High Temperature Reactions And Colour Development In Brick Clays

by

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The motivation behind this study was primarily commercial - in the brick industry the colour of the finished article is a very significant commercial factor.

Initially a series of mineralogical analyses, selective chemical extraction procedures and firing trials were undertaken to investigate and identify the potential colour-inducing constituents of fired and unfired brick clays.

Iron-rich clay minerals were identified as a major 'source' of colour in the fired bricks. This study then concentrated on the investigation of the role of iron and related colour-inducing transition metals in the thermal reaction sequence(s) of fired clays primarily by means of X-ray Diffraction and Transmission Electron Microscopy.

Electron Microscopy identified iron oxide (Fe₂O₃) as the primary coloured phase in fired brick clays and successfully correlated changes in colour with firing temperature with changes in oxide crystallite size and composition.

Some inconsistencies were evident between the results of this study and the previously accepted mechanism behind the high temperature transition series of layer silicates. Consequently, in line with an additional aim of identifying the precise reaction mechanism(s) responsible for the transition series and the development of the coloured phases, an alternative hypothesis is put forward to cover the (lower temperature) transitions.
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'The real constitution of things is accustom to hide itself'
1. Introduction

In the brick industry the colour of the finished article is a very important property. Indeed, from a commercial point of view it may be the most important feature. Architects now select bricks, be they for a functional outdoor application or for an internal decorative project, not only for their mechanical properties but also for aesthetic reasons.

Brick producers are well aware of the potential sales value of colour modifications in their clay. Every brick maker has available a clay or clays with known fired colour and texture. Some are fortunate in that they have clays that, when fired singly or in combination, will produce a range of natural colours from red to buff, while others are not so fortunate. These brick manufacturers realise the limitations of their own natural products as well as the need to provide their customers with a wider choice.

The methods for effecting a control of surface colour are many and varied. Apart from controlling the oxidising-reducing nature of kiln atmospheres, they range from the use of ceramic pigments to glazes and engobes. The exact choice depends on technical and/or commercial considerations. In the United Kingdom most have specialised in the use of ceramic pigments. These pigments tend to be transition metal oxides (of spinel type) such as oxides of Mn, Zn, Zr, Ti, Sn, V, Cr, Ni, Cu and Co. They are often required to be used in large quantities to produce suitable colours, and are generally rather expensive.

There is therefore a commercial aim to replace or reduce the need for such pigments. To accomplish this one must understand the reasons for natural colour development in clay ceramics. Few systematic fundamentally based investigations of the factors controlling the
The colour of fired brick clays appear to have been carried out and they are not well understood, apart from the recognition that Fe oxides are generally the chief colouring agents and that the colour relies in part on the state of oxidation of the iron. It was however appreciated that the link between colour and iron content is not straightforward – for the colour appears to be sensitive not only to amount of iron but also to its source.

This study, sponsored by Redland Technology Ltd, is aimed at discovering the sources and role(s) of iron and related colour-inducing transition metals in the thermal reaction sequence(s) of fired clays and so identifying the fundamental reactions responsible for the colour development in fired bricks.

The approach adopted is based on preliminary investigations by Redland Technology Ltd. on a number of commercial brick clays used by Redland Bricks Ltd. As little in the way of detailed information from prior research was available from the literature, it was decided to start with a relatively simple situation. Of the 'available' clays, mineralogical investigations identified Warnham clay as having a relatively simple mineralogy and so this was adopted for use in this study.

The mineralogical analysis identified a number of iron-containing phases. The initial approach made attempted to simplify the situation still further by using selective chemical extraction procedures to remove single or combinations of these iron containing phases, so permitting their respective effects to be estimated.

This approach was successful in identifying the two main sources of colour generating iron. However, it became apparent that pretreatment prior to firing not infrequently resulted in unforeseen side effects. It was also discovered that the mineralogy of Warnham
clay was slightly more complex than at first thought and this further complicated the detailed interpretation of the results obtained from chemically treated material. Despite the reduction in usefulness of this approach from that at first envisaged, it did succeed in identifying iron-rich clay minerals as one of the main sources of 'active' colour-generating iron.

Once it became apparent that the chemical pretreatments were not quite as selective and side effect free as expected, their use was restricted. Instead the detailed study of the high temperature reactions of the clay minerals was switched to a 'mechanically' produced clay concentrate. A hydrocyclone was used to separate out particles with a mean diameter of <5μ - effectively concentrating the clay minerals into this fraction. What was in effect the second stage of this study - a Transmission Electron Microscopy based investigation - was conducted almost exclusively on this hydrocycloned Warnham clay.

Optical microscopy and X ray diffraction revealed that the high temperature products of the clay minerals had a very small crystallite size. Detailed crystallographic and chemical information on materials with such small crystallite sizes can be obtained by combining Electron Microscopy, Electron Diffraction and Energy Dispersive X Ray Analysis. The aim of this stage was to identify the phases that developed on firing and as far as possible to determine the reaction sequence(s) and mechanism(s) governing those transitions, with particular attention being given to those yielding coloured phases.

As little in the way of such research appears to have been conducted on brick clays, a thorough literature survey was carried out into the high temperature reactions of layer silicates in general, and in particular kaolinite → mullite as it is the most studied reaction. The current consensus view regarding the kaolinite - mullite and
related transition series was constructed - and the 'hypothetical' transition mechanism determined. An outline of some of the similarities and discrepancies between the observed results of this study and some of those elsewhere in the literature and the 'predictions' of the generally accepted transition mechanism are included in the discussion. The outline of an alternative transition mechanism is put forward which appears to take account of some of the observed anomalies.

Also included in the discussion is a detailed explanation of the main colour generating processes. The two main sources of 'colour-generating' iron are identified and some of the factors governing their effects are outlined. While in many instances colour is often a disregarded physical attribute, it is in fact a visible and even conspicuous manifestation of some of the subtle effects that determine the structure of matter. It is dependent on the actual atomic structure of the material in question. This study has concentrated on the identification of the constituents of fired and unfired brick clays so as to identify any potential colour-inducing components. Detailed consideration of colour-generating mechanisms on the atomic scale has not proved practical in such a multicomponent material - though the general principles outlined in section 2.2 can and have been applied to the individual components.
2. Literature Review

2.1.1 Colour Development in Fired Clays: Introduction

Despite the commercial significance of colour development in clay ceramics, surprisingly little has been published on this subject. Thorough literature surveys (by Redland Technology Ltd, the British Ceramic Research Association and this study) have revealed only about 100 related papers published since 1900. This is a surprisingly low number compared to say, clay mineralogy or even colour formation in glasses, and even of these less than half have any truly useful scientific content. The early ones tend to be primarily concerned with influencing firing conditions, while the rest, particularly the pre-1950 ones, often suffer from the limitations of the relatively crude analysis techniques available at the time. Comment will be restricted in the main to work in which the 'measurements', eg the identification of the phases, is reasonably reliable, eg XRD.

2.1.2 Iron Content

It has long been appreciated that while the colour of a fired clay is related to the total iron content, there is no direct correlation. Clays containing less than 1% iron (as oxide generally) fire white, while 1-2% imparts a yellow colour, 2-3% produces a buff and 4-5% plus gives a red, but there are exceptions. White firing clays usually contain 0.1-1.0% iron oxide though the more iron-rich ones occasionally have a higher iron content than some buff burning ones; likewise some buff burning clays contain more iron than some red (Keane, 1916). The
colour therefore is not due solely to the iron content. Similarly it is not related to the colour of the unfired clays; some red clays can fire buff or even white.

The colour and shade was found by Keane (1916) to depend on:

1) The amount of iron
2) The firing temperature
3) The oxidation state of the iron oxide
4) The kiln atmosphere

He noted that red firing clays darkened with increased firing temperature and suggested that the colour change from yellow to red is associated with an increase in the particle size of iron oxide.

Like others (e.g. Orton 1908), he found that the natural fired colours could not be matched (synthesised) by adding iron oxide pigments to a light firing clay and attributed this to the inability to match the 'colloidal' dispersion of the natural system. Keane also observed that an increase in $\text{Al}_2\text{O}_3$ or $\text{CaO}$ content increased the tendency of a clay to fire to buff colour.

Norton & Duplin (1932) studied colour formation in vitreous bodies and like Keane, considered the colour to be due to particles of iron oxide embedded in the 'body' rather than dissolved in the glass phase.

Mellor's hypothesis (1933) gained wide acceptance. He postulated that $\text{Fe}_2\text{O}_3$ dissolved in $\text{Al}_2\text{O}_3$ over a limited temperature range to produce a buff or a bleached iron oxide colour, but that unless the iron was available as $\text{Fe}_2\text{O}_3$ over this temperature range the alumina:ferric oxide solid solution would not form, and a pink colour would develop due to free $\text{Fe}_2\text{O}_3$. Mellor considered that $\text{Al}_2\text{O}_3$ heated above 700°C would not readily dissolve ferric oxide but the solid solution was stable once formed, provided the $\text{Al}_2\text{O}_3$ content was high; otherwise it would break down if the $\text{Fe}_2\text{O}_3$ content was high.
In studies of purer pigments Meir & Mellor (1936) observed that the colour of iron oxide varied with the source salt and also on the temperature of calcination. They also noted that the colour could be affected by the inclusion of Zn, Al and Mn salts and postulated that the colour series from orange red to deep violet red was associated with particle size - for the darker coloured powders lightened on grinding.

Differences in colour with calcining temperature had been observed earlier by Hedvall (1922) who attributed the colour change to 'hereditary' lattice defects. Bronwell (1958) suggested it was due to an increase in disorder with increasing temperature while Sandford and Liljegren (1963) suggested it was due to an increase in order. Dissociation has also been postulated (Moore, 1948). Ferric oxide is known to dissociate at high temperatures to FeO and Fe$_3$O$_4$. In pure material this occurs at about 1350°C plus but has been said to occur at temperatures as low as 1050°C if suitable fluxes or reducing atmospheres are present (Collier, 1976). Whatever the cause, the variation in colour with calcining temperature has been reported by numerous researchers, eg Norton, 1980, who gives the range for oxides derived from ferrous sulphate as:

- 600°C orange
- 700°C scarlet
- 800°C violet red
- 900°C deep violet
- 1000°C grey

Zimmerman & Favejee (1941) and Bronwell (1959) found that Fe$^{3+}$ substituting for Al$^{3+}$ in mullite influenced the colour of fired bricks, and that delayed oxidation during firing tended to result in the formation of free iron oxides. Mellor (as quoted by White, 1977)
subsequently suggested that the buff colour of fire bricks was due to Fe substitution into mullite. He too noted that Fe oxidation must be complete before mullite formation. If it was not, or if a brick was reduced and reoxidised, a pink colour developed which he attributed to ferric oxide. A similar phenomenon was observed by Richardson et al (1951) in reduced then reoxidised fire clays. They also found a similar situation prevailed in mixtures of china clay and ferrous oxalate when they were fired in nitrogen or sulphur dioxide and then refired in air - pink or buff colours were produced depending on the subsequent firing temperature. If the original firing did not exceed 900°C then the effects of the previous reduction were eliminated by the subsequent oxidation. However, if it exceeded 900°C then slight differences in colour could be detected (probably associated with less of the iron going into solution in the mullite).

As already mentioned, an increase in CaO content is often associated with a tendency of the material to fire buff or yellow and this was often attributed to the formation of calcium silicates or ferrites (Krauss, 1936 and Richardson et al, 1951). Sandford & Liljegren (1963), in studying fired synthetic mixtures of CaO, SiO₂ and Fe₂O₃ found free ferric oxide in red systems but report finding only 2CaO Fe₂O₃ - a yellow calcium ferrite spinel - in yellow material. They noted that this material is normally brown-black and suggested that if thin films of it developed on CaO grains, a yellow colour could be produced. (Note: CaO had to be in excess of Fe₂O₃ to give a yellow colour, otherwise a red colour prevailed.)

Richardson et al (1950) found that mixtures of china clay and ferric oxide gave buff colours when the material was heated to about 1300°C but the presence of CaO and/or TiO₂ caused a buff colour to develop at lower temperatures. Mixtures of china clay, CaO and Fe₂O₃
in addition to mullite formed gehlenite if fired between 800-1000°C and anorthite above 1230-50°C. They thought the resultant buff colour could be due to Fe substitution into mullite but noted that CaO:SiO₂:Fe₂O₃ mixtures fired to form anorthite also gave a buff colour. They found that if the anorthite was synthesised first and then refired with Fe₂O₃, the mixture stayed pink. They found no explanation for this because microscopic investigation indicated the anorthite was colourless in both cases.

They never found the alumina content of fired clay as free Al₂O₃ and there was no evidence in favour of the colour being caused by Al-Fe oxide solid solution as suggested by Mellor (1933) and Wanie (1967). They suggested the colour of red bricks was associated with the crystallite size of iron oxide and buffs with the substitution of Fe³⁺ for Al³⁺ in mullite.

2.1.3 Reducing Atmosphere

It has long been realised that firing in a reducing atmosphere produces grey or 'blue' bricks, the colour of which is still commonly assigned to the presence of magnetite - Fe₃O₄ (eg Procter, 1981). Though magnetite may often be present it is not necessarily the only or even the main cause.

The typical metallic surface colour of the Staffordshire blue brick was found by Roberts et al (1960) to be due to a well developed orientated 'skin' of plate-like hematite crystals and not to the development of magnetite or ferrous silicates (eg fayalite-Fe olivine), as had been suggested. The hematite was probably due to minor surface oxidation during the cooling stages of the firing process.
Roberts et al (1960) found hematite, iron rich spinels, magnetite and hercynite FeAl$_2$O$_4$, mullite, anorthite, cristobalite and residual quartz in a glassy matrix in the outer reduced zone of the bricks. The hematite occurred as a skin near the surface while magnetite and hercynite were found just below this zone. Mullite was seen to decrease in size away from the surface. Anorthite was developed locally from Ca rich precursors. The inner reduced zone was found to contain iron-rich cordierite, magnetite, anorthite, mullite and residual quartz.

The blue-grey colour of the core of many bricks has also been attributed in whole or in part to disseminated carbon (Hopwood & Jackson, 1903 and Orton, 1908) as well as to ferrous iron compounds. Ferrous iron:titanium spinel has also been suggested as a possible cause. (Krauss, 1936 and Houseman & Koenig, 1971).

2.1.4 Conclusions

Most researchers have attributed the colour of fired ceramics to their crystalline components. In contrast, Shelton (1935) reported that the composition of the glassy phase was an important factor in the colour of fired clays. The idea had been echoed by Richardson et al (1950) and Sandford & Liljegren (1963) who have also suggested that the yellow colour of some bricks may at least in part be due to an iron containing glass phase, for alkali rich Fe$^{3+}$ doped glasses are known to have a yellow colour. Similarly ferrous glasses are often a blue-green colour and could in part be responsible for the blue-grey colour of some non-oxidised/reduced brick colours. Iron usually occurs in both Fe$^{2+}$ and Fe$^{3+}$ states in glasses (Paul, 1980). In silicate glasses it
is usually in four-fold coordination. The alkali content tends to affect the oxidation potential of a glass. Thus increasing the alkali content favours the formation of $\text{Fe}^{2+}\text{O}_4$ network groups rather than $\text{Fe}^{2+}\text{O}_4 - \text{Na}$ having more effect than $\text{K}$ (Bishay, 1959). This in turn changes the colour.

Most recent investigators, however, have suggested systems similar to that of Ayscough (1968) who postulated that the common red colours were due to the precipitation of $\text{Fe}_2\text{O}_3$ from a $\text{CaO}\text{Al}_2\text{O}_3\text{SiO}_2$ glassy phase. Similarly Aston (1978) attributed the colour of Warnham Clays to the precipitation of $\text{Fe}_2\text{O}_3$ derived from vermiculite.

So while many observations of colour changes in clay ceramics have been made and numerous explanations offered, very little in the way of substantiated fact appears to exist. It would appear that in most cases the constituents of fired ceramics are not precisely known, therefore the identification of those generating colour are uncertain. As outlined in the following section, the exact causes of colour are very dependent on the precise nature of the colour-generating atom/material (crystalline or amorphous). The basic requirement in any study of colour formation in clay ceramics would appear to be a detailed mineralogical analysis of the fired material, identifying the components present (coloured ones included) and determining the reactions involved in forming them.
Light is more appreciated by man for what it does than for what it is - we still do not fully understand it. We know that it behaves in part like a wave as well as a beam of discrete particles of energy and can be characterised in terms of frequency, wavelength or energy (fig. 2.2.1.1). We also know that it reacts in some way with almost every object it comes into contact with. One of the more obvious interactions is the 'effect' known as 'colour' - the colour of an object depends primarily on its innate ability to absorb, transmit and reflect in a selective way, the collection of wavelengths comprising white light - these differences being detected by the eye and interpreted by the brain as 'colour'.

There are fourteen known types of mechanism which generate colour, some are quite similar and can be grouped into 5 basic genres (see table 2.2.1.1). In all but one of these mechanisms (vibrations), the colour is due in some way to the interaction of light with electrons as described by Quantum Theory. (Loeffler & Burns, 1976).

