clay deposits
The samples were first air dried, then gently crushed by means of an agate mortar and pestle to pass through a 2-mm sieve. Total carbon (TC) and total nitrogen (TN) contents in the soils were determined with a C/N analyzer (Elementar Vario EL, Hanau, Germany). The total content of Fe-oxyhydroxides was estimated as dithionite-citrate-bicarbonate extractable iron (Fe\textsubscript{d}) (AAS, Perkin Elmer, Waltham, Massachusetts, USA) using the method of Mehra and Jackson (1960) and Holmgren (1967). Mn-oxide and short-range-order (oxalate extractable) Fe- and Al-(hydr)oxide (Fe\textsubscript{o} and Al\textsubscript{o}) contents were measured using the method of Searle and Daly (1977). Field water content was determined by drying soil samples at 105°C for 24 h. The soil pH\textsubscript{H\textsubscript{2}O} was also measured (1:2.5 v/v ratio). The CEC of the soils was determined using the method of Hendershot and Duquette (1986). Major cations (Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, and K\textsuperscript{+}, and Na\textsuperscript{+}) and major anions (Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, and PO\textsubscript{4}\textsuperscript{3-}) were measured using an ICP-OES (Perkin Elmer-Optima 3000XL) and San\textsuperscript{++} Automated Wet Chemistry Analyzer-Continuous Flow Analyzer (CFA), respectively.

Before determining the grain size distribution of the studied soils, they were treated with 1 M HCl and H\textsubscript{2}O\textsubscript{2} (30%) to remove respectively carbonates and organic matter contents. Grain size distributions were determined on the basis of sieving for the coarse component (> 150 µm) and a SediGraph (model 5100 grain size analyzer) for the fine component (< 150 µm) according to Stein (1985) and Jones et al. (1988). Silt and clay fractions (< 63µm) were separated from the remaining portion by sieving. Then, the clay fraction (< 2 µm) was separated using the sedimentation-decantation technique according to Jackson (1969).

SSA measurements were performed at the Van ’t Hoff Institute for Molecular Sciences, University of Amsterdam, The Netherlands, using CO\textsubscript{2} at 273 K on Thermo Scientific Surfer instrument. CO\textsubscript{2} gas adsorption was used. Given the higher temperatures it employs as opposed to N\textsubscript{2} physisorption and it is considered more suitable for SSA determination of
sediments and soil material (e.g., Echeverría et al., 1999; Kwon & Pignatello, 2005; Eusterhues et al., 2011).

Four samples (KW-2, KO-2, W-2, and AH-2) were selected for SSA measurement from the soils sampled in the study area; representing one sample for each area. The selection was such that the samples represented a variation in physico-chemical characteristics. The SSA was calculated according to the Dubinin-Radushkevich equation (Dubinin & Radushkevich, 1947). Prior to the measurements, the samples were outgassed for at least 24 h at 200 °C in vacuum to remove adsorbed water.

2.4. Qualitative and semi-quantitative analysis of clay assemblages using XRD

2.4.1. Sample preparation for XRD analysis

The separated clay fraction was divided into two parts; the first one was saturated with K⁺ and the second one with Mg²⁺. Demineralized water and centrifugation were then used (2575 x g) to remove excess salts after saturation (Whittig, 1965). Afterwards, the samples were freeze-dried and kept for mineral identification.

To prepare oriented aggregates for XRD analysis about 25 mg from each freeze-dried clay fraction sample was added to 10 ml demineralized water in a 25 ml volume tube and mixed well ultrasonically (5 sec). The mixture was deposited gravimetrically on a porous mounting medium (ceramic tile, 37.2 mm in diameter and 6.2 mm thick) connected to a funnel under vacuum that provided the preferred orientation. After subsequent air-drying, the samples were ready for XRD analysis. For each sample, five X-ray diffractograms were taken; Mg-saturated samples were X-rayed in the air-dried and glycerol solvated states. The K-
saturated samples were X-rayed after air drying and heating to 300 and 550 °C for 2 h (Bouchet et al., 1988).

