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MINERALOGY OF A NORWEGIAN POSTGLACIAL CLAY AND SOME GEOTECHNICAL IMPLICATIONS

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ABSTRACT

Crystalline and amorphous phases present in a sensitive clay from Oslo are examined using several independent analytical techniques. Major crystalline phases are feldspars (50 wt. %), hornblende (~18 wt. %), quartz (8 wt. %), clay mica (12 wt. %) and chlorite (~7 wt. %). Selective-dissolution studies in association with energy-dispersive X-ray investigations reveal polymictic assemblages that are cemented by amorphous iron oxide. Amorphous iron compounds (~2 wt. %) also form discrete particles and coatings on hornblende. The dissolution technique (Segalen 1968) disaggregates these cemented mineral assemblages and affords an improved definition of the constituent particles. It is inferred that the minute particles (<0.2 μm) and the amorphous iron oxide which make up the polymictic assemblages probably are common constituents of Norwegian and Canadian clays. Although these materials can appear as one bonded mass, their roles in the formation of sensitive-clay microstructures are considered to be independent. By enhancing interparticle bonding at low stresses, the glacially derived colloidal particles may promote the development of high-porosity structures. The amorphous coatings, produced by *in situ* chemical weathering, act as cementing agents and augment the established soil structure. Variations in the degree of cementation exhibited by the engineering characteristics of clays reflect differences in timing of the cementation.

Keywords: amorphous iron oxide, cementation, energy-dispersive X-ray analysis, high-porosity structure, polymictic assemblages, sensitive clay, thermogravimetry, Oslo.

SOMMAIRE

Les phases cristallines et amorphes qui constituent une argile sensible d'Oslo ont été analysées par plusieurs techniques indépendantes. Les phases cristallines principales sont: feldspath (50% en poids), hornblende (≃ 18%), quartz (8%), mica argile (12%) et chlorite (≃ 7%). Une étude par dissolution sélective et aux rayons X à dispersion d'énergie montre que ces assemblages polymictes sont cimentés par de l'oxyde de fer (amorphe). Des composés de fer amorphes (≃ 2% en poids) forment également des particules distinctes et un enduit sur la hornblende. On désagrège ces assemblages cimentés, par la technique de dissolution de Segalen (1968), ce qui permet une résolution améliorée des particules composantes. Les particules très petites (< 0.2 μm) et le matériau amorphe seraient des composants courants d'argiles sensibles canadiennes et norvégiennes. Quoique ces composants puissent se présenter agglutinés en une seule masse, leurs rôles dans la formation de microstructures d'argiles sensibles semblent indépendants. En améliorant les liaisons interparticulaires à faible charge, les particules à l'état colloïdal dérivées de source glaciaire peuvent produire des structures d'une grande porosité. Les enduits amorphes, produits d'un lessivage chimique *in situ*, agissent comme ciment et renforcent la structure pré-existante du sol. Les variations dans le degré de cimentation, décelées dans les propriétés mécaniques des argiles, illustrent les différents stades de cimentation.

(Traduit par la Rédaction)

Mots-clés: oxyde de fer amorphe, cimentation, analyse aux rayons X à dispersion d'énergie, structures à grande porosité, assemblages polymictes, argile sensibles, thermogravimétrie, Oslo.

INTRODUCTION

Considerable research has been directed towards the contribution of amorphous material to the engineering properties of Canadian sensitive clays. Few similar studies have been concerned with Norwegian clays, probably because the amorphous material was believed to act as a cementing agent, and the engineering characteristics of Norwegian clays do not reflect cementation in the microstructure to the same degree as Canadian clays. If similar amorphous materials are present in Norwegian clays, their role in the development of sensitive microstructures appears to be different. The objects of this research are to obtain mineralogical data for an Oslo clay, to provide improved definition of any amorphous materials and to consider the contribution of cementation in the formation of sensitive clays.

Amorphous phases in the Oslo clay were removed by the dissolution procedure described by Segalen (1968). Before-and-after studies involving energy-dispersive X-ray spectroscopy (EDS) were then used to provide information concerning the dissolved material. The suitability of thermogravimetry and the method of Kiely & Jackson (1965) for quartz and feldspar determinations as routine analytical techniques for investigating sensitive clays is assessed by comparing these results with EDS data.

A study of the Norwegian literature concerned with sensitive clays reveals that there are few quantitative determinations of the mineral constituents. Reporting some of the early observations on these clays, Rosenqvist (1953) stated that "... the clay mineral of the finest fraction seems always to be made up of the hydrous mica 'illite'. Together with illite, the finest fraction of all quaternary Norwegian clays contains considerable amounts of inactive (non-clay) minerals. Quantitative determinations of the amount of illite is rarely made and statistical material is not available."

Since this statement was made, the scientific investigation of Norwegian clays has been focused on the chemistry of the pore water and the changes in the mechanical properties resulting from variation in the constituents of this medium. For such geochemical studies the mineral composition is important if the observations are to be interpreted correctly; in many cases a brief account of the mineralogy was provided and this was usually obtained by semiquantitative XRD and DTA. A summary of such analyses, performed on clays from Alna (Moum *et al.* 1968), Oslo (Løken 1970) and Drammen (Moum *et al.* 1971), is given in Table 1.

Sufficient data have not been published to enable an average composition to be calculated or indeed to assess the regional variation of each mineral phase. However, some insight may be obtained from the work of Moum *et al.* (1971), who reported the clay from Drammen as "typical" of Norwegian marine clay.