Quantum Mechanical Theory places important constraints on the interactions of all electromagnetic radiation with matter; for it states that atoms can have only certain discrete states, each with a precisely defined energy: intermediate energies are forbidden. The overall state of an atom is most easily seen in terms of the distribution of its electrons. One useful simplified model depicts an atom as a nucleus surrounded by shells of electrons in various orbits around the nucleus, with each electron having different possible energy levels. Light, or any electromagnetic radiation, can only be absorbed if it has precisely the right energy to promote an electron from one energy level to a higher one. Similarly, if it falls back from an
<table>
<thead>
<tr>
<th>Categories</th>
<th>Mechanisms</th>
<th>Typical Examples</th>
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<tbody>
<tr>
<td>Electronic transitions in free atoms and ions</td>
<td>electronic excitations</td>
<td>incandescence, flames, arcs, gas discharges, some lasers</td>
</tr>
<tr>
<td>Vibrational transitions in molecules</td>
<td>vibrations</td>
<td>blue-green tint of pure water and ice</td>
</tr>
<tr>
<td>Crystal field colours</td>
<td>transition-metal</td>
<td>olivine, goethite, some fluorescent materials, some lasers</td>
</tr>
<tr>
<td></td>
<td>compounds</td>
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<tr>
<td></td>
<td>Transition-metal</td>
<td>ruby, emerald, citrine</td>
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<tr>
<td></td>
<td>impurities</td>
<td>some fluorescence</td>
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<td></td>
<td>colour centres</td>
<td>amethyst, smoky quartz</td>
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<tr>
<td>Transitions between molecular orbitals</td>
<td>charge transfer</td>
<td>blue sapphire, magnetite, cordierite kyanite, pyrite etc</td>
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<tr>
<td></td>
<td>conjugated bonds</td>
<td>organic dyes, lapis lazuli, graphite</td>
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<tr>
<td></td>
<td></td>
<td>dye lasers, some fluorescence</td>
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<tr>
<td>Transitions in materials having energy bands</td>
<td>metallic conductors</td>
<td>copper, silver, gold, iron</td>
</tr>
<tr>
<td></td>
<td>pure semiconductors</td>
<td>silicon, galena, diamond</td>
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<td></td>
<td>doped semiconductors</td>
<td>pyrite, sulphur</td>
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<td></td>
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<td>blue diamond, light-emitting diodes, semiconductor lasers</td>
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<tr>
<td>Geometrical and physical optics</td>
<td>dispersive refraction</td>
<td>'fire' in gemstones</td>
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<td></td>
<td>scattering</td>
<td>chromatic aberration</td>
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<td></td>
<td>interference</td>
<td>moonstone, star sapphire</td>
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<td></td>
<td>diffraction grating</td>
<td>oil film on water holds, chalcopyrite</td>
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<td></td>
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<td>opal, liquid crystals</td>
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Table 2.2.1.1

The 14 types of 'colour generating' processes
'excited' high state to a lower one it must emit radiation (eg a photon) with the precise energy difference between the two levels (fluorescence). The exact position of the energy levels depends on the environment, more specifically on the following:

1. On what atom, ion or group the electron is located.
2. The nature of ions surrounding or connected to the 'ion'.
3. At what distance they occur.
4. In what geometrical arrangement they occur.

Quantum Theory selection rules control the probability of the occurrence of various possible changes between energy levels and so further limit absorption and explain the intensity ('frequency') with which the transitions occur.

In the majority of minerals and ceramics the specific causes of colour are unknown and it is not uncommon for more than one colour-generating process to be active in any one mineral. The observed colour is then the complimentary colour of their combined absorptions. Most instances of colour generation in minerals, ceramics and glasses can be explained by Crystal Field Theory and/or Molecular Orbital Theory. The basic outline of such explanations will be given in the following sections. For detailed considerations of these and other approaches, eg Band Theory, the reader is referred to Burns (1970), K. Nassau (1978 & 1980) and Kittel (1976).

2.2.2 Crystal Field Theory

Crystal field theory is most applicable to ionic crystals and can explain colour that is due to unpaired electrons.

In an isolated atom the valency electrons are unpaired and are the
Figure 2.2.1.1  Colours, wavelengths (Å) and energy (eV) for spectral pure light (SW is short and LW long wavelength ultraviolet).

Fig. 2-2-2-1 The five $d$ orbitals.
primary source of colour (e.g., Na+ vapour in a sodium lamp). In a molecule or crystalline solid, on the other hand, the valence electrons of one atom form pairs with the valence electrons of adjacent atoms, and it is these pairs that constitute chemical bonds. As a result of pair formation, the absorption band of valence electrons is displaced to higher energy in the UV. The atoms of elements in the transition metal series and the rare earth elements have inner shells that can remain only partially filled—d shell in the case of transition metals, f shell in the case of the actinides and lanthanides. These unfilled inner shells can hold unpaired electrons which have excited states equivalent to visible wavelengths. Transition metals seem to be the main colour generating agents simply because they are much more abundant than the rare earth elements. Iron is the most plentiful transition metal (~5% of the earth's crust) and therefore is the dominant colour contributor in minerals and is probably the major transition metal involved in the colour of fired clays. The following synopsis is based on Burns (1970) and Nassau (1978 & 80).

As stated, it is the d electrons of the transition metals that are responsible for their colour-generating properties. As illustrated in figure 2.2.2.1, the d orbitals fall into 2 categories based on their orientation relative to a cartesian coordinate system. The lobes correspond to the electron density of a given orbital and represent where the electrons are likely to be with a 90% probability. Two of the five have probability lobes along the axes ('eg' sets), three have lobes projecting between the axes ('t2g' sets).

In an isolated atom or a free ion, these electrons have the same energy, i.e., they are 'degenerate'. However, if the ion is located in a coordination site in a mineral, it is no longer surrounded by a
spherically symmetrical charge distribution - it probably has as its nearest neighbour oxygen, with localised negative charges.

In a typical six coordinate octahedral site, the adjacent anions can be regarded as defining the apices of an octahedron as well as the axes of a cartesian system. This octahedral crystal field has a profound effect on the d orbital's energy levels due to their particular spatial distributions of electron density. The eg d orbitals which have lobes pointing along the metal-oxygen axes are increased in strength relative to the t2g d orbitals. (This can be viewed crudely as due to electrostatic/coulombic repulsion between like charges, negative oxygen ions and negative electrons.) This changes the system from 5 'degenerate' orbits to one where the electrons may be excited from the lower energy t2g levels to the excited eg levels.

In a real system the perfect octahedra is never attained, therefore the effect is to further split the d orbital energy levels. The d orbits have a fixed geometric arrangement so it is the exact position of the oxygen which determines which orbits suffer the greatest degree of coulombic repulsion. The geometry of metal coordination sites determines the order and separation of d orbital energy levels. Depending on the site, some or all of the degeneracy of the d orbitals may be removed. The greater the number of non-degenerate levels, the greater the number of possible electronic transitions between the levels.

The actual calculation of energy levels in a real mineral is complex and for a given atom includes:

1. Site symmetry (octahedral or tetrahedral) and degree of distortion, if any.

2. Valency

3. Strength of crystal field - nature and strength of bonding.
Another feature of crystal field caused colour is that the same ion can enter several sites in a mineral lattice thus creating several sets of energy levels and resulting in superimposed absorption bands.

The crystal structure of olivine \((\text{Fe,Mg})_2\text{SiO}_4\) (a possible constituent of clay ceramics) consists of independent SiO tetrahedra linked by divalent metal ions in 6-fold coordination with oxygen. There are two sites - designated M1 and M2. The M1 can be approximated to a tetragonally distorted octahedron (D4h), M2 closely approximates to a trigonally distorted octahedron with C3v symmetry (Loeffler & Burns, 1976). The optical spectra of olivine show features at 8,300 and 11,700cm\(^{-1}\) and at 9,500cm\(^{-1}\) which correspond to the spin allowed transitions of Fe\(^{2+}\) in M1 and M2 sites respectively (Burns, 1970). The green colour of many Fe\(^{2+}\) silicates like olivine is not so much due to absorption in the visible but a window in the visible between strong UV absorption and the characteristic Fe\(^{2+}\) crystal field absorption in the near infrared.

Many minerals, including olivine, are anisotropic and have different physical properties in different crystallographic directions. Materials that are not cubic often have unsymmetrical cation sites, hence the environment round a colouring ion is not necessarily spherically symmetrical and in such instances neither is the crystal field nor the resultant absorption spectra. Different wavelengths of light are absorbed along the various optical directions - the mineral is seen to change colour if viewed from different directions, and is described as pleochroic. Olivine is not visibly pleochroic as most of the differential absorption occurs in the infrared - the visible portion of the spectra of the 3 optical axes are essentially identical.

Variable valency is another factor. The same element can produce differing effects depending on the valency of the ion present. There
are, for example, no unpaired electrons when the electron shells are empty or completely full and therefore no colour, eg:

\[ \text{Cr}^{6+}, \text{V}^{5+}, \text{Sc}^{3+}, \text{Ti}^{4+} \quad \text{no d electrons - orbit empty.} \]
\[ \text{Zn}^{2+}, \text{Cu}^{+} \quad 10 \text{ d electrons - orbit full.} \]

Crystal field transitions in Fe\(^{3+}\) occur at higher energy and are much weaker than those in Fe\(^{2+}\). There are five unpaired d electrons in Fe\(^{3+}\), one in each orbit. Therefore any crystal field transition in Fe\(^{3+}\) must result in the pairing of at least two electrons in one orbital. This reduces the number of unpaired electrons from 5 to 3. Transitions which change the number of unpaired electrons and hence the spin of the cation are 'spin forbidden' and are 'not allowed' by quantum mechanics. However, they do occur due to spin orbit coupling, but are much weaker and occur at higher energies than normal 'spin allowed' d-d transitions.

Fe\(^{3+}\) transitions are thus unlike those of Fe\(^{2+}\) where the spin allowed transition of the 6th d electron from a t\(_{2g}\) to an e\(_{g}\) orbital maintains the number of unpaired electrons (Loeffler & Burns, 1976).

The effect of changing the crystal field strength can be seen by comparing ruby and emerald. The colour of both is due to Cr\(^{3+}\) substituting for Al\(^{3+}\) in a 6 coordinate site. The oxygen bond lengths are similar in both cases, but the higher degree of covalency in the beryl type crystal structure of emerald results in a shift in absorption (see Nassau, 1978).
The unpaired electron which produces colour does not need to be located on a transition metal, it can occur in the form of a colour centre. These are usually due to defects in the crystal structure which either trap an electron or leave a vacancy at a site usually occupied by a pair of electrons. Both result in one unpaired electron.

The best known colour centre is the 'F' centre which gives rise to the purple colour of fluorite, which is due to the trapping of an electron in place of a fluoride ion. Colour centres are also known to occur in certain glasses (Nassau, 1978) and in quartz - a mineral often present in clay ceramics.

The purple colour of amethyst is due to a special type of iron contamination. If the iron in quartz enters two types of site, Fe\(^{3+}\) substituting for Si\(^{4+}\) giving an S1 centre with interstitial Fe\(^{3+}\) producing an I4 centre, one can get transitions of the type:

\[
\text{Fe}^{3+} (\text{S1}) + \text{Fe}^{3+} (\text{I4}) \rightarrow \text{Fe}^{4+} (\text{S}) + \text{Fe}^{2+} (\text{I4})
\]

\[\text{donor} \quad \text{acceptor}\]

The visible colour is dominated by Fe\(^{4+}\). Fe\(^{2+}\) gives a weak band at 6000cm\(^{-1}\) and a charge transfer band at above 50,000cm\(^{-1}\) (Lehmann, 1975). Al\(^{3+}\) substituting for Si\(^{4+}\) can, in certain circumstances, give rise to the brown cast typical of 'smoky quartz', ie an ejection of an electron from an oxygen adjacent to an Al by radiation.
2.2.3 Molecular Orbital Theory

In the crystal field approach the unpaired electrons remain localised on a single ion or at a defect. If unpaired electrons are in orbit around two or more ions in a predominantly ionic structure or two or more atoms are predominantly covalently bonded, then Molecular Orbital Theory is more appropriate.

This theory is similar to CFT (having similar energy levels and selection rules) but it is applicable to electrons with multi-centred orbits. While CF transitions occur within one ion, reactions do occur between atomic centres. The most common of these fall under the heading of Charge Transfer Transitions (CTT), since they may be regarded as a shift from one atomic centre to another. There are three main types of orbit centre combinations:
metal:metal
metal:non-metal
non-metal:non-metal

2.2.3.1

Metal:Metal or intervalence CTT involves the transfer of an electron between two transition metal ions of variable valency in adjacent cation sites. Due to elemental abundances the following examples are the most common:

A) $\text{Fe}^{2+} + \text{Fe}^{3+} \rightleftharpoons \text{Fe}^{3+} + \text{Fe}^{2+}$
B) $\text{Fe}^{2+} + \text{Ti}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ti}^{3+}$
C) $\text{Fe}^{3+} + \text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+} + \text{Fe}^{4+}$
The energies required to promote this reversible electron hopping generally correspond to visible wavelengths. The energy of a given CTT depends not only on the type of ion but also on the metal:metal distance, as one might expect. As the distance increases, so too does the energy but the probability of transition decreases. The geometry of a charge transfer couple (e.g., octahedral/tetrahedral, edge or face sharing) also affects the energy. In general, the greater the adjacent oxygen electron density, the greater the energy between the cations involved.

Thus with other factors held constant, the energy increases in the order: face sharing (oct:oct) < edge sharing (oct:oct) < edge sharing (oct:tet) < corner sharing (Loeffler & Burns, 1976). The most diagnostic feature of CTT is that they are highly polarization dependent and occur at maximum intensity when light is parallel to the metal:metal axis.

Charge transfer transitions usually have high transition probabilities and thus give intense colours. They therefore tend to dominate CFT colours when both are present. It is probable that the majority of dark blue-black colours in iron, manganese, and titanium containing minerals are due to such mechanisms. Example A, and perhaps C, could be responsible for the black colour of magnetite Fe₃O₄. A and B have been suggested, either singly or combined, as the cause of the blue colours in iron doped α-Al₂O₃ (sapphire) and kyanite (Faye, 1971 and Lehmann & Harder, 1970), though the precise causes are still contentious.
Metal: non-metal charge transfer is also a common occurrence, at least in the form of an oxygen→metal transition where an electron of essentially oxygen 2p character is transferred to a metal 3d orbital. It is for instance likely to occur when transition metals occur in octahedral coordination sites. The O→Fe³⁺ transition may be the cause of many Fe³⁺ colours, e.g. the yellow colour of citrine (Fe³⁺ doped SiO₂). Crystal field transitions with Fe³⁺ occur at the blue end of the spectrum but are spin forbidden and therefore weak. The stronger O→Fe³⁺ absorption in the UV may extend a tail into the visible causing a yellow colour (Loeffler & Burns, 1976, Nassau, 1978).

Metal: non-metal transitions could also apply to sulphides and selenides, e.g. pyrite FeS, but these have semiconductor type properties and are probably best understood using Band theory.

Non-metal: non-metal transitions are not so common in minerals and are normally associated with, for example, organic dyes. One example is seen in graphite. The 'π' electrons of the six carbon atom rings are free to move not only throughout the whole ring but also through the whole crystal in the plane of the ring. This produces the electrical conductivity, specular reflection and almost complete absorption of light - hence black colour.
2.3 The Kaolinite → Mullite Transition

The kaolinite → mullite reaction sequence is relevant to the study of colour formation in industrial clay materials primarily for one reason. It provides a "simple" model on which the initial stages of the important colour-producing thermal reaction sequence can be based. If one does not have a reasonable appreciation of the mechanisms involved in what is essentially the simplest and certainly the most studied clay ceramic reaction sequence, then one is unlikely to appreciate fully the intricacies involved in a more complex situation, e.g. in a mixed-layered clay.

Indeed very few studies have been made of the thermal reaction sequence of illite or illite:vermiculite mixed-layered clay - the main clay mineral(s) of interest here. The basic model will therefore be constructed using kaolinite and the important parameters described. Once this has been done the model can be extended (in the next section) to cover illitic mixed-layered clays.

Kaolin, and therefore its reaction products, are found in Warnham Clays. Whilst they do not normally have a significant effect on the colour of the fired clays, they do influence it. Iron, the main colouring agent, can for example dissolve in the kaolin reaction products, so it can dilute them. The kaolinite → mullite reaction sequence does therefore have some significance in its own right.

As stated, the kaolinite → mullite transition is the most studied ceramic type reaction sequence. A very large amount of material has been published on this sequence and it is not practicable to review more than a small percentage of it here. Comment will therefore be restricted to the main papers.
The hypothesis that is now generally accepted, at least in its basic format if not in detail, was first proposed by Brindley and Nakahira in 1959 (See fig.2.3.1.1). The reader is referred to the first part of their paper for the pre-1959 historical background. Their review covers most of the developments from the pioneering thermal analysis and acid dissolution experiments of Le Chatelier in 1887, to the early electron microscopy of Eitel, Muller & Radczewski (1939), Comfero, Fisher & Bradley (1948) and Comer, Koenig and Lyons (1957).

Ordinary XRD powder patterns of normal, finely crystalline kaolinite heated to >470°C generally gives a broad diffuse peak at about 3.5-4.5Å. As a result metakaolinite was generally regarded as 'amorphous'.

Brindley and Nakahira (1959), using single crystals of kaolinite (flakes about 0.1mm) succeeded in obtaining X-ray patterns of metakaolinite. Rotation and oscillation photographs taken around the a and b axes of kaolin particles previously heated to between 490 and 800°C gave hexagonal patterns that could be indexed in terms of a and b. The spots were too diffuse for exact measurement but the parameters were essentially the same as those for kaolinite. Patterns around c, that is normal to a and b, gave diffuse and continuous scattering.

These results were interpreted as indicating that 'metakaolinite' had a modified layer structure similar to kaolinite, but without periodicity normal to the layers. On the basis of density measurements, Brindley and Nakahira calculated a theoretical value for
Proposed kaolinite transition series

\[
\begin{align*}
& a) \text{ Kaolinite} \rightarrow \text{ Metakaolinite} \rightarrow \text{ Al Si Spinel} \rightarrow \text{ Mullite} \rightarrow \text{ Mullite} \\
& \text{ Si}_4 \text{ Al}_4 \text{ O}_{14} \quad \text{Si}_3 \text{ Al}_4 \text{ O}_{12} \quad 1:1 \text{ Transitional} \quad \text{Al}_6 \text{ Si}_2 \text{ O}_{13} \\
& \quad \begin{array}{c}
(001) \quad \parallel \quad \text{III} \\
\text{ab plane} \quad \parallel \quad [111] \\
\text{b axis} \quad \parallel \quad [110] \quad \rightarrow \parallel \quad \text{c axis}
\end{array}
\end{align*}
\]

\[
\begin{align*}
& b) \text{ Kaolinite} \rightarrow \text{ Metakaolinite} \rightarrow \gamma\text{Al}_2\text{O}_3 \rightarrow \text{ Mullite} \\
& \text{ SiO}_2 \quad \text{Amorphous} \rightarrow \text{ Cristobalite} \\
& c) \text{ Kaolinite} \rightarrow \text{ Metakaolinite} \rightarrow \text{ Al Si Spinel} \rightarrow \text{ Mullite} \\
& \text{ Si}_{4.9} \text{ Al}_{3.1}[\text{Al}_{11.7}\Box_{4.3}] \text{ O}_{32}
\end{align*}
\]

Figure 2.3.1.1
Proposed kaolinite → mullite transition series
c of about 6.3Å. Using this value and measurements of a and b and taking 'likely bonding situations' into account, they proposed the structure shown in fig.2.3.1.2 for metakaolin. Though still commonly quoted as 'correct'; some discrepancies are now known, which will be discussed later.