2.4.2. XRD analysis

XRD analysis was performed at the Van der Waals-Zeeman Institute, University of Amsterdam, The Netherlands, using a Philips (now PANalytical) PW 1830 instrument, with a Philips PW 3710 control unit (Cu Kα radiation with wavelength 1.54056 Å produced at 50 mA and 40 kV). Minerals were identified by characteristic reflections as discussed in Brindley and Brown (1980) and Moore and Reynolds (1997). The relative percentages (semi-quantitative) of clay minerals were determined using empirically estimated weighting factors of Biscaye (Biscaye, 1965). The low chlorite and illite contents in studied samples were estimated from the relative peak height (Johns et al., 1954) because they could not to be detected in the glycerol solvated states.

3. Results

3.1. Physico-chemical properties of Pliocene clay deposits

Field observations showed that the Pliocene sediments have slickensides and desiccated under formation of deep cracks in a roughly polygonal structure (Fig. 3a; b; c).
Fig. 3. a) Pliocene deposits upon swelling and shrinking in wet and dry conditions display slickenlines on slickensides (polished and striated) (WQ area), b) deep wide cracks forming wedge-shaped or parallel-sided aggregates (KO area), and c) polygonal patterns (AH area).

The studied samples had large CECs ranging from 32.3-65.4 cmol/kg (Table 1). The CEC, water content of air-dried samples and amount of clay fraction were strongly correlated (both $R^2 = 0.75$). Crystalline iron-oxide contents were small to moderate (3.7-17.6 g kg$^{-1}$), while soil organic carbon (SOC) contents were low in all samples (0-5.35 g kg$^{-1}$; Table 1).

The pH was always slightly basic (Table 1). Na$^+$ was the dominant exchangeable cation with the highest abundance of Na$^+$ in sediments sampled from the KW area, while Ca$^{2+}$, Mg$^{2+}$ and K$^+$ provided minor contributions (Table 1).

<table>
<thead>
<tr>
<th>pH</th>
<th>EC</th>
<th>H$_2$O</th>
<th>CEC</th>
<th>SOC</th>
<th>CBD ext.</th>
<th>Oxalate ext.</th>
<th>Major cations</th>
<th>Major anions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>µS cm$^{-1}$</td>
<td>%</td>
<td>cmol kg$^{-1}$</td>
<td>Fe-oxide</td>
<td>MnO$_2$</td>
<td>Na$^+$</td>
<td>Ca$^{2+}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>g kg$^{-1}$</td>
<td></td>
<td>g kg$^{-1}$</td>
<td>g kg$^{-1}$</td>
<td>g kg$^{-1}$</td>
<td>g L$^{-1}$</td>
<td>g L$^{-1}$</td>
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<td>Samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>KW-1</td>
<td>7.38</td>
<td>9.9</td>
<td>8.40</td>
<td>60.48</td>
<td>0.43</td>
<td>17.13</td>
<td>31.54</td>
<td>5.34</td>
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<tr>
<td>KW-2</td>
<td>7.53</td>
<td>8.8</td>
<td>8.88</td>
<td>64.23</td>
<td>0.28</td>
<td>18.63</td>
<td>35.08</td>
<td>5.44</td>
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<td>KW-3</td>
<td>7.80</td>
<td>14.5</td>
<td>6.90</td>
<td>43.21</td>
<td>0.21</td>
<td>17.42</td>
<td>35.90</td>
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<td>KW-4</td>
<td>8.21</td>
<td>3.1</td>
<td>4.02</td>
<td>32.28</td>
<td>5.35</td>
<td>3.67</td>
<td>5.64</td>
<td>1.48</td>
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<td>KW-5</td>
<td>7.81</td>
<td>5.9</td>
<td>7.58</td>
<td>51.38</td>
<td>0.36</td>
<td>5.12</td>
<td>3.59</td>
<td>2.77</td>
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<tr>
<td>KO-1</td>
<td>7.77</td>
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<td>8.43</td>
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<td>17.64</td>
<td>23.30</td>
<td>1.22</td>
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<td>KO-2</td>
<td>7.61</td>
<td>5.0</td>
<td>10.86</td>
<td>60.36</td>
<td>1.72</td>
<td>9.69</td>
<td>13.05</td>
<td>2.09</td>
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<td>7.20</td>
<td>7.9</td>
<td>9.99</td>
<td>51.26</td>
<td>0.69</td>
<td>14.34</td>
<td>17.06</td>
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<td>WQ-1</td>
<td>7.50</td>
<td>5.8</td>
<td>9.44</td>
<td>58.76</td>
<td>1.24</td>
<td>17.46</td>
<td>12.12</td>
<td>2.41</td>
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<td>9.3</td>
<td>9.44</td>
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<td>0.41</td>
<td>16.05</td>
<td>5.07</td>
<td>1.51</td>
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<tr>
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<td>4.1</td>
<td>7.47</td>
<td>50.09</td>
<td>0.00</td>
<td>4.49</td>
<td>70.51</td>
<td>1.28</td>
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<td>8.90</td>
<td>55.40</td>
<td>0.30</td>
<td>11.54</td>
<td>51.66</td>
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<td>AH-1</td>
<td>7.73</td>
<td>7.5</td>
<td>7.96</td>
<td>55.36</td>
<td>0.85</td>
<td>10.63</td>
<td>20.96</td>
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</tr>
<tr>
<td>AH-2</td>
<td>8.07</td>
<td>3.9</td>
<td>8.22</td>
<td>59.07</td>
<td>0.80</td>
<td>9.18</td>
<td>10.75</td>
<td>2.09</td>
</tr>
</tbody>
</table>