Of the minerals present in these clays, perhaps the clay micas are the most geotechnically significant. Rosenqvist (1953) discussed the development of a sensitive microstructure in terms of the leaching of a flocculated clay-mineral fabric, and studies concerning the contribution of illite and pore-water chemistry to the properties of these clays were continued by Bjerrum (1954). Illite determinations, quoted by Bjerrum (1954), were performed by Rosenqvist using DTA, and the results for seven samples showed an illite content of 25 to 40 wt. %. These results compare almost precisely with those of Moum *et al.* (1971) for the "typical" marine clay from Drammen. The presence of amorphous material in sensitive clays has been recognized by several Norwegian workers (Moum 1967, Bjerrum *et al.* 1969, Løken 1970). The amorphous matter appears to be insoluble iron and aluminum compounds that are liberated from mineral phases by *in situ* weathering. Other soluble cations, notably K^+, Ca^{2+} and Mg^{2+}, are also liberated by mineral disintegration. These do not usually form amorphous precipitates but they can have an important electrochemical influence on the clay. It is evident from laboratory observations that mineral disintegration becomes active when the leaching process in-

TABLE 1. QUANTITATIVE MINERAL DATA FOR NORWEGIAN MARINE CLAYS (wt. %)

Reference	Organic, %C	$CaCO_3$	Quartz	Feldspars	Hornblende	Illite	Chlorite	Others
Alna (Moum et al. 1968)	0.2-0.6	0.5-2.5	15-20	∿25	∿5	∿30	∿20	
City of Oslo (Løken 1970)	0.5	0.5	5	10		65	15	5
Drammen (Moum et al. 1971)	0.35	1-3	22-30	17-24		25-35	10-15	

troduces freshwaters that result in a change of pH and oxidation capacity (Bjerrum 1967, Moum 1967).

For a "normal" clay in an environment of *in situ* weathering, leaching must continue and must effectively remove the soluble cations as they are liberated if a sensitive-clay fabric is to be maintained. In this case, the Fe^{3+} and Al^{3+} that are liberated either must be removed by water seepage or their presence in the clay must maintain and not restrict the development of sensitivity. A cementing rôle for these compounds is acceptable, but the quantity produced and the emplacement process must be such that a marked reduction in sensitivity does not occur.

For many Canadian clays Sangrey (1972) recognized a suite of minerals that are found only in cemented sediments, and it was suggested that the *in situ* weathering of these minerals must lead to the liberation of suitable chemicals that can precipitate as amorphous cementing agents. Amphiboles and pyroxenes, if present in the fine fractions, would decompose rapidly during the postdepositional period. Loughnan (1969) described the decomposition of hornblende as a rapid process that produces chlorite and vermiculite and liberates iron, aluminum and manganese oxides. The amorphous nature of these compounds suggests that they are present in a hydrated oxide form; amorphous hydrated ferric oxide is particularly common in natural clays (Mackenzie 1957).

PRELIMINARY ANALYSES

The sample of sensitive clay from Oslo, supplied by Professor I.T. Rosenqvist, was received "undisturbed", at field moisture content. It was dispersed and separated by gravitational sedimentation into two fractions, <2 μm (54 wt. %) and >2 μm (46 wt. %). X-ray diffraction was used to identify qualitatively the mineral species present in the whole sample and the sized fractions. Orthoclase, sodic plagioclase, quartz, mica, calcite and chlorite were recognized in all three samples. Hornblende was identified in all but the <2 μm fraction.

The bulk chemistry of the samples was evaluated in terms of elemental oxides using X-ray-fluorescence spectroscopy; these data are shown in Table 2.

The presence of amorphous materials in Canadian sensitive clays has been recognized for many years, although their nature remains ill-defined. The quantity detected is highly dependent on the extraction technique employed, but significant quantities, >10 wt. %, have been recognized (McKyes *et al.* 1974, Yong *et al.* 1979). A method to dissolve any amorphous constituents in the Oslo clay by alternate washings with acid and alkali was adopted.

TABLE 2. X-RAY-FLUORESCENCE DATA FOR OSLO CLAY

	<2μm	>2μm	Whole
SiO_2	52.2	65.6	58.6
TiO_2	1.0	0.7	0.8
Al_2O_3	17.0	14.5	16.2
FeO	10.2	5.3	7.9
MnO	0.2	0.1	0.1
MgO	5.1	2.1	3.7
CaO	2.1	2.9	2.5
K_2O	5.7	4.2	4.9
P_2O_5	0.2	0.3	0.3
Na_2O	2.9	3.7	3.2
Total	96.6	99.4	98.2

As amorphous materials dissolve more rapidly than wholly crystalline phases, an extended period of treatment enables the two dissolution profiles to be "identified". The method used, described by Segalen (1968) for the dissolution of amorphous iron-bearing phases, has been applied to sensitive clays by other researchers (McKyes *et al.* 1974, Yong *et al.* 1979). The whole-clay sample was washed with 3*N* HCl and 0.5*N* NaOH. Following each alkali treatment, the residue was carefully dried and weighed. Although this weighing procedure may cause some error, it allows information concerning dissolution losses to be obtained directly. The final percentage of material dissolved during the treatment was ~20 wt. %.

In order to determine the damage sustained during this treatment, we used XRD to examine a residue (after 5 cycles). A much clearer diffractogram was obtained, and peak definition was much better than in a similar trace obtained for the untreated whole clay. The only mineral to show a poorer reflection pattern was the 10 Å layer-silicate. This probably suggests that much of the original clay mica in the sample is poorly crystalline illite. All the other minerals showed an enhancement of difraction peaks;

the relative peak heights in the treated and untreated samples were used to provide multiplication factors. The peak heights for quartz, plagioclase, orthoclase and hornblende increased by 200 to 300%, the chlorite reflections were enhanced by 10 to 15%, and the mica reflection was one-eighth of its original height. Although not intended to be precise, these comparisons do indicate the errors that may arise from quantitative and semiquantitative XRD procedures if no pretreatments are used to ensure the absence of amorphous material.

In order to elucidate the nature of the dissolved material, we subjected untreated and treated whole-clay samples to rigorous analysis using energy-dispersive X-ray spectrometry (EDS).