Brindley and Nakahira obtained good XRD patterns of a cubic spinel-type phase, together with residual metakaolin and a very faint mullite pattern from samples heated to 950°C. Additional samples showed that the cubic spinel phase existed over a temperature range of 925-1075°C with maximum development at about 950-980°C, after which the cubic phase declined while mullite increased in intensity. The mullite pattern was too diffuse for accurate lattice measurements below about 1200°C.

Their significant breakthrough came with the discovery that the XRD patterns showed that the [110] direction of the spinel developed parallel to the b axis of the kaolinite → metakaolinite, while the [111] direction was normal to the c axis (ie 002) of the kaolinite. It was realised that these planes correspond to the close packed oxygen layers in their respective lattices. This indicated a structurally dominated transformation in which the oxygen lattice remains relatively intact while the cations migrate. In view of this structural dominance it was considered unlikely that complete segregation of alumina and silica followed by recombination would occur. Rather, most of the cations, including silicon, would probably be retained in the oxygen framework. This indicated that the cubic phase was an Al-Si spinel and not γAl2O3 - a defect spinel, as proposed by Hyslop and Rooksby (1928). This identification is still a controversial issue and will be dealt with later in detail.

Despite looking for an indication of a structural continuity in
the spinel-mullite transition, they failed to find one. They did postulate one, however. Their hypothesis suggests that a rotation of the octahedral chains of the spinel (along (110)) could transform spinel into a mullite type lattice. That is, the c axis of mullite parallel to the [110] of spinel, and hence b axis of kaolinite.

The structure of mullite was not known in detail at that time, though it was known to be orthorhombic and similar to sillimanite (chains of Al-O octahedra parallel to c axis and cross-linked by Al to Si ions in tetrahedral positions).

The existence of mullite in preferred orientation is important as it supports the idea of an epitaxial type of transformation. Brindley and Nakahira reasonably expected to find such evidence; Comefero et al had reported finding mullite developed in a preferred orientation with respect to the original kaolin, while Bradley and Grim (1951) reported that mullite sets developed with their c axis parallel to the [020] [110] [110] axes of pyrophyllite on firing.

Comer (1960) partly solved the problem when, during an EM study, he found that mullite forms with a preferred orientation in well-crystallised kaolin, but not in poorly crystalline material. Preferred orientation occurs consistently only in well-crystalline material when the particles are left undamaged (eg by not pre-grinding). This suggests that particle size and/or degree of crystallinity are important.

Comer (1961) was subsequently able to prove by electron diffraction that the (111) of the spinel type structure develops parallel to the ab plane of metakaolinite (ie ⊥ C) and that [110] is parallel to the main b axis, while mullite develops with the c axis parallel to the 110 axes of the spinel. Comer found that the degree of crystallisation of the new phases and the temperatures at which they
were formed were lower in well-crystallised kaolinite than in poorly crystalline kaolinite. Poorly crystalline material was found to be transformed into a spinel at 850°C with few specimens showing mullite development. The moderately crystalline ones, in contrast, did develop mullite at that temperature.

These findings, along with those of Von Gehlen (1962), corroborate those of Brindley and Nakahira and support their hypothesis. This hypothesis is now more or less generally accepted, though various workers have suggested slight modifications to it, mainly in alterations to the proposed crystal structures and the precise chemical composition of the various phases. Some of the more important ones will be outlined in the following sections.

The arguments for and against many modifications to the above reactions are quite 'involved' and usually centre on experimental limitations and inappropriate cross correlation of results. Many different experimental techniques have been used, eg XRD, XRF, TEM, DTA, IR, XPS etc, but as each has its own advantages and disadvantages, one must know what these are so as to measure only what one thinks one is measuring. This has not always been the case. Also, comparing one published result with another is hazardous - eg different degrees of crystallinity of starting material and/or different heating rates are probably responsible for many a dubious conclusion. With most papers one should look more closely at the experimental method section than the conclusion and discussion.
2.3.1.1 Metakaolinite

The precise structure and composition of metakaolinite is still unknown. The model proposed by Brindley and Nakahira (1959) is shown in fig.2.3.1.2; as previously mentioned, it is now known to contain discrepancies. Despite this, it is still commonly quoted as the basic model.

For example, their model leads to the unlikely conclusion that at about 500°C the number of oxygen atoms per unit volume drops sharply, only to be brought back to approximately its original value when the spinel is formed at about 950°C (Brindley and Nakahira account for this by postulating oxygen diffusion - yet the basis of their model is a stable oxygen framework). It also proposes that the Al in metakaolinite is exclusively Al₄, while proposing that both kaolin and spinel are exclusively Al₆ (i.e. octahedral cf tetrahedral - see figs. 2.3.1.6-7).

In addition to these apparent crystal chemical discrepancies, structural differences have been observed. Brindley and Nakahira (1959) reported little or no periodicity along the c axis of metakaolinite. Radczewski and Schadel (1962) however, on the basis of electron microscopy, concluded that there can be a definite, though restricted periodicity - this was subsequently corroborated by McConnell and Fleet (1970). Electron diffraction on single crystals gave values of 6.8 to 5.6Å with an average of 6.2Å for c.

Brindley and Gibbon (1968) made refined measurements of the b parameter. Electron diffraction of "exceptionally well crystallised" material heated to 700°C gave b=9.145 ± 0.035Å, compared to an initial value of b=8.95 ± 0.03Å for the kaolinite used. This 2.2% expansion led them to postulate a slight modification of the metakaolinite structure of Brindley and Nakahira. If an Al-O sheet is to be
maintained after dehydroxylation, some reduction in a and b are to be expected - not expansion, for this suggests some disruptions of the octahedral sheet.

Brindley and Gibbon (1968) found they could explain the increase in b by postulating a relaxation of the tetrahedral layer following the disruption of the octahedral layer.

The tetrahedral sheets of the kaolinite structure are normally distorted from true hexagonal symmetry towards ditrigonal, due to the rotation of the tetrahedra through angles of about 11.3° in order to fit the constraints of the bonds to the Al-O, OH layer. If, when the octahedral layer is disrupted, the constraints on the tetrahedra are removed, so that the Si ions repel each other to the maximum limit of the Si-O bond length (1.62Å), then the maximum relaxation can correspond to a hexagonal network. As Brindley and Gibbon (1968) showed from the geometry of the tetrahedron (See fig.2.3.1.3), it follows that;

\[ b = 4\sqrt{2}(\text{SiO}_2) = 4\sqrt{2}(1.62) = 9.15\text{Å} \]

This value corresponds exactly with their measured parameter for metakaolinite. This suggests a hexagonal arrangement of the tetrahedra and shows that some disruption of the octahedral layer must occur.

Additional evidence for the disruption of the octahedral layer in the coordination of Al comes from a number of studies using a variety of techniques, eg Mossbauer, IR, ESCA and XRF. For example, Pampuch (1966), on the basis of an IR study, postulated that the tetrahedral sheets take up a hexagonal instead of the ditrigonal arrangement while the Al-O,OH sheets break down to an arrangement of corner and edge shared Al-04 tetrahedra forming chains. The partial change form 6 to 4 coordination for Al is also supported by the IR data of Stubican and Roy (1961).
The Brindley and Nakahira model (1959) for metakaolinite contains exclusively Al 4 as opposed to kaolinite and spinel which contain exclusively Al 6. Brindley and McKinstry (1961) reported that Al in metakaolinite was apparently tetrahedrally coordinated (XRF), while also noting a partial reversal of coordination number from 4 to 6 in material heated to 1024°C - a trend more marked in disordered forms (Fig. 2.3.1.4). Likewise Udagawa et al (1969) apparently showed that during the dehydroxylation of kaolin to metakaolinite, Al 6 was totally converted to Al 4; they too noted a reversal if fired to a higher temperature, thus corroborating Brindley and Nakahira's model.

XRF results, however, should only be used as a guide and not be regarded as conclusive. It should be remembered that the changes in Δ2θ are very small and depend on a number of factors, not just coordination state, eg degree of covalent bonding, nature of nearest neighbour, crystallinity, defect structure, impurity content and perhaps dominantly on bond length. Wardle and Brindley (1971) found that the shifts in Δ2θ between different materials correlated significantly with bond length. (See fig. 2.3.1.5)

So these (and other) XRF results may actually reflect changes in Al-O bond length rather than changes in coordination. The decrease in Δ2θ could simply indicate a decrease in Al-O distance and not a change from Al 6 to Al 4. Al 4 and Al 6 proportions can probably be estimated by XRF only if the Al 4 and Al 6 'standards' used have the same bond length as the material under study. However, as the bond length of Al-O in metakaolinite is unknown as yet, this is somewhat difficult.

Even though XRF data is inconclusive, IR studies do give some indication of coordination state. Mackenzie (1969) reports that the broad IR bands of both metakaolinite and spinel fall between the
frequencies of Al-04 and Al-06 groups (as deduced by Tarte, 1967). This would seem to suggest an extremely distorted configuration containing both Al 4 and Al 6. (The maxima are separated by 300cm-1 so they are easily distinguishable). This would be consistent with a metakaolinite formed by the type of dehydroxylation process described by Taylor (1962) (See later) - ie certain regions of the crystal retaining an extremely distorted octahedral layer while in others a more nearly tetrahedral situation develops. This lack of regularity is consistent with the broad IR bands and absence of an XRD pattern. Similarly Mossbauer results described later indicate a general loosening of the structure and an increase in distortion along with cation migration at dehydroxylation.

One of the basic premises of Brindley and Nakahira's model is that the dehydroxylation process is homogeneous i.e. H2O is lost from all regions of the crystal equally. In contrast, Taylor (1962 & 1964) proposed an inhomogeneous dehydroxylation, the essential steps of which can be described as:

1. Cation migration from donor regions into acceptor regions and counter diffusion of H+ ions (maintaining charge balance).

2. Loss of oxide ions (O / (OH) ) from exposed or donor regions and their combination with H+ from all regions to form water, which evaporates, leaving pores.

3. Changes in oxygen packing in acceptor regions which have received metal cations - new packing being orientated with respect to original lattice.
In Taylor's model for the dehydroxylation mechanism, (fig.2.3.1.6) the essential feature is that the crystalline order in metakaolin, such as it is, resides chiefly in the oxygen packing. No oxygen is lost from the acceptor regions and the type of packing initially tends to remain unchanged (ie as kaolin). The additional cations are incorporated into the structure to restore imbalance, caused by loss of H+. It is assumed both Si and Al migrate from donor to acceptor regions where they occupy, largely at random, the available tetrahedral interstices in the oxygen framework.

This model is to some extent corroborated by Rouxhet et al (1969) who proposed that an oxygen-containing species is involved in 'long range' proton transfer.

The 'difficulty' in explaining how a transformation involving oxygen transport could be topotactic and preserve a close relationship between the oxygen packing of the starting and final phases was overcome by 'assuming' that "the lattice in its initial configuration orientates the nucleation and the formation of the new phase." (Rouxhet et al., 1969) (See section 2.3.3, ie cations of oxygen lattice).

There is some additional evidence which is consistent with an inhomogeneous process. McConnel and Fleet (1970), in their electron optical study of the thermal decomposition of kaolin, report the development of 'micropores' in kaolin crystals heated to about 850°C. The kaolin broke down to an 'amorphous' defect oxide phase which was homogeneous and finely porous - as indicated by a mottled microstructure of approximately 50Å scale. This mottled structure increased in scale, reaching about 100Å in 900°C samples, apparently persisting into the defect spinel phase. It seemed to be an integral part and possibly essential in stabilising the structure (See section 2.3.1.6).
If, as seems probable, the micropores do grow with temperature, as suggested by Taylor, then if they exist on a much smaller scale than 50Å in kaolin heated to a lower temperature, say 400-800°C, the disruption of the lattice on this sort of scale could account for the low degree of crystallinity exhibited by metakaolin. In contrast, the metakaolin of Brindley and Nakahira (1959) appears relatively crystalline (See fig. 2.3.1.2) and does not adequately explain the lack of crystallinity.

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**Fig. 2.3.1.7** Layer sequence of atoms perpendicular to (001) in kaolinite and metakaolinite and parallel to [111] in spinel. (After W.D. Johns, 1965)
Fig. 2.3.1.2 Proposed structure of metakaolin. (a) Projection on the (001) plane; (b) elevation seen along the a axis. (After Brindley and Nakahira.)
FIG. 2-3-1-4 Graphical representation of $\Delta (2\theta)$, difference in diffraction angle of AlK$\alpha$ radiation from Al (metal), and Al ions in various minerals and coordination states. Angular ranges are marked corresponding to AlO$_4$ and AlO$_6$ coordinations.

FIG. 2-3-1-5 $\Delta (2\theta)$ = $2\theta$(Al metal) - $2\theta$(Al, substance), and $\Delta \lambda$ plotted against Al-O distances, Å. Upper curve and circles, present data, lower curve and triangles, from data of Läuger (1971). The numbers correspond to the numbers in Table 1. In addition in Läuger's data sp = spinel, Al-O = 1.927 (Bacon, 1952), and ma = margarite, Al-O = 1.841 (Takéuchi, 1960).
Fig. 2.3.1.6  Kaolinite spinel transition via an inhomogeneous dehydroxylation mechanism. Left - schematic representation of pore formation. Right - schematic representation of corresponding crystal structures. (After Taylor, 1962).
2.3.1.2 Spinel Phase

The main controversial issue in the kaolinite-mullite transition over the last twenty years, and at present, is the exact nature of the spinel type phase. (A second, closely associated issue is the precise significance of the exotherm at 980°C seen in DTA experiments - see section 2.3.1.4.)

Many accept the suggestion of Brindley and Nakahira that it is an Al-Si spinel, while others keep to the previous suggestion by Hyslop and Rooksby (1928) that it is $\gamma$Al$_2$O$_3$. There is some evidence to support both views. There is however one additional possibility that is generally overlooked (in effect a compromise) which is presented later.

The basis of the $\gamma$Al$_2$O$_3$-Si spinel controversy is in effect one of experimental limitations. Hyslop and Rooksby identified the cubic phase as $\gamma$Al$_2$O$_3$ on the basis of chemical extraction and the similarity of its XRD pattern. Brindley and Nakahira (1959) thought that, given a topotactic transformation, complete segregation of silica and alumina, followed by recombination, was unlikely and that in addition the 'real' cell size of the cubic phase was smaller than the J.C.P.D.S standard for $\gamma$Al$_2$O$_3$, so they proposed Si spinel. This phase has a smaller cell size than $\gamma$Al$_2$O$_3$ and is closer to the measured value than $\gamma$Al$_2$O$_3$. Over the years, many workers reported that their XRD pattern was closer to one value or the other and indicated $\gamma$Al$_2$O$_3$ or Si spinel. Few, if any, have looked at it objectively.

Isomorphous substitution of Si$^{4+}$ for Al$^{3+}$ and vice versa is a well known phenomena in aluminosilicate structures, including clay minerals. It should therefore not be unexpected in their reaction products. The resultant change (if any) in Si substituting for Al in a cubic spinel
structure must be determined by considering the nature of the substituting species (i.e., ionic sizes), their coordination number, the extent of substitution and the original structure, packing and vacancies of the phase in which substitution occurs.

The ionic sizes of Si$^{4+}$ and Al$^{3+}$ are similar; Si$^{4+} = 0.4\text{Å}$, Al$^{3+} = 0.5\text{Å}$. The oxygen bond distances are Si-O = 1.62Å, Al-O = 1.78Å—a difference of about 10%.

The structure of γ$\text{Al}_2\text{O}_3$ is spinel type face centered cubic (Fd$\text{3m}$). Two crystallographic models have been proposed, based on a 32 oxygen atom unit: in one the 8 tetrahedral sites are occupied by Al with the remainder present in the 16 octahedral sites. This results in 2 $\frac{2}{3}$ octahedral sites being left vacant, i.e., 8 Al $[\text{Al}_{13.3} \square_{26.7}]_0\text{O}_3$ In the other, vacancies are thought to occur in both sites $\text{Al}_{7.1} \square_{0.9} [\text{Al}_{14.2} \square_{1.8}]_0\text{O}_3$.

Since Al has dual valency and Si does not, if a Si spinel forms the Si would be expected to occupy the tetrahedral sites with Al shifting to the octahedral. The number of vacancies could also change.

Since there is also a small difference in atomic sizes and bond length, it could be expected that an Al-Si spinel would have a slightly smaller unit cell size than γ$\text{Al}_2\text{O}_3$. Since during substitution a slight push-pull adjustment occurs before final positions are established, the actual change cannot be predicted theoretically. So even with a difference of about 10% in bond lengths, a large difference in unit cell size need not necessarily occur.

In reality, the cubic phase is poorly crystalline and of very small crystallite size (approximately 75 – 125Å, Comer 1961). Usually, only the (400) and (440) reflections are detectable and both are usually weak and broad. The difference in cell size for the two types corresponds to a difference in 2θ for the two phases of about
400=0.098° and 440=0.0329° (KαK). However, given the broad reflections and their low intensity, it seems unlikely that accurate cell measurements can genuinely be made unless rigorous calibration and experimental conditions are applied, e.g., slow oscillatory scanning with a known standard added. All researchers appear to have used conventional powder diffraction techniques. Only one or two (Chakraborty and Gosh 1977 & 1979 and Yamada and Kimura 1962) have even expressed caution at interpreting their measurements as absolute, as most do. Given the limitations involved, it is unlikely that XRD will ever give a definitive cell size and certainly not until experimental conditions are tailored to suit the situation. Likewise (at present) electron diffraction under good conditions is generally thought to give a maximum accuracy of no more that 1-5%.