# CBD ext. (Citrate Bicarbonate Dithionite extraction).
3.2. Grain size distribution

Table 2 presents the grain size distribution, i.e. percentages of clay, silt and sand in the various samples. The silt content along the study area did not vary greatly in the studied samples (Table 2). The silt fraction dominated over the other fractions in all studied samples (75-89%); the clay fraction varied from 6 to 20% and the sand content fluctuated between 2 and 15% (Table 2). As a result, the grain size distribution of all studied samples classified as silt.

Table 2. Grain size distribution (% of total mass) of the studied samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Depths</th>
<th>Clays</th>
<th>V. F. silt</th>
<th>F. silt</th>
<th>M. silt</th>
<th>C. silt</th>
<th>V. C. silt</th>
<th>V. F. sand</th>
<th>F. sand</th>
<th>C. sand</th>
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<tbody>
<tr>
<td></td>
<td>µm</td>
<td>&lt; 2</td>
<td>2-4</td>
<td>4-8</td>
<td>8-16</td>
<td>16-31</td>
<td>31-63</td>
<td>63-125</td>
<td>125-250</td>
<td>500-1000</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KW-1</td>
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<td>5.4</td>
<td>7.2</td>
<td>12.2</td>
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<td>32.7</td>
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<td>10.9</td>
<td>14.8</td>
<td>18.5</td>
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<tr>
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<tr>
<td>KO-1</td>
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<td>7.2</td>
<td>6.5</td>
<td>9.3</td>
<td>15.8</td>
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<td>14.8</td>
<td>17.8</td>
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<td>17.3</td>
<td>8.4</td>
<td>1.1</td>
<td>0.0</td>
<td>2.2</td>
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# V.F. = Very fine; F. = Fine; M. = Medium; C. = Coarse; V.C. = Very coarse.

3.3. Clay mineral composition

3.3.1. Smectite
The XRD patterns of Mg- and K-saturated clay fraction patterns confirmed that smectite is present (Fig. 4). The basal spacing of smectite (001) in Mg-saturated expanded from ~16 Å to ~18 Å after the glycerol solvation treatment. Upon treatment with K+, the ~16 Å of smectite contracted to ~12.5 Å at room temperature (25°C), slightly collapsed to ~12 Å following heating to 300°C, and highly collapsed to ~11 Å at 550°C (Fig. 4).

Fig. 4. Selected XRD patterns of oriented mounts of the < 2 µm size soil fraction in the KW (a), KO (b), WQ (c), and AH (d) areas. Lower panels (Green & blue): Mg-saturated slides in air-dried state (Mg-AD) and after glycerol solvation (Mg-GI). Upper panels (violet, brown, and red): K-saturated slides in air-dried state (K-AD) after thermal treatment (K-300°C & K-500°C). S: smectite; K: kaolinite; I: illite; Q: quartz; C: chlorite; F: Fe-oxide

Second-, third-, and fourth-order basal reflections were identified in the XRD patterns of the untreated and glycerol solvation treated samples. Only the first-, second-, and third-order reflections were present in the heated samples (Fig. 4). The absence of reflection in the
glycerol solvated samples (Mg-Gl-treatments) between 6 and 9°2θ (Fig. 4), confirm that in all samples smectite was well crystallized and did not contain interlayers of illite (Raigemborn et al., 2014).

