

The mineralogy, geochemistry and surface area of mudrocks from the London Clay Formation of southern England

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The mineralogy, geochemistry and surface area of mudrocks from the London Clay Formation of southern England

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Front cover

<2 µm X-ray diffraction traces, sample Brambledown, Kent.

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Foreword

This report is the published product of a study by the British Geological Survey (BGS) and forms part of the ongoing BGS project, 'Ground Movements: Shrink/Swell'. This report aims to provide mineralogical and geochemical data to help explain the geotechnical behaviour of the UK London Clay Formation. This project follows similar projects dealing with soils and rocks of the Gault Clay, the Mercia Mudstone Group, the Lambeth Group and the Lias Group.

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Summary

This report describes the results of mineralogical and geochemical analysis of a suite of mudstones from the London Clay Formation of southern and south-eastern England. The work was carried out as part of the ongoing 'Ground Movements: Shrink/Swell' project under the Physical Hazards Programme.

The first part of the report gives an introduction to the geology of the London Clay Formation and a summary of previous mineralogical studies of these rocks. A summary of analytical methods employed (X-ray diffraction analysis, X-ray fluorescence spectrometry and surface area determinations) is then provided and the results discussed with reference to their likely effect on the engineering performance of the London Clay Formation.

The study has generally confirmed the findings of previous workers with typical non-clay mineral assemblages composed of quartz, feldspar (albite and K-feldspar), carbonates (dolomite, siderite and calcite), 'mica', pyrite, gypsum and goethite while clay mineral assemblages are generally formed of smectite, illite, kaolinite and chlorite. However, the wide geographic and stratigraphic distribution of the analysed samples has provided important new information which will aid not only interpretation of the engineering behaviour of these rocks but also their diagenetic and geological histories.

The engineering properties of the London Clay Formation are heavily influenced by its clay mineralogy and the proportion of clay minerals present. This study has shown that while the composition of the clay mineral assemblages is similar across the London Clay Formation outcrop, the proportion of clay material increases from west to east.

The most clay-rich samples are found in the London Basin and particularly around the Thames estuary, central Essex and just west of London in eastern Berkshire/Surrey. These clay-rich samples also contain the most smectite and are therefore likely to undergo the greatest shrink-swell volume changes during wetting and drying and provide the most problems in terms of their engineering behaviour.

It would appear most likely that the smectite in the London Clay Formation was contributed by the reworking of ash-rich soils while kaolinite was sourced from tropical weathering of granites to the west. A rare occurrence of a pure interlayered kaolinite/smectite clay assemblage in a sample from Studland Bay, Dorset is likely to have developed due to the acidic, tropical weathering of a volcanic-ash or smectite-rich deposit.

The very common presence of pyrite, together with gypsum in the London Clay Formation means that concrete engineering sited in these rocks may require sulphate-resistant compositions to avoid acid attack and thaumasite formation.

1 Introduction

This report summarises the results of a mineralogical, geochemical and surface area study of a suite of predominantly mudrock samples from the London Clay Formation of south and south-east England. This study forms part of the BGS geotechnical project, 'Ground Movements: Shrink/Swell' under the Physical Hazards Programme.

Since the early 1990's, the ongoing 'Engineering Geology of UK Rocks and Soils' project has examined soils and rocks from different formations and attempted to database, characterise and explain their geotechnical behaviour. Previous studies have included the Gault Clay (Forster *et al.*, 1994), the Mercia Mudstone Group (Hobbs *et al.*, 2001), the Lambeth Group (Entwisle *et al.*, 2005) and the Lias Group (Hobbs *et al.*, 2005).

The main aims of the 'Ground Movements: Shrink/Swell' project are to specifically determine the shrinkage and swelling properties of UK clays and mudrocks, and to investigate the relationship between them.

Due to their high surface area, residual charge and interaction with water, clay minerals (and smectite in particular) are most frequently cited as the reason for the shrink-swell behaviour noted in many fine-grained sedimentary rocks. For this reason, this study principally aimed to evaluate the nature of the clay minerals present to help explain the geotechnical behaviour of the London Clay Formation.

In addition, this study also focussed on detecting the presence of sulphate-bearing species (e.g. pyrite, gypsum etc). Oxidation of pyrite in the environment leads to the formation of sulphuric acid which considerably reduces the pH of groundwater. Where such acidic groundwaters make contact with concrete engineering at low temperatures (e.g. foundations, motorway bridges etc), the main cementitious binder (calcium silicate hydrate, C-S-H) is converted to thaumasite (a non-binding calcium carbonate silicate sulphate hydrate) resulting in deterioration and failure (e.g. Hobbs & Taylor, 2000; Bensted, 1999; Burkart, *et al.* 1999). Greater awareness of the potential problems that thaumasite can cause has arisen with the increased use of limestone fillers in cements, the common employment of limestone aggregates in concrete and the introduction of Portland limestone cements, together with the realisation that structural foundations of buildings are, on average, below ambient temperature and are within the optimum temperature range for thaumasite to be formed (Bensted, 1999). A knowledge of the presence of sulphate-bearing species in the London Clay Formation is therefore crucial to planning foundation construction in such strata.

2 Geology

The early Eocene (Ypresian) London Clay Formation, part of the Thames Group, was deposited during the most widespread Tertiary marine advance from the North Sea which covered the whole of Eastern Britain from East Anglia to Dorset and southwards over the Low Countries, North France and North-west Germany. In Britain, the onshore London Clay Formation is only preserved in the London and Hampshire basins where it rests unconformably on the Woolwich and Reading Formations respectively (Figure 1).

The Formation is principally formed of a fairly monotonous, stiff, sometimes intensely bioturbated, bluish grey mudstone that weathers brown and commonly contains selenite (gypsum) crystals. Generally uniform in lithology, it becomes sandier to the west (King, 1981). It can be subdivided into five coarsening-upward divisions indicating repeated transgressive pulses that were followed by shoreline progradation and shallowing. It is characterised by an

abundant and diverse marine fauna of molluscs (bivalves, gastropods and more rarely nautiloids), an exotic macrofauna including crustaceans, fish and reptiles and microfauna of essentially pelagic forms, such as diatoms, radiolaria and globigerine foraminiferans. The London Clay Formation also contains a wealth of terrigenous plant material (>500 species) including pollen, spores, logs and fruits which has enabled the production of detailed palaeoclimate and paleoecological reconstructions. During the deposition of the London Clay Formation, southern England lay at approximately 40°N and the Tertiary climate was at its warmest with the surrounding land covered by dense tropical to temperate forest and mangrove swamps.

The London Clay Formation is the thickest and most widespread Tertiary unit in Britain and reaches a thickness of over 200 m in the east of the London Basin. It thins to c.100 m at Windsor and even less further west. A similar trend is noted in the Hampshire Basin, where a thickness of c.100 m at eastern end of the Isle of Wight thins to less than c.25 m in Purbeck.

In the London Basin, the London Clay Formation grades upwards into the nearshore, tidally influenced sands of the Bagshot Beds indicating a general regression. In the Hampshire Basin, the tops of the coarsening-upward divisions are sandy with cross-bedding suggesting deposition in nearshore tidal channels. Towards the western end of the basin, rootlet-bearing palaeosols occur near the top of the unit, in the Christchurch Member, recording the seawards encroachment of tidal flats (Anderton, 2000).