ENERGY-DISPERSIVE X-RAY ANALYSES

Analytical procedure

Clay samples were examined using a Philips 301 transmission electron microscope fitted with an EDAX 711 energy-dispersive spectrometer and 32K minicomputer. To facilitate routine analytical work we modified the second condenser lens to incorporate a third "mini" lens. With this assembly it was possible to obtain a focused spot size down to 0.05 μm; the beam current for a given spot size was also enhanced by a factor of about ten (Haines 1977).

Each sample was dispersed by mild ultrasonic treatment in deionized water and mounted on 3-mm-diameter carbon-coated gold grids. Gold specimen-grids were chosen to support the samples because the X-ray emission lines of this metal do not interfere with any of the $K\alpha$ X-ray lines of elements present in silicate minerals. Samples were transferred to the grids by pipetting small drops of the suspension taken from near the bottom of the test tube immediately on removal from the ultrasonic bath. Several grids of each sample were prepared in this way; the grids were left to dry above warming plates until the water had evaporated, leaving the particles adhering to the carbon film. Care was taken to ensure that the particles were sufficiently dispersed to avoid overlap during analysis.

The grids were mounted in low interference holders coated with graphite to reduce the generation of stray X-rays. All analyses were performed at an accelerating voltage of 60 kV. The beam current was not monitored, as this has been shown by previous experimentation not to interfere with the form of the X-ray data collected, only with the rate at which the data accumulate (Pooley 1975).

Single-particle analyses were used to define the various phases. Between 100 and 150 particles taken from several areas of the grid were observed during each examination. Three examinations of each sample were made. Each area was scanned in a regular manner at magnification of 10,000 or 20,000 x. All particles falling within the 16- or 8-μm-wide strip, created by moving the specimen across the circular field of view, were analyzed. Each particle was allocated to one of a number of phase categories depending on its chemical and morphological character. Spectra were recorded at a maximum peak height of 500 counts and later averaged to obtain the chemical composition (dry) of each phase.

Using constant operating conditions, we collected cumulative beam analyses to provide bulk-chemical data. Each bulk spectrum was created by the summation of analyses, each 10 seconds long. A 50-μm-diameter beam was positioned on ten grid openings in turn.

The X-ray counts for the various elements detected in the particles analyzed were collected in an EDAX 711 multichannel analyzer and processed in a minicomputer. Counts were obtained by integrating the $K\alpha$ X-ray peaks for the various elements over three channels, each 20 eV wide. Background measurements, taken at suitable positions, were used to correct the peak integrals. The background-corrected counts were then used to calculate an average phase (or bulk) chemistry. The averaged X-ray counts from several spectra were converted to oxide weight proportions using conversion factors for each element obtained from analyses of standards (Pooley 1977). The chemical data obtained in this manner do not include the water of crystallization nor any trace elements. Detailed discussions of these analytical techniques are given by Pooley (1975, 1977) and Pooley & Clark (1979).

Results

Samples of Oslo clay (whole) treated in the manner described by Segalen (1968), and others in an untreated state, were analyzed. The bulk chemistry, the average chemical composition of each major phase and the percentage of each phase present (based on percentage by number) were determined.

The chemistry of some of the phases in the untreated sample could not be associated with

TABLE 3. AVERAGE CHEMICAL COMPOSITION OF THE MAJOR CRYSTALLINE PHASES

	Albite	Oligoclase	Labradorite	Orthoclase	Hornblende	Mica	Chlorite
SiO_2	71.9	65.1	60.7	64.8	46.4	50.9	36.1
Al_2O_3	19.8	22.8	25.4	18.5	9.4	30.3	19.5
FeO	0.0	0.2	0.0	0.1	18.3	3.6	19.9
MnO	0.0	0.1	0.2	0.2	0.7	0.2	0.5
MgO	0.7	0.7	0.1	0.4	9.9	2.6	22.0
CaO	0.4	4.7	9.7	1.0	12.2	0.9	0.2
Na_2O	7.2	6.3	3.4	0.8	1.3	1.0	1.2
K_2O	0.2	0.2	0.6	14.1	1.1	10.2	0.6
TiO_2	0.0	0.0	0.0	0.2	0.6	0.3	0.0
Total	100.2	100.1	100.1	100.1	99.9	100.0	100.0
Number of particles analyzed	8	12	3	8	14	7	3

TABLE 4. PARTICLE MORPHOLOGY FOR THE MAJOR PHASES†

Phase	*Description*	
Orthoclase Plagioclase	Opaque	Subrectangular to rectangular
Quartz	Opaque to translucent	Irregular to polygonal
Mica	Translucent	Platey or shard-like, some with pitted surface textures
Chlorite	Translucent	Platey with "frilled" edges
Hornblende	Opaque to slightly translucent	Irregular to subfibrous
Phase γ	Translucent, with shadow patterns	Flakey with irregular surface textures

†Observations from TEM studies

well-defined mineral standards; two such phases were present in significant quantities (phases γ and δ). Following the dissolution treatment, these phases were apparently removed and mineral identification became more straightforward. The average chemical compositions of the major crystalline phases, obtained from the treated sample, are shown in Table 3, and the morphological characteristics of the particles are described in Table 4. It will be noted that the plagioclase analyses are stoichiometrically alkali deficient owing to low Na values. Feldspar analyses from both the treated and untreated samples show the same deficiency; although it is difficult to monitor light-element contents by EDS, the most likely cause of this deficiency is the natural history of the clay. The analyses are sufficiently accurate to characterize the phases, and these errors do not affect the manipulation of the bulk composition. The nature of the mica phase in the Oslo clay requires some consideration. Although illite has been recognized as an important constituent in many Norwegian and Canadian sensitive clays, after treatment in the Oslo clay the residual clay mica appeared to be muscovite. Mackenzie (1954) has classified clay micas on the basis of $K_2O + Na_2O$ percentages; the value of 11.2% in this Oslo clay is well above the 6–8% quoted for illite and approaches the theoretical maximum for muscovite.

