Influence of early diagenesis on geotechnical properties of clay sediments (Romania, Black Sea)

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Abstract :

The geotechnical properties of clay sediments were investigated using laboratory and in-situ measurements as part of the geohazard assessment in the Romanian sector of the Black Sea affected by landslides and seafloor deformation features. The sediments were characterized as predominantly high plastic silty clay of high compressibility, low undrained shear strength, low cohesion and moderate sensitivity. A shallow increase in shear strength exceeding the general trend could have been reconciled with evidence for the precipitation of iron sulfides and calcium carbonates related to early diagenetic reactions of sulfate reduction (e.g. cryptic sulfur cycle) and anaerobic oxidation of methane. Comparison of the compression behaviour of natural and reconstituted samples indicated that precipitation of these materials at particle contacts produced cementation. The analysis of deeper sediments sharing similar geochemical properties illustrated that the early precipitation of even low quantity of sulfur and carbonate cements allowed clays to develop sufficient strength to preserve an abnormal high water content even under tens of meters burial depth. Because this cementation process was observed to be associated with an enhanced sensitivity and a strain softening response to undrained shearing it was concluded that such early diagenesis should be considered as a key environmental factor, leading to weak layer formation that may influence the susceptibility of seafloor to failure.

Highlights

► Sulfide and carbonate cements induced by early diagenetic reactions (AOM, SR). ► Structured clay materials with high water content and shear strength ► Sediments with metastable structure and slight sensitivity ► Early diagenesis considered as a key factor in the seafloor instability hazard control.

Keywords : Lacustrine clay sediment, Structured material, Sulfur cement, Carbonate cement, Early diagenesis, Weak layer

Notation

AOM

Anaerobic Oxidation of Methane

c'

effective cohesion

C_c

compression index

C_c^*

compression index of remoulded material

C_v

consolidation coefficient

e

void ratio

e_{100}^*

void ratio of remoulded material at 100 kPa

f_s

sleeve friction

ICL

Intrinsic Compression Line

I_v

void index = $(e - e_{100}^*)/C_c^*$

K

hydraulic conductivity

K_0

coefficient of earth pressure at rest

p'

effective mean stress = $(\sigma_1 + 2 \sigma_3)/3 - u$

Nkt

cone factor

PI

plasticity index = $w_L - w_p$

q

deviatoric stress = $\sigma_1 - \sigma_3$

q_c

tip resistance

q_t
corrected tip resistance

SCL
sedimentation compression line

SR
sulfate reduction

Su_{peak}
peak undrained shear strength

Su_{res}
residual undrained shear strength

St
Sensitivity

TOC
total organic carbon

u
pore pressure

YSR
yield stress ratio = σ'_p / σ'_v

w
water content

w_l
liquid limit

w_p
plastic limit

Δu_2
penetration-induced pore pressure

ε_a
axial strain

φ'
effective friction angle

σ'_{v0}
in-situ vertical effective stress

σ'^{yield}
yield stress

1. Introduction

Coastal and offshore areas are subjected to increasing urban development in response to the increasing worldwide population (Pelling and Blackburn, 2014), exploitation of hydrocarbons (the example of Black Sea in Georgiev, 2012) or development of renewable energy (Pérez-Collazo et al., 2015). In such environments, sediment deposits could be extremely heterogeneous in composition and architecture (Holland and Elmore, 2008). A sound understanding of the mechanical behaviour of these soils is thus necessary for human structures founded on it, such as traffic infrastructures, oil rigs, wing-turbines or any

urban planning (Suganya and Sivapullaiah, 2016). It is also of first importance in the prevision of submarine landslides which are mainly controlled by the geotechnical properties of the sedimentary column and the presence of favourable weak layers (Volpi et al., 2003; Sultan et al., 2004; Locat et al., 2014; Zhou et al., 2017).

It is widely accepted that the soil structure controls its mechanical behaviour (Cotecchia and Chandler, 2000; Mitchell and Soga, 2005). This structure is subject to a variety of physical and chemical phenomena (Boudreau et al., 2014) and reflects all facets of soil solid and fluid composition, history, present state, and environmental influences. The factors controlling the soil structure and evolution upon burial are complex and generally not constrained, especially in surficial aquatic sediments inducing several geotechnical engineering problems (D'Ignazio et al., 2007; Horpibulsuk et al., 2013). For example, changes in environmental conditions can result in significant changes in sediment structures and properties through their influence on temperature, chemical reactions and transport of large variety of chemical and mineralogical species (Mitchell and Soga, 2005). This has long been recognised as a major factor underlying the evolution of sediments upon deep burial in depositional basins (Skempton, 1969; Bjørlykke and Høeg, 1997; Nygård et al., 2004; Chandler, 2010; Dewhurst et al., 2015; Favero et al., 2016). Comparatively little is known about the mechanical consequences of early diagenetic reactions involving sulfur species (solid sulfur, sulfate, sulfide) and carbonate or phosphate precipitation.