In short, to try to differentiate the cubic phase on diffractional evidence is, to say the least, optimistic. The most useful indicators so far have come from chemical and crystal chemical studies.

Chakraborty and Gosh (1978) proposed a new alternative; that the Al-Si spinel has the same composition as mullite and contains both Al4 and Al6. They showed that metakaolinite does not lose amorphous silica gradually with increasing temperature, rather it loses SiO2 only at the temperature of the exothermic reaction and that the liberated SiO2 is very soluble in alkali -ie it remains in a free state.

They compared the amount of amorphous silica extracted by boiling 10% NaOH against leaching time. They found that initially silica was extracted rapidly. Up to 30-35% SiO2 and minor Al2O3 was extracted for leaching times less than 30-40 minutes. For leaching times greater than 40 minutes the spinel and mullite were attacked and a sodium zeolite type phase was formed. The cubic phase gradually disappeared
with prolonged extraction while the amount of SiO₂ and Al₂O₃ extracted did not increase significantly. Under similar conditions they found a mixture of synthetic γAl₂O₃ and amorphous SiO₂ did not form a zeolite.

The fact that a zeolite formed supports an Al-Si composition for the spinel. Zeolite type materials are generally synthesised in one of two ways, by homogeneous or heterogeneous reaction (Breck, 1974). In the former, a soluble silicate reacts with an aqueous solution of alumina (eg in Na form), resulting in the precipitation of an amorphous aluminosilicate, the subsequent nucleation and crystallisation of which gives a zeolite phase. In a heterogeneous reaction a solid aluminosilicate, eg. an Al-Si spinel, reacts directly with an aqueous solution of a base (eg NaOH) to form a zeolite.

The results of Chakraborty and Gosh (1978) and Chakraborty (1979) suggest that the cubic phase transforms directly to a zeolite via a heterogeneous reaction. There was no evidence of significant Al₂O₃ dissolving in the NaOH (eg soluble NaAl₂O₃ formation) or of it precipitating, or of soluble SiO₂ uptake by any residue (ie its reaction with SiO₂).

Chakraborty and Gosh (1978) also found that if kaolin was heated to 980°C and leached, then reheated to 1200°C, mullite formed as usual. This too suggests that the residue is an Al-Si spinel as the removal of about 35% silica could reasonably be expected to hamper the formation of mullite and so the γAl₂O₃ would be expected to change to αAl₂O₃ – at least some αAl₂O₃ should form; but none did.

In addition they noted that while 35% silica could be extracted at the metakaolinite spinel transition, no further silica was liberated at the spinel-mullite transition. According to the thermodynamic data of Schieltz and Soliman (1966), of the reactions they considered, the following one is the most likely as it has the maximum - ΔG.
According to this equation, about 37% amorphous silica should be released - this is in close agreement with observed data.

Hence it seems that the spinel is an Al-Si spinel and that all the SiO$_2$ liberated in the kaolin $\rightarrow$ mullite reaction is liberated at the metakaolinite $\rightarrow$ spinel transition. Therefore the spinel probably has the same composition as mullite. Chakraborty and Gosh (1978), assuming the standard mullite composition (i.e. 3:2) proposed the formula for the spinel as Si$_{Al_6}O_{13}$ or Si$_{49}Al_{31}[Al_{11.7}O_{4.3}]O_{32}$.

If they are correct, and the spinel does contain Al 4 and Al 6, it could explain some of the IR and XRF studies that have been done. Percival et al (1974) and Mackenzie (1969), during infrared investigations, observed both Al 4 and Al 6 in kaolin heated to 1000°C. Both Al 4 and Al 6 are present in mullite and since some mullite will coexist with spinel at this temperature, both should be detected. As spinel is usually considered to be the major phase at this temperature, then given the apparent strong development of AlO$_4$ absorption, this does not seem compatible with a formula of Si$_3$Al$_4$O$_{12}$. This formula, proposed by Brindley and Nakahira (1959), makes no provision for Al to occupy tetrahedral sites.

There has been some support for the Brindley and Nakahira's formula from Weiss et al (1969), who claim to have isolated a spinel of composition Si$_{2.95}$Al$_{4.07}$O$_{12}$ by means of "exhaustive leaching of heat treated kaolin" with pyrocatechol at pH8. (These authors give almost nothing in the way of experimental details so it is difficult to assess this and other claims (i.e. other topotactic transformations), and no further details appear to have been published since.)
Chakraborty (1979), in a study of coprecipitated $\text{SiO}_2/\text{Al}_2\text{O}_3$ gels of differing ratios, found that all showed an exotherm at 980°C followed by crystallisation of a cubic phase, with silica being liberated in gels where $\text{SiO}_2 > 30\%$. The gel with a ratio corresponding to mullite (3:2) gave the largest exotherm. The height of the exotherm increased with increasing $\text{Al}_2\text{O}_3$, reaching a maximum at the above ratio, then declined, confirming the results of Demediuk and Cole (1958).

This too suggests the spinel has a composition corresponding to mullite, since the heat of formation is at a maximum at that ratio while in others silica or alumina acts as a dilutent.

The results of investigations using gels are the subject of as much controversy as the kaolinite reaction itself. Other investigators have obtained different results, for example Horte and Weigmann (1956) found equimolar gels gave highest exotherm whereas mullite composition was $1/3$ lower; Segawa (1949) and West and Grey (1958) found a maximum at 0.5 $\text{SiO}_2:\text{Al}_2\text{O}_3$.

To sum up:

The overall bulk of the evidence now favours the spinel to be an Al-Si spinel which contains both Al 4 and Al 6 and has a bulk composition close to that of primary mullite. In other words, most of the silica lost in the Kaolin $\rightarrow$ mullite transition is lost at the metakaolinite $\rightarrow$ spinel transition. (fig.2.3.1.1). It is also quite probable that vacancies occur in both octahedral and tetrahedral lattice sites.
<table>
<thead>
<tr>
<th>Material</th>
<th>Reflection</th>
<th>d</th>
<th>a</th>
<th>Mean a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Diffractometer)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-Si Spinel</td>
<td>400</td>
<td>1.973</td>
<td>7.892</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>440</td>
<td>1.394</td>
<td>7.885</td>
<td>7.886</td>
</tr>
<tr>
<td>γAl₂O₃</td>
<td>400</td>
<td>1.977</td>
<td>7.908</td>
<td>b</td>
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<tr>
<td></td>
<td>440</td>
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<tr>
<td></td>
<td>(Powders)</td>
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<tr>
<td>Al-Si Spinel</td>
<td>400 s</td>
<td>1.971</td>
<td>7.884</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>440 vs</td>
<td>1.394</td>
<td>7.885</td>
<td>7.886</td>
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<tr>
<td></td>
<td>444 w</td>
<td>1.138</td>
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</tr>
<tr>
<td>γAl₂O₃</td>
<td>400 s</td>
<td>1.976</td>
<td>7.904</td>
<td></td>
</tr>
<tr>
<td></td>
<td>440 vs</td>
<td>1.397</td>
<td>7.900</td>
<td></td>
</tr>
<tr>
<td></td>
<td>444 w</td>
<td>1.142</td>
<td>7.905</td>
<td>b</td>
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<tr>
<td></td>
<td>731 w</td>
<td>1.030</td>
<td>7.911</td>
<td></td>
</tr>
<tr>
<td></td>
<td>800 vw</td>
<td>0.9879</td>
<td>7.903</td>
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<tr>
<td></td>
<td>840 vw</td>
<td>0.8845</td>
<td>7.910</td>
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Table 2.3.1.1

<table>
<thead>
<tr>
<th>Material</th>
<th>Formula</th>
<th>Al-4 %</th>
<th>Al-6 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>Al₂O₃ 2SiO₂ 2H₂O</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Metakaolinite</td>
<td>Al₂O₃ 2SiO₂</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(60)</td>
<td>(40)</td>
</tr>
<tr>
<td>Al Spinel</td>
<td>Al₈&quot; (Al₁₃₃₂₆₆)&quot; O₃₂</td>
<td>37.5</td>
<td>62.5</td>
</tr>
<tr>
<td>Al Spinel</td>
<td>(Al₇₁₂₉₂₂₄₂)&quot; (Al₁₄₂₁₈)&quot; O₃₂</td>
<td>33.3</td>
<td>66.6</td>
</tr>
<tr>
<td>Al-Si Spinel</td>
<td>Si₈ (Al₁₀₆₆₂₅₃₃) O₃₂</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Al-Si Spinel</td>
<td>Si₄₉ Al₃₁ (Al₁₁₇₂₄₃) O₃₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3:2 Mullite</td>
<td>3 Al₂O₃ 2SiO₂</td>
<td>55.5</td>
<td>44.5</td>
</tr>
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<td>2:1 Mullite</td>
<td>2 Al₂O₃ SiO₂</td>
<td>58.3</td>
<td>41.7</td>
</tr>
<tr>
<td>Na Zeolite</td>
<td>Na₇ (Al₁₉₂₄₋₇₂) O₃₈₄ nH₂O</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>Al(OH)₃</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 2.3.1.3
Theoretical Aluminium Valency of Reaction Products
(After Bulens et al., 1978)
Mullite is known to be the stable high temperature aluminosilicate at close to atmospheric pressure. A lot of the assumptions about the course of the transitions phases are based on mullite. The structure and nature of mullite is therefore important. Detailed study of the literature would now suggest that mullite too may not be quite what it has often been assumed to be.

For most of the early years of the kaolin → mullite research, the structure of mullite was not known. Wyckoff et al (1926) pointed out that its XRD pattern was very similar to one of the four Al2SiO5 polymorphs, sillimanite.(1:1) Agrell and Smith (1960) showed it is possible to distinguish the two only by careful measurement of lattice parameters. Both are known to be made up of Al-O chains parallel to the c axis, cross-linked by (Si-Al)4 tetrahedra.

Recent observations suggest, however, that their short range order schemes are fundamentally different.

Sillimanite has Si and Al ordered on the tetrahedral sites (Burnham, 1962) giving rise to a double c repeat (2 x 2.9Å). Mullite solid solution, generally assumed to lie between 3:2 and 2:1 (Al2O3 : SiO2), is thought to be arrived at by a substitution scheme of 2 Si4+ + O2− → 2 Al3+ + □. Sadanaga et al (1967) and Burnham (1964), in structural determinations of the 2.9Å cell in mullite (fig.2.3.1.8), found no evidence of the sillimanite type (Al-Si)4 ordering. Rather a new tetrahedral site containing Al2* is adopted adjacent to the position where each oxygen atom is lost. (Oc -see fig.2.3.1.8)

Given such a scheme, there is no reason why mullite solid solution should not extend fully between sillimanite and alumina. In practice it is restricted by the encroachment of the αAl2O3 stability field.
Natural mullite, however, has a very restricted solid solution field from 57 - 60 mole percent Al$_2$O$_3$ (Cameron, 1977). In a study of natural and synthetic mullite, Cameron (1977) found that mullite which developed by crystallisation from liquids can have a compositional range of 57 - 71 mole percent Al$_2$O$_3$, depending on the temperature of crystallisation and cooling rate. For a given rate, then, Al$_2$O$_3$ content increased with temperature, but rapid quenching can further increase it.

Mullite formed by solid state reactions, in contrast, has a temperature dependent range of only 60 - 66 mole percent - the higher composition being that at which melting commences.

Perhaps very importantly, it was noted that, contrary to popular belief based on Bowen and Greig (1924), there was NO apparent preference for either 3:2 or 2:1 stochiometric composition.

Structural determinations, verified by density measurements (Cameron, 1977) for Al + Si = 6 and a c=2.9Å cell give the mullite solid solution scheme to be:

$$\text{Al}^{\text{VI}}_2 \left[\text{Al}_{2+2x} \text{Si}_{2-2x}\right]_{\text{IV}}^4 \text{O}_{10-x}$$

with Z=1 and x equivalent to the number of oxygen (Oc) atoms missing per unit cell (Burnham, 1964). The silica-rich end of the solid solution (x=0.17) occurs where sillimanite and mullite coexist.

Cell dimensions for mullite in 60 - 71 mole percent range vary linearly with composition, (fig.2.3.1.9) but are subject to small systematic variations when Ti and Fe substitute for Al.(fig.2.3.1.10). Chemical composition, and not Al-Si order, is evidently the main variable (Cameron, 1977 cf Aramaki and Roy, 1962).
Fig. 2.3.1.8  Projection on (001) of model 2 for the mullite structure. Two unit cells show the effect of removing one O atom. Note that the O\(_c\) atom that has become three-coordinated has shifted to the O\(_c^*\) position, not on the symmetry centre at O, \(\frac{1}{2}\), O.

Fig. 2.3.1.9  Variation of lattice parameters with mullite composition, with speculative extrapolations to the pure alumina end-member.
FIG 2.3.10a Variation of lattice parameters as a function of composition and temperature for mullite-Fe$_2$O$_3$ solid solutions.

FIG 2.3.10b Variation of lattice parameters as a function of composition and temperature for mullite-titania solid solutions.
If one extrapolates the \(a\) and \(b\) cell parameters seen in fig.2.3.1.9, they appear to cross near \(x=0.63\) ie 79 mole percent \(\text{Al}_2\text{O}_3\) - so the alumina rich phases could be either tetragonal or orthorhombic.

Foster (1959) synthesised a tetragonal metastable polymorph of alumina, known as \(\text{i Al}_2\text{O}_3\) (iota). Its XRD pattern is very similar to that of mullite - hence it could represent the alumina rich end phase of the solid solution. Direct evidence for an orthorhombic \(\Leftrightarrow\) tetragonal transition at 79 mole percent \(\text{Al}_2\text{O}_3\) (at liquidus) is unlikely to be forthcoming as \(\text{i Al}_2\text{O}_3\) is unstable.

Saalfeld (1962) and Du Vigneaud (1974) report finding an orthorhombic version of \(\text{i Al}_2\text{O}_3\) - albeit possibly contaminated with NaOH.

If \(a\) and \(b\) are simply taken to cross over, as postulated by Cameron (1977) then the orthorhombic form of \(\text{i Al}_2\text{O}_3\) should have \(a=7.74\text{Å}\) and \(b=7.60\text{Å}\) - in good agreement with Saalfeld. \((a=7.591\text{Å} \ b=7.675\text{Å} \ c=2.876\text{Å})\)

Regardless of the symmetry of the end member phase - the cell parameters composition relationship, fig.2.3.1.9, would still appear consistent, with complete solid solution between \(\text{i Al}_2\text{O}_3\) and silicious mullite.

The precise crystal structure of mullite is still under debate, but it almost certainly varies with composition and relative site occupancy. An average structure is shown in fig.2.3.1.8 (Burnham,1964). Essentially, it is similar to a disordered sillimanite type structure in which some of the oxygen atoms (Oc) linking the Al:Si tetrahedra are missing at random. Cations whose positions are rendered untenable by oxygen removal take up positions in tetrahedrally coordinated sites \(\text{Al}_2^*\), that are unoccupied in sillimanite. Since the \(\text{Al}_2^*\) sites also require coordination to Oc, their occupancy increases
Oc coordination from 2 to 3 - the atoms moving to Oc* sites accommodate this.

Changes in composition necessitate differing site occupancy which in turn changes the structure. The octahedral units in Burnham's model are slightly distorted along the Z axis. His high resolution electron density maps provide evidence of distortions arising from Oc* asymmetry, caused by changes in coordination. For a detailed consideration of the crystal structure, see the literature, e.g. Burnham 1964, Cameron 1977, Nakajima et al 1981.

2.3.1.4 Infrared Spectroscopy

Numerous IR studies of the kaolin → mullite transition have appeared in the literature. The replacement of the 1010, 1032 and 1112 cm⁻¹ bands (Table 2.3.1.4) by one at 1060 cm⁻¹ has already been mentioned (section 2.3.1) and is thought to correspond to a change in symmetry of the silica layer from ditrigonal to open hexagonal (Pampuch, 1966, Blaszczak et al, 1972).

IR apparently shows that silica polymerisation starts immediately after metakaolinite formation, at 450-600°C. At temperatures of 600-800°C the 1060cm⁻¹ band is progressively replaced by one at 1080cm⁻¹ which, coincident with the appearance of a band at 800cm⁻¹, indicates the appearance of silica (free silica = 1080, 800, and 475cm⁻¹).

As for the Al, one of the general features is the apparent shift from octahedral to tetrahedral coordination as the reaction proceeds. Tarte (1967) recognised, condensed (ie X-O-X cf X-O-Y) and isolated AlO₄ and AlO₆ units with ranges of 650-900 and 400-680cm⁻¹.
respectively.

Mackenzie (1969) noted a peak (probably an amalgamation of an octahedral and tetrahedral peak) which initially occurred at about 790cm⁻¹ in metakaolinite then shifted progressively, becoming the characteristic square-shaped mullite peak at about 870cm⁻¹. This shift was found to give a positive linear correlation to percentage mullite formation - hence a possible quantitative technique. The frequency shift on heating could be interpreted as an increase in tetrahedral Al at the expense of octahedral during mullite formation - at least the direction of shift is consistent with such a change. It is true that it is at variance with the XRF data, but then that is suspect. (Section 2.3.1.1).

Mackenzie (1972) calculated the IR frequencies of an ideal 3:2 mullite on the basis of the simplified crystal model in fig.2.3.1.11. Despite simplifying it by treating it as discrete Al-O and SiO tetrahedra and Al-O octahedral groups, he succeeded in showing each (Si,Al) tetrahedra could have 3 active IR bands which, combined with the two F_w bands from the octahedral layer, gave the observed number of eight. The frequencies calculated on this model (table 2.3.1.5) agree well with his observed frequencies spectrum. Some of the assignments are supported by, or at least are consistent with, those found elsewhere in the literature.