Quantifications of the major crystalline phases present in the untreated and treated

TABLE 5. MINERALOGICAL DATA OBTAINED BY EDS ANALYSES (wt.%)

Phase	a Untreated	b Treated*	c Whole Clay†
Orthoclase	11.2	31.5	24
Plagioclase	12.6	31.0	24
Hornblende		11.7	9+ (≥7.5)
Quartz	4.3	8.3	6
Chlorite	4.6	7.9	6+ (≤4.5)
Mica	10.9	7.5	6+ (7.5)
Sphene		1.7	1
δ	3.2		
γ	53.1		
Calcite	1.0		(1.0)
Ilmenite		0.6	0.5+(1.5)
Amorphous Iron Oxide			(~2)
Total	100.9	100.2	100.5

* Sample treated using Segalen's (1968) procedure.

† Approximate mineralogy, including the constituents dissolved or removed in the treatment (bracketed values).

TABLE 6. COMPARISON DATA FOR COATED PARTICLES: ELEMENTAL PROPORTIONS

	Elemental oxides wt.%		Based on 100 SiO_2 molecules			
	a	b	c	d	e	f
	Phase γ	Phase δ	Phase γ	Orthoclase	Phase δ	Hornblende
SiO_2	41.7	44.0	100.0	100.0	100.0	100.0
Al_2O_3	14.5	11.0	34.7	28.6	25.0	20.3
FeO	18.0	24.7	43.2	0.2	56.1	39.4
MnO	0.6	0.9	1.4	0.3	2.1	1.5
MgO	11.0	5.1	26.4	0.6	11.6	21.3
CaO	3.8	9.6	9.0	1.5	21.8	26.3
Na_2O	0.5	2.1	1.2	1.2	4.8	2.8
K_2O	7.3	2.2	17.5	21.8	5.0	2.4
TiO_2	1.6	0.3	3.8	0.3	0.7	1.3
Total	99.0	99.9				

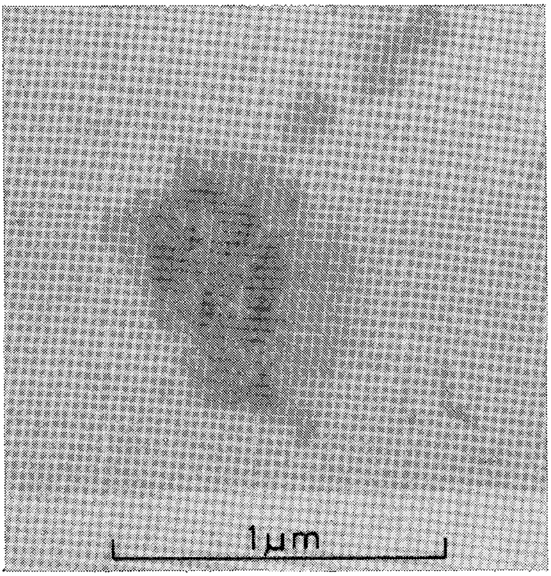

FIG. 1. Electron micrograph of a polymictic assemblage, phase γ.

clays are given in Table 5a, b. The apparent enhancement of hornblende, feldspar and quartz is consistent with the preliminary XRD findings; these minerals seem to be masked in the original sample by the presence of amorphous coatings. These coated minerals, with their complex but distinct chemistry, have been denoted as phases γ and δ in Table 5a and their chemistry is shown in Table 6a, b. The δ phase has a subrectangular to rectangular morphology and a composition similar to that of hornblende. A comparison of the chemistry of these two phases, normalized to 100 SiO_2 molecules, provides a clear indication that phase δ is hornblende with an iron oxide coating (Table 6e, f).

The chemical composition of phase γ is similar in some respects to that of orthoclase and muscovite; the high iron content may be interpreted as an amorphous coating (Table 6c, d). However, the nature of phase γ appears to be more complex. In TEM studies the particles appeared flaky, with irregular surface textures, and translucent but exhibited shadow effects. This morphology, in association with chemical and major phase determinations, suggests that phase γ particles may be polymictic assemblages that are bonded together by iron oxide compounds. Large particles (1–3 μm) form nuclei onto which smaller particles (<0.2 μm) adhere (Fig. 1). It appears that the nuclei are mainly orthoclase with some muscovite whereas the smaller particulate minerals are plagioclase, quartz, hornblende, ilmenite and poorly crystalline clay mica and chlorite. The proportion of finer particulate minerals in these assemblages is approximately 20%. Therefore, these colloidal particles (<0.2 μm) represent ~10% of the whole Oslo clay. The 18.3% FeO in phase γ (Table 6a) represents 9.7% FeO in the whole clay. Most of this iron can be attributed to the constituent phases of the polymictic assemblages, notably clay micas, hornblende, chlorite and ilmenite. Tentative calculations suggest that <2% FeO is available as a bonding agent in these aggregates.

These mineralogical results do indicate that amorphous material is present as coatings on certain crystalline phases and as a bonding agent in mineral aggregates, but in addition, discrete particles of almost pure iron oxide were identified. These amorphous particles have ill-defined boundaries and no visible structure, and diffraction patterns could not be obtained.

The overall effect of Segalen's dissolution treatment was assessed by studying the bulk chemistry of the untreated and treated clay (Table 7a, b). The results have been normalized to 100 SiO_2 molecules to enable a direct comparison to be made (Table 7c, d). Reductions were observed in the elemental oxides of magnesium, calcium, potassium and, particularly,

TABLE 7. BULK CHEMICAL ANALYSES

	Elemental oxides wt.%		Based on 100 SiO_2 mol.	
	a	b	c	d
	Untreated	Treated	Untreated	Treated
SiO_2	62.6	68.3	100.0	100.0
Al_2O_3	11.9	14.3	19.0	20.9
FeO	8.7	3.5	13.9	5.1
MnO	0.3	0.4	0.5	0.6
MgO	3.3	1.4	5.2	2.0
CaO	5.4	4.1	8.6	6.0
Na_2O	2.6	2.7	4.2	4.0
K_2O	5.1	4.7	8.2	6.9
TiO_2	1.6	0.7	2.5	1.0
Total	101.5	100.1		

iron. These reductions should represent the dissolution of amorphous iron oxide phases; that the losses are not restricted to FeO indicates that additional phases are involved. The sodium-rich feldspars appeared to be unaffected by the treatment.