Reactions in cryptic sulfur cycle, including the sulfate reduction (SR) coupled with anaerobic oxidation of methane (AOM) or organic matter degradation, are well-known early diagenetic processes by which sulfides can precipitate in the sedimentary column (Barnes and Goldberg, 1976; Wakeham et al., 1995; Boetius et al., 2000; Neretin et al., 2004; Egger et al., 2016). These reactions are identified under various environmental conditions such as those encountered in coastal, estuarine, or lacustrine environments (Bottrell et al., 1998; Holmer and Storkholm, 2001; Tudryn et al., 2014). This process and its preservation upon burial depend on the availability of each species involved in the reaction (organic matter or

methane, sulfate and iron oxide) and the reaction pathways (bacteria, Treude et al. (2005)) which themselves depend on various factors such as the mineralogical composition of sediments, the rate of deposition (sediment, organic matter), the chemistry of pore fluids, fluid flow events or other processes occurring in the water column (Won and Chang, 2007). The products of the reactions are involved in other precipitation processes such as carbonate and pyrite (Hendry, 1993; Greinert and Derkachev, 2004; Rajasekaran, 2005, Wright and Wacey, 2005), which can also affect the geotechnical behaviour of sediments (Bozzano et al., 1999; Rajasekaran, 2006; Won and Chang, 2007). A better characterization of the influence of early diagenesis on the properties of surficial aquatic sediments and their evolution upon burial thus appears fundamental to geotechnical engineering dealing with urban project and geohazard management. This study combines the results of geotechnical investigations with those of sedimentological and geochemical analyses to identify and characterize how early diagenesis affects the mechanical behaviours of lacustrine sediments and its evolution upon burial.

2. Geologic setting

The study site is located in the Romanian sector of the Black Sea, North-East of the Danube canyon (Fig. 1). It extends from the shelf edge (160-170 m of water depth) to the deep-sea (around 1600 m) where thick deposits of mostly clayey sediments were mainly supplied by the Danube and Dniepr Rivers (Soulet et al., 2013; Matenco et al., 2016). The present-day seafloor morphology is marked by the presence of several submarine canyons, landslides scars and deformation features (Riboulot et al., 2017). The area is also characterized by a well-developed fluid flow system inferred by the presence of pockmarks (i.e. craters in the seabed caused by focussed fluid flow, (King and MacLean, 1970), gas seeps and gas hydrates (Popescu et al., 2007; Riboulot et al., 2017) (Fig. 1). This study site has been submitted to large changes in environmental conditions as a function of the global ocean level fluctuations and the induced connection-disconnection of the Marmara-Mediterranean Sea during last glacial-interglacial cycles (Soulet et al., 2011; Constantinescu et al., 2015; Wegwerth et al., 2015). These fluctuations have led to: (1) Alternating freshwater lake and marine conditions (Badertscher et al., 2011). (2) Connection-

disconnection between the Danube-Dniepr Rivers, the canyons and the deep-sea deposit system (Lericolais et al., 2009; Constantinescu et al., 2015). (3) Alternating oxic-anoxic conditions in the water column (Soulet et al., 2011). (4) Development of early diagenetic reactions including sulfate reduction, anaerobic oxidation of methane, precipitation of sulfides and dissolution-precipitation of carbonates (Wakeham et al., 1995; Jørgensen et al., 2004; Egger et al., 2016). These specificities make this site favourable for the analysis of early diagenesis and its influence on the geotechnical properties of sediments which appears necessary to constrain seafloor stability and establish their link with the environmental conditions and the fluid flow system.

Most of the sediments analysed in this study correspond to the lacustrine or limnic deposits which were described as massive to coarsely banded calcareous clays formed during the last glacial period (Unit III in Dean and Arthur (2011)). These sediments are overlain by organic-rich sapropel and coccolith-rich layers (Unit II and I respectively) deposited under marine conditions (Hay et al., 1991; Constantinescu et al., 2015). Because Units I and II form very fine levels (few centimeters), we concentrated our analysis on the properties of the lacustrine sediments of the unit III.

3. Material and methods

This study uses eight piston cores (called Calypso) recovered from 547 to 1623 m below sea level during the GHASS oceanographic cruise on the *R/V Pourquoi Pas?* (see Table 1 for detailed characteristics of these cores and Fig. 1 for their location). We selected the sediment cores GAS-CS03 and GAS-CS17 as key to illustrate the variability of material properties. However, to complete the picture of this variability, data from other cores have been integrated.

3.1. Onboard analyses

Each core was cut in one-meter long sections before being sealed and transported to the shipboard laboratory at 4°C for pore water extraction at a sampling interval of 40 cm. This was achieved by drilling

small holes along core liners to place Rhizon samplers (Seeberg-Elverfeldt et al., 2005; Ruffine et al., 2013) connected to 10 mL syringes for water collection. The concentrations of chloride, sulfate and dissolved methane in sampled pore waters were determined using an ion chromatograph 861 Advanced Compact IC from Metrohm with an accuracy of 3%.

Two-dimensional X-ray scans and bulk density measurements were also undertaken onboard using a GEOTEK MSCL-XCT system. This allowed to select and preserve samples for oedometer and triaxial tests. Core sections were otherwise split in two halves: one half for visual analyses and the other for vane shear testing and water content determination.

3.2. Laboratory analyses

Once ashore a series of classification, mechanical and chemical tests were conducted on preserved samples. Sediments were also subsampled from split core sections to perform additional classification and chemical tests.

3.2.1. Classification tests

Tests were performed to determine the water content, consistency limits and indices as well as the particle size distribution of sediments. Because the water content is higher or close to the liquid limit, we used the fall cone method described by Koumoto and Houlsby (2001) on samples that were left naturally drying in five successive stages to obtain consistency limits. The particle size distribution was determined using a Malvern Mastersizer 3000 laser granulometer.

3.2.2. Oedometer and hydraulic conductivity tests

Twenty five specimens of intact sediment were placed in 50 mm diameter oedometers and incrementally-loaded to determine their consolidation coefficient (C_v), compression index (C_c), vertical yield stress (σ'_{yield}) and yield stress ratio (YSR). The hydraulic conductivity (K) was measured each 24 hours at the end of successive loading stages using the falling-head method. The linear relations obtained by plotting

void ratio values against the logarithm of hydraulic conductivities were used to derive values of hydraulic conductivities representative of *in-situ* conditions (*in-situ* void ratio).