3 Previous mineralogical studies of the London Clay Formation

The mineralogy of the London Clay Formation has been investigated by several workers including Gilkes (1966, 1968), Weir & Catt (1969), Perrin (1971), Burnett & Fookes (1974), Lake *et al.*, (1986), Bloodworth *et al.* (1987), Edwards & Freshney, (1987), Huggett (1994) and Huggett & Gale (1997, 1998). Most recently, Huggett & Knox (2006) provided some new data for the London Clay Formation as part of a synthesis of the clay mineralogy of the onshore and offshore Tertiary strata of the UK.

3.1 LONDON BASIN

The first investigations (Gilkes 1966, 1968) examined a few specimens from Harefield and Hampton, Middlesex and found a predominantly montmorillonite (smectite)-illite mineralogy.

Samples of London Clay Formation from northeast Kent, examined by Weir & Catt (1969) lacked appreciable quantities of sand and had average clay fraction compositions of 60% montmorillonite (smectite), 25% mica (illite), 5-10% kaolinite and 2-5% chlorite. The detrital sand and coarse silt minerals in the lower parts of the formation were formed of quartz, flint, glauconite, K-feldspars, chlorite, muscovite and deep-green biotite and were similar to the underlying Oldhaven and Thanet Beds. Heavy mineral suites in the higher beds of the London Clay Formation were similar to the overlying Claygate and Bagshot Beds; zircon, tourmaline, kyanite and staurolite are less common in the lower parts, whereas the amounts of garnet, epidote and amphiboles are greatly increased. The main authigenic sand and silt minerals were glauconite, calcite, pyrite with siderite at some levels.

Weir & Catt (1969) also noted the unusually great depths to which weathering could be detected in the London Clay Formation e.g. 20ft (~6.5 m) beneath 8ft (~3 m) of river terrace gravels at Shelford sand quarry. This was attributed to Tertiary or Early Quaternary times and caused a colour change from dark grey (5Y 3/1 of the Munsell Color Chart) to yellowish-brown (commonly 10 YR hues). The most-strongly weathered horizons often contain small selenite crystals or nodular segregations of jarosite while large, twinned selenite crystals occur at lower horizons. Such weathering was attributed to pyrite oxidation and subsequent leaching by sulphuric acid. In studying the morphology of the smectite present, Weir & Catt (1969) described a mixture of lath-shaped and rounded particles at the base, with the proportion of rounded particles increasing up the sequence.

Lake *et al.* (1986) described clay assemblages that were dominated by smectite and illite with minor kaolin and rare chlorite from the *c*.130 m of the London Clay Formation intercepted by the BGS Hadleigh borehole in Essex. An upward increase in the proportion of kaolin, associated with an overall upward increase in grain size, was also noted with a maximum of 15% quoted for the Claygate Beds (now the Virginia Water Formation). Interstratified illite-smectite was recorded in the lower part of the London Clay Formation (Divisions B/C of King, 1981).

As part of a site investigation for a low-level radioactive waste repository at Bradwell, Essex, Bloodworth *et al.* (1987) carried out an extensive mineralogical and lithogeochemical study of a *c*.45 m borehole interval of the London Clay. The samples were predominantly composed of mica (*c*.38%), smectite (*c*.30%), kaolinite and chlorite (*c*.12%) and quartz (*c*.15%) with subordinate feldspar and siderite. Trace quantities of calcite and dolomite were also detected in the upper parts of the interval. Surface area values for the mudstones varied from 157 to 281 m²/g with a mean of 231 m²/g and cation exchange capacities (CEC) ranged from 21.7 to 35.7 meq/100g with a mean of 27.3 meq/100g. Evolved gas and X-ray diffraction analyses revealed that pyrite was ubiquitously developed below a depth of *c*.16 m, typically forming <3% of the London Clay Formation.

Huggett (1994) examined the diagenesis of mudrocks and concretions from the London Clay Formation in the London Basin. Mineralogically, the three lithofacies – laminated silty claystone, partially bioturbated silty claystone and partially bioturbated claystone, showed little variation but considerable differences in the suites of trace cements such as apatite, siderite, barite, calcite, silica and pyrite.

Glauconite was reported to occur in minor amounts (~1%) throughout the London Clay Formation, although at some burrowed horizons it forms up to 10% of the bulk sediment (Huggett & Gale, 1997, 1998).

Most recently, Huggett & Knox (2006) suggest that in the London Basin, the clay mineral assemblages of the London Clay Formation are uniformly dominated by smectite and illite with minor chlorite and kaolin. Chlorite increases with decreasing depth in the Hampstead Heath borehole.

3.2 HAMPSHIRE BASIN

The first published studies describing the clay mineralogy of the London Clay Formation in the Hampshire Basin were produced by Gilkes (1966, 1968). This $<5 \mu m$ XRD study found a wide range of compositions. At Whitecliff Bay for example on the Isle of Wight, he found a wide range of compositions from illite-rich with minor smectite and kaolin, to smectite-rich with minor illite and kaolin. In contrast, at Alum Bay he found the $<5 \mu m$ fraction to be dominated by illite and kaolin with no smectite. Glauconite, in the form of pellets and finely dispersed pigment was common but impossible to distinguish from illite on the XRD charts.

Gilkes (1966, 1968) suggested an overall lateral increase in kaolin, and a decrease in smectite from east to west across the Hampshire Basin in the clay fraction. Burnett & Fookes (1974) suggested a similar trend when considering whole-rock mineralogy.

Examination of the London Clay Formation using a transmission electron microscope (TEM), Gilkes (1966) found that the majority of particles in smectite-dominated samples from Whitecliff Bay are $0.1-0.3 \mu m$ in size and were composed of anhedral "fluffy" aggregates and very thin lath-shaped particles. Samples from Alum Bay, however, included a much higher proportion of

thick lath-shaped euhedral particles $0.3 \times 0.6 \mu m$ which resembled those identified as smectite by Weir & Catt (1969). Gilkes (1966) argued that these lath-shaped euhedral particles were either kaolin or illite with the smaller particles representing smectite.

At both Alum Bay and Whitecliff Bay on the Isle of Wight, Huggett & Gale (1997, 1998) noted that the clay mineral assemblages are notably kaolin-rich in some sand units due mostly to replacement of glauconite by kaolin at, or soon after, deposition. These authors also noted that in the Hampshire Basin, replacement of detrital mica grains by kaolin is extremely rare, whereas in the London Basin it is widespread.

The London Clay Formation intercepted by BGS boreholes in the Southampton area show different proportions of clay minerals. In the Bunker's Hill borehole, illite > smectite > kaolin, while further east in the Shamblehurst borehole smectite > illite > kaolin (Edwards & Freshney, 1987). In both boreholes, there is a gradual upward increase in smectite to the top of Division B.

No clay mineral data are available for the Aller Gravel of Devon which has been correlated with the London Clay Formation (Daley & Balson, 1999).

3.3 REGIONAL SYNTHESES

Previously published regional syntheses of the mineralogy of the London Clay Formation in both the London and Hampshire basins have been produced by Burnett & Fookes (1974) and Huggett & Knox (2006).

Burnett & Fookes (1974) carried out their study to help explain engineering properties, along similar lines to this study but with a more limited dataset.

Quartz typically formed between 20 and 33% mineral assemblage with the upper London Clay clearly more quartz-rich than lower parts of the formation. Quartz concentrations were greater in the west than the east, particularly in the Hampshire Basin perhaps due to a river entering the London Clay sea. High quartz contents (and low clay content) were detected close to palaeontological zone or subzone boundaries.