Table 2.3.1.4 shows average values of absorption features obtained from the literature by Percival et al (1974) for the main phases in the kaolinite → mullite sequence, along with suggested attributions.

One additional point to mention - Blaszczak et al (1972) report that the metakaolinite bands at about 450 and 565cm⁻¹ can revert to about 412 and 539cm⁻¹ on protonation, eg with 2M HCl, thus indicating the former are due to OH free analogues of the Al-O-H group.
### Assignment of Kaolinite Band Wave Numbers (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Si-O bond from SiO(_4)</th>
<th>(Al(^{1+})-O)-H bond from Al[O(OH)]</th>
<th>Al(^{1+})-O bond from Al[O(OH)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1114 ms</td>
<td>938 m,(sh)</td>
<td>540 s</td>
</tr>
<tr>
<td>1095 m, (sh)</td>
<td>914 ms</td>
<td>370 mw</td>
</tr>
<tr>
<td>1072 s, br</td>
<td>789 m,(sh)</td>
<td>345 ms</td>
</tr>
<tr>
<td>1060 s,sh</td>
<td>782 m</td>
<td></td>
</tr>
<tr>
<td>1035 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1012 s</td>
<td>794 m</td>
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<td>752 m</td>
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<td>430 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>411 mw,sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>370 mw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>345 ms</td>
<td></td>
<td></td>
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</tbody>
</table>

### Assignment of Metakaolinite Band Wave Numbers (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Si-O bond from SiO(_4)</th>
<th>Al(^{1+})-O bond from AlO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1260 w,sh</td>
<td>807 m,br</td>
</tr>
<tr>
<td>1203 s,sh</td>
<td>807 m,br</td>
</tr>
<tr>
<td>1152 s,sh</td>
<td>807 m,br</td>
</tr>
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<td>1071 s,br</td>
<td>807 m,br</td>
</tr>
<tr>
<td>665 w,sh</td>
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<td>479 m</td>
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</tr>
<tr>
<td>456 m,br</td>
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</tr>
<tr>
<td>428 s,sh</td>
<td>807 m,br</td>
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</table>

### Assignment of Mullite Band Wave Numbers (cm\(^{-1}\))

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<tr>
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</thead>
<tbody>
<tr>
<td>1171 s</td>
<td>832 s,br</td>
<td>613 m,sh</td>
<td>1081 w</td>
</tr>
<tr>
<td>1120 ms,sh</td>
<td>740 m,(sh)</td>
<td>613 m,sh</td>
<td>1000 m,sh</td>
</tr>
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<td>960 ms,sh</td>
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<td>613 m,sh</td>
<td>725 w,sh</td>
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<td>927 s,sh</td>
<td>740 m,(sh)</td>
<td>613 m,sh</td>
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</tr>
<tr>
<td>901 s,br</td>
<td>740 m,(sh)</td>
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<td>542 s,sh</td>
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<td>306 w,sh</td>
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<tr>
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<td>445 m,(sh)</td>
<td>740 m,(sh)</td>
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<td></td>
</tr>
<tr>
<td>362 w,sh</td>
<td>740 m,(sh)</td>
<td>613 m,sh</td>
<td></td>
</tr>
</tbody>
</table>

s=strong m=medium w=weak  br=broad sh=shoulder (sh)=shoulder in some spectra

Table 2.3.1.5 Observed and Calculated Infrared Frequencies of Mullite. (After Mackenzie, 1972)

![Fig. 2.3.1.11](image)

(A) Simplified Model of Mullite Structure (not to scale)

(B) Possible Variations of AlO\(_6\) Symmetry in Simplified Model
2.3.1.5 Thermal Analysis - significance of

The literature includes numerous papers that are based in whole or in part on thermal analysis techniques, e.g. DTA, DTG or DTC. They are far too numerous to go into in detail so only the basic outline can be given.

In essence, the DTA trace of kaolinite contains three, or perhaps more accurately, four important features, which can be summarised as follows: An endothermic reaction at between 400 - 600°C, corresponding to the loss of hydroxyls and the formation of metakaolinite. This is followed by another, much smaller endotherm, just before the intense exothermic reaction at 950 to 980°C. The endotherm at about 900°C is often not recognised as it frequently manifests itself only as a decrease in upward slope at the onset of the exotherm (i.e. it is swamped) (Tsuzuki and Nagasawa, 1969). The cause of these two features is controversial and will be dealt with shortly. The final feature is a second exotherm at about 1250°C corresponding to the crystallisation of 'secondary' mullite (Johns, 1953).

Traces of this general format are obtained for all clay minerals, though they differ in detail. It has been apparent for quite some time, however, that one must be careful in comparing fine detail of DTA traces as they are very sensitive to experimental conditions, e.g. heating rate, particle size, crystallinity, degree of sample packing etc. (e.g. Spiel et al, 1945 and Grim, 1968). So while detailed comparison is very useful in specific circumstances, in general it ought to be treated with a degree of caution.

Genuine differences do however occur. Traces of poorly crystalline kaolin are essentially flat between the 400 - 600°C endotherm and the exotherm at about 950°C, while in well-crystallised
kaolin they slope slightly upwards and the faint endotherm just prior to the exotherm is more likely to be seen. (Grim, 1953).

As mentioned, the cause of the 980°C exotherm is controversial and has been attributed to the crystallisation of both of the known crystalline phases, spinel (Brindley and Nakahira, 1959, Tsuzuki and Nagasawa, 1969) and mullite (Roy et al 1955, Glass, 1955). The silica present is generally regarded as amorphous but the crystallisation of quartz (Nicholson and Fulrath 1970) and cristobalite (Mackenzie, 1971) have also been proposed.

The most likely cause of this reaction is the crystallisation of the spinel phase. Few of the researchers mention the small endotherm just prior to the exotherm, possibly because it is not always very obvious. It is probably always present, in which case any proposed reaction ought to take both features into account.

Tsuzuki and Nagasawa (1969), by means of simultaneous DTA and XRD, have shown that the appearance and increase in the (440) reflection of the spinel is coincident with the exotherm. In addition electron microscopy revealed that 'dots' which appeared during the endotherm changed to spinel crystallites during the exotherm. The rate of crystallisation did not follow a simple rate formula - there appeared to be an induction period at low temperature.

Chakraborty (1979), in a study of coprecipitated SiO2 : Al2O3 gels, found that all showed a 980°C exotherm followed by crystallisation of a cubic phase - the only crystalline phase present. He also noted a small endothermic peak analogous to that seen in kaolin prior to the exotherm, which he attributed to the expulsion of the last traces of water from the aluminosilicate gel.

A similar explanation could apply to kaolin. De Keyser (1963) suggested metakaolin may be stabilised by OH groups - he noted that
even though metakaolin contains $<1\%$ H$_2$O, this water is evolved only with difficulty between 650 and 900°C, eg by prolonged heating.

The evidence from both real and synthetic systems suggests that the 980°C exotherm is due to the crystallisation of spinel. The arguments put forward to support the other phases are somewhat weak. For example, one of the main arguments used against spinel are the reports of its occurrence at temperatures significantly below the exotherm, eg at about 850°C (Comer, 1961, Roy et al, 1955), the argument being that if it already exists, it could not be responsible. However, as the heat treatment regimes used by the aforementioned researchers are significantly different from those of DTA, this argument seems invalid.

The argument put forward by Glass (1955) to indicate that mullite is responsible for the exotherm is somewhat vague. Basically, it is the general view that while hard, dense, crystalline phases could be expected to give a sharp, strong, exothermic reaction on crystallisation, soft, irregularly constituted phases would not evolve significant energy in slow development and probably would not in a moderately fast one. This view, however, does not seem consistent with the observations of Tsuzuki and Nagasawa (1969). Similarly, Chakraborty and Gosh (1978) have shown that the crystallisation of either quartz or cristobalite is essentially an untenable suggestion.

Thus most direct observations indicate spinel as being responsible for the exotherm.
Strictly speaking, thermodynamic functions are only meaningful for accurately defined single processes and not for complex reactions of this type - so in this instance they are best used only as a guide and not given precise physical significance. As the transformation of kaolinite to mullite involves a series of intermediate products, each with its own, though overlapping, temperature range, it is very difficult to obtain precise parameters as one can never be quite certain of precisely what one is measuring. Hence any values can be regarded only as approximate.

This said, a number of general observations can be made. It is clear from the quite wide range of activation parameters for mullite development, obtained by different researchers using kaolinite from different localities, that activation enthalpies of 50-200 k cal mole-1 are possible. Duncan et al (1969) measured $\Delta H^*$ to be 74-84±15 k cal mole-1, Lundin (1959) measured 190-220 k cal mole-1, Nicholson et al (1970) 38-48 k cal mole-1 and Budnikov about 50 k cal mole-1. Fyfe et al (1958) obtained 67.8 k cal/g mole for activation energy.

The spread of results is probably due to the combined effects of impurities, morphology of sample and strain causing defects, eg dislocations. Duncan et al (1969) have shown that it is not entirely due to impurities.

Measurements of parameters aside, the main processes in a solid state reaction are;

1. Interfacial growth of products from previously formed nuclei.
2. Transport of materials in the system.
3. Lattice reordering in the reaction leading to nucleation.
Each is a potential rate-determining step.

Duncan et al (1969) reported that the formation of mullite from kaolin is consistent with a nucleation controlled model - mainly by 'eliminating' alternative models. The 'total' lack of parabolic kinetics at the beginning of the reaction was considered to obviate a diffusion controlled process. Mechanisms requiring control at the reactant-product interfaces (i.e., phase boundary model), though in reasonable agreement with the rate of reaction up to about 80% conversion to mullite, were regarded as not being totally consistent with electron microscopy evidence.

Jacobs and Tompkins (1955) proposed a model involving exponential nucleation from flat surfaces of plate-like reactant particles followed by crystal growth. Their equation used both nucleation and crystal growth constants. Duncan et al (1969) found that in the case of mullite the growth rate is significantly greater than nucleation rate and so it had little effect (i.e., \( \ln(1-\alpha) = 0 \) at \( t=0 \)).

If nucleation is primarily a surface reaction along the lines of the Jacobs and Tompkins model, then the area of particles can be expected to be an important variable in determining reaction rate. It is well known that the progress of the kaolin-mullite reaction is affected by particle size. Furthermore, the dehydroxylation of kaolinite is thought to start at the surface (Freund, 1969).

As mentioned, Duncan et al (1969) regarded a phase boundary model as inconsistent with electron microscopy evidence, despite the close fit of the reaction profile. TEM shows the resultant mullite forms as needles which are orientated with respect to the original kaolin.
The general model

\[ \alpha = 1 - \left( \frac{k_2 t}{a} \right)^3 \]

where \( k_2 \) = rate constant
\( a \) = constant radius
\( \alpha \) = fraction reacted at time \( t \)

assumes the reactant crystal is spherical. The boundary conditions being invoked seemed inappropriate and therefore so did the concept of a migrating reactant interface. It is therefore of interest to find that McConnell and Fleet (1970), on the basis of a TEM study, conclude almost precisely the opposite for the intermediate spinel phase. These authors suggest, on the basis of the similarity of the microstructure of the spinel to that of CoO formed from dehydroxylated Co(OH)\(_2\), that it too is a porous defect oxide. They proposed that it also forms via a migrating reaction product interface. Their model is very similar to the dehydroxylation model of Taylor (1962) described earlier, and it is probably not coincidence that the initiation of dehydroxylation at the surface, noted by Freund (1969), was thought to be followed by the migration of an interface into the crystal at higher temperatures.

In this model, dehydroxylation occurs at a sharp interface which moves into the crystal. Counter diffusion of cations occurs across the interface, forming the defect oxide, while the coherence across the interface is maintained by the development of pores/voids in the reaction product. The pores are randomly developed and subsequently the pore structure continues unchanged from the metakaolin into the spinel phase.

Over the temperature range over which the spinel is found (about 900-1100°C), McConnell and Fleet (1970) report that the microstructure remains relatively constant - that is, the scale of inhomogeneity increases only slightly (50-100Å). Over the same temperature range,
defect aluminium spinels ($\gamma Al_2O_3$) sinter or readily produce a coarse system of micropores. (Lippens, 1961).

These observations would suggest that the spinel is microporous and that the fine structure may actually be necessary to stabilise this phase. It also seems reasonable to assume that all the available Al and Si is incorporated into the spinel and could perhaps be differentiated to some extent, thus stabilising the dimensions of the microstructure.

As pointed out by McConnell and Fleet, given the potential thermodynamic stability (metastability) of the microporous product, it is worth noting that not only does it have an excess energy due to internal surface and possible lattice defects, but it also has appreciable configurational entropy. This suggests that the initial reaction at the interface defines a local free energy minimum in which the excess energy due to defects is balanced, at least in part, by a configurational entropy term - hence appreciable stability. Huckel (1951) gives values of several $k$ cal mole$^{-1}$ for excess energy in activated porous oxides.

A number of other general observations can be included at this point. The breaking of bonds and loosening of a structure is associated with a large entropy increase. Where this process occurs in an activation incident, the reaction has a very high entropy of activation.

The water vapour pressure for a dehydroxylation reaction under equilibrium conditions may be hundreds or even thousands of atmospheres. So for a reaction at atmospheric pressure, as in a laboratory test, where the vapour pressure is by comparison relatively insignificant, the potential overall change in free energy (effectively $-RT \ln p_1/p_2$) may be of the order of tens of $k$ cal g mole. This would
mean the driving force in the reaction is extremely large and the reaction is likely to proceed by the fastest possible mechanism, regardless of the consequences. Non-equilibrium thermodynamics relate the magnitude of this driving force to the production of entropy in the reaction process. Hence a highly disordered, intrinsically metastable product is not just possible, but is actually favoured. The potential change in free energy must be insufficient below about 850°C for complete breakdown/dehydroxylation - hence metakaolin. Permissible fast reactions therefore must have a high activation energy. This in turn is only likely where the activated state is itself disordered and of high entropy - a condition that is inherited by the reaction product - hence defect spinel. (McConnell).

"In conclusion" in can be suggested that the apparent confusion over the reaction mechanism put forward by Duncan et al, as opposed to that of McConnell and Fleet, could be simply that they do not apply to the same phases. That is, McConnell and Fleet (1970), Freund (1969) and Taylor (1962) were looking essentially at the dehydroxylation of kaolin to metakaolinite and its transformation into spinel, while Duncan et al were looking at mullite development. Thus they do not necessarily have to follow the same mechanism. The transformation of spinel to mullite could well be a nucleation-controlled process. It need not necessarily follow that the early dehydroxylation process is aswell - it could be a phase boundary mechanism.

2.3.1.7 Iron - Its Reaction With Kaolin and Its Products

The work of Bronwell (1958) has shown that ferric iron is capable of entering into the mullite lattice by substituting for Al and is associated with increases in lattice parameter and refractive index
as well as changes in colour (cream-buff).

As shown in fig. 2.3.1.12, the amount of Fe III capable of entering into solid solution varies with top firing temperature. Fig. 2.3.1.10 shows that a 0-12% range of Fe₂O₃ in solid solution gives an average linear increase in lattice dimensions of 0.3% - equivalent to a volume change of about 1% in the unit cell.

Bronwell observed that if mullite with a relatively high Fe content was reheated at a lower temperature then the iron in excess of the amount soluble at that temperature exsolved, forming α-Fe₂O₃.

Iron II, in contrast, does not enter into solid solution in mullite. Bronwell (1958) observed that kaolinite heated with FeO in argon reacted to form ferrous aluminate and ferrous silicate - the sample was black. Similarly, Segnit et al (1972) found that kaolinite fired in nitrogen above 830°C reacted with FeO to form hercynite and fayalite. Though predicted by the FeO - SiO₂ - Al₂O₃ phase diagram, no Fe cordierite was observed in the temperature range (750-1100°C) investigated by Bronwell.

In contrast, Inagaki and Torii (1965) report finding firing in nitrogen rather than oxygen increases the amount of iron (II) that dissolves in mullite.

![The solid solution of iron oxide in mullite.](After Bronwell, 1958)
2.3.2 Layer Silicate High Temperature Reactions

The previous section (2.3.1) gave a comprehensive literature review of the current perception of the kaolinite-mullite transition. Relatively few accounts of the thermal transitions of other clay minerals are to be found in the literature. The few that do exist seem to show that the situation in each case is at least as confused as in the case of kaolinite - they are full of a similar series of inconsistencies.

2.3.2.1 Halloysite

As stated in section 3.4., Warnham clay contains some halloysite. This is structurally and chemically very similar to kaolinite (section 3.4.6). It is not surprising therefore, that the few accounts in the literature suggest that their high temperature reactions are essentially the same. As may be expected, the dehydration reactions differ in detail due to the additional water halloysite contains and on average take place at slightly lower temperatures.

Stubican and Gunthard (1957), however, observed water in halloysite heated to 850°C, (by IR spectroscopy). Kaolin, in contrast, loses it at about 650°C. Roy et al (1955) found metahalloysite formed at about 450°C and persisted until 640-670°C, $\gamma$Al$_2$O$_3$ developed between 650-690°C and this was followed by mullite development. Grim (1968) reports that mullite and cristobalite are the only crystalline products in halloysite fired to 'high' temperatures.
2.3.2.2 Illite - Vermiculite

The major phase of interest in Warnham clay is illite - illite:vermiculite mixed layered clay. Illite has essentially a mica-type structure (section 3.4) and therefore could be expected to behave in a similar way to muscovite.

The $K_2O-Al_2O_3-SiO_2$ phase diagram of Yoder and Eugster (1955) predicts that below 1140°C leucite, potassium feldspar and mullite could be expected while $1140 < T < 1315°C$ leucite, mullite and liquid should be found, giving way to leucite, corundum and liquid above 1315°C.