In order to quantify the effect of the sediment structure on the compression behaviour, compression tests were carried out on four samples reconstituted at 1.5 x liquid limit. Following the method proposed by Burland (1990), compression test data could thus have been normalized using the void index (I_v) concept.

3.2.3. Triaxial tests

Sixteen cylindrical specimens of 50 mm diameter and 100 mm in height were prepared for triaxial compression testing. Ten of them were anisotropically consolidated under K_0 conditions as determined from the method recommended by Lunne et al. (2006) based on piezocone data. Two series of three triaxial compression tests were also carried out on specimens of two different sediment types that were isotropically consolidated at effective confining stresses corresponding to σ'_{v0} , $1.5 \cdot \sigma'_{v0}$ and $3 \cdot \sigma'_{v0}$. All the specimens were sheared undrained at the constant rate of axial deformation of $0.01 \text{ \%} \cdot \text{min}^{-1}$. We used MOHR circles to determine the effective friction angle (ϕ') and the effective cohesion (c').

3.2.4. Mineralogical, chemical and microstructural analysis

X-ray powder diffraction and fluorescence were carried out on selected samples for quantitative estimates of mineralogical and chemical composition using the methods reported in Chéron et al. (2016). The total Organic Carbon Content (TOC) was quantified using a TOC-L CPH Shimadzu analyzer. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) analysis were used to investigate the microscale characteristics of the sediments. For SEM and EDS analysis, a small amount of sediment was mounted on pin stubs and coated with carbon. SEM secondary electron images and EDS element maps were performed with a FEI Quanta 200 coupled with an OXFORD X-MAX^N Silicon Drift Detector (detector size: 80 mm^2 , Collins et al. (2009)).

3.3. Cone penetration testing with pore pressure measurement

Cone penetration testing with pore pressure measurement (CPTu) has been carried out with the Penfeld penetrometer developed by IFREMER. The Penfeld penetrometer is a seabed rig developed to ensure piezocone penetration at a constant rate of 2 cm/s down to 30 m below seabed (Sultan et al., 2007). The piezocone continuously measures the tip resistance (q_c), the sleeve friction (f_s) and the penetration-induced pore pressure (Δu_2). The cone has a projected area of 10 cm² with an apex angle of 60°. The friction sleeve is 15 cm long and 3.6 cm in diameter. Two different load cells are used to measure the tip resistance and sleeve friction. The pore pressure measured with a differential pressure sensor located immediately behind the cone (u_2 position) is used to obtain values of corrected tip resistance (q_t). Geotechnical data from 61 CPTu measurements were collected in the study area during the GHASS cruise and 2 of them were used in the current study (CPT01-07 and CPT04-01). Normalized piezocone data ($Q_t - \Delta u_2 / \sigma'_{v0}$) allowed the sediment to be classified using the soil behaviour chart proposed by (Schneider et al., 2008). Profiles of undrained shear strength (S_u) were derived from tip resistance data using the empirical method recommended by Lunne et al. (2006) with a site specific N_{kt} factor of 12. This value is consistent with that of 13.6 ± 1.9 commonly reported for soft clays (Low et al., 2010).

4. Experimental results

4.1. Sediment description

Core photographs and X-ray radiographs were used to define sedimentary classes (Fig. 2). Profiles of physical properties (Figs. 3 and 4), chemical properties (Fig. 5), and SEM images (Fig. 6) were used to support the distinction of four main sediment classes:

Class 1: Silty clays: The first class comprises well-laminated materials (Fig. 2, sections S1-S12) which are observed in all sediment cores and reach depths up to 7.5 m and 14 m in cores GAS-CS03 and GAS-CS17 respectively. These materials are silty clays (Fig. 3d) classified as inorganic clays of high to very high plasticity in the USCS chart (Fig. 4). They are composed of 3 sub-units: (1a) a carbonate-rich unit at the top (Fig. 2, section S1: 0-50 cm), (1b) a reddish-brown unit over 1-2 m thickness (Fig. 2, section S1:

50-100 cm and entire section S3, also called “Red Layers” in Constantinescu et al. (2015) and references therein), and (1c) a well-laminated grey unit deeper (Fig. 2, sections S4-S12). The organic content is commonly lower than 2.5 % except at the top of the carbonate-rich unit where it reaches 7.8% (Fig. 5c). Progressive increases in bulk density, from 1.41 to 1.65 g/cm³, and Su , from 2.6 to 19.2 kPa, are recorded with increasing burial depth ($Su/\sigma'_v = 0.16$) (Figs. 3a and 3e). This is accompanied by a progressive decrease in water content while the PI drops from 70 % to 35 % (Figs. 3b and 3c). The carbonate-rich sub-unit has the lowest plasticity with an average plasticity index (PI) value of 44 % $\pm$ 2 %. The clay content slightly decreases with depth, and this is coupled with the progressive increase in carbonate content from 2.6 to 9.5 % after the peak value of 20 % is reached in the sub-unit 1a at the top of the core (Figs. 5a and 5d). It is interesting to note that carbonates are mainly of detrital origin as revealed by the presence of Eocene and Pliocene coccoliths provided by continental erosion (J. Giraudeau, personal communication) (Fig. 6a). The colour change between red and grey sediments corresponds to a change in clay mineralogy with higher proportions of illite and kaolinite and very low smectite proportion in red materials (Fig. 5b). A very low and uniform sulfur content (%S) is measured in these sediments away from spikes at the top of the cores and from where dark stains are observed in the upper part of the grey unit (Fig. 5e and see section S4 in Fig. 2). These materials show moderate and constant sensitivity between 1 and 2 (Fig. 3f).