The authors also noted a fairly clear-cut line of separation along the London Ridge (Watford to Streatham) between silty or sandy sediments to the west and clayey sediments to the east. Clay minerals typically form between 50 and 75% of the total mineral assemblages but particularly high values were obtained in the middle London Clay and around Staines, the London 'upland' region and the Thames Estuary. Lower clay mineral contents were shown by samples from the Hampshire Basin.

In terms of clay minerals, increased kaolinite contents were noted in the upper London Clay and in the near-shore Hampshire Basin and were ascribed to emergence of the deposition surface from the sea. Illite distribution was found to be similar to the total clay minerals suggesting that supply seems to have been very constant and ubiquitous. Divalent smectite contents usually form 10-25% of the clay mineral assemblages and generally increases from west to east, from shoreline to deep water. Decreasing smectite contents were also noted from the base to the top of the London Clay Formation.

Huggett & Knox (2006) suggest that there are no trends apparent between the Hampshire and London basins (Table 1). However, new data that they present from Alum Bay and Whitecliff Bay suggests that the clay mineral assemblages of the London Clay Formation in the Hampshire Basin display much more vertical variability than in the London Basin, with notably kaolin-rich assemblages in some sand-units. These kaolin-rich assemblages result from glauconite replacement at, or soon after deposition. Kaolinisation of detrital micas is common in the London Basin but rare in the Hampshire Basin.

Basin	Location		Mean %cl	ay mineral	
		illite	kaolinite	chlorite	smectite
Hampshire	Alum Bay	41	13	2	44
··· ·	Whitecliff Bay	40	15	5	40
London	Staines	40	11	5	44
	Hampstead Heath	35	12	Inite chlorite smectite 13 2 44 15 5 40 11 5 44 12 7 46	

Table 1. Mean semi-quantitative XRD estimate of clay minerals present in <2 μm fraction of the London Clay Formation (from Huggett & Knox, 2006)

4 Samples

During 2004, field visits were made by BGS staff to sample the London Clay Formation at 19 locations across southern England. The aims of these visits were to collect undisturbed samples for geotechnical tests and disturbed samples for a suite of geotechnical, mineralogical, geochemical, petrographical and micropalaeontological analyses. The results of petrographical analyses were reported by Bouch (2005), micropalaeontological ages were provided by Wilkinson (2004a, b, 2005) and geotechnical results by Nelder & Jones (2005) and Freeborough & Jones (2006).

A total of 25 disturbed, outcrop samples (Figure 1, Table 2) were submitted for mineralogical analysis using X-ray diffraction (XRD) and surface area techniques. Of these 25 samples, 16 were also selected for major and trace element geochemical analysis by X-ray fluorescence spectrometry (XRFS).



Figure 1. The distribution of the London Clay Formation at surface and the location of the study sites.

Table 2. Summary of sample details

BGS Code	Basin	Location	NGR	Hand specimen description, field notes	Stratigraphic division (King, 1981)	XRD, surface area	XRFS
MPLK205		Knowl Hill, Berkshire (quarry)	SU 816 795	Brown-blue grey, stiff mudstone with sand lenses	B-C	\checkmark	\checkmark
MPLK206		Bulmer, Essex (quarry)	TL 832 382	Brown-blue-grey, stiff silty mudstone	Upper D-E	\checkmark	\checkmark
MPLK207		Whitehall Farm 1, Kent (quarry)	TQ 882 762	Brown, stiff mudstone (Top Section)	B-C	\checkmark	-
MPLK208		Whitehall Farm 2, Kent (quarry)	TQ 882 762	Brown, stiff, homogeneous mudstone (Lower Section)	B-C	\checkmark	\checkmark
MPLK209		Warden Point, Kent (cliff face)	TR 020 724	Brown-grey, stiff, homogeneous mudstone	B-C	\checkmark	-
MPLK210		Brambledown, Kent (clay pit)	TQ 967 715	Brown, stiff, homogeneous mudstone	B1	\checkmark	\checkmark
MPLK612	Ŀ.	Ockendon 1, Essex	TQ 614 820	Medium grey, stiff, homogeneous mudstone	Α	\checkmark	\checkmark
MPLK613	Bas	Ockendon 2, Essex	TQ 614 820	Buff, stiff, homogeneous mudstone	Α		-
MPLK614	don	Bulls Lodge, Essex	TL 747 085	Dark brown-grey, stiff, homogeneous mudstone	Α	\checkmark	\checkmark
MPLK615	Lone	Colchester 1, Essex	TL 955 226	Dark brown, stiff, homogeneous mudstone	Α		\checkmark
MPLK616		Colchester 2, Essex	TL 955 226	Medium grey, stiff, homogeneous mudstone with ?gypsum efflorescence	Α		-
MPLK617		Farnham, Surrey	SU 877 475	Light blue-grey, stiff, homogeneous mudstone		\checkmark	\checkmark
MPLK618		Poyle, Berkshire	TQ 028 766	Dark brown, stiff homogeneous mudstone		\checkmark	\checkmark
MPLK619		Stanwell, Surrey	TQ 049 746	Medium brown, stiff, homogeneous mudstone	B1	\checkmark	\checkmark
MPLL005		Roxwell, Essex	TL 657 088	Brown, laminated silty mudstone	B-C		-
MPLL006		Hollingson Meads, Hertfordshire	TL 453 126	Brown, laminated silty mudstone	Α		\checkmark
MPLK211		Fair Oak Sand Pit, Hampshire (sand pit)	SU 504 183	Brown, stiff, sandy mudstone, below stone horizon		\checkmark	\checkmark
MPLK212		Southleigh, Sussex (quarry)	SU 886 043	Brown, stiff, homogeneous mudstone	С	\checkmark	-
MPLK213	sin	Whitecliff Bay 1, Isle of Wight (cliff face)	SZ 643 858	Brown, stiff, silty mudstone, Lower Basement Beds	Α	\checkmark	-
MPLK214	Bas	Whitecliff Bay 2, Isle of Wight (cliff face)	SZ 643 858	Grey, stiff, silty mudstone, higher in succession	Α	\checkmark	-
MPLK215	hire	Alum Bay 1, Isle of Wight (cliff face)	SZ 307 853	Brown, stiff, sandy mudstone, near Basement Beds	Α		\checkmark
MPLK216	sdun	Alum Bay 2, Isle of Wight (cliff face)	SZ 307 853	Brown, stiff, sandy mudstone, higher in succession	Α	\checkmark	-
MPLK217	Ha	Knoll Manor 1, Dorset (clay pit)	SY 977 973	Grey-orange, stiff, mudstone with Fe-oxides		\checkmark	\checkmark
MPLK218	1	Knoll Manor 2, Dorset (clay pit)	SY 977 973	Yellow-brown, stiff, sandy clay, above S1		\checkmark	\checkmark
MPLK219	1	Studland, Dorset (cliff face)	SZ 043 824	Dark brown, stiff, sandy clay		\checkmark	\checkmark

5 Laboratory methods

5.1 GENERAL SAMPLE PREPARATION

Representative portions of each sample were separated, dried at 55°C and jawcrushed. Approximately ¹/₄ of the jawcrushed material was then hammer-milled to pass a 125 μ m screen for surface area and whole-rock X-ray diffraction analyses.