The correlation between CEC vs. water content ($R^2 = 0.75$) and CEC vs. amount of clay fraction ($R^2 = 0.75$) in the studied samples (Tables 1 and 2) confirms once again the predominance of smectite clays and strongly influences the ability of the smectite-rich sediments to retain water in interlayer sites (e.g., Henry, 1997; Eisenhour & Brown, 2009).

$Na^+$ was the dominant exchangeable cation in all studied samples (Refaey et al., 2014) and this indicates that the type of smectite is Na-smectite (Weaver, 1956; Murray, 1999). Furthermore, the Na/Ca ratio of tested samples in the KW (3.4-16.5), KO (2.1-3.1), WQ (1.5-4.9), and AH (7.5-16) sites revealed a high expanding capacity of the Pliocene sediments (Karakaya et al., 2011). The alternate swelling and shrinking of expanding smectite clays in the study area resulted in deep cracks, slickensides and wedge-shaped structural elements (Fig. 3a, b) during the dry season (Gray & Nickelsen, 1989; Youssef, 2008; Ismaiel, 2013). The large content of $Na^+$ over $Ca^{2+}$ and $Mg^{2+}$ cations in the studied sediments which occupy most of the wadi terraces and part of the wadi floors in the low desert zone of the study area probably was responsible for swelling and cracking in the foundations in the new planning area (Mitchell, 1976; Youssef, 2008).

### 3.3.2. Kaolinite

Reflection peaks of kaolinite at ~7.15 Å and ~3.57 Å remained unchanged when the samples were subjected to solvation with glycerol (Mg-saturated) and upon heating to 300 °C but they disappeared upon heating to 550 °C (K-saturated) as a result of the destruction of the
structure. Such behavior is characteristic of kaolinite (Moore and Reynolds, 1997; Refaey et al., 2008; Hong et al., 2012; Tsao et al., 2013).

Kaolinite in the WQ and AH areas displayed narrow and sharp peaks (Fig. 4c, d), indicating that it was highly crystalline (Brindley and Brown, 1980). Less narrow but well-defined peaks (Fig. 4a, b) were also present at infrequent levels in the KW and KO areas, suggesting a slightly poorer degree of crystallinity (Arslan & Aslan, 2006).

3.3.3. Illite and chlorite

Illite and chlorite were scarce or absent in most of the studied samples. The presence of illite was confirmed in the current study by reflection peaks at 10.13, 4.53, and 3.33 Å d-spacing, which remained unchanged when the samples were subjected to heating treatments (300 °C and 500 °C). Furthermore, the 3.33 Å (003) reflection of illite was developed with quartz (010). The K⁺ content in all tested soil samples was the lowest among all exchangeable cations, which is in line with the scarcity of illite as a mineral constituent of the clay fractions (Hower and Mowatt, 1966; Inoue and Utada; 1983; Brusewitz, 1986; Velde, 1986; Refaey et al., 2014).

Chlorite minerals were detected only in the WQ and AH areas as a very weak peak appeared in the position of the kaolinite peak after heating treatment to 550°C (Fig. 4c). Also, a weak peak was recognized as a shoulder at 3.46 Å that showed no change upon glycerol solvation and heating to 550°C (Fig. 4c).

3.3.4. Non-clay minerals
Non-clay minerals such as quartz and hematite were recognized as weak reflection peaks at 4.21 and 2.69 Å d-spacing respectively, indicating that only trace amounts of non-clay minerals were present. To exclude the possibility of the quartz peaks having originated from the ceramic tile itself, we compared X-ray analyses of the tile with and without sample material present. None of the characteristic peaks found for the empty tiles (results not shown) appeared in the analyses when sample material was present.

3.4. Qualitative and semi-quantitative description of experimental XRD patterns

The intensity of the clay mineral peaks changed notably in the different sampled areas, indicating variations in relative proportions of clay species of the studied samples (Fig. 4). On the one hand, in all studied samples smectite had the highest, sharpest and most symmetrical peaks (001 reflection) indicating predominance of smectite over the other clay minerals in the assemblage. On the other hand, the illite and chlorite mineral groups, as well as the non-clay minerals such as quartz and Fe-oxide (hematite/goethite), were present as weak peaks indicating trace amounts (Fig. 4). There was no indication of the presence of any regularly stratified mixed-layer clay. Therefore, all expandable clay is treated here as highly expandable smectite.