The loss in iron is attributable to the dissolution of muscovite, chlorite, hornblende and amorphous iron oxide compounds. The apparent resistance of feldspars to dissolution and the reduced peak heights for mica observed in the XRD studies suggest that the K_2O loss is due to the removal of clay mica. Calculations based on the discrepancy in K_2O and the chemical composition of muscovite (Table 3) indicate a 7.5 wt. % loss in clay micas; this would incorporate 0.3% FeO. The reduced value for CaO may be due to calcite and hornblende. If the entire CaO loss is attributed to the dissolution of hornblende, then 12.5 wt. % is involved. The dissolution of this hornblende would account for the MgO discrepancy and would involve 2.3% FeO. The small estimated content of calcite in the untreated sample ($<$ 1 wt. %) would reduce this hornblende loss. The residual MgO and FeO are probably attributable to the destruction of poorly crystalline chlorite; $\leq$ 4.5 wt. % would be required.

These findings indicate that when Segalen's dissolution procedure is applied to sensitive clays it removes not only amorphous iron-rich phases but also significant quantities of chlorite, hornblende and muscovite. The analyses suggest that a minimum of 1.6% FeO is present in the Oslo clay and that this material takes the form of discrete particles, coatings and bonding compounds in mineral aggregates.

It is difficult to obtain accurate data concerning the dissolution of pure silica phases but this possibility must not be excluded. Segalen's (1968) treatment appears to disaggregate the polymictic assemblages and affords an improved definition of the constituent minerals. The mineralogy for the Oslo clay has been recalculated, using data obtained from the treated sample (Table 5b), to incorporate the probable dissolution losses (see Table 5c).

The usefulness of EDS in providing detailed mineralogical data is undeniable, but basic mineralogy required on a routine basis by geotechnical engineers must be obtained by less specialized methods. Thermal analysis is an established technique for mineral determinations in soils; indeed many of the mineralogical analyses that had been performed at the Norwegian Geotechnical Institute included DTA. Of the thermal techniques available, thermogravimetry has the advantage of giving weight changes due to decomposition reactions directly; these can readily be incorporated into simple calculations. Thermogravimetry alone does not permit one to draw mineralogical conclusions for the whole sample; it must be augmented by analyses of the thermally stable phases.

THERMOGRAVIMETRY

Samples for thermogravimetric analysis were prepared in two ways. The first procedure involved drying to a constant weight at 105°C and then equilibrating, *in vacuo,* at a relative humidity of 55% (at 18°C) for four days. In the second procedure, the pretreatments described by Mackenzie (1956) were used to saturate the clays with magnesium cations and to ensure the removal of carbonate and lignus–humus material. The samples were analyzed using a Stanton-Redcroft TR-02 thermobalance at a heating rate of 8°C/min. The derivative thermogravimetric plots are of percentage weight-loss *per* minute *versus* temperature. Additional TG information is given in the appendix. DTG plots for the whole, <2 μm and $>$ 2 μm samples are shown in Figures 2a, 2b and 2c, respectively.

Seven weight-loss events have been recognized in the DTG plots for the Oslo clay; these correspond to reactions involving adsorbed water (event A), organic matter (event B), hydrated iron oxide (event B_1), clay mica (event C), calcite (event D) and chlorite (events C_1 and E).

The accuracy of quantitative thermogravimetry is controlled by (1) the precision with which the weight losses can be attributed to individual mineral phases and (2) the values of percentage weight-loss used in the calculations. To allow comparisons with other thermogravimetric studies, the thermal characteristics of each mineral must be considered, as these provide the basis of each calculation.

The reaction interval involving calcite (event D) was identified by before-and-after studies on samples treated with 20% acetic acid; a percentage weight loss of 44% was used in the calculations. The selective removal of minerals by chemical pretreatments can improve the definition of weight-loss reactions for other minerals. Treatments with hydrogen peroxide were also used to remove the lignus–humus material and to clarify events in the 200–400°C temperature range.