5.2 SURFACE AREA DETERMINATION

Surface area determinations were performed on all samples using the 2-ethoxyethanol (ethylene glycol monoethyl ether, EGME) technique. The method is based on the formation of a monolayer of EGME molecules on the clay surface under vacuum. Aluminium dishes containing approximately 1.1 g hammer-milled sample/clay standard (Patterson Court Blue bentonite) were placed in a desiccator containing anhydrous phosphorus pentoxide. The desiccator was evacuated and allowed to stand overnight before the dishes were reweighed. The samples were then saturated with 2-ethoxyethanol and placed in a second desiccator containing dry calcium chloride. After 1½ hours, the desiccator was evacuated and left overnight. The sample was then rapidly re-weighed and the weight of 2-ethoxyethanol absorbed determined and the surface area calculated. Finally, a correction based on the Patterson Court Blue standard was applied.

Smectite has a surface area of c.800 m²/g while other clay minerals and quartz have surface areas typically less than 100 m²/g and 1 m²/g respectively. Such a difference in value means that the surface area of a sample can provide a useful estimate of its smectite content.

5.3 X-RAY DIFFRACTION ANALYSIS

5.3.1 Preparation

In order to achieve a finer and uniform particle-size for whole-rock XRD analysis, approximately 3 g portions of the hammer-milled material was micronised under acetone for 5 minutes and dried at 55°C. The dried material was then disaggregated in a pestle and mortar and back-loaded into a standard aluminium sample holder for analysis.

Approximately 15 g subsamples of the jawcrushed material was dispersed in distilled water using a reciprocal shaker combined with treatment with ultrasound. The suspension was then sieved on 63 μ m and the <63 μ m material placed in a measuring cylinder and allowed to stand. In order to prevent flocculation of the clay crystals, 2 ml of 0.1M 'Calgon' (sodium hexametaphosphate) was added to each suspension. After a period dictated by Stokes' Law, a nominal <2 μ m fraction was removed and dried at 55°C. 100 mg of the <2 μ m material was then re-suspended in a minimum of distilled water and pipetted onto a ceramic tile in a vacuum apparatus to produce an oriented mount. The mounts were Ca-saturated using 2 ml 0.1M CaCl₂.6H₂O solution and washed twice to remove excess reagent.

5.3.2 Analysis

XRD analysis was carried out using a Philips PW1700 series diffractometer fitted with a cobalt-target tube and operated at 45kV and 40mA. Whole-rock samples were scanned from 3-50 °20 at 0.69 °20/minute. The <2 μ m samples were scanned from 2-32 °20 at 0.54 °20/minute as airdry mounts, after glycol-solvation and after heating to 550°C for 2 hours.

Diffraction data were firstly analysed using Philips X'Pert software coupled to an International Centre for Diffraction Data (ICDD) database running on a Gateway personal computer system.

5.3.3 Whole-rock quantification

Following identification of the mineral species present in the samples, mineral quantification was achieved using the Rietveld refinement technique (e.g. Snyder & Bish, 1989) using Siroquant v.2.5 software. This method avoids the need to produce synthetic mixtures and involves the least squares fitting of measured to calculated XRD profiles using a crystal structure databank. Errors for the quoted mineral concentrations are typically $\pm 2.5\%$ for concentrations >60 wt%, $\pm 5\%$ for concentrations between 60 and 30 wt%, $\pm 10\%$ for concentrations between 30 and 10 wt%, $\pm 20\%$ for concentrations between 10 and 3 wt% and $\pm 40\%$ for concentrations <3 wt% (Hillier *et al.*, 2001).

5.3.4 XRD-profile modelling

In order to gain further information about the nature of the clay minerals present in the samples, modelling of the XRD profiles was carried out using Newmod-for-WindowsTM (Reynolds & Reynolds, 1996) software.

Modelling was also used to assess the relative proportions of clay minerals present in the $<2 \mu m$ fractions by comparison of sample XRD traces with Newmod-for-WindowsTM modelled profiles. The modelling process requires the input of diffractometer, scan parameters and a quartz intensity factor (instrumental conditions), and the selection of different sheet compositions and chemistries. In addition, an estimate of the crystallite size distribution of the species may be determined by comparing peak profiles of calculated diffraction profiles with experimental data. By modelling the individual clay mineral species in this way, *mineral reference intensities* were established and used for quantitative standardization following the method outlined in Moore & Reynolds (1997).

5.4 X-RAY FLUORESCENCE SPECTROMETRY

X-ray fluorescence spectrometry (XRFS) analysis was carried out using sequential, fully automatic wavelength-dispersive spectrometers (2 x Philips PW2400 and 1 x Philips PW2440) controlled via PCs running SuperQ (version 3.0H) XRF application package.

Fused beads for major element analysis were prepared by fusing 0.9 g sample plus 9.0 g flux ($66/34 \text{ Li}_2\text{B}_4\text{O}_7$ and LiBO₂) at 1200°C. Loss on ignition (LOI) was determined on *c*.1 g sample heated at 1050°C for one hour.

6 Results

The results of whole-rock XRD and surface area analyses are shown in Table 3. <2 μ m clay mineral XRD analyses are summarised in Table 4. Major and trace element geochemical analyses are summarised in Tables 5 and 6. Labelled whole-rock and <2 μ m clay mineral XRD traces are shown in the Appendix.

6.1 WHOLE-ROCK MINERALOGY AND SURFACE AREA

Whole-rock XRD analysis indicates that the samples from the London Clay Formation are composed of variable amounts of quartz (20-70%), feldspar (albite, K-feldspar, <10%), phyllosilicates/clay minerals (40-80%), carbonate minerals (calcite, dolomite, siderite, generally <3%) together with traces of pyrite, goethite and gypsum.

As shown in Figure 2, it is noticeable that samples from the London Basin have higher proportions of phyllosilicates/clay minerals (mean c.66%) compared to those from the Hampshire Basin (mean c.36%). Additionally, the samples from the Hampshire Basin appear more quartz-rich (mean c.60%) than those from the London Basin (mean c.28%). Within the Hampshire Basin, quartz contents appear to decrease and phyllosilicates/clay mineral content increases northwards. In the London Basin, quartz contents show an overall increase northwards while phyllosilicates/clay mineral content decreases.

Surface area analyses for the sample suite (Figure 2) indicate a range of values from 74 – 260 m²/g, which assuming a surface area of 800 m²/g for pure smectite is equivalent to smectite contents of 9 – 33%. Values for the London Basin (mean 207 m²/g) are significantly higher than those recorded for the Hampshire Basin (mean 111 m²/g). The London Basin samples from Colchester 1 (260 m²/g), Ockenden 1 (255 m²/g), Roxwell (254 m²/g) and Whitehall Farm (251 m²/g) have the highest values equivalent to >30% smectite.

6.2 CLAY MINERALOGY

With the exception of the sample from Studland, Dorset, the samples analysed in this study show broadly similar clay mineral assemblages composed of smectite, illite, kaolinite and chlorite (Figure 3).

The London Basin samples have mean clay mineral assemblages of 38% smectite, 26% illite, 25% kaolinite and 12% chlorite while samples from the Hampshire Basin have an average composition of 36% smectite, 29% illite, 23% kaolinite and 12% chlorite.

However, the single sample from Studland, Dorset has a rare clay mineral assemblage consisting of an interlayered kaolinite/smectite only. Newmod-modelling suggest that this is an *RO*-ordered species with the composition 88% kaolinite, 12% smectite.