Class 2: Shallow sulfur-rich sediments: A dark-black facies of 0.40 to 1 m thick is systematically observed intercalated within the first 2-3 meters of the class 1 material (Fig. 2, section S2: 100-170 cm). Class 2 bulk density, water content, and plasticity indices follow the trend of the surrounding material (Figs. 3a-c). This material shows equivalent silt and clay distribution (Fig. 3d), organic content around 1% (Fig. 5c), and it corresponds to inorganic clays of high to very high plasticity (Fig. 4). However, class 2 material differs by showing slightly higher values of Su_{peak} (Fig. 3e) along with noticeably higher sulfur contents (up to 1.7 %, Fig. 5e). Sulfur enrichment occurs where iron sulfides (e.g. greigite, pyrite) are observed pervasively disseminated between silt and clay particles in secondary electron images and EDS

element maps (Fig. 6b) while the sulfate concentration in pore water approaches zero (Fig. 5f). The class 2 material is also characterized by a low carbonate content (%Ca) compared to surrounding material. The decrease in carbonate content however varies from one core to another (Fig. 5d).

Class 3: Sand-rich clays: A material composed of alternating fine-sand, silt and clay laminae is generally observed beneath the sediment of class 1 (Fig. 2, S13-S14). Its thickness ranges from few tens of centimeters to 3-5 m in cores GAS-CS03 and GAS-CS17. It shows higher density values (about 1.8 g/cm³), lower water content, and larger grain size (median grain size up to 57.8 µm) compared to other materials (Figs. 3a, 3b and 3d). Class 3 also shows low plasticity with PI ranging from 19 % to 58 % and an average value of 36 % ± 13.5 % (Figs. 3b and 3c). Few high plasticity values are observed in locally more clayey laminae. The class 3 sediment mainly corresponds to inorganic clays of moderate plasticity in the USCS chart even if it sometimes shows sandy laminae (Fig. 4). These sand-rich clays also differ from previous sediments by showing higher proportions of silica and calcite-dolomite, whereas chlorite replaced a part of smectite and kaolinite contents (Figs. 5a and 5b). The geotechnical properties of these materials are not developed in the following sections.

Class 4: Deep sulfur-rich sediments: Dark-grey materials containing black layers and stains constitute the last class identified in the study area (Fig. 2, S20-S22). Their thickness ranges from few tens of centimetres to 3-4 m in cores GAS-CS03, GAS-CS04 and GAS-CS17. A similar pattern is also observed deeper in cores GAS-CS07, GAS-CS08 and GAS-CS12, alternating with sediment of class 3. They are characterized by anomalously low density and high water content given their burial depth; i.e. around 1.6 g/cm³ and 60-70% respectively which is about 30% above the general trend of the class 1 material (Figs. 3a-b). A significant increase in Su_{peak} values is measured, whereas Su_{res} values follow the trend of class 1 sediments (Fig. 3e). In core CS03 and CS17, Su_{peak} is respectively up to 25 kPa and 36 kPa higher than expected for sediments of class 1. This leads to a significant increase in sensitivity St with values ranging from 3 to 7, whereas sensitivity never exceeds 3 in the overlying sediments (Fig. 3f). With PI values

ranging from 46 % to 78 % (Fig. 3c) they correspond to inorganic clays of high to very high plasticity but sometimes lie close to or below the A-line in the unified classification chart (Fig. 4). Their high clay fraction is mainly composed of smectite and kaolinite, similarly to sediments of class 1. They show a systematic enrichment in sulfur content even if lower than class 2 (Fig. 5e), and a relatively low calcite-dolomite content compared to surrounding materials (Figs. 5a and 5d). Secondary electron images and EDS element maps reveal the presence of iron sulfides in the form of nodules and aggregates in the surrounding of pore spaces but also elemental sulfur in the form of microparticles pervasively distributed between clay particles (Figs. 6c-d and 6f). Calcium carbonate is also observed in the form of calcite mineral overgrowths, microcrystal aggregates or elemental particles pervasively distributed in the clay matrix (Figs. 6c, 6e, and 6g).

4.2. Consolidation properties

The compression curves obtained from the oedometer tests are reported in e -log σ'_v diagrams (Fig. 7). Depth profiles were used to reveal the specificity of the different materials (Fig. 8), whereas I_v -log σ'_v diagrams were used to illustrate the influence of sediment structure by comparing natural and reconstituted samples (Fig. 9).

Class 1: The sediments from class 1 follow a well-defined sedimentation compression line (SCL) (Fig. 7a). Only the deeper specimens (GAS-CS05-S11 and GAS-CS17-S13b) show slightly flatter curves compared to other samples. A progressive increase in yield stress (σ'_{yield}) is observed with depth (Fig. 8a) whereas YSR values are close to 1 which suggests no significant structuration in these sediments. One specimen shows a YSR of 2.5, but this value is related to a discrepancy in the calculation of σ'_v for such shallow depth (Fig. 8b). The compression index (C_c) shows an average value of 1.0 ± 0.20 and ranges from 1.25 at the top of the cores to 0.63 for the two deeper specimens (Fig. 8c). Conversely, the coefficient of consolidation (C_v) increases with depth and ranges from $5.9 \cdot 10^{-9}$ to $8.66 \cdot 10^{-8}$ m²/s (Fig.

8d). The hydraulic conductivity (K) calculated at the *in-situ* void ratio ranges from 2.3×10^{-9} to 7.03×10^{-9} m/s and shows no clear evolution with depth (Fig. 8e).

Class 2: The sample of class 2 shows a compression line above the SCL of class 1 samples (Fig. 7b) and a YSR reaching 1.9 (Fig. 8b). It has a slightly higher C_c value whereas its C_v and K values are in the same range as that of the class 1 sediment (Fig. 8).