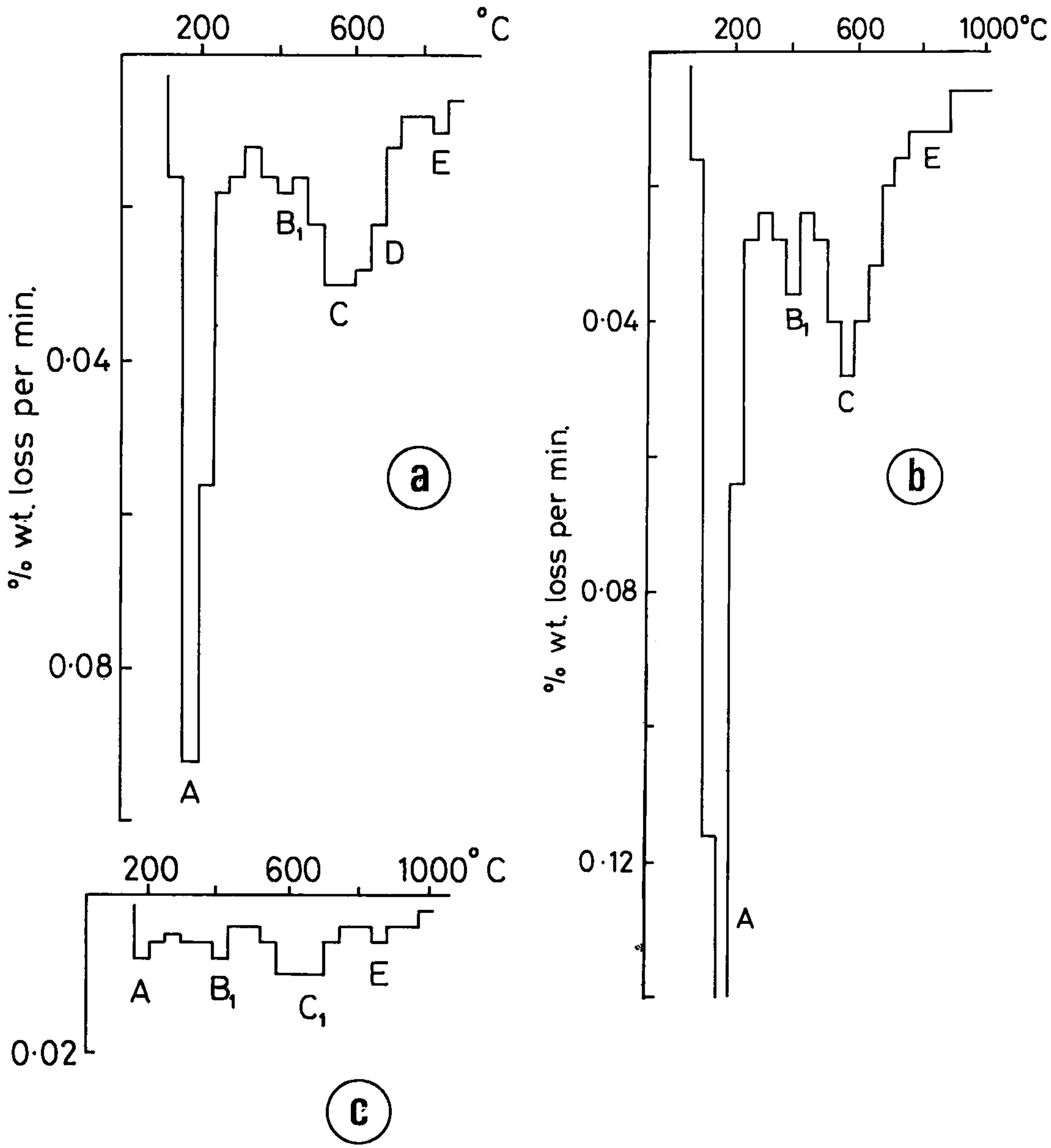

FIG. 2. DTG results for Oslo clay; (a) whole soil, untreated; (b) <2-μm-sized fraction; (c) >2-μm-sized fraction. Sized fractions treated to remov lignus-humus and carbonate minerals.

Clay micas

The dehydration characteristics of clay micas show a relatively distinct weight loss between 300 and 700°C; the maximum rate of weight loss generally occurs at 550°C (event C). Published chemical analyses and TG curves for the different clay micas show surprisingly little variation in the content of structural water (Grim *et al.* 1937, Roy 1949, Mackenzie *et al.* 1949, Mackenzie & Caillère 1979). The average values of weight loss during dehydration for clay-sized muscovite and illite are 6.2 and 7.3%, respectively, in the range 110–1000°C. However, these weight-loss events are often more discernible in the temperature range 300–700°C. The average percentage weight-losses for muscovite and illite in this temperature range are 4.2 and 5.0%, respectively.

Chlorite

The dehydration of chlorites has been discussed at length by Caillère & Hénin (1957). Two periods of weight loss, corresponding to the dehydration of the brucite-like and mica-like layers, occur at about 600° (event C_1) and 850°C (event E). Reducing the particle size by grinding causes a lowering of these reaction temperatures to 550 and 775°C, and the events become more pronounced (Sabatier 1950). The percentage weight-loss during the dehydration of chlorite is approximately 13%, of which 3.7% is attributed to the high-temperature reaction (Brindley & Chang 1974). Using the high-temperature reaction (event E) for calculation purposes enables the overlap of the clay mica and the other chlorite event to be resolved.

Amorphous ferric oxide hydrate

Although amorphous compounds of hydrated ferric oxide commonly occur in nature (Kurnakow & Rode 1928, Mackenzie 1949), most of the information concerning their thermal properties has been obtained by studying synthetically prepared gels. Studies have shown two main groups of gels, classified by their color to be "red-brown" and "yellow". Although the thermal behavior of these gels at low temperatures is ill-defined, it has been suggested that when heated to ~200°C they adopt identical behavioral and chemical characteristics (van Bemmelen 1899). Subsequent experiments have shown that variation of the peak temperature within a 250–500°C range is related to the pH of the solution in which the gels were formed. For pH values in the 7–10 range, peak temperatures of 350–400°C have been observed (Kulp & Trites 1951). Reviewing the thermal properties of clay soils, Mackenzie (1957) stated, "... a sharp peak in this region (250°–500°C) and especially at about 350°C is, in the absence of organic matter, almost invariably due to ferric oxide gel" (event B_1).

Dehydration studies with amorphous hydrated ferric oxide have yielded weight losses of 8–9%; these values correspond to a molecular ratio of combined water to ferric oxide of approximately unity (Fischer 1910, Posnjak & Merwin 1919).

The calculations for calcite, clay mica, chlorite and amorphous iron present in a mono-hydrated oxide form were performed using the appropriate values of percentage weight-loss. In all calculations the sample weight was adjusted for adsorbed water; the results are shown in Table 8.

FELDSPAR AND QUARTZ DETERMINATIONS

A brief review of Norwegian literature on sensitive clays indicates that the major components, accounting for over 50 wt. %, are feldspars, clay micas and quartz. Quantification of these minerals by X-ray diffraction can result in large errors, due not only to the presence of amorphous-coating material. As much as 15 wt. % quartz is commonly undetectable in X-ray diffractograms in the presence of appreciable mica because of the coincidence of the 3.35 Å peak of quartz with the 3.33 Å peak of mica and because the 4.26 Å quartz peak is relatively weak.