The kaolinite in the other samples appears to be relatively poorly-ordered with Newmod-modelling suggesting a mean defect-free distance of 13 layers and a size range of 1 to 60 (7Å) layers.

BGS Code	Basin	Location		-	-	-	-	mineral	ogy (%)			-		-	$\widehat{\mathbf{D}}$
			quartz	albite	K- feldspar	calcite	dolomite	siderite	goethite	pyrite	gypsum	'mica'	kaolin & chlorite	smectite	Surface area (m2/§
MPLK205		Knowl Hill, Berkshire	20.8	1.6	2.0	nd	nd	nd	nd	0.8	< 0.5	37.3	20.7	16.4	187
MPLK206]	Bulmer, Essex	47.7	3.8	5.3	nd	nd	nd	nd	nd	0.9	16.2	13.1	13.0	120
MPLK207		Whitehall Farm 1, Kent	16.2	4.0	4.1	nd	nd	nd	nd	0.5	0.7	25.5	22.0	27.0	251
MPLK208]	Whitehall Farm 2, Kent	20.4	2.8	3.3	nd	< 0.5	nd	nd	0.8	< 0.5	33.7	18.0	20.4	218
MPLK209]	Warden Point, Kent	24.9	< 0.5	< 0.5	nd	1.0	nd	nd	< 0.5	0.5	33.4	20.7	18.8	193
MPLK210		Brambledown, Kent	35.9	1.7	2.9	nd	< 0.5	nd	nd	< 0.5	< 0.5	25.7	13.2	19.8	212
MPLK612	asin	Ockendon 1, Essex	23.4	0.6	< 0.5	nd	nd	nd	nd	1.0	0.7	30.4	16.4	27.2	255
MPLK613	nBå	Ockendon 2, Essex	33.7	1.3	3.5	nd	nd	nd	< 0.5	nd	2.6	25.0	15.2	18.5	188
MPLK614	opu	Bulls Lodge, Essex	18.6	0.5	< 0.5	nd	0.6	7.2	nd	1.3	0.6	34.5	16.2	20.2	208
MPLK615	Loi	Colchester 1, Essex	25.4	2.1	1.6	nd	nd	nd	nd	1.3	0.5	16.4	22.4	30.3	260
MPLK616		Colchester 2, Essex	28.7	0.7	1.9	nd	nd	nd	nd	4.1	3.1	20.5	18.0	23.0	201
MPLK617		Farnham, Surrey	17.5	nd	nd	nd	nd	nd	nd	nd	1.2	33.4	28.5	19.4	197
MPLK618		Poyle, Berkshire	20.3	nd	nd	0.6	2.9	nd	nd	0.8	1.3	34.1	18.1	21.9	221
MPLK619		Stanwell, Surrey	26.8	nd	nd	nd	3.4	nd	nd	1.1	1.2	23.4	26.5	17.6	175
MPLL005		Roxwell, Essex	20.1	nd	nd	0.5	2.8	nd	nd	0.8	0.9	24.3	24.7	25.9	254
MPLL006		Hollingson Meads, Hertfordshire	49.1	2.1	2.3	nd	< 0.5	nd	nd	2.8	1.7	15.9	7.3	18.6	177
MPLK211		Fair Oak Sand Pit, Hampshire	57.0	1.4	3.3	nd	nd	< 0.5	nd	0.5	0.9	10.3	14.4	12.1	125
MPLK212		Southleigh, Hampshire	36.6	nd	1.0	2.1	2.6	nd	nd	1.0	0.9	24.3	17.5	14.0	165
MPLK213	usin	Whitecliff Bay 1, Isle of Wight	60.8	1.8	1.1	0.8	< 0.5	nd	< 0.5	0.8	1.6	11.9	11.5	9.0	100
MPLK214	e B٤	Whitecliff Bay 2, Isle of Wight	46.3	0.9	1.5	nd	2.3	nd	nd	0.6	1.0	18.5	15.6	13.3	139
MPLK215	shire	Alum Bay 1, Isle of Wight	72.4	nd	2.0	nd	0.9	nd	nd	< 0.5	0.9	9.2	8.7	5.7	74
MPLK216	sdur	Alum Bay 2, Isle of Wight	75.3	nd	1.7	nd	0.7	0.9	nd	0.5	0.5	7.6	7.2	5.6	74
MPLK217	Ha	Knoll Manor 1, Dorset	44.0	nd	0.6	nd	nd	nd	nd	2.6	1.1	25.0	16.6	10.1	130
MPLK218]	Knoll Manor 2, Dorset	59.8	nd	0.5	nd	nd	nd	nd	<0.5	<0.5	18.4	14.4	6.4	90
MPLK219		Studland, Dorset	83.4	< 0.5	nd	nd	nd	< 0.5	nd	< 0.5	nd	nd	16.0	nd	101

Table 3. Summary of whole-rock XRD and surface area analyses



Figure 2. The whole-rock mineralogy and surface area of the London Clay Formation samples, ordered approximately north-south.

BGS Code	Basin	Location		Other minerals				
			smectite	illite	chlorite	kaolinite	kaolinite/ smectite	
MPLK205		Knowl Hill, Berkshire	30	36	12	22	nd	quartz, goethite
MPLK206		Bulmer, Essex	42	28	10	19	nd	quartz, goethite
MPLK207		Whitehall Farm 1, Kent	41	25	nd	34	nd	quartz, goethite
MPLK208		Whitehall Farm 2, Kent	39	25	12	24	nd	quartz, goethite
MPLK209		Warden Point, Kent	38	27	11	23	nd	quartz, goethite
MPLK210		Brambledown, Kent	46	24	9	21	nd	quartz
MPLK612	asin	Ockendon 1, Essex	45	23	11	20	nd	quartz
MPLK613	1 B	Ockendon 2, Essex	37	27	12	23	nd	quartz
MPLK614	юри	Bulls Lodge, Essex	37	22	13	28	nd	quartz
MPLK615	Loi	Colchester 1, Essex	49	16	12	23	nd	quartz
MPLK616		Colchester 2, Essex	40	21	14	26	nd	quartz
MPLK617		Farnham, Surrey	15	34	19	33	nd	quartz
MPLK618		Poyle, Berkshire	30	27	14	28	nd	quartz
MPLK619		Stanwell, Surrey	25	31	15	29	nd	quartz
MPLL005		Roxwell, Essex	29	26	15	30	nd	quartz
MPLL006		Hollingson Meads, Hertfordshire	65	17	9	9	nd	quartz
MPLK211		Fair Oak Sand Pit, Hampshire	49	23	9	19	nd	quartz
MPLK212		Southleigh, Hampshire	38	29	12	21	nd	quartz
MPLK213	Isin	Whitecliff Bay 1, Isle of Wight	28	41	12	19	nd	quartz, goethite
MPLK214	ββ	Whitecliff Bay 2, Isle of Wight	41	26	11	22	nd	quartz
MPLK215	shire	Alum Bay 1, Isle of Wight	55	19	9	17	nd	quartz
MPLK216	jdu	Alum Bay 2, Isle of Wight	45	21	11	23	nd	quartz
MPLK217	Ha	Knoll Manor 1, Dorset	15	41	15	29	nd	quartz
MPLK218		Knoll Manor 2, Dorset	18	34	15	32	nd	quartz
MPLK219		Studland, Dorset	nd	nd	nd	nd	100	quartz

Table 4. Summary of <2 µm clay mineral XRD analyses



Figure 3. The clay mineralogy of the London Clay Formation samples, ordered approximately north-south.