In practice, the situation is somewhat different. Eberhart (1963) reports that spinel and small amounts of mullite and leucite formed on heating muscovite to 1050°C and that the (111) and (110) planes of the spinel were parallel to the original (001) and (010) mica planes respectively. Sundius and Bystrom (1953) observed three sets of orientated mullite needles in the a-b plane of fired muscovite. This suggests a very similar situation to that seen in kaolin.

Other reports have been somewhat different though. Roy (1949) reported finding that the muscovite structure was destroyed between 940-980°C and was followed by the crystallisation of $\gamma Al_2O_3$ or spinel at about 1000°C, $\alpha Al_2O_3$ at about 1100°C and $\alpha Al_2O_3$ plus glass above 1400°C. Zwetch (1934) observed $\gamma Al_2O_3$, $\alpha Al_2O_3$ and leucite at 1050° while at 1300° the only crystalline phases were leucite and $\alpha Al_2O_3$.

Sundius and Bystrom (1953) studied several muscovites of variable composition and found mullite and/or corundum in various ratios. The presence of Fe impurity apparently promoted the formation of $\alpha Al_2O_3$ at the expense of mullite. Bye and Simpkin (1974) noted that additions of 2-5 wt% Fe decreased the minimum temperature and increased
the rate of conversion of γAl₂O₃ via δ to αAl₂O₃. (The cubic → hcp transition in the oxygen lattice is by synchroshear and is analogous to the γFe₂O₃ → αFe₂O₃ transition. αAl₂O₃ and αFe₂O₃ have almost identical crystal structures.)

Eberhart (1963) also noted that the unit cell of the spinel phase varied with the composition of the original mica (see table 2.3.2.1). Pure mica gave a value close to γAl₂O₃ while ones with a high impurity content (Fe and Mg) gave values closer to Mg spinel. Electron density measurements showed the site occupancy in the cation layers of the Al₂O₃ type material was uniform in contrast to Mg type spinel, in which octahedral and octahedral-plus-tetrahedral distributions alternate.

Brindley and Maroney (1960) found αAl₂O₃ was the only crystalline phase in pure muscovite fired to 1100-1300°C, while in muscovite quartz mixtures of <75% muscovite, only mullite formed. Intermediate mixes gave intermediate final compositions. (See fig.2.3.2.1). The amount of glass increased very rapidly with mica content. Cole and Segnit (1963) reported glass formation to be greater in Fe rich micas.

It would appear, therefore, that the high temperature phases that develop from muscovite can be influenced significantly by impurities, both in the crystal structure itself and admixed with the mica, eg quartz.

Illites differ from well-crystallised micas in that there is less replacement of Si by Al and therefore less interlayer potassium in addition to a more random stacking of silicate layers. Substitution of Fe for Al is common and the formation of an oxyhydroxide interlayer
forming a dioctahedral vermiculite component in the illite, as in Warnham clay, is also quite common and results in increasing the Fe content relative to muscovite.

Illite therefore could be expected to behave rather like a disordered iron-rich mica. In this case there is likely to be limited structural inheritance due to the reduced order in the original crystal, and one could expect the formation of α-Al$_2$O$_3$ at moderately high temperatures containing significant Fe substituted for Al.

In reality, the situation appears to be slightly different. Grim and Bradley (1940) carried out one of the few studies on illitic clays. The reaction sequence they observed can be summarised as:

\[
\text{Illite} \xrightarrow{600\degree C} \text{Illite Anhydride} \xrightarrow{850\degree C} \text{Spinel} \xrightarrow{1100\degree C} \text{Mullite} \xrightarrow{1400\degree C} \text{Glass}
\]

The dehydrated state 'illite anhydride' was stable up to about 850°C. Its XRD trace was similar to illite though the 001 reflection is shifted slightly and corresponds to a 1-2% increase in unit cell height. The (004) and (008) reflections were noticeably enhanced. Illite anhydride gave way at 600-850°C to a spinel thought to be (Mg-Fe)(Al$_2$Fe$_2$)O$_4$ (a = 8.15Å) which persisted until about 1200°C. Mullite appeared at about 1100°C and lasted until 1400°C - the amount appeared complimentary to the spinel. A small amount of α-Fe$_2$O$_3$ appeared at about 850°C but was attributed to a limonite impurity. No new quartz development occurred - residual quartz that had not been extracted from the original clay did not invert to cristobalite but 'dissolved' between 850-1050°C. Grim & Bradley postulated that the octahedral layer of the illite containing Al, Mg and Fe gives rise to the spinel while the silica and potassium give the amorphous glass.

Grim and Kulbicki (1957) found that the XRD reflections of illite
were lost between 950-1000°C and the intensities of the products were weak or non-existent if Fe or K impurities were high. Spinel was seen in Fithian illite between approximately 1000 and 1150°C. They observed mullite above about 1250°C but no cristobalite at all.

A high temperature XRD study by Bohor (1964) of illites from various localities identified quartz, spinel and mullite as the only three crystalline high-temperature phases commonly found. "Some form of iron oxide" developed in nearly all the samples, but most were thought to come from impurities. No cristobalite was observed, but amorphous silica was suspected to be present.

The initial effect of heating was to sharpen and intensify the basal peaks with the maxima shifting closer to 10Å as the hydrated mixed layers collapsed. Above about 475-500°C the formation of illite anhydride was manifested by a decrease in the (001) intensity (returning to approximately original value) while the (003) increased. Illite anhydride was stable to about 850°C but was lost by 1000-1080°C. Spinel and quartz both formed at about 1000°C and were present up to about 1300°C. Mullite appeared at about 1150°C and was stable to 1400°C. The samples used were orientated and it was observed that the mullite reflections lacking the c axis were relatively enhanced, which Bohor interpreted as showing that the mullite c axis was parallel to the a or b axes of the clay. Potassium feldspar, kalsilite, corundum and cordierite were found at about 1050°C in some of the samples.

Brindley and Udagawa (1960) observed an apparent iron-rich spinel as distinct from an Al-Si spinel in the kaolin - Fithian illite - quartz mixtures they studied. Hematite was seen in the fired mixtures but was attributed to Fe impurities. Similar experiments (see fig.2.3.2.1), using 2M muscovite in place of illite showed no spinel development.
Furlong (1967) studied the high temperature changes in illite under continuous heating conditions by electron microscopy. He heated the samples in the microscope - ie in a vacuum and not air. The octahedral iron in illite is dominantly ferrous. Fe\(^{2+}\) does not enter into solid solution in mullite - therefore if it is not oxidised it cannot dissolve in mullite as Fe\(^{3+}\) can, and so the reactions under these conditions (ie vacuum) are likely to be different from those observed in air. It is not obvious whether he appreciated this.

Furlong (1967) found the precise temperature at which the reactions occurred varied with the material used. Illite appeared stable up to about 700°C, when small so-called 'liquid spots' formed within the platelets. Up to about 850°C all diffraction patterns were equivalent to the a-b plane of illite, but at about 900-1000°C "all diffraction effects ceased", until the appearance of spinel at 1000-1100°C. This developed with its (111) plane parallel to the a-b plane of the illite, but unlike kaolinite, no distinct orientation with respect to [110] was observed. Furlong thought this reflected the smaller particle size of illite. As there was always more than one particle in the diffraction area, any orientation that might exist in any single particle would be masked by patterns from adjacent particles. The spinel phase was followed by mullite, which reached maximum development at about 1200°C. Mullite developed with its c axis lying in the (111) plane of the spinel.

Segnit and Anderson (1972) performed a rather imprecise XRD and SEM study of Fithian illite. They too recorded illite anhydride, quartz, hematite, mullite glass and residual feldspar appearing over similar temperature ranges to those mentioned. They suggested that 'at least some' of the hematite that appeared at about 800°C came from the breakdown of illite.
### Table 2.3.2.1
Cell dimensions of spinel phase compared to original mica compositions (Eberhart, 1963).

<table>
<thead>
<tr>
<th>Location</th>
<th>Mg</th>
<th>Fe</th>
<th>Fe</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mont. Mica</td>
<td>0</td>
<td>0</td>
<td>0.19</td>
<td>7.92</td>
</tr>
<tr>
<td>Bengate</td>
<td>0.15</td>
<td>0.28</td>
<td>0.15</td>
<td>7.92</td>
</tr>
<tr>
<td>Uto</td>
<td>0.15</td>
<td>0.09</td>
<td>0.36</td>
<td>7.96</td>
</tr>
<tr>
<td>Miasc</td>
<td>0.14</td>
<td>0.20</td>
<td>0.40</td>
<td>7.95</td>
</tr>
<tr>
<td>Easton</td>
<td>0.37</td>
<td>0.27</td>
<td>0.55</td>
<td>7.97</td>
</tr>
<tr>
<td>Pensbury</td>
<td>0.44</td>
<td>0.10</td>
<td>1.10</td>
<td>7.99</td>
</tr>
<tr>
<td>Bamle</td>
<td>0.54</td>
<td>0.22</td>
<td>0.39</td>
<td>7.97</td>
</tr>
<tr>
<td>Aschaffenburg</td>
<td>0.68</td>
<td>0.45</td>
<td>0.61</td>
<td>7.99</td>
</tr>
</tbody>
</table>

**Fig. 2.3.2.1**
High temperature phases derived from quartz and layer and layer silicate mixtures (After Brindley & Udagawa, 1960)

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**Fig. a** Qualitative variation of mineral content in fired mixtures containing muscovite.

**Fig. b** Qualitative variation of mineral content in fired mixtures containing illite. Key to mineral representation is given in Fig. a.
Partially Dehydrated Phase

1. Kaolinite $\rightarrow$ Metakaolinite $\rightarrow$ Si-Al spinel $\rightarrow$ Mullite

2. Muscovite $\rightarrow$ $\gamma$Al$_2$O$_3$ or spinel $\rightarrow$ $\alpha$Al$_2$O$_3$ $\rightarrow$ $\alpha$Al$_2$O$_3$ + glass

3. Muscovite $\rightarrow$ anhydride $\rightarrow$ $\gamma$Al$_2$O$_3$ + Leucite $\rightarrow$ $\alpha$Al$_2$O$_3$ + glass

4. Biotite $\rightarrow$ Fe magnetic Spinel $\rightarrow$ Fe Spinel + Leucite $\rightarrow$ Olivine + Leucite + mullite + glass

5. Biotite $\rightarrow$ Spinel, $\gamma$Fe$_2$O$_3$ + Leucite $\rightarrow$ $\gamma$Fe$_2$O$_3$ + glass

6. Illite $\rightarrow$ Illite anhydride $\rightarrow$ Spinel + glass $\rightarrow$ Mullite + glass

7. Vermiculite 14.4 $\rightarrow$ 13.8Å $\rightarrow$ 11.6Å $\rightarrow$ 20.6Å $\rightarrow$ 9.0Å $\rightarrow$ Enstatite

8. Vermiculite 14.4 $\rightarrow$ 13.3 $\rightarrow$ 11.5 $\rightarrow$ 10.3 $\rightarrow$ 9.6 $\rightarrow$

9. Pennite $\rightarrow$ Brucite layer $\rightarrow$ Mica layer $\rightarrow$ Olivine dehydroxylated dehydroxylated

$\rightarrow$ Olivine + Spinel $\rightarrow$ Enstatite, Olivine + Spinel

10. Sheridanite $\rightarrow$ Brucite layer $\rightarrow$ Mica layer $\rightarrow$ Olivine $\rightarrow$ Olivine + Spinel $\rightarrow$ Enstatite

11. Fe Chlorite $\rightarrow$ dehydroxylation $\rightarrow$ Spinel $\rightarrow$ Enstatite + $\alpha$Fe$_2$O$_3$

12. Serpentine $\rightarrow$ Fosterite + Quartz $\rightarrow$ Enstatite.

Fig. 2.3.2.2 Layer silicate reaction sequences

1. Roy, 1949
2. Roy, 1949
3. Grim & Bradley, 1940
4. Grim & Bradley, 1940
5. Roy, 1949
6. Grim & Bradley, 1940
7. Walker
8. Weiss & Rowland, 1956
9. Brindley & Ali
10. Brindley & Ali
11. Shirozawa, 1962
12.
2.3.2.3 Vermiculite

The vermiculite component in Warnham clay is very unlikely to behave along the lines of the Trioctahedral Mg vermiculite transitions described by Walker (1957), see fig.2.3.2.2. Trioctahedral Mg vermiculite, like other trioctahedral materials, does not normally form an anhydride structure, but first shows a series of partially dehydrated phases before transforming directly into enstatite. An iron-rich form, should it exist, should give rise to ferrosilite - the synthetic Fe equivalent of enstatite.

As explained in section 3.4.6, the vermiculite in Warnham clay is due to an oxyhydroxide layer in a dioctahedral mica/illite type structure, and so could be expected to behave more like an iron-rich illite. However, there are no reports in the literature relating to the high temperature reactions of such a material.

Byrne (1954) showed that absorbed interlayer organic complexes can influence the high temperature reaction of expanding lattice clays, even though the molecules themselves are eliminated at far lower temperatures. So it is possible that the actual reactions of the illite:vermiculite component may be modified by any interlayer organic material present.
2.3.3 Diffusional Aspects - Crystal Chemical Considerations

The basic lattice of all the proposed high temperature phases is normally thought of as being an oxygen one into which fit the smaller cations. The relative immobility of oxygen is an important basic feature of the accepted topotactic transformation of kaolinite to mullite, the rearrangement apparently taking place about the close packed oxygen layers with the smaller cations doing most of the necessary moving.

2.3.3.1

There is a general preconception that oxygen is immobile due to its large ionic size. In recent years isotope studies in silicate systems (eg Taylor and Epstein 1963 & 68, Garlick and Epstein 1966, O'Neil and Taylor 1967 and many more) however, have shown that this is not necessarily true. If anything, oxygen is rather more mobile than most cations.

If it is acknowledged that oxygen anions, as well as cations, could be mobile, then it is possible that crystal chemical diffusional factors along the lines of those postulated by Dowty (1980) could shed some light on the high temperature reactions of clay minerals. Dowty postulated three basic factors which could affect diffusion in silicate type systems:

1. Anion Porosity of the Structure

   defined as the volume of the unit cell, minus the volume of the included anions, divided by the unit cell volume and expressed
as a percentage. Could also include cation volume if appropriate, eg large cations.

2. Electrostatic Site Energy of the Ion

For cations this is proportional to the charge squared divided by the cation-anion distance.

3. Size of the Ion

Site energy appears more important except in compact structures.

Anion porosity strongly influences the relative mobility of different ions in different minerals or lattices. Table 2.3.3.1 shows some typical values of some relevant phases. As pointed out by Dowty (1980), there is a general positive correlation between porosity and increased polymerisation (linkage) of the Si-O tetrahedra. An oxygen bridging two tetrahedra is in contact with only six other oxygen ions (cf 12 in ideal c.p.), hence an increase in Si content effectively reduces the average cation coordination number, which generally implies a looser packing. There are exceptions - fayalite (high) and quartz (low).

Most oxides and orthosilicates have oxygen in either hexagonal or cubic close packing arrangements, but the actual density is highly variable and always less than that of ideally packed spheres. This is to be expected as anions repel each other and their closeness of packing is determined by the way the cations hold them together.

Electrostatic (Madelung) site energy is normally defined as the work required to bring the ion into the site from an infinite distance. This strongly correlates with $Z^2/d$, the formal charge squared, divided
Ideal c p 26.0

Kyanite 27.7 \(\text{Al}_2\text{SiO}_5\) triclinic
Rutile 33.0 \(\text{TiO}_2\) tetragonal
Sillimanite 35.7 \(\text{Al}_2\text{SiO}_5\) orthorhombic
Zircon 35.9 \(\text{Zr(SiO}_4\) tetragonal
Spinel 37.2 \(\text{MgAl}_2\text{O}_4\) cubic
Enstatite 39.8 \((\text{Mg},\text{Fe}^{2+})\text{SiO}_3\) orthorhombic
Ilmenite 40.9 \(\text{FeTiO}_3\) rhombohedral
Kaolinite 42.5 \(\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8\) triclinic/monoclinic
Diopside 42.8 \(\text{Ca(Mg,Fe)}[\text{Si}_2\text{O}_5]\) monoclinic
Magnetite 43.6 \(\text{Fe}_3\text{O}_4\) cubic spinel
Quartz 44.6 \(\alpha\text{SiO}_2\) rhombohedral
Fosterite 46.4 \((\text{Mg,Fe})\text{SiO}_4\) orthorhombic
Muscovite 46.6 \(\text{K}_2\text{Al}_4[\text{Si}_6\text{Al}_2\text{O}_{20}](\text{OH, F})_4\) monoclinic
Gehlenite 51.3 \(\text{Ca}_2[\text{Al}_2\text{Si}_7\text{O}_{17}]\) tetragonal
Cordierite 51.8 \(\text{Al}_3(\text{Mg,Fe}^{2+})(\text{Si}_5\text{Al}_2\text{O}_{18})\) orthorhombic
Orthoclase 53.8 \(\text{K(Si}_3\text{Al)}\) monoclinic
Rhyolite glass 54.3

Table 2.3.3.1
Anion Porosity

<table>
<thead>
<tr>
<th>Ion</th>
<th>-kcal/mole</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Na}^+,\text{K}^+)</td>
<td>270-320</td>
<td>Mica, feldspar</td>
</tr>
<tr>
<td>(\text{OH}^-)</td>
<td>280-315</td>
<td>Mica</td>
</tr>
<tr>
<td>(\text{Fe}^{2+})</td>
<td>1030-1210</td>
<td>Mica, olivine</td>
</tr>
<tr>
<td>(\text{O}^{2-})</td>
<td>1200-1500</td>
<td>Silicates, oxides</td>
</tr>
<tr>
<td>(\text{Al}^{3+})</td>
<td>2500</td>
<td>Feldspar</td>
</tr>
<tr>
<td>(\text{Al}^{3+})</td>
<td>2600</td>
<td>Garnet</td>
</tr>
<tr>
<td>(\text{Si}^{4+})</td>
<td>4200-4700</td>
<td>Silicates</td>
</tr>
</tbody>
</table>

Table 2.3.3.2
Typical Site Energies
by the average cation distance. Typical values are shown in Table 2.3.2. In silicates and oxides the Madelung energy is the principal contributor to the forces holding an atom in place.