The clay mineral assemblages of the Pliocene clay deposits showed an overall similar composition with smectite as the most abundant class, followed by moderate amounts of kaolinite and scarce amounts of illite and chlorite (1-7% and < 1% abundance respectively) (Table 3). Therefore, representative XRD patterns were selected to illustrate clay mineral assemblages with different treatments as shown in Fig. 4. The average of the smectite content as determined by the Biscay method (Biscay, 1965) and the peak intensity methods (Johns et al., 1954) in the KW, KO, WQ, and AH areas was 91, 80, 74, and 69 %, whereas the
The proportion of kaolinite equaled 9, 18, 24, and 29 %, respectively (Table 3). The smectite proportional percentages in all studied areas increased in the order KW > KO > WQ > AH.

Table 3. Relative clay mineral abundance in the clay fraction of sediment samples (method according to Johns et al., 1954) and Biscay (1965)).

<table>
<thead>
<tr>
<th>Method</th>
<th>Peak height method (Johns et al., 1954)</th>
<th>Biscay’s method (1965)</th>
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<tr>
<td>Samples</td>
<td>Clay fraction</td>
<td>Smectite</td>
</tr>
<tr>
<td></td>
<td>mg g⁻¹</td>
<td>Rel. %</td>
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<tr>
<td>KW-1</td>
<td>92</td>
<td>94</td>
</tr>
<tr>
<td>KW-2</td>
<td>176</td>
<td>87</td>
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<tr>
<td>KW-3</td>
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<td>AH-2</td>
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# Rel. % = relatively peak height % of each clay mineral; Wt. % = relative weight percentages of each clay mineral.

3.5. The SSA of the clay fraction

The SSAs in the representative samples of KW-2, KO-2, W-2, and AH-2 were 34.0, 47.8, 129.0, and 26.2 m²/g respectively, whereas the micropore volumes were 6.02, 8.48, 22.86 and 4.65 cm³/g respectively. The results show SSA to be related to the type of exchangeable cations, in the following order: K⁺ > Ca²⁺ > Na⁺. In all samples, strong correlations were observed of the SSA with the amount of K⁺ (R² = 0.96), Ca²⁺ (R² = 1.0), and micropore volumes (R² = 1.0).

4. Discussion

4.1. Origin and genesis of clay minerals
The grain size distribution and clay mineral assemblage in the Sohag area can give an important first idea about the palaeoclimate conditions and weathering processes at the source area (Velde & Meunier 2008; Agha et al., 2013). The fact that the grain size distribution of the studied samples exhibited no large variation in sand, silt, and clay fraction contents nor distribution of individual clay minerals suggests that the sediments derived from one source area. Moreover, the high amounts of silt in comparison to sand in all studied samples (Table 2) suggest that the sediments were deposited from suspension and were formed under uniform conditions of slow moving water (Ghandour et al., 2004).

During the Pliocene, East Africa was characterized by seasonal, arid and warm environments (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 (e.g., Griffin, 2002; Swezey, 2009; Talbot & Williams, 2009; Agha et al., 2013). A study by El-Shahat et al. (1997) of Pliocene sediment from the North western desert, Egypt, indicates an initial provenance of metamorphic and acidic igneous rocks from the Red Sea highlands. The weathered regolith of the Red Sea basement rocks must have been eroded by several tributaries that fed a master stream (Paleo-Nile) during the late Pliocene pluvial (Said, 1981; El-Shahat et al., 1997). The genesis of smectite is favored by dry seasons alternating with less pronounced wet seasons (Singer, 1984), poorly drained environments (Schaetzl & Anderson, 2005) as well as low-lying topography such as in marine environments (Odoma et al., 2013). All these features, in particular the dominance of smectite, also indicative of chemical weathering (Raigemborn et al., 2014), are present in the study area. This suggests the Pliocene deposits in the Sohag region were deposited in a marine environment under arid to semi-arid climatic conditions (Salman et al., 2013), in particular in a warm climate with alternating pronounced dry and less pronounced wet seasons (Lewis & Berry, 1988;
In general, the presence of abundant smectite in the studied area is generally linked to a transgression of the sea in the Pliocene (Tantawy et al., 2001).