6.3 GEOCHEMISTRY

In general terms the major element geochemistry concurs with the identified mineralogical assemblages.

SiO₂ and Al₂O₃ contents are predominantly controlled by variations in the major mineral components of quartz, feldspar and phyllosilicate/clay minerals. CaO contents are low due to a lack of major calcium-bearing minerals and are largely controlled by the presence of traces of dolomite and gypsum. MgO contents are higher, reflecting its presence in smectite and chlorite clay minerals as well as dolomite. The positive correlation of K₂O and Al₂O₃ content provides evidence that most of the K₂O is hosted by 'mica' and K-feldspar species. The much smaller Na₂O concentrations are indicative of the presence of traces of plagioclase (albite) feldspar. Fe₂O_{3t} is likely to be associated with chlorite and smectite clay minerals, pyrite and in the case of the Bulls Lodge sample, siderite. TiO₂ is likely to be hosted by trace amounts of rutile, anatase and ilmenite which are beyond the lower detection limit of the XRD technique.

No significant trace-element geochemical anomalies are apparent from the limited number of samples analysed in this study. In general terms the concentration of all trace elements increase with decreasing SiO_2 content due to a decreasing quartz-dilution effect.

BGS Code	Location	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ t	Mn ₃ O ₄	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Cr ₂ O ₃	SrO	ZrO ₂	BaO	NiO	CuO	ZnO	PbO	LOI
MPLK205	Knowl Hill	59.08	0.98	18.00	5.95	0.03	2.80	0.48	0.33	3.50	0.14	0.4	0.02	0.02	0.03	0.05	0.01	< 0.01	0.02	< 0.01	7.35
MPLK206	Bulmer	71.90	0.86	11.28	4.83	0.05	1.33	0.52	0.46	2.67	0.14	0.7	0.02	0.01	0.05	0.04	0.01	< 0.01	< 0.01	< 0.01	4.65
MPLK208	Whitehall Farm	57.99	0.99	17.51	7.38	0.04	2.99	1.14	0.38	3.32	0.13	0.4	0.02	0.01	0.03	0.05	0.01	< 0.01	0.01	< 0.01	6.64
MPLK210	Brambledown	61.28	0.96	15.88	6.47	0.03	2.65	0.92	0.47	3.10	0.10	0.8	0.02	0.02	0.04	0.05	0.01	< 0.01	0.02	< 0.01	6.74
MPLK612	Ockendon 1	61.09	1.04	17.30	6.13	0.03	3.10	0.77	0.40	3.21	0.15	0.4	0.02	0.02	0.02	0.04	< 0.01	< 0.01	0.01	< 0.01	6.50
MPLK614	Bulls Lodge	50.39	0.91	15.71	14.17	0.16	2.71	1.65	0.29	2.87	0.14	0.3	0.02	0.01	0.03	0.04	0.01	< 0.01	0.01	< 0.01	10.34
MPLK615	Colchester 1	56.56	1.11	18.24	8.02	0.04	2.76	1.07	0.35	3.13	0.16	0.5	0.02	< 0.01	0.03	0.05	< 0.01	< 0.01	0.02	< 0.01	6.96
MPLK617	Farnham	55.06	0.96	23.02	5.61	0.02	1.97	0.69	0.11	3.85	0.05	0.8	0.02	0.01	< 0.02	0.06	0.02	< 0.01	0.02	< 0.01	7.74
MPLK618	Poyle	54.47	0.98	17.87	7.92	0.05	3.16	2.12	0.27	3.21	0.16	0.6	0.02	0.01	0.03	0.04	< 0.01	< 0.01	0.01	< 0.01	8.49
MPLK619	Stanwell	54.05	0.97	17.97	7.85	0.05	3.29	1.93	0.26	3.29	0.15	0.7	0.02	0.01	0.02	0.05	< 0.01	< 0.01	0.01	< 0.01	8.58
MPLL006	Hollingson Meads	66.38	0.81	12.03	5.55	0.02	1.76	0.91	0.45	2.59	0.13	1.6	0.02	< 0.01	0.03	0.04	< 0.01	< 0.01	0.01	< 0.01	6.86
MPLK211	Fair Oak Sand Pit	69.05	0.89	12.84	5.15	0.03	1.71	0.50	0.24	2.71	0.14	0.7	0.02	0.03	0.05	0.05	0.01	< 0.01	0.02	< 0.01	5.04
MPLK215	Alum Bay	79.55	0.65	7.35	3.49	0.02	1.28	0.73	0.18	2.13	0.10	0.3	0.01	< 0.01	0.05	0.04	< 0.01	< 0.01	< 0.01	< 0.01	3.23
MPLK217	Knoll Manor	65.49	0.95	14.53	5.20	0.02	1.18	0.35	0.14	2.55	0.05	0.6	0.02	< 0.01	0.05	0.05	0.01	< 0.01	0.01	< 0.01	7.90
MPLK218	Knoll Manor	75.97	0.98	11.93	3.13	0.01	0.65	0.27	0.13	1.95	0.04	< 0.1	0.02	< 0.01	0.06	0.04	< 0.01	< 0.01	< 0.01	< 0.01	3.82
MPLK219	Studland	80.64	0.60	11.72	0.72	< 0.01	0.15	0.30	0.05	0.22	0.01	< 0.1	0.01	< 0.01	0.02	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	4.21

Table 5. Summary of the major element (%) geochemistry and loss-on-ignition (LOI) of the London Clay Formation samples.

BGS Code	Location	V	Cr	Со	Ni	Cu	Zn	As	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Nd	Pb	Th	U
MPLK205	Knowl Hill	165	125	24	65	35	116	19	150	132	34	214	18	343	48	88	42	25	13	4
MPLK206	Bulmer	119	112	20	46	22	78	8	96	75	28	367	15	334	38	56	30	17	10	3
MPLK208	Whitehall Farm	185	130	23	60	30	102	12	138	112	29	197	16	315	40	79	36	20	12	3
MPLK210	Brambledown	163	141	17	49	22	87	11	126	121	27	241	16	336	32	71	30	20	11	3
MPLK612	Ockendon 1	176	128	19	55	41	109	9	129	178	34	195	16	280	46	73	41	20	11	3
MPLK614	Bulls Lodge	173	128	41	87	32	118	11	119	83	29	176	15	262	46	75	36	18	11	3
MPLK615	Colchester 1	247	140	24	70	52	122	16	127	97	37	201	17	356	46	87	42	21	12	3
MPLK617	Farnham	161	134	94	134	28	117	11	180	114	35	159	19	388	59	116	52	25	16	3
MPLK618	Poyle	183	128	21	59	29	110	13	140	116	31	184	17	301	46	87	40	21	12	3
MPLK619	Stanwell	186	132	22	62	29	107	15	141	115	31	192	18	354	50	90	39	21	13	3
MPLL006	Hollingson Meads	127	109	17	45	29	82	11	96	93	28	233	13	341	34	58	30	17	8	3
MPLK211	Fair Oak Sand Pit	141	130	28	80	21	129	18	100	214	34	345	14	325	37	89	42	16	10	2
MPLK215	Alum Bay	69	89	11	23	9	46	6	64	75	20	381	10	327	21	42	20	12	7	2
MPLK217	Knoll Manor	145	123	28	58	26	116	21	125	81	55	400	17	347	42	90	46	24	12	4
MPLK218	Knoll Manor	111	97	6	18	21	45	13	93	62	31	450	18	301	33	65	29	18	12	4
MPLK219	Studland	89	79	5	30	10	21	4	46	20	10	195	11	118	<6	<6	2	16	6	7

Table 6. Summary of the trace element (ppm) geochemistry of the London Clay Formation samples.