An alternative procedure for the assessment of quartz and feldspar, described by Kiely & Jackson (1965), was used. The <2 μm- and >2 μm-sized fractions were fused with sodium pyrosulfate to decompose the layer silicates. The relics of these minerals were then removed by hydrochloric acid and sodium hydroxide washings, leaving quartz and feldspar in the residue. The feldspar contents were determined by the allocation of K_2O, Na_2O and CaO in the residue to their equivalent end-member feld-

TABLE 8. MINERALOGICAL DATA OBTAINED BY TGA AND THE KIELY & JACKSON (1965) PROCEDURE

	SPSM^2	Iron oxide monohydrate^1	Clay^1 Mica	Chlorite^1	Calcite^1	Feldspars^2 K	Na	Ca	Quartz^2	Total
Whole	$\sim$25†	2.0	10.2	2.4	0.1	21†	22†	6†	11†	99.7
<2μm	$\sim$26	2.5	22.0	1.1	0.2	21.4	17.8	4.5	4.1	99.6
>2μm	$\sim$22	1.0	1.0	2.2	trace	19.5	26.5	8.6	19.3	100.1

1. TGA results 2. Kiely & Jackson (1965) results. †Calculated from sized fractions

SPSM^2: mainly hornblende; inferred data from EDS analyses.

spars, with suitable correction for mineral solubility and for the increase of Na from the pyrosulfate. Quartz content was calculated from the percentage residue by subtraction of the feldspars and by the use of the appropriate dissolution-correction factor (Table 8). The elemental oxides in the residue were measured by X-ray-fluorescence spectroscopy.

Additional information can be obtained by adapting the analytical procedure of Kiely & Jackson (Bentley & Smalley 1978). The sodium pyrosulfate-soluble material (SPSM) consists of some feldspars and quartz, mica, chlorite, calcite and iron compounds; each of these constituents has been evaluated. The differences between the recorded SPSM values and the sum of the detected constituents were 26 and 22 wt. % in the <2 μm and >2 μm fractions, respectively. It may be inferred from the EDS results (Table 5c) that the majority ($\sim$20 wt. %) of this additional material is hornblende.

DISCUSSION

As the particles analyzed by EDS were <3 μm in diameter, the results may be subject to a sampling bias; minerals in this restricted size-range may not be representative of the whole soil. However, feldspar determinations by the method of Kiely & Jackson (1965) compare well with EDS data (Tables 5c, 8). The most likely result of any sampling bias is an overestimation of the layer silicates. This may explain discrepancies between the EDS and TGA results for chlorite and clay mica. Alternatively, the errors may be a function of the weight-loss distribution between reaction intervals C and E. Thermogravimetry seems to provide a reasonable basis for the identification of hydrated ferric oxide; the next stage in the investigation of this compound should be studies of synthetic gel–clay mixtures. Published DTG plots for Canadian clays (Bentley & Smalley 1978) also show reaction intervals resulting from hydrated ferric oxide (event B_1). These are approximately the same size as in the Oslo clays and represent a content of <3 wt. %.

Previously, where the dissolution technique of Segalen (1968) was used on Canadian clays, large quantities (10–20 wt. %) of amorphous material were detected (McKyes *et al.* 1974, Yong *et al.* 1979). McKyes *et al.* (1974) defined the amorphous constituent as an iron–silicon–hydroxyl complex with small amounts of aluminum. The present mineralogical findings suggest that the elements removed during Segalen's treatment are not representative of the chemistry of the amorphous phase. The considerable quantities of amorphous material, previously reported for Canadian clays, may be a function of this nonselective dissolution treatment.

A fundamental flaw in the Segalen approach is the assumption that the crystalline layer-silicate minerals in clays are sufficiently homogeneous to react uniformly during dissolution. Clays produced by glacial erosion are not the best subjects for this treatment, and careful consideration must be given to the attack upon the nonamorphous clay-mineral fraction.

Geotechnical implications

The identification of polymictic assemblages has important sedimentological and geotechnical implications. Although the colloidal primary-mineral particles and the amorphous iron oxide can appear as one bonded mass, their roles in the development of sensitive-clay microstructures are probably quite independent, because the provenances of these materials are different. The glacially derived colloidal particles influence the clay microstructure during formation. The amorphous-iron compounds, which may form cementitious links, are introduced at a later stage, as a result of postdepositional chemical weathering.

It has been proposed that sensitive-clay microstructures are formed by the leaching of a flocculated clay-mineral fabric (Rosenqvist 1953, 1975). Sedimentation of layer-silicate minerals into a marine environment leads to the development of an open "card-house" structure. Subsequent decrease in the cation concentration of the pore water during the postdepositional period increases the effective zeta-potentials and therefore the mutual repulsion between the layer-silicate particles. This leaching process has the effect of reducing the plasticity, frequently to a level at which the natural moisture content is in excess of the liquid limit. Hence, a change in the electrolytic environment is seen as modifying the liquidity index, strength and sensitivity in the undisturbed state while maintaining a constant water content and structure. Subsequent research has shown that in most sensitive-clay deposits the layer silicates have been subjected to leaching, but a comprehensive theory for sensitivity should accommodate contributions from other mineral phases and cognate sediment processes. In Norwegian clay, additional factors do not mask the relationship between sensitivity and salt concentration in the pore water (Bjerrum 1954). However, in Canadian clays the additional factors are sufficiently variable to obscure a similar relationship (Penner 1965). The behavioral characteristics of colloidal-mineral particles and amorphous iron oxide may be important in this respect.

As the size of colloidal particles diminishes, the surface area *per* unit mass increases and the effectiveness of surface forces is enhanced. The colloidal-mineral particles in sensitive clays adhere to larger particles; van der Waals forces, augmented later by cementation, may provide a bond of sufficient strength to promote and maintain this aggregation. This interaction with other crystalline components could promote the development of high-porosity and sensitive structures. Defects in the mineral lattice of these colloidal particles may produce a surface charge that allows some double-layer activity. In this case the particles could undergo pseudoflocculation in the manner envisaged by Gadd (1975) and, in response to changes in porewater chemistry, they could contribute to low remolded strengths.