Class 4: The consolidation behaviour of sediments from class 4 varies from one sample to another (Figs. 7b and 8):

- The samples from section GAS-CS17-S28a shows a compression curve reaching the SCL of the class 1 sediment (Fig. 7b). Their consolidation properties are in the range of those observed for the class 1 but they show significantly lower K values (Fig. 8).

- Compression curves from GAS-CS12 samples are slightly above the SCL of the class 1 (Fig. 7b). However, they show clearly higher values of σ'_{yield} and a YSR ranging from 1.5 to 2.3 (Figs. 8a and 8b). Their C_c and C_v values are in the same ranges as those of the sediment of class 1 but do not evolve with depth in the same way (Figs. 8c-d). Low K values are generally recorded in these specimens (Fig. 8e).

- Specimens from GAS-CS03 show compression curves significantly above the SCL of the class 1 (Fig. 7b). However, their values of σ'_{yield} and YSR remain low (Figs. 8a-b). High values of C_c are obtained on these specimens (Fig. 8c) whereas their values of C_v and K are low, similarly to specimens from GAS-CS12 (Figs. 8d-e).

The normalized compression data of all reconstituted samples plot close to or along the Intrinsic Compression Line, ICL, determined by Burland (1990) (Fig. 9a). When normalized the post-yield compression curve of natural sediment from class 1 follows the ICL (Fig. 9b). By contrast, the sediments from classes 2 and 4 show post-yield compression curves lying to the right of the ICL and reaching it only

at very high stresses (Fig. 9b). It is interesting to note that compression curves of specimens from both classes 2 and 4 follow the same trend at high stress.

4.3. Strength properties

Results from triaxial tests were plotted in deviatoric stress (q) versus axial strain (ε_a) space (Fig. 10a) and deviatoric stress (q) versus effective mean stress (p') space (Fig. 10b). Mohr circles were used to calculate the effective friction angle (ϕ') and cohesion (c') of these materials (Fig. 11).

Class 1: Specimens of class 1 (samples GAS-CS12-S04, GAS-CS12-S05, and GAS-CS07-S09) generally exhibit contractive behaviour with slight to moderate strain softening (Fig. 10ai and 10bi). The tendency to strain soften increases with increasing confining pressure. The effective friction angle and cohesion obtained from isotropically consolidated specimens from section GAS-CS07-S09 coupled with additional tests from GAS-CS12 are 26.6° and 2.6 kPa, respectively (Fig. 11a).

Classes 2 and 4: Specimens of class 2 exhibit ductile failure. By contrast, specimens of class 4 show pronounced strain-softening except for the specimen from section GAS-CS12-S12 which behaves in a dilatant manner before reaching peak strength (Figs. 10aii and 10bii). The results obtained on isotropically-consolidated samples from section GAS-CS03-S16 indicate an effective friction angle of 16° and potentially a higher cohesion than sediment 1 (Fig. 11b). However, these tests were performed under high effective stresses (222 to 473 kPa) which is known to reduce the value of the friction angle (Mitchell and Soga, 2005; Le et al., 2008) and then prevent us to determine the cohesion consistently. Coupled with the test performed on the sediment from class 2, a friction angle of 30° and a cohesion of 2.1 kPa was obtained at low effective stress (Fig. 11b).

4.4. In-situ geotechnical properties

The cone penetration tests CPTu01-07 and CPTu04-S01, corresponding respectively to cores GAS-CS03 and GAS-CS17, are used to estimate the *in-situ* geotechnical properties of the different sediment classes described above. The corrected tip resistance (q_t), the sleeve friction (f_s), and the pore pressure (Δu_2) induced by the penetration are reported as a function of depth (Figs. 12a-c). These data are used to estimate the soil type (Fig. 12d), and derive profiles of peak undrained shear strength (S_u) (Fig. 12e).

(i) A quasi-linear increase with depth of q_t , f_s , Δu_2 and S_u is recorded in the upper 15 m of CPTu01-07 (Fig. 12i). Gradients of $dq_t/dz = 37.1$ kPa/m, $df_s/dz = 0.71$ kPa/m, $d\Delta u_2/dz = 16.25$ kPa/m, and $dS_u/dz = 1.94$ kPa/m can be derived from these profiles ($S_u/\sigma'_v = 0.35$). Based on normalized CPTu data, sediments following these trends are classified as clays (Fig. 12d). This applies to the sediments previously identified as sub-units 1b and 1c while the surficial carbonate-rich sediments of sub-unit 1a behave more like sensitive clays. The presence of sulfur-rich clay sediments of class 2 is only revealed by a slight increase in S_u . The sediments identified in cores as sand-rich clays of class 3 typically show high values of q_t and a partially-drained response characteristic of silt and transitional (i.e. mixed) soils. In class 4 sulfur-rich sediments, high q_t values are also observed but penetration occurred fully undrained as in typical clay soils (Fig. 12di). An increase in S_u of up to 40 kPa, is observed in this sediment compared to the general trend of the class 1 material (Fig. 12e). Piezocone responses suggest that alternations of class 3 and class 4 sediments occur from 15 to 30 m below seabed.

(ii) In the upper 19.5 m below seabed, the CPTu04-01 profiles follow the trends previously observed at site CPTu01-07 with gradients $dq_t/dz = 36.8$ kPa/m, $df_s/dz = 0.64$ kPa/m, $d\Delta u_2/dz = 16.27$ kPa/m ($S_u/\sigma'_v = 0.36$) (Figs. 12a-cii). However, following a sudden drop at about 3 m below seabed, the tip resistance readings appear to have been temporarily impaired with the consequence of distorting the sediment interpretation down to 7.8 m below seabed (Fig. 12dii). An increase in S_u is also observed in the class 4 sulfur-rich sediments similarly than CPTu01-07 (Fig. 12e). The noticeable change from the previously

described CPTu01-07 is that on CPTu04-01, the pore pressure increased markedly above the general trend when penetrating the sulfur-rich sediments of class 4 (Fig. 12cii).