7 Discussion

Mineralogical analysis of a suite of samples from the London Clay Formation representing a relatively large geographic and stratigraphic range have generally similar mineralogies to those described in previous studies (e.g. Burnett & Fookes, 1974; Huggett & Knox, 2006 and others discussed in section 3). Non-clay mineral assemblages are typically composed of quartz, feldspar (albite and K-feldspar), carbonates (dolomite, siderite and calcite), 'mica', pyrite, gypsum and goethite. Clay mineral assemblages are generally formed of smectite, illite, kaolinite and chlorite.

The relatively complex, clay mineral-rich mineralogies of the London Clay Formation samples are difficult to quantify, even by employing state-of-the-art software modelling packages. For this reason the quoted mineral concentrations must be regarded with some caution. However, calculations using whole-rock XRD data and theoretical surface area values for the individual clay minerals, reveal similar whole-rock surface area values to those determined empirically (Figure 4).



Figure 4. Scatter plot to illustrate the strong correlation between measured and calculated surface area

Although the samples reveal similar mineral assemblages, this study has provided further evidence for important differences in the concentration of individual mineral phases that may have a profound effect on the engineering behaviour of the London Clay Formation.

As previously suggested by several authors (e.g. King, 1981, Burnett & Fookes, 1974), the London Clay Formation becomes sandier towards the west and the palaeo-shoreline. This study

has also shown that samples from the Hampshire Basin have higher quartz contents than those from the London Basin. Moreover, within the Hampshire Basin, quartz contents increase southwards and westwards. In the London Basin, quartz content increases in the north-east of the basin. Bouch (2005) confirms these findings by grain-size observations made with a scanning electron microscope.

As a consequence of this variation in quartz content, the proportion of phyllosilicate/clay minerals present in the London Clay Formation also varies. The most clay-rich samples are therefore found in the London Basin and particularly around the Thames estuary, central Essex and just west of London in eastern Berkshire/Surrey. As the clay mineral assemblages are approximately uniform in character across the two basins, and as indicated by both XRD and surface area analysis, these clay-rich samples also contain the most smectite. Since smectite clay mineral species undergo the greatest shrink-swell volume changes during wetting and drying, these clay-rich samples are likely to provide the most problems in terms of their engineering behaviour.

7.1 ORIGIN OF THE CLAY MINERAL ASSEMBLAGES

In order to more fully understand the nature and distribution of the clay mineral assemblages of the London Clay Formation, and their engineering behaviour, it is necessary to consider their origins.

Studies suggest that the London Clay Formation has experienced only relatively light diagenetic overprints (e.g. Bouch, 2005) and that the clay mineral assemblages are largely detrital in nature. Huggett & Knox (2006) consider that the detrital assemblages are the result of several factors including climate, tectonic setting, periods of pyroclastic activity and the reworking of pre-existing clay-rich sediments.

Early attempts to account for the detrital clay mineral assemblages (Gilkes 1966; Weir & Catt, 1969) favoured the Chalk as the source for the smectite and illite in the lowermost part of the London Clay Formation. Tropical, rapid chemical weathering resulted in high rates of clay mineral neoformation e.g. deep kaolin-rich soils in southwest England (Bristow, 1968). The greater abundance of kaolin in the western parts of the Hampshire Basin suggest derivation from the southwest Armorican granites and is probably accentuated by the preferential settling of coarser kaolinite over finer smectite particles.

Later, the first identification of volcanic ash or its argillization products in the Eocene of southeast England (Elliot, 1971) was followed by numerous similar descriptions in the London Basin in pre-London Clay Formations (e.g. Knox *et al.*, 1990; Knox, 1983). Huggett & Knox (2006) argue that the ash also contributed to sediments in the Hampshire Basin although dilution by non-volcanogenic detrital clays was much greater here, especially in the west.

Gilkes (1966) suggested that the detrital illite in the Hampshire Basin was sourced from the Upper Greensand of Devon. However, reworked palynomorphs in the Hampshire Basin are dominated by Middle and Upper Jurassic species suggesting that Middle and Upper Jurassic rocks, with their illite-dominated with minor smectite, kaolin and chlorite clay mineral assemblages, were an important sediment source.

The more smectitic nature of the London Clay Formation compared to the main clay-bearing Middle and Upper Jurassic sediments of southern England (the Oxford Clay Formation and Kimmeridge Clay Formation) suggests a requirement for an additional smectite-rich source. Although the clay fraction of the Chalk is indeed smectite-rich, it could not have provided sufficient smectite for the London Clay Formation (Huggett & Knox, 2006). Weathering of Upper Greensand glauconite to smectite may also have contributed. However, the homogeneous composition of the London Clay Formation, particularly in the London basin, suggest that reworking of soils containing air-borne ash was the principal volcanogenic source.

The limited evidence for diagenetic alteration of the clay mineral assemblages has chiefly been reported from the sandier units within the London Clay Formation. For example, Huggett & Gale (1998) reported the widespread occurrence of coarsely crystalline kaolin (>4 μ m) and Feoxyhydroxides in the sandstones of the London Clay Formation and suggest that these developed by the penecontemporaneous oxidation of glauconite during sub-aerial emergence and prior to the deposition of overlying mudstone.

Kaolin/mica stacks and kaolin pseudomorphs after mica are abundant in the London Clay Formation of the London Basin but are rare elsewhere (Huggett, 1994). They appear to have developed through the partial-replacement of mica grains by kaolin during early diagenesis, prior to compaction.

The smectite at the base of the London Clay Formation displays a lath-like morphology similar to that observed in the underlying Harwich Formation and other sandy formations. This lath-like morphology is gradually replaced by aggregates of very small platy particles with decreasing age in the London Clay Formation. Although pure smectite and smectite-dominated clay assemblages can frequently be proven to have formed through the replacement of ash, evidence for such an origin is limited to the occurrence of occasional aggregates of smectite with a high proportion of face-to edge contacts in the London Clay Formation (Huggett & Knox, 2006).

In summary, it would appear most likely that the smectite in the London Clay Formation was contributed by the reworking of ash-rich soils while kaolinite was sourced from tropical weathering of granites to the west.

7.2 KAOLINITE/SMECTITE CLAY MINERAL ASSEMBLAGE AT STUDLAND

The identification of a pure kaolinite/smectite (K/S) clay mineral assemblage in the sample from the cliff face at Studland Bay, Dorset represents a relatively rare occurrence, particularly in the UK.

Kaolinite/smectite interstratifications most commonly occur due to hydrothermal alteration (e.g. Linares, 1985) or soil development (e.g. Bühmann and Grubb 1991; Churchman *et al.* 1994; Hughes *et al.* 1993) over basic igneous or volcanic rocks or more rarely over bentonites (e.g. Hillier *et al.*, 2002; Schultz *et al.*, 1971). The K/S usually forms as an intermediate product of the conversion of smectite into kaolinite due to acid weathering.

In the case of the Studland sample, the K/S is likely to have developed due to the tropical weathering of a volcanic-ash or smectite-rich deposit.