In addition, the presence of kaolinite as second abundant clay mineral is indicative of chemical weathering of acidic igneous and metamorphic rocks or their detrital weathering products under tropical to subtropical humid climatic conditions (Hendriks, 1985; Marzouk, 1985; Chamley, 1989; Refaey et al., 2008). The lower abundance of kaolinite relative to smectite in the present study, especially in the KW area (West bank of Nile River; Fig. 1), situated at lower altitude than the other sampling sites (East bank of Nile River), further confirms the earlier mentioned deposition from suspension as a primary sedimentation mechanism. Kaolinite tends to concentrate in relatively near-shore shallow water settings, in line with its tendency to flocculate as coarser grains than smectite that tends to settle as finer particles in deeper offshore settings (Raucsik & Merenyi, 2000; Thiry, 2000).

The absence of mixed layer minerals (Illite-smectite) implies that the origin of clay minerals in the Pliocene deposits is of detrital origin where there is no evidence for the influence of burial diagenesis which lead to conversion of smectite to illite (Hoffman & Hower, 1979; Chamley, 1989; Ghandour et al., 2004). Furthermore, it is implausible that the clay mineral assemblages in the studied area originated from deep burial diagenetic alteration due to the lower overburden thicknesses in the studied area (Agha et al., 2013). Nor was any evidence for hydrothermal alteration observed during field sampling.

4.2. Implications for HM retention

It is well known that smectites have higher CEC values than kaolinites (e.g., Babel & Kurniawan, 2003; Aparicio et al., 2010; Hong et al., 2012). In the KW and KO areas, soil
KW-2 and soil KO-2 had the highest CEC values in line with their having the largest clay fraction and highest proportion of smectite compared to kaolinite (Table 1, 2). However, in the WQ and AH areas, soil WQ-2 and soil AH-2 had the highest CEC values (Table 1) in spite of the fact that they did not have the largest absolute clay content of the samples from the area (Table 2). Therefore, in the KW and KO areas, in contrast to the WQ and AH areas, it is the clay mineralogical composition rather than the absolute amount of clay that determined the CEC. This observation is in line with the results from other studies and is linked to the previously mentioned large difference in CEC between smectites and kaolins, which in soils with appreciable kaolinite contents overrides absolute amounts of clay minerals as dominant factor (e.g., Rice et al., 1985; Youssef, 2008; Parfitta et al., 2008; Usman, 2008). As a result of these differences in CEC, although our previous study showed the capacity for HM (Cu, Ni and Zn) adsorption was high in all soils, a higher affinity was found in the soils from the KW and KO than from the WQ and AH areas (Refaey et al., 2014).

The measured SSA values (26.25-128.97 m²/g) of the Pliocene clay fraction all fell within the normal range (33-130 m²/g) for pure Na⁺, K⁺, Ca²⁺, and Mg²⁺-smectite as determined by gas adsorption (Volzone & Ortiga, 2004; Kaufhold et al., 2010). Compared with the KW-2, KO-2, and AH-2 samples, the WQ-2 sample showed a significantly higher SSA and micropores volume in line with its higher K⁺ and Ca²⁺ contents (Volzone & Ortiga, 2004, Ayari, et al., 2007). This can be explained by the fact that the ionic radius of the exchangeable cations has a strong effect on the CO₂ gas adsorption and consequently on the value of SSA in the interlayer positions of this sample (Rutherford et al., 1997; Volzone & Ortiga, 2004). Also in line with previous findings, the measured SSAs and micropore volumes of our samples both decreased in the following sequence: K-clay > Ca-clay >> Na-clay (e.g., Rutherford et al. 1997; Volzone & Ortiga, 2004; Afsin et al., 2009). The large
primary surfaces of the investigated clays explain the previously observed large adsorption capacity of the deposits in the study area for the Cu, Ni, and Zn (Refaey et al., 2014).

4.3. Application in the region

Pliocene smectite-rich deposits in the studied area can be used as a potential raw material for purification of wastewater from toxic HMs because of their very fine particle size and physical and chemical properties, including SSA, that are related to their clay mineralogical composition. Particularly for the Sohag region, discharge of large amounts of wastewater (sewage) used as irrigation water for wood production as well as the use of high amounts of fertilizers in new reclamation areas causes infiltration and accumulation of many pollutants to ground water reservoirs, including HMs (Ayman & Mohamed, 2011). The Pliocene clay deposits in the study area might be used to reduce the load of HMs as well as organic pollutants from such sources. Furthermore, crude water purification using Pliocene clay deposits may extend the applicability of the treated water from wood production alone to include the irrigation of crops (Rashed & Soltan, 2002).