5. Discussion

5.1. Geotechnical properties of lacustrine Black Sea sediments

Sediments from class 1 are mainly composed of very soft silty clays showing high water content, high plasticity (USCS chart), high compressibility, low cohesion and moderate sensitivity. These characteristics are in agreement with a clay fraction mainly composed of smectite and illite and the presence of organic content in these shallow materials (0.5-2.5 %) (Mitchell and Soga, 2005). No overconsolidation and no structure were detected in this sediment class as revealed by the compression curve reaching the ICL and then following it at high vertical stress (Fig. 9). The progressive increase in density and undrained shear strength with depth, coupled with the decrease in water content reveals a normal compaction process during burial. This process is combined with a progressive increase in detrital carbonate content (calcite and dolomite), together with a decrease of plasticity indices (Figs. 3, 4 and 5). The class 3 “sand-rich clays” at the base of this facies follows the same trends.

Class 2 sulfur-rich materials share sedimentological properties similar to class 1 materials but exhibit S_u and YSR values slightly above the general trend. These distinctive properties can be ascribed to the influence of structure as revealed by a compression curve lying to the right of the ICL (Fig. 9b). This supports the interpretation that distinctive physical and/or chemical conditions applied during the formation of class 2 sediments.

The same applies to the deep sulfur-rich sediments of class 4 whose compression and strength behaviour (Figs. 3e, 8c-d, 9b, 10bii, 12e) are consistent with slightly sensitive and structured clay soils. The water content 30% above the trend of class 1 sediment (Fig. 3b), the slightly lower permeability values (Fig. 8e), and the pore pressure response during piezocone penetration (Fig. 12c) are also consistent with

structured materials. When compared to the general trend displayed by class 1 sediment, class 4 sediments appear to be up to 25.4 kPa and 40kPa stronger (Figs. 3e and 12e). An increase in sensitivity was also noted with St values ranging from 3 to 7 whereas it never exceeds 3 in class 1 material (Fig. 3f). The results of triaxial tests confirm this increase in shear strength and suggest that the strengthening of class 4 sediments is associated with a strain softening response (Fig. 10bii) and potentially to a small friction angle (Fig. 11b) although this value could also be related to high effective stresses applied during these tests (Le et al., 2008).

5.2. *Evidences of early diagenesis (AOM, SR) and triggering factors*

No significant changes in bulk and clay mineralogy, grain size, organic content or pore fluid composition are measured in materials from classes 1, 2, and 4 which permits to exclude the potential impact of these constitutive parameters and the influence of present-day cation exchange on the geotechnical properties of the materials (Sultan et al., 2000). This observation indicates that silicate diagenesis accompanied with clay formation is not responsible for the difference in mechanical properties. No evidence of recent erosion is detected where cores GAS-CS03 and GAS-CS17 were recovered which suggests that sediments have not been overconsolidated (Chandler, 2010) (Fig. 1). There are however chemical evidence suggesting that early diagenesis affected sediments of both class 2 and 4.

The class 2 material shows a significant enrichment in sulfur content (reaching 1.7 % in core CS17, Fig. 5d) and, to a lesser extent, a decrease in carbonate content (Figs. 5a and 5d). The SEM images and EDS element maps confirm the presence of iron sulfides pervasively disseminated between clay-silt particles in class 2 sediments (Fig. 6b) where the sulfate content in pore water approaches zero (Fig. 5f). These characteristics are consistent with early diagenesis described by a series of studies in the Black Sea (Calvert et al., 1996; Wilkin and Arthur, 2001; Jørgensen et al., 2004; Neretin et al., 2004; Egger et al., 2016). These studies have established that the shift from freshwater lake to marine conditions initiated 9000 years ago the sudden and massive input of marine sulfate into sulfate-free environment and its

downward diffusion into methane-bearing lacustrine sediments (Soulet et al., 2011). The sulfide ion produced from the AOM reacts with the underlying iron-bearing solid phases such as Fe-Oxide, Fe-carbonate and Fe-Phosphate (Egger et al., 2016) and precipitate in solid-phase iron sulfides evidenced by black bands visible on the sediment core. Visual observations and chemical analyses reported in the present study attest that these reactions have occurred in the shallow sediments of class 2.

The class 4 sediments reveal evidence of early diagenesis involving an enrichment in sulfur content (Fig. 5d), the presence of sulfides in the form of nodules and aggregates in pore spaces (Figs. 6d and 6f), and S as elemental particles pervasively distributed between clay particles (Fig. 6c). However, given their burial depth, class 4 sediments are out of the influence of the present-day sulfate diffusion. Because these sediments correspond to the lacustrine unit III of Dean and Arthur (2011), they are too young to be influenced by the previous marine intrusion (Eemian interglacial, Wegwerth et al., 2015), and thus cannot be related to intrusion of sulfate-rich marine water. This suggests the occurrence of a cryptic sulfur cycling (Lovley and Phillips, 1994; Holmkvist et al., 2011; Egger et al., 2016) under freshwater lake conditions where sulfur-involving redox reactions and AOM are also documented, and inferred to depend on several controlling factors such as oxygen, sulfate concentration, iron, temperature and organic matter availability (Holmer and Storkholm, 2001). Organic matter is rather constant along the studied sediment cores (Fig. 5c), and the temperature is considered constant at such deep water depths (variation of more or less 1°C, Wegwerth et al. (2015)). However, alternating oxic – anoxic conditions are reported to have occurred during the last glacial period as a result of climate-driven changes in water column stratification (Soulet et al., 2011). This environmental process can lead to episodic changes in sulfate, oxygen or iron concentration in bottom sea water and can affect the bacteria population mediating sulfate reduction (Treude et al., 2005; Baumgartner et al., 2006). These episodic changes can explained the development of the cryptic sulphur cycle during periods corresponding to the formation of the class 4 sediments whereas the conditions are not in place during the formation of class 1 and class 3 materials. The limited sulfur enrichment in class 4 could be the result of lower concentration of the downward diffusing dissolved