It is often assumed and now appears to have been verified (Dowty, 1980) that there is a rough proportionality between site energy and activation energy.

In the process of diffusion an energy barrier or activation energy is encountered, which is often the principal determinant of rate. This activation energy is the difference between the total energy of the crystal when an atom is in its initial position and that when it is in a high energy interstitial position in the process of motion.

The purely electrostatic contribution to the activation energy would, if there were no readjustments of the structure or atomic polarizations, be of similar magnitude to the site energy. Since these do occur, the net activation energy is typically <10% of the site energy (Dienes et al, 1976).

2.3.3.2

Site energy considerations may hold the key to the kaolinite-mullite transition. It may appear that oxygen is immobile, but this is not necessarily correct, as already stated.

In a given structure, ions with a lower, less negative site energy should, subject to geometric constraints (size:porosity) be more mobile. Large ions will not be able to diffuse in a very compact structure however low the site energy. The converse should also be true, small ions, eg Si^{4+}, should have site energy dominant over geometric factors, ie be immobile. Measurements on oxides (Kofstad,
apparently bear out that oxygen's much larger size makes it relatively immobile in all but the most porous structures despite its site energy being roughly the same as Fe$^{2+}$ or Mg$^{2+}$.

When water is present the situation is very different. It is known that water vapour greatly enhances mullite development from kaolin (Mackenzie, 1969a) and has a catalytic effect on nucleation in silicate melts (Weyl, 1962). It is also known to catalyse the transformation of $\gamma$Fe$_2$O$_3 \rightarrow \alpha$Fe$_2$O$_3$ (Ridge et al, 1967), another proposed topotactic reaction, and enhance the rate of reaction between $\beta$ quartz and CaO $\rightarrow$ Ca$_2$SiO$_4$ (Burte et al, 1972).

This effect is apparently due to a weakening of (or ?attack on) the Si-O and Fe-O bonds. On entering a silicate, each water molecule probably reacts with an oxygen ion to form two hydroxyls (Burnham, 1975) –ie proton attack. The result can be seen in terms of one hydroxyl in a regular oxygen site and another as an interstitial. The mobility of the oxygen in the form of hydroxyls depends on the binding energy. If the oxygen ion in a regular site is converted to OH– the site energy is halved (at least), since the formal charge is halved. Local readjustments of the structure would probably reduce the site energy of an OH substituting for oxygen towards that of a normal hydroxyl which is about 25% that of an oxygen ion. The site energy of an interstitial cannot be predicted, but there is no apparent reason to expect it to be above normal.

Therefore in the form of an hydroxyl the barriers to diffusion should be no greater than those for large alkali ions, eg K+, their site energies and size being of the same order.

The effect of the conversion of one oxygen to hydroxyl on the electrostatic site energy of an adjacent cation can be estimated (Dowty, 1980).
\[ \Delta E = Z \frac{e^2}{d} \]

e = charge reaction
d = bond length
Z = formal charge

For a Si-0 bond \( \Delta E + 200 \text{ kcal} \) cf site energy of 4400 kcal (4.5%)

Fe-0 bond \( \Delta E + 160 \text{ kcal} \) cf site energy of 1200 kcal (13.3%)

The conversion of more distant oxygens would change the site energy but by a lesser amount. The conversion of oxygen ions changes their site energies by about 50-75\%, while the conversion of an adjacent oxygen would change the cation site energy by about 5-15\% (Dowty, 1980). As it is unlikely that more than one of the adjacent oxygen atoms surrounding a given cation would be replaced at any one time, it is unlikely that water vapour will have a significant effect on cation mobility - as observed (Sipling and Yund, 1972). It is, however, possible that the presence of water or other hydroxyl bearing species may have an indirect effect on some cations through various types of reaction, eg oxidation state is important in different Fe\(^{2+}\) minerals, eg fayalite, where it affects the concentration of vacancies.

2.3.3.3

In a polymorphic transition, a rearrangement of the structure of a framework silicate could be affected without removing more than one oxygen at a time from the first 'coordination sphere' of each silicon. This is probably the correct way to envisage the process of 'prying
open' the silicate tetrahedra, postulated by Donnay et al (1959) rather than envoke actual escape and long range diffusion of silicon.

Polymorphic transformations and especially ones involving large changes in composition may also take place by solution and reprecipitation. The transformation of kaolin through metakaolin and spinel type phase to mullite involves a fairly large change in composition. Breakdown of kaolin to 'amorphous' metakaolin occurs at approximately 500°C with the loss of some water but it is thought (see section 2.3.1.1) that the last traces of water (ie OH) do not leave the amorphous phase until just before the first crystallisation of the spinel. Thus one has in the metakaolin an ordered, but non-crystalline phase in which oxygen may be mobile in the form of hydroxyls. It would appear to have an open 'porous' structure (the structure is not certain, therefore one cannot calculate a figure) and is probably the stage at which most of the cation and oxygen diffusion occurs. Thus one could postulate that kaolin breaks down to an amorphous material at which point most of the long range diffusion occurs. Once this has occurred and nucleation begun, there is probably relatively little long range diffusion - most of the further changes take place with minimal movement of the oxygen (the last of the OH has probably gone). Also the porosity of the structure has decreased between the metakaolinite and spinel phases. Hence the transition from spinel to mullite is topotactic. The continuity of the full topotactic reaction depends on the degree of order in the metakaolin, which in turn depends on the crystallinity of the initial material and possibly on the heating regime.

This view would fit in with Chakraborty and Gosh (1978), that the composition of the spinel is the same as that of mullite, that is, all the silica that is lost in the transformation is lost at the metakaolin
to spinel stage. Also, if as suggested, it is site energy that affects diffusion, then Si and Al should be immobile compared to oxygen. So it could be the converse of the accepted theory that is true; that is, it is the Si and Al ions that are relatively stationary and hold the oxygen network in place, not the other way round.

In other words, cations, not oxygen or the oxygen lattice, could well be the dominant factor in determining the course of the reaction. In this case, the degree of ordering, vacancies, substitution, amount and type of impurities present in the octahedral and tetrahedral site in the raw clay are likely to affect considerably the extent to which the kaolinite to mullite transformation follows an apparently topotactic reaction path. This would appear to be compatible with the observed facts, since 'crystallinity' and impurities have long been known to be important factors affecting the transition.

2.3.3.4

Studies of the role and effects of impurity cations on this reaction sequence confirm their importance and are consistent with an hypothesis that relates their behaviour to crystal chemical factors such as site energy.

Mossbauer spectroscopy studies on the role of iron impurities in the high temperature reaction of kaolinite do give an indication of the diffusional movements and structural changes of the lattice.

Mackenzie (1969b) studied the role of lattice iron impurities and cation exchange iron in the kaolin-mullite reaction. Fig. 2.3.3.1 shows the Mossbauer spectra obtained by Mackenzie for an English China Clay containing 0.8% natural iron. The single peak of the unfired
kaolin has an isomer shift (δ value) characteristic of high spin Fe³⁺, while the small line width indicated a compact high energy bond. This is consistent with the view that iron impurities substitute for lattice Al³⁺ - changes in the iron should parallel changes in Al, up to a point.

The 650°C 'metakaolinite' spectra shows two very broad, ill-defined peaks, indicating a general loosening of the iron bonds and therefore of the whole structure, after dehydroxylation. The spectrum indicated a mixture of several very distorted Fe³⁺ sites, they are too diffuse to classify as either octahedral or tetrahedral.

The 980°C 'spinel phase' spectrum is sharper and the peak is still in the Fe³⁺ region, with a δ value apparently corresponding to octahedral coordination. Thus if the iron has gone into the spinel, it has not gone into the tetrahedral sites.

The 1100°C sample shows a slightly broader peak with a δ value intermediate between octahedral and tetrahedral, so both sites could be present. By 1280°C, with mullite development nearing completion, the Fe³⁺ is tightly bound in two sites. This could be interpreted either as indicating two octahedral sites, one high spin, the other low, or they could correspond to the octahedral and tetrahedral sites in mullite proposed for Al³⁺ (Day, 1963). The δ value of 0.9mm/s is rather high for tetrahedral Fe³⁺ unless lattice distortions are present. Mullite is generally thought to exhibit distortions (Burnham, 1964) but the magnitude of their likely effect is not known.

Mackenzie (1969b) studied the effect of iron in cation exchange sites, by means of ⁵⁷Co²⁺ doped kaolin - the same one used in the previous example. ⁵⁹Co²⁺ decays into ⁵⁷Fe²⁺ with the emission of a 14.4kV γ ray, so this in contrast to the last experiment is a source study, not an absorber study. The results are shown in figure 2.3.3.2.
Fig. 2.3.3.1 Mossbauer spectra with a palladium source of kaolinite absorbers starting as follows: A, 20 C; B, 650 C; C, 980 C; D, 1100 C; E, 1280 C. The error bars indicate ±σ.

Fig. 2.3.3.2 Mossbauer spectra for $^{57}$Co$^{2+}$ doped kaolinite sources with a stainless steel absorber after heating as follows: A, 200 C; B, 650 C; C, 980 C; D, 1100 C for 10hr; E, 1100 C for 17.5hr; F, 1280 C. The error bars indicate ±σ.
Graph of metal-oxygen bond strengths versus percentage mullite formation.

Kinetic growth curves of mullite from copper-treated and untreated halloysite.

A. Cu-treated at 1050°C. B. Cu-treated at 1100°C.
C. Untreated at 1100°C. D. Untreated at 1160°C.
E. Untreated at 1220°C.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Mullite present (%)</th>
<th>Cation</th>
<th>Mullite present (%)</th>
</tr>
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<tbody>
<tr>
<td>Li⁺</td>
<td>51</td>
<td>Ni²⁺</td>
<td>22</td>
</tr>
<tr>
<td>Na⁺</td>
<td>25</td>
<td>Pb²⁺</td>
<td>19</td>
</tr>
<tr>
<td>K⁺</td>
<td>15</td>
<td>Co²⁺</td>
<td>14</td>
</tr>
<tr>
<td>Rb⁺</td>
<td>12</td>
<td>Cu²⁺</td>
<td>56</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>10</td>
<td>Ag⁺</td>
<td>65</td>
</tr>
<tr>
<td>H⁺</td>
<td>8</td>
<td>Tl⁺</td>
<td>0.5</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>18</td>
<td>Bi³⁺</td>
<td>67</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>16</td>
<td>Fe³⁺</td>
<td>26</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>11</td>
<td>Ti³⁺</td>
<td>16</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>10</td>
<td>Ce³⁺</td>
<td>13</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>65</td>
<td>Cr³⁺</td>
<td>11</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>47</td>
<td>Al³⁺</td>
<td>10</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>14</td>
<td>La³⁺</td>
<td>46</td>
</tr>
<tr>
<td>Hg²⁺</td>
<td>14</td>
<td>untreated</td>
<td>33</td>
</tr>
<tr>
<td>Be²⁺</td>
<td>8</td>
<td></td>
<td>0.015</td>
</tr>
</tbody>
</table>

Table 2.3.3.3 Mullite formation from homo-ionic halloysite fired at 1100°C for 4h.
As perhaps expected for cation exchange material at low temperatures, a number of low energy, high spin Fe II sites can be seen. After dehydroxylation at 650°C, the iron is found in several well-defined sites, two high spin Fe II sites, one octahedral, one tetrahedral and a third high spin Fe III site that could be either coordination. There is little change until about 1280°C or after prolonged heating at lower temperature, when two types of site can be distinguished, one divalent and of uncertain coordination, the other trivalent and apparently octahedral. The broad peaks suggest that even at high temperatures, the cation structure is rather random.

Both series of Mossbauer results give an indication of the type of movements involved, not just of the cations, but also of the lattice. It is difficult to interpret them precisely, but a number of general points can be made.

Following dehydroxylation, a significant change in the lattice can be observed, lattice iron indicates a loosening of the lattice structure, while cation exchange material diffuses into and is incorporated in the lattice. The lattice iron studies suggest a degree of octahedral coordination in the metakaolin phase, suggesting that Al$^{3+}$ is not exclusively tetrahedrally coordinated, as proposed by Brindley and Nakahira (1959).

These results are consistent with the view that the breakdown of kaolin to metakaolin produces an 'ordered' but open structure in which long range diffusion of cations can occur and possibly also oxygen diffusion.

The final redistribution of lattice cation impurities apparently occurs only when mullite development is well advanced. However, a noticeable lattice change occurs at about 980°C, which then remains relatively unaltered up to about 1280°C, the stage when secondary
mullite develops. This final redistribution probably coincides with the known increase in mullite crystallinity that occurs in this temperature range.

Between 980 and 1280°C, the iron is apparently in a small number of high energy sites, probably of both octahedral and tetrahedral type, while once the secondary mullite has developed, two sites, probably octahedral and tetrahedral, can be distinguished. This would appear to be consistent with an increase in mullite crystallinity. The final change does not necessarily reflect a major change in the lattice, perhaps just enough to permit the sites to be resolved.

The results of a similar $^{57}$Co experiment on a halloysite showing a similar trend to lattice iron in kaolin (Mackenzie, 1968) suggest that the slight differences that do occur do not necessarily imply a difference between the role of iron in the two sites, but perhaps simply different diffusional parameters for Fe$^{3+}$ and Fe$^{2+}$/Co$^{2+}$ in that kaolin lattice.

2.3.3.5

Crystal chemical considerations have in addition been shown to be important in a study of the effects of cation impurities on the kaolin-mullite reaction sequence.

In a study of the catalytic effects of cations on mullite development from kaolin Mackenzie (1969a) found that while there was a relationship between mullite formation and ionic size for alkali and alkaline earth cations, there was a better relationship between cation-oxygen bond lengths - as expressed by heats of formation of respective oxides and percentage mullite formation (fig. 2.3.3.3).
For all series of ions except the trivalent ones, the trend is consistent with the idea that cations facilitate mullite formation by weakening the Al-O and Si-O bonds. Since the formation of mullite from kaolin requires the loss of Si from the aluminosilicate phase, it is probably caused by cation attack on the Si-O bond of the aluminosilicate in a manner similar to the proton attack on Si-O bonds described earlier - i.e., catalysis of silicate nucleation by water vapour.

In the case of trivalent ions the tendency seems to be towards isomorphous substitution for trivalent lattice ions, resulting in those ions with strong cation-oxygen bonds tending to suppress mullite formation. (It should be noted that trivalent ions normally have a relatively high site energy, therefore hindering their and/or their attached oxygen's movement - hence suppression.)

Duncan et al (1969) succeeded in showing that the mechanism of mullite formation had as a rate-determining step, either a nucleation controlled or a phase boundary controlled process with electron optical evidence suggesting a nucleation process. Mackenzie (1969) found that Cu$^{2+}$ addition catalysed mullite formation, it did not affect the mechanism (see fig. 2.3.3.4) Thus, if Cu$^{2+}$ behaved similarly to 57Fe$^{2+}$, it would be feasible that its incorporation into the lattice at a relatively low temperature provided an increased number of suitable nucleation sites.

Small amounts of such impurities could thus have a significant effect on nucleation rates - the relative effects of the impurities could perhaps be gauged from figure 2.3.3.3. The overall effect of one or more impurity is, however, difficult to predict.
2.4 Selective Chemical Extraction Techniques

The mineralogical investigation of Warnham Clay by Hall (1978) suggested that it was feasible to use chemical treatments selectively to remove the iron-rich components thus allowing their effect on the fired colour to be investigated. The iron-rich components identified in Warham clay and the treatments employed in attempts to extract them are outlined in Table 3.5.2.1. This section of the literature search was carried out to establish as accurately as possible the actual effects of the various treatments.

Their effects tend not to be restricted solely to the phase at which they are aimed. It is now apparent that it is almost inevitable that chemical pretreatment will result in some alteration of the other phases present. However, this need not be disadvantageous; provided one can determine exactly what is being done to the clay, carefully controlled degradation of clay materials can provide valuable information.