7.3 SULPHATE-BEARING SPECIES

Mineralogical analysis from this study also suggests that pyrite is very commonly developed throughout the London Clay Formation, typically forming c.1% mineral assemblage. Gypsum, most probably the result of the reaction of acidic water with carbonate species, is also ubiquitously present as a minor-trace component of the formation mudstones.

Therefore concrete engineering sited in mudstones from the London Clay Formation may require sulphate-resistant compositions to avoid acid attack and thaumasite formation.

8 Conclusions

This mineralogical, geochemical and surface area study of a suite of mudstones from the London Clay Formation of southern and south-east England has generally confirmed the findings of previous workers. Non-clay mineral assemblages are typically composed of quartz, feldspar (albite and K-feldspar), carbonates (dolomite, siderite and calcite), 'mica', pyrite, gypsum and goethite while clay mineral assemblages are generally formed of smectite, illite, kaolinite and chlorite. However, the wide geographic and stratigraphic distribution of the analysed samples has provided important new information which will aid not only interpretation of the engineering behaviour of these rocks but also their diagenetic and geological histories.

The engineering properties of the London Clay Formation will be heavily influenced by its clay mineralogy and the proportion of clay minerals present. This study has shown that while the composition of the clay mineral assemblages is similar across the London Clay Formation outcrop, the proportion of clay material increases from west to east.

The most clay-rich samples are found in the London Basin and particularly in the vicinity of the Thames estuary, central Essex and just west of London in eastern Berkshire/Surrey. These clay-rich samples also contain the most smectite and are therefore likely to undergo the greatest shrink-swell volume changes during wetting and drying and provide the most problems in terms of their engineering behaviour.

It would appear most likely that the smectite in the London Clay Formation was contributed by the reworking of ash-rich soils while kaolinite was sourced from tropical weathering of granites to the west. A rare occurrence of a pure interlayered kaolinite/smectite clay assemblage in a sample from Studland Bay, Dorset is likely to have developed due to the acidic, tropical weathering of a volcanic-ash or smectite-rich deposit.

The very common presence of pyrite, together with gypsum in the London Clay Formation means that concrete engineering sited in these rocks potentially risk acid attack and thaumasite formation.

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Appendix: X-RAY DIFFRACTION TRACES:

KEY

Vertical axis - Intensity (counts per second)

Horizontal axis - °2θ Co-Kα

For the whole-rock traces, only the most intense/diagnostic peak of each identified mineral is labelled.

For the <2 μ m traces. Black trace (air-dry), red trace (glycol-solvated) and green trace (heated 550°C/2 hours). Only the d_{001} of each identified clay mineral is labelled on the glycol-solvated trace.









Knowl Hill, Berkshire, <2 μm fraction



Bulmer, Essex, whole-rock



Bulmer, Essex, <2 µm fraction



IR/06/060; Version 1

Whitehall Farm 1, Kent, whole-rock



28
Whitehall Farm 1, Kent, <2 µm fraction



Whitehall Farm 2, Kent, whole-rock



30

Whitehall Farm 2, Kent, <2 µm fraction



IR/06/060; Version 1

Warden Point, Kent, whole-rock



Warden Point, Kent, <2 µm fraction



Brambledown, Kent, whole-rock



Brambledown, Kent, <2 µm fraction



Ockendon 1, Essex, whole-rock



Ockendon 1, Essex, <2 µm fraction



IR/06/060; Version 1

Ockendon 2, Essex, whole-rock



Ockendon 2, Essex, <2 µm fraction



Bulls Lodge, Essex, whole-rock



Bulls Lodge, Essex, <2 µm fraction



Colchester 1, Essex, whole-rock



42

Colchester 1, Essex, <2 µm fraction



Colchester 2, Essex, whole-rock



Colchester 2, Essex, <2 µm fraction



Farnham, Surrey, whole-rock



Farnham, Surrey, <2 µm fraction



Poyle, Berkshire, whole-rock



Poyle, Berkshire, <2 µm fraction



IR/06/060; Version 1

Stanwell, Surrey, whole-rock



Stanwell, Surrey, <2 µm fraction



IR/06/060; Version 1

Roxwell, Essex, whole-rock



Roxwell, Essex, <2 µm fraction





Hollingson Meads, Hertfordshire, whole-rock

Peak List						
01-083-0539; Quartz; Si O2	I					
00-007-0042; Muscovite-3T; (K , Na) (Al , Mg , Fe)2 (Si3.1 Al0.9) O10 (O H)2						
01-079-1270: Clinochlore: (Mg2.96 Fe1.55 Fe.136 Al1.275) (Si2.622	2 Al1.376 O10) (O H)	8				
······································	()	-				
00-006-0710; fools gold, pyrites; Fe S2						
00-009-0466; Albite, ordered; Na Al Si3 O8						
00-011-0078; Dolomite; Ca Mg (C O3)2						
00-013-0135; Montmorillonite-15A; Ca0.2 (AI , Mg)2 Si4 O10 (O H)2	2 •4 H2 O					
00.010.0022: Microclino, intermediate: KALSi2.08						
00-019-0932, Microcine, internediate, KAI 515 06						
00-033-0311; Gypsum, syn; Ca S O4 ·2 H2 O						
00-014-0164; Kaolinite-1A; Al2 Si2 O5 (O H)4						

Hollingson Meads, Hertfordshire, <2 µm fraction





Fair Oak Sand Pit, Hampshire, whole-rock

Fair Oak Sand Pit, Hampshire, <2 µm fraction



Southleigh, Sussex, whole-rock



Southleigh, Sussex, ${<}2~\mu m$ fraction



Courts

Whitecliff Bay 1, Isle of Wight, whole-rock



Whitecliff Bay 1, Isle of Wight, <2 µm fraction





Whitecliff Bay 2, Isle of Wight, whole-rock

Whitecliff Bay 2, Isle of Wight, <2 µm fraction





Alum Bay 1, Isle of Wight, whole-rock
Alum Bay 1, Isle of Wight, <2 µm fraction





Alum Bay 2, Isle of Wight, whole-rock

Alum Bay 2, Isle of Wight, <2 µm fraction



Knoll Manor 1, Dorset, whole-rock



Knoll Manor 1, Dorset, <2 µm fraction



IR/06/060; Version 1

Counts 3600 -Knoll Manor 2, Dorset 1600 · 400 her and a state of the state of hennyane phanyane nyanganyanya yanganya Maynolygyddiadd *** 0 10 20 30 40 50 Position [°2Theta] Peak List 01-070-3755; Quartz; Si O2 00-003-0849; Nuscovite; H4 K2 (AI , Fe)6 Si6 O24 01-083-1365; Clinochlore IIb-4; Mg9.8 Al1.6 Fe0.6 (Si6.32 Al1.68 D20.24) (OH) 15.72 00-001-0527; Kaolinite; Al2 S 2 O5 (O H)4 01-075-1759; Dolomite; Ca Mg (C O3)2 00-006-0710; fools gold, pyrites; Fe S2 3-0135; Montmorillonite-15A; Ca0.2 (AI , Mg)2 Si4 O10 (O H)2 -4 H2 0-024-0027; Calcite; Ca C O3 00-033-0311; Gypsum, syn; Ca S O4 ·2 H2 O

Knoll Manor 2, Dorset, whole-rock

Knoll Manor 2, Dorset, <2 µm fraction



Studland, Dorset, whole-rock



Studland, Dorset, <2 µm fraction