sulfate comparatively to the development of the class 2 material (Fig. 5e). This limited sulfur enrichment is associated with evidence of carbonate precipitation such as calcite showing rhombohedral crystal and overgrowths, and microcrystal aggregates of calcium carbonate which seem to rise out from the clay matrix as reported by Bozzano et al. (1999) (Figs. 6c, 6e and 6g). The calcium carbonates observed pervasively distributed rather than the scatter silt detrital particles observed in sediment from class 1 (see Fig. 6a) suggests a part of them was dissolved and reprecipitated to form a cement. The low values of permeability obtained in this class (Fig. 8e) despite of their relatively high water content (Fig. 3b) are consistent with the dissolution followed by reprecipitation of cement between particles. A part of dissolved calcium could have been transported by diffusion in the pore water which explains the decrease in carbonate content in this class. Carbonate dissolution is thought to have been induced by acidity generated during bacterial oxidation of organic matter and methane (Hendry, 1993), whereas carbonate precipitation would have been typically linked to sulfate reduction by bacteria, releasing HS^- and HCO_3^- , the latter of which triggers and enhances the carbonate formation (Greinert and Derkachev, 2004).

5.3. Influence of early diagenesis on shallow sediment geotechnical properties

The formation of sulfur and carbonate cements triggered by early diagenetic reactions is thought to have delayed normal consolidation and strengthened the sediment framework by occurring at the contact points between particles (Figs. 6b and 6c). This phenomenon preserved high water content values upon burial compared to normally consolidated sediments (Bartetzko and Kopf, 2007), that is about 30% above the general trend of the class 1 sediment (Fig. 3b). The observed increases in sensitivity of these cemented sediments indicate however that their structure is metastable (Mitchell and Soga, 2005) (Fig. 3f). Metastable structures have already been described in other soft materials such as carbonate-cemented loess deposits (Luo et al., in press; Xu et al., in press) or organic soils (Horpibulsuk et al., 2007; Jannuzzi et al., 2015). These different materials have comparable sensitivity values to the sulfur-rich sediments described in this study (with St between 3 and 9). They can be considered to be a significant value as proposed by Schlue et al. 2011 (with a St higher than 4.8 although much lower than $St = 30$ for highly

sensitive materials, Gylland et al., 2013). Although cementation appears to have strengthened class 4 sediments, their anomalously high water content and sensitivity can lead to the development of excess pore pressure and strength reduction upon undrained shearing. Following Locat et al. (2014) and Zhou et al. (2017) these properties and corresponding strain softening behaviour can be considered as factors contributing to strain localization and the development of a so-called ‘induced’ weak layer. Accordingly, these sulfur and carbonate cemented sediments may influence the location and development of failure in the sedimentary column.

Because high pyrite (sulfide) and sulfur contents are observed deeper in the Black Sea sediments (Stoffers and Degens, 1978) and several environmental fluctuations occurred during the last glacial-interglacial cycles (Badertscher et al., 2011); the presence of such weak layers can be considered as a potential preconditioning factor for causing the submarine landslides observed in this area (Riboulot et al., 2017) (see the many landslide scars and seafloor deformation features around the location where these sediments were recovered in Fig. 1). Beyond the implications for the study areas, the western Black Sea is also rich in hydrocarbon fields (oil, gas, gas hydrate) with many exploitation and exploration projects (Georgiev, 2012). It is thus expected that the presence of such material (both class 2 at the surface and class 4 sediment deeper) may have implications on the design of offshore facilities such as pipelines, foundation systems or wellheads. This consideration could be reasonably extended to the whole Black Sea which has undergone regional-scale environmental changes. It could be extended to other places such as estuaries and lakes where environmental conditions ; i.e. methane-bearing, iron and carbonate-rich sediments, the diffusion of sulfate and variations in oxic-anoxic conditions ; could have contributed to the development of these early diagenetic reactions (Holmer and Storkholm, 2001; Won and Chang, 2007; Tudryn et al., 2014).

6. Conclusions

A suite of laboratory and *in-situ* measurements have been carried out to characterize the geotechnical properties of lacustrine sediments from the Romanian sector of the Black Sea and investigate the influence of early diagenetic reactions on their hydro-mechanical behaviour. Four main sediment classes were identified:

- The material mainly consists of soft silty clays (class 1) and sand-rich clays (class 3) containing a significant proportion of detrital carbonate (until 20 %) and organic content (0.5-2.5 %). These sediments show high plasticity (high PI values), high compressibility, low undrained shear strength, low cohesion and moderate sensitivity.
- A reaction of early diagenesis, involving sulfate reduction and anaerobic oxidation of methane has affected shallow silty clay sediments by inducing the precipitation of sulfur-sulfide cement pervasively disseminated between clay particles. The resulting sulfur-rich sediment (class 2) appears to be structured with consolidation and strength properties consistent with cemented clays.
- Evidences of early diagenesis detected deeper in the sediment column suggest older and buried cryptic sulfur cycles inducing sulfur and carbonate cementation (class 4). It results from changes in anoxic-oxic conditions in the water column and thus in the sediments. The occurrence of such reactions at shallow depth allowed the sediment to preserve an open structure, a high water content and high plasticity upon burial. In the cementation process the sediment has developed high strength as well as a metastable structure and consequent sensitivity.