The engineering characteristics of Norwegian clays do not reflect cementation in the microstructure to the same degree as Canadian sensitive clays. In fact, one of the major differences between the two is that Canadian clays almost invariably have higher undisturbed strengths. The degree of structural cementation in these clays is related to the amorphous ferric oxide. However, the emplacement process is probably more significant than any small variations in quantities present. Introducing cementing compounds at different stages of sediment consolidation can have a pronounced effect on the geotechnical properties of the resulting clay mass. If the interparticle bonds form at low stresses, the high initial porosity of the sediment will be preserved to a considerable degree; sensitivity will be enhanced by virtue of the cementation. If cementitious materials are introduced into a partially or wholly consolidated clay, then the influence of brittle interparticle links on this established fabric will not be as great. The high-porosity sensitive structure will have been produced by the original constituents of the sediment, and cementation will cause a modest increase in undisturbed strength and presumably decrease the rapidity number. Clearly, cementation is a factor that may obscure the relationship between sensitivity and salt concentration.

Considering the engineering behavior of Canadian clays, Crawford (1968) concluded that cementitious links do form at low stresses during the first stages of deposition. The formation of cementing compounds, by *in situ* chemical weathering, appears to be a function of increased oxidation capacity and changes in pH that are promoted by the influx of freshwater during the leaching process (Bjerrum 1967, Moum 1967). Therefore, the environmental conditions during the depositional and postdepositional periods influence the timing of the cementation. The emplacement of iron oxide compounds may have commenced earlier, and possibly at a higher rate, in Canadian clays as a response to regional rather than global changes in environmental conditions.

CONCLUSIONS

Mineralogical data for the Oslo clay have been obtained using EDS, XRF, XRD and TG analysis in conjunction with selective dissolution procedures. Mineralogical results obtained from TGA and the procedure of Kiely & Jackson (1965) compare well with EDS data. Although the former do not give a direct assessment of hornblende contents, they provide a relatively straightforward method of obtaining accurate mineralogical information. The major crystalline phases are feldspar (50 wt. %), hornblende (~18 wt. %), quartz (8 wt. %), clay mica (12 wt. %) and chlorite (~7 wt. %). The clay mica includes a significant proportion of muscovite.

Polymictic assemblages have been distinguished that are composed of single orthoclase or muscovite particles (1–3 μm) covered with colloidal-mineral particles (<0.2 μm). The assemblages are cemented together by iron compounds, probably in the form of an amorphous hydrated oxide. The amorphous iron compounds (~2 wt. %) also appear as discrete particles and as coatings on individual hornblende particles. Iron compounds in the Oslo clay are probably derived from the *in situ* chemical weathering of hornblende. The presence of cemented-particle aggregates masks the actual grain-size distribution of the clay, and by incorporating layer silicates the apparent plasticity of the material may be reduced.

The dissolution technique described by Segalen (1968) disaggregates these cemented-mineral assemblages and affords an improved definition for the constituent particles. In addition, this treatment appears to dissolve significant quantities of chlorite, hornblende and mica. The considerable quantities of amorphous material (>10 wt. %), previously reported for

Canadian clays (McKyes *et al.* 1974, Yong *et al.* 1979), may be a function of this nonselective dissolution.

The colloidal particles (<0.2 μm) and the amorphous iron compounds are probably common constituents of Norwegian and Canadian sensitive clays. By contributing to the formation of microstructures, these materials influence the engineering properties of clays. The glacially derived mineral particles are constituents of the sedimenting assemblage, and their colloidal nature may promote van der Waals' and electrochemical bonding. The potential for forming interparticle linkages suggests that during sedimentation the colloidal-mineral particles may interact with other crystalline components to assist in the formation of high-porosity structures. The amorphous iron compounds are introduced at a later stage of sediment development, and the cementing role previously suggested appears to be satisfactory. Regional changes in environmental conditions influence the timing of the cementation, and this may partly explain variations in the degree of cementation exhibited by sensitive clays from different localities. From a geotechnical viewpoint the presence of this cementitious material in sensitive clays is undoubtedly important, but it may be a mistake to attach too much significance to the variation in contents from sample to sample. Until improved determinative procedures are developed, the actual proportion of amorphous compounds that contributes directly to the behavioral characteristics of the clay mass will remain unknown.

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APPENDIX: THERMOGRAVIMETRIC INFORMATION FOLLOWING ICTA FORMULATION

1. Substance investigated: Sensitive-clay sample from Oslo, Norway.
2. The clay samples were supplied by Professor I.T. Rosenqvist of the Institute of Geology, Oslo.
3. Heating rate: 8°/minute; the heating rate departed from linear below 100°C. The temperature range for the analysis was 20 to 1000°C.
4. Furnace atmosphere: Air at atmospheric pressure.
5. Sample container: Alumina crucibles (diameter 21 mm and depth 25 mm).
6. Identification of the abscissa: Time and temperature were recorded simultaneously.
7. Identification of the final products: XRF analyses were performed for each sample; the results are presented as elemental oxides (Table 2).
8. Reproducibility of weight change: A reproducibility of ± 5% was recorded; there also was fluctuation of the reaction interval within ± 20°C.
9. Reference to XRD and TGA of standard minerals allowed the thermal events to be identified.
10. Instrumentation: Stanton-Redcroft TR-02 thermobalance.
11. The weight-change axis on the DTG plots is presented as a percentage weight loss *per* minute.
12. The DTG curves were constructed by plotting the weight change during a predetermined time; the five-minute interval of the thermobalance timer made this the most convenient interval. In order to characterize the behavior of the thermobalance, we calibrated the system at intervals during the test program by using potassium hydrogen phthalate as a temperature standard (Smalley *et al.* 1977). The four major thermal events associated with the decomposition of PHP occurred at 340, 540, 760 and 980°C. The spread of events across a relatively wide heating range makes PHP a useful standard for clay-mineral thermogravimetry.