In addition to potential use in regional wastewater (pre)treatment, the studied Pliocene deposits could be utilized as liners (barrier) in landfills to control the seepage of HM containing leachate into the surrounding environment (Abollino et al., 2003; Talaat et al., 2011), a particular problem in the desert areas of the Sohag region. The suitability of soil material as liners relates to its particle size distribution, Atterberg limits, swelling potential, CEC and hydraulic conductivity (Taha & Kabir, 2005). Specifically for landfill liners, preferred value ranges for such parameters that have been specified in the literature include: percentage of clay (< 2µm) ≥ 20, percentage of fines (< 75 µm) ≥ 50%, CEC ≥ 10 meq/100g , plasticity index (PI) ≥ 12%, activity ≥ 0.3 (Rowe et al., 1995; Daniel 1998; Taha & Kabir,
The studied Pliocene clay deposits from the Sohag area contain clay percentages between 8-20% and percentages of fines between 81-98% (Table 1). In particular the more clay rich samples (i.e. locations KO, WQ and AH) thereby come close to the mentioned preferred values with respect to clay percentages, while always exceeding the threshold values for the percentage of fines. Moreover, a study by Youssef (2008) of the Pliocene deposits in the studied area revealed that these deposits had the following Atterberg limits: liquid limit (LL)=44-62%, plastic limit (PL)=26-38%, plasticity index (PI)=14-36% and activity (AC)=0.41-0.72. These index properties fall within the mentioned preferred value range and are indicative of a high shrinkage limit that will result in little volume change of the material when used as landfill liners (Taha & Kabir, 2005). Note that the high AC value of the studied Pliocene deposits is indicative of the low hydraulic conductivity as well as of the high SSA of the clay fraction (Benson et al., 1994; Taha & Kabir, 2005). In addition, the high CEC and SSA values of Pliocene deposits will result in a greater amount of inorganic contaminants being removed from the leachate when used as liner or in water treatment (Kayabali 1997; Taha & Kabir, 2005). Altogether this makes that the studied clay deposits, in particular the ones with the higher clay percentages, seem well suited for regional application as cheap landfill lining. Our present study can serve as a foundation on which to build further explorations into such regional applications.

In general, the present work supports the potential of the studied sediments as a natural and inexpensive material for removing toxic HMs that was tentatively established in our previous study (Refaey et al., 2014), and established the underlying mechanisms of such applications. Specifically, Originally, we recommended materials from the KW area for treatment of wastewater rich in HMs such as Zn and Ni, as they showed a high affinity for these materials. On the other hand, we proposed clay-rich materials from the KO, WQ and AH areas to be most effective in the treatment of wastewater rich only in Cu (Refaey et al.,
2014) which is known to form strong inner-sphere complexes with surface of Fe-(hydro)oxides in sediments even when the smectite content is less. However, the new information obtained from the present study shows that, given the significantly higher SSA and microporosity of the WQ-2 sample, material from this area warrants extra research attention to be used as starting point for further exploration in waste water treatment, not only for HM removal but possibly also for toxic gas adsorption (Volzone, 2007).

5. Conclusions

The grain size distribution of the studied samples was dominated by silts (75-89 %) with lower quantities of clays (6-20 %) and sands (2-15%). XRD analysis demonstrated that the clay mineral composition of the Pliocene clay deposits studied was composed almost exclusively of smectites and kaolinite, with the former always being the most abundant class of clay minerals. The presence of a large amount of smectite in association with a low quantity of kaolinite minerals in our study suggests an origin from chemical weathering conditions under warm and semi-arid conditions. Furthermore, the absence of mixed layer clays confirmed that the tested sediments were derived from transported weathered materials. The physico-chemical properties of the studied sediments as well as the type and amount of smectites indicate that they have a high capacity to immobilize large amount of dissolved HMs. The present study has shown that there are strong relationships between the SSA and soil chemical properties such as exchangeable cations where $K^+$ and $Ca^{2+}$-rich clay fraction tends to have higher SSA and micropore volume values. This makes the studied sediments potentially useful in high-value-added markets, e.g., as environmentally friendly and inexpensive raw material for waste water treatment. To further examine such application, additional research should focus on unraveling the mechanisms of such interactions,
specifically in quasi-realistic operational and field settings such as in column experiments. Particularly interesting is the exploration of the material from the WQ area giving its significantly higher SSA and microporosity than material from the other areas.

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