Because such early diagenetic reactions (cryptic sulfur cycle including sulfate reduction coupled with anaerobic oxidation of methane) can occur in lacustrine and estuarine environments, their influence on geotechnical properties should be considered in engineering design problems and geohazard studies.

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Figure captions

Fig. 1. Bathymetric map showing the location of sediment cores and cone penetration tests (GHSZ = Gas Hydrate Stability Zone).

Fig. 2. Photographs of selected half-sections from core GAS-CS03. (1a) Carbonate-rich silty clays. (1b) Reddish-brown silty clays. (1c) Grey silty clays. (2) Shallow sulfur-rich sediment. (3) Sand-rich clays. (4) Deep sulfur-rich sediments.

Fig. 3. Graphs of density (*a*), water content and consistency limits (*b*), plasticity index (*c*), particle size (*d*), undrained shear strength (*e*), and sensitivity (*f*) as a function of depth in cores GAS-CS03 (*i*) and GAS-CS17 (*ii*). (The upper dark band outlines shallow sulfur-rich sediments of class 2; the dotted band outlines sand-rich clays of class 3; the lower dark band outlines deep sulfur-rich sediments of class 4) (w_l = liquid limit; w_p = plastic limit).

Fig. 4. Soil plasticity chart from Unified Soil Classification System. Class 1: Silty clays. Class 2: shallow sulfur-rich sediments. Class 3: Sand-rich clays. Class 4: deep sulfur-rich sediments.

Fig. 5. Profiles of bulk mineralogy (*a*), clay mineralogy (*b*), organic carbon content (TOC) (*c*), Calcium oxides (CaO) content (*d*), Sulfur (S) content (*e*), and dissolved sulfate (SO_4^{2-}) content (*f*) in cores GAS-CS03 (*i*) and GAS-CS17 (*ii*). (The upper dark band outlines shallow sulfur-rich sediments of class 2; the dotted band outlines sand-rich clays of class 3; the lower dark band outlines deep sulfur-rich sediments of class 4).

Fig. 6. (*i*) EDS element maps. (*ii*) Secondary electron images. (*a*) Class 1 showing clay material with detrital particles of calcium carbonate (GAS-CS17-S13). (*b*) Class 2 showing iron sulfur (sulfide) covering clay particles. (*c*) Widespread distribution of sulfur and calcium carbonate particles observed in class 4 (GAS-CS12-S20). (*d*)-(*e*) Detail of sulfur aggregates and microcrystal aggregates of calcium carbonate from the same specimen. (*f*) Aggregate of iron sulfur in pore space in class 4 (GAS-CS03-S19). (*g*) Calcite mineral overgrowths observed in the same specimen.

Fig. 7. Graphs of void ratio (e) vs. logarithm of vertical effective stress (σ'_v) for (a) Class 1: Silty clays. (b) Class 2 and 4: Shallow and deeper sulfur-rich sediments. The SCL is the linear regression of the average values of void ratio obtained at each post-yield loading stage.

Fig. 8. Graphs showing the vertical yield stress (σ'_{yield}) (a), the yield stress ratio (YSR) (b), the compression index (C_c) (c), the coefficient of consolidation (C_v) (d), and the hydraulic conductivity (K) (e) as a function of depth.

Fig. 9. Graphs showing the evolution of the void index, I_v , as a function of the logarithm of vertical effective stress for (a) samples reconstituted at 1.5 x liquid limit, and (b) natural samples. ICL was calculated with Burland's equation from Chandler (2000).

Fig. 10. (a) Stress-strain curves and (b) Effective stress paths from undrained triaxial tests on (i) specimens from class 1 and (ii) specimens from class 2-4.

Fig. 11. Mohr circles and failure envelopes of material from class 1: Silty clays (a) and class 4: Deep sulfur-rich clays (b). ϕ' = Effective friction angle. c' = effective cohesion.

Fig. 12. Depth profiles of (a) corrected tip resistance (q_t), (b) sleeve friction (f_s), (c) pore pressure (Δu_2), (d) soil type (based on normalized data, Q_t/σ_0 vs. $\Delta u_2/\sigma_0$ and the classification chart by Schneider et al. (2008) and (e) undrained shear strength (S_u) derived with a N_{kt} factor of 12, from CPTu01-07 (GAS-CS03) (i) and CPTu04-01 (GAS-CS17) (ii). (Soil type classification: 1 = sensitive clays; 2 = clays; 3 = silts and clays of low Rigidity Index (i.e. $I_r = G/S_u$); 4 = transitional soils; 5 = drained sands; diamonds: data from triaxial tests).

FIGURE 01

FIGURE 02

FIGURE 03

FIGURE 04

FIGURE 05

FIGURE 06

FIGURE 07

FIGURE 08

FIGURE 09

FIGURE 10

FIGURE 11

FIGURE 12

Table 1. Characteristics of sediment cores used in this study

Core	Latitude	Longitude	Water Depth [mbsl]	Core Length [m]
GAS-CS03	N44°58,038	E031°03,114	842	22.99
GAS-CS04	N43°42,549	E031°06,558	1623	26.58
GAS-CS05	N43°58,398	E030°59,735	794	11.69
GAS-CS07	N43°56,035	E030°50,664	819	11.59
GAS-CS08	N43°56,035	E030°50,664	821	19.94
GAS-CS12	N43°57,994	E030°45,020	547	23.5
GAS-CS17	N44°00,587	E030°57,552	651	26.41
GAS-CS18	N43°55,785	E030°45,298	638	26.92