Selective dissolution, more accurately termed 'differential dissolution' techniques, have been employed for many years in soil science, for quasi quantitative analysis. The techniques devised are of two fundamental types; acid or alkali, the acid techniques essentially being used to dissolve crystalline materials and alkali the amorphous ones.
### Equilibrium Equations

<table>
<thead>
<tr>
<th>Equation</th>
<th>Form</th>
<th>log $K_a$</th>
<th>log $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(OH)$_2$*H$_2$O $= \text{Fe}^{3+} + 3\text{OH}^-$</td>
<td>Goethite</td>
<td>-44.0</td>
<td></td>
</tr>
<tr>
<td>am. FeOx</td>
<td></td>
<td>-35.5</td>
<td></td>
</tr>
<tr>
<td>frequently used</td>
<td></td>
<td>-38.5</td>
<td></td>
</tr>
<tr>
<td>Fe$^{3+} + \text{H}_2\text{O} = \text{Fe(OH)}^+ + \text{H}^+$</td>
<td></td>
<td>-2.60</td>
<td></td>
</tr>
<tr>
<td>Fe(OH)$_2^+ + \text{H}_2\text{O} = \text{Fe(OH)}^+ + \text{H}^+$</td>
<td></td>
<td>-4.70</td>
<td></td>
</tr>
<tr>
<td>2Fe$^{3+} + \text{H}_2\text{O} = \text{Fe}_2(\text{OH})^4^+ + 2\text{H}^+$</td>
<td></td>
<td>-2.85</td>
<td></td>
</tr>
<tr>
<td>Fe(OH)$_3$*H$_2$O $= \text{Fe}^{3+} + 2\text{OH}^-$</td>
<td>Gibbsite</td>
<td>-15.1</td>
<td></td>
</tr>
<tr>
<td>Fe$^{3+} + \text{H}_2\text{O} = \text{FeOH}^+ + \text{H}^+$</td>
<td></td>
<td>-7.15</td>
<td></td>
</tr>
<tr>
<td>Al(OH)$_2$*H$_2$O $= \text{Al}^{3+} + 3\text{OH}^-$</td>
<td></td>
<td>-33.51</td>
<td></td>
</tr>
<tr>
<td>Al(OH)$_3$*H$_2$O $= \text{Al}^{3+} + \text{OH}^-$</td>
<td></td>
<td>-29.92</td>
<td></td>
</tr>
<tr>
<td>frequently used</td>
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<td>-31.7</td>
<td></td>
</tr>
<tr>
<td>Al$^{3+} + \text{H}_2\text{O} = \text{Al(OH)}^+ + \text{H}^+$</td>
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<td>-12.4</td>
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</tr>
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<td>2Al$^{3+} + \text{H}_2\text{O} = \text{Al}_2(\text{OH})^4^+ + 2\text{H}^+$</td>
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<td>-4.96</td>
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</tr>
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<td>Al$^{3+} + 4\text{H}_2\text{O} = \text{Al(OH)}^4^- + 4\text{H}^+$</td>
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<td>-8.06</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$*2H$_2$O $= \text{Si(OH)}_2^-$</td>
<td>Quartz</td>
<td>-3.7</td>
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</tr>
<tr>
<td>Si(OH)$_2^-$</td>
<td></td>
<td>-2.85</td>
<td></td>
</tr>
<tr>
<td>Si(OH)$_3^-$</td>
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<td>-9.46</td>
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</tr>
<tr>
<td>4Si(OH)$_4^- = \text{Si}_4\text{O}_4(\text{OH})_4^- = 2\text{Si}^4^+ + 4\text{H}_2\text{O}</td>
<td></td>
<td>-12.56</td>
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<td>H$^+ + \text{T}^4^+ = \text{HT}^3^-</td>
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<td>12.6</td>
<td></td>
</tr>
<tr>
<td>H$^+ + \text{HT}^3^- = \text{H}_2\text{T}^2^-</td>
<td></td>
<td>7.66</td>
<td></td>
</tr>
<tr>
<td>Fe$^{3+} + \text{HT}^3^- = \text{FeT}^2^-</td>
<td></td>
<td>10.0</td>
<td></td>
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<td>Fe$^{3+} + \text{H}_2\text{T}^2^- = \text{FeT}</td>
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<td>15.2</td>
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<td></td>
</tr>
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<td>Al$^{3+} + \text{T}^4^+ = \text{AlT}^-</td>
<td></td>
<td>19.92</td>
<td></td>
</tr>
<tr>
<td>Al$^{3+} + \text{T}^4^+ = \text{AlT}^-</td>
<td></td>
<td>12.08</td>
<td></td>
</tr>
<tr>
<td>Al$^{3+} + \text{T}^4^+ = \text{AlT}^-</td>
<td></td>
<td>2.64</td>
<td></td>
</tr>
</tbody>
</table>

### Fig. 2.4.0.1a
Equilibrium equations related to oxides or hydroxides of aluminium iron and silicon in aqueous medium at 25°C (Silien & Martell, 1964; Stumm & Morgan, 1970). T=Titron

### Fig. 2.4.0.1b
Solubility diagram of Al(OH)$_3$, Fe(OH)$_3$, SiO$_2$ and related complexes as a function of pH at 55°C (After Hiersmans and Haert, 1977)
Perhaps the most rudimentary alkali method was developed by Hashimoto and Jackson (1960), who discovered that large quantities of allophane, free silica and alumina could be dissolved by boiling clay samples in 0.5M NaOH for 2.5 minutes. (100ml of 0.5M could dissolve up to 110mg Al₂O₃ and 130mg of SiO₂.) The degree of dissolution was found to be directly related to the logarithm of concentration - hence 0.5M was found to be convenient but three extractions with 0.2M was equally effective. An increase in time resulted in dissolution of the crystalline silicates. They also noted that if kaolin was heated to its dehydroxylation temperature (~500°C for 4 hours), it too could be dissolved in the 2.5 minute treatment. (Most clay minerals will dissolve if heated to their dehydroxylation temperature first.)

Wada and Greenland (1970), in their infrared study of the effects of differential dissolution techniques, found that the difference spectra of NaOH treated clay rich material corresponded to poorly ordered layer silicates. The spectra showed relative enhancement in absorption at 3500 and 910cm⁻¹ (see table 2.3.1.4), which may signify selective dissolution of kaolin type minerals or possibly their poorly ordered peripheral portions. Only minor traces of an amorphous silicate component were seen in the difference spectra.

Other reports of crystalline layer silicates being dissolved by boiling in 0.5M NaOH have appeared in the literature: kaolinite (Langston & Jenne, 1964), halloysite (Askenasy et al, 1973; Fey & Le Roux, 1975) and nontronite (Briner & Jackson, 1970; Dudas & Harward, 1971). The latter report that KOH has less of an effect on the crystal
lattice than NaOH, so its use in place of NaOH may be preferable.

2.4.2 Sodium Carbonate $\text{Na}_2\text{CO}_3$

A hot $\text{Na}_2\text{CO}_3$ solution is often used to aid dispersion of clay materials by dissolving amorphous alumina-silica cementing materials (Jackson, 1956).

Follet et al (1965) studied the effect of $\text{Na}_2\text{CO}_3$ extraction conditions on various clay minerals. The technique they used was; 100mg of sample treated with 80ml of 5\% $\text{Na}_2\text{CO}_3$ agitated for 16 hours, with repeat treatments until the silica extracted was less than 0.2\% of the initial amount (ie 3-4 times). The residue was then heated on a steam bath for 2 hours with 80ml of 5\% $\text{Na}_2\text{CO}_3$ - again extractions were repeated until both SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} were low and constant.

This version, a more vicious one than is normal, did not significantly attack any of the crystalline clay minerals investigated. It was found that cold $\text{Na}_2\text{CO}_3$ solution in general dissolved much more silica than alumina, while hot $\text{Na}_2\text{CO}_3$ removed more alumina, except from chlorite. An observed rapid fall off in dissolution with repeated extraction could indicate the removal of a separate amorphous phase, though the continued low level solution could be interpreted as continued low level attack on the layer silicates. The improvement seen in the XRD background of treated samples suggested a dominantly amorphous source. The cold $\text{Na}_2\text{CO}_3$ treatment effectively 'sharpened' the kaolin and quartz patterns in the IR spectra and reduced absorption at 2.79-2.92\mum and could be interpreted as a reduction in hydrous oxide. There was no obvious attack on the clay minerals in cold solutions. In hot solutions in contrast, kaolin absorption decreased
after treatment. Partial dissolution of kaolin was also indicated by electron microscopy, though it indicated that the bulk of the material being dissolved took the form of a cement-like coating which was holding the clay flakes together.

It should also be mentioned that Follet et al (1965) noted that the successive cold and hot treatments removed considerably more alumina and silica than did one extraction with 0.5M NaOH for 2.5 minutes. The alkali reagents appear to have the extraction effect expected as a result of their chemical reactivity, that is:

\[ \text{NaOH} \succ \text{hot Na}_2\text{CO}_3 \succ \text{cold Na}_2\text{CO}_3 \]

As can be seen in figure 2.4.0.1, iron oxide is almost insoluble in alkali solutions. It is not surprising, therefore, that Follet et al (1965) found their treatment removed no iron.

2.4.3 Tiron - Catechol Disulphonic Acid Disodium Salt

As can be seen in figure 2.4.0.1, no simple acid or alkali solution simultaneously dissolves alumina, iron oxide and silica in equivalent proportions. Silica acts as the limiting factor in acid solutions, whereas in alkali solutions iron oxides are virtually insoluble. However, as it is easier to increase the solubility of iron oxides by, for example, complexation or chelation than to increase silicate solubility, an alkali solution of a complexing agent should dissolve all these oxide groups.

Biermans and Baert (1977) proposed the use of an alkali (pH 10.5) tiron solution because of its known complexing ability of Al and Fe
from its use in colourimetry. Based on theoretical considerations, they predicted that crystalline phases should remain practically undissolved in tiron solutions if amorphous oxides are present. They reported finding that tiron has a greater affinity for amorphous iron oxide than for aluminium - as predicted.

Despite an apparently thorough theoretical analysis of the potential solubility of the likely ion species, Biermans and Baert (1977) are somewhat vague about the experimental conditions they used to verify their predictions. They do not specify which isomer of tiron they used (equations imply 1-4). They loosely describe using a tiron concentration "as high as possible but within the practical limit of 0.1M" and claim to have buffered this solution with a 0.1N Na₂CO₃ solution to pH values of 9.5-11.0.

Experiments (section 3.5.3) have shown that tiron solution is quite acid. A 0.1M 1-4 tiron solution could not be buffered to these pH values using 0.1N Na₂CO₃ or indeed a 0.1M solution. That pH range could not be attained without complete loss of the 'designated' tiron molarity. The actual conditions used in this study for the tiron treatment of Warnham clay are given in section 3.5.3.

It is clear from the literature that tiron extracts less Fe and Al than other alkali treatments. Its milder action could therefore be expected to be restricted to the amorphous component, but as no detailed study of any potential side effects has been made, its full effect is still unknown.
2.4.4 Potassium Pyrophosphate

Bascomb (1968) proposed the use of 0.1M potassium pyrophosphate, $\text{K}_4\text{P}_2\text{O}_7$, for extracting organic iron and aluminium complexes. As prepared, the solution is naturally alkaline with a pH of about 10. If used in a neutral solution, iron silicates and amorphous oxides may partially dissolve.

Arshad et al (1972) compared alkaline pyrophosphate to DCB and acid ammonium oxalate and found it extracted the least quantity of iron oxide from the minerals they tested (mostly 'fresh' trioctahedral layer silicates). They considered this to be the least destructive extraction technique. Similarly, McKeague et al (1971) found it to be a relatively mild Fe extraction method - at least for synthetic hydrated oxides.

It has the advantage of removing organic carbon along with organic Al and Fe (Bascomb 1968, McKeague et al, 1971) and it is probable that it only extracts organic based material (Schwertmann, 1973), though it may result in some K+ cation exchange.

2.4.5 Sodium Dithionite

One of the most widespread techniques for removing Fe and Al oxides from soils and clays is based on sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$). The original proposal came from Galabutskaya and Gorova (1934). Following this, Deb (1950) proposed using a solution of 4% $\text{Na}_2\text{S}_2\text{O}_4$ in an acetate/tartrate buffer (pH 5.4-6.0), - the buffer being used to prevent the solution from becoming too acid and to prevent precipitation of iron sulphides, his recommended extraction being:
0.25-1.0gm of clay in 50ml of 1N acetate/0.2N tartrate solution plus 2gm of dithionite, at 40°C for 30-50 minutes, followed by washing with 50ml of 0.02N HCl to dissolve any precipitated iron sulphides. (If distilled water is used in place of the buffer solution, then pH is 2.9-3.4)

Mitchell and Mackenzie (1954) later modified this technique by replacing the organic buffer with NaOH. In their technique 20-40mg of clay in suspension (~5ml) is treated with 10ml of a fresh solution of 0.4g Na₂S₂O₄ in approximately 0.6M NaOH at 40°C for 15 minutes. The pH of 4% Na₂S₂O₄ in distilled water is about 3.5 - while that 'desired' is 5.8-6.0. So the NaOH molarity is adjusted accordingly. Two treatments with dithionite were recommended with intermediate and final washing with 0.05M HCl (3 minutes at 40°C) to remove any sulphides that formed.

Aguilera and Jackson (1953) developed a more significant version. Its main advantage over the previous techniques is that it does not cause the precipitation of sulphur or metal sulphides. They proposed the combined use of Na₂S₂O₄ and sodium citrate solutions (with or without iron specific versene) adjusted to pH 7.3 by 10% NaOH and 5M citric acid (respectively), at 80°C. Almost immediately Jackson (1956) suggested a minor modification to the procedure - adding the dithionite as 1g of powder and omitting the NaOH. However, it was soon realised (Mehra and Jackson, 1960) that the order in which the solutions were dissolved and mixed in the previous method affected the pH which markedly influenced the effectiveness of the extraction and the precipitation of sulphur and iron sulphides.

The technique as it is now commonly used, is based on that of Mehra and Jackson (1960) (see section 3.5.4). They too used a dithionite-citrate solution buffered at pH 7.3, but employed sodium bicarbonate (NaHCO₃) as the buffer. Sodium bicarbonate proved to be a
more effective buffer than NaOH as it is not prone to the sudden changes in pH, and hence oxidation potential, experienced with NaOH. Mehra and Jackson found the oxidation potential of dithionite increased over the pH range of 6 to 9, with a sharp increase occurring up to about pH 8 - i.e. became a more effective reducing agent. However, the amount of iron oxide dissolved decreases with increasing pH. An optimum pH for maximum reaction kinetics occurs at about pH 7.3.

Follet et al. (1965b) found that in clays pretreated with 5% Na₂CO₃ (section 2.4.2), up to 40% more iron oxide was extracted than in clays treated with dithionite alone (Mitchell and Mackenzie 1954 technique). The Na₂CO₃ solution appeared to dissolve no iron oxides only Fe deficient aluminosilicate 'cements'. This presumably aided dispersion and with it solution of the Fe-Al-Si dithionite soluble material.

2.4.5.1

A great many studies have been conducted over the years using one or other of these techniques, and some side effects have been reported. Some of the authors mentioned have suggested that slight attack on layer silicates may be occurring. The results of a differential infrared spectroscopic examination of clays subjected to 'selective' alkali dissolution treatments by Wada and Greenland (1970) appears to confirm this.

The attack on crystalline layer silicates by 0.5M NaOH has already been mentioned. Similarly, all the clays treated with dithionite-citrate-bicarbonate (DCB) by Wada and Greenland (1970) were also attacked. Si-0 stretching and (Al)-OH bending bands characteristic of layer silicates predominated in the difference
spectra of treated clay materials. The OH bands were strong and rather broad, giving maxima at wave numbers lower than those of well crystallised kaolinite.

The results obtained by Wada and Greenland may well indicate a close association between the dissolved layer silicates and iron oxide, eg incorporation of iron or iron hydroxy groups into the disordered peripheral structure of clay minerals, or even perhaps interlayer material.

As outlined in Appendix 1, under certain conditions at least, sodium citrate solution is capable of changing dioctahedral mica into dioctahedral vermiculite, by removing interlayer K+ etc (Rich & Cook, 1963). Given the results of Wada and Greenland, it is quite possible that DCB extraction could significantly affect the interlayer material of the illite:vermiculite component of Warnham clay as well as dissolving the 'free oxide' coatings thought to be present. This is especially likely to occur in the case of repeated extraction.

DCB extraction could have a significant adverse effect on layer silicates in general, especially those containing iron, eg illite. Dudas and Harward (1971) reported that structural iron was removed by DCB from nontronite, a 2:1 dioctahedral iron-rich montmorillonite type mineral.

Roth and Tullock (1972) observed that Na₂S₂O₄ solution (NOTE-No citrate etc) could reduce structural ferric iron in nontronite. A complete exchange of structural hydroxyls by deuteroxyls accompanied the reduction of structural ferric iron with Na₂S₂O₄ in D₂O at room temperature. The OH stretch band at 3560cm⁻¹ was replaced by an OD stretch band at 2630cm⁻¹, as observed in cases of complete hydrothermal
substitution of D for H in nontronite. Similarly, a reduction of hydrothermally deutrated nontronite with dithionite in H$_2$O resulted in complete H for D exchange. The reduction of ordinary nontronite with Na$_2$S$_2$O$_4$ in H$_2$O resulted in a change in structural OH absorption from 3560 to 3540 cm$^{-1}$, while subsequent reoxidation (H$_2$O$_2$) restored it. This decrease is consistent with a change to OH associated with Fe$^{2+}$ – Fe$^{3+}$ octahedral cations (Farmer et al., 1967). The hydrothermal deuteration of nontronite resulted in the Fe-OH bending band at 810 cm$^{-1}$ being replaced by an Fe-OD band at 595 cm$^{-1}$. The increase observed by Roth and Tullock in the OH bending absorption bands, e.g., FeOH at 810 cm$^{-1}$ on reoxidation of a reduced nontronite, could be accounted for only by an increase in the OH content.

An increase in the 810 cm$^{-1}$ band occurred when dry deuterated nontronite was reduced by anhydrous hydrazine vapour (N$_2$H$_4$) indicating that reduction in the absence of excess H$_2$O is still accompanied by exchange of structural protons.

The investigation by Roth and Tullock (1972) shows that the reduction of nontronite involves a decrease in structural OH and is accompanied by complete exchange of structural hydrogens and that reoxidation restores the original OH content without complete exchange of structural hydrogen. In the case of nontronite at least, chemical reduction apparently involves the migration of electrons to the ferric iron with simultaneous formation of H$_2$O due to the condensation of two structural hydroxyls. This water is free to diffuse out of the structure. The remaining oxygen is immediately protonated (Roth & Tullock, 1972).

The use of dithionite or any other reducing agent on clay minerals ought to be treated with caution since there is now some evidence that reduction of octahedral cations can result in structural as well as chemical changes.
2.4.6 ACID

As described in Appendix 1, in the process of natural weathering of micas, hydroxy Al and Fe groups accumulate in the interlayer space. These groups occupy exchange sites, reduce CEC and inhibit expansion and contraction of the mineral. The process of interlayer filling can be reversed when natural chelating agents (organic matter) are abundant. The interlayer can be removed in the laboratory with complexing agents.

Though it was not always recognised, acid extraction techniques developed for removing crystalline material from soils act by attacking the octahedral and interlayer material of the clay minerals present.

2.4.7 Fluoride

Rich (1966) described a technique for 'concentrating' dioctahedral mica and vermiculite (section 3.5.7). The technique does not enrich the sample in dioctahedral mica and vermiculite by simply dissolving the other layer silicates, as Rich appears to have envisaged. This treatment appeared to result in rather rapid and in some cases total dissolution of halloysite, nontronite, Mg montmorillonite, trioctahedral micas and vermiculite. The attack on kaolinite was slightly slower. In the case of halloysite, \((\text{NH}_4)_3\text{AlF}_6\) precipitated, while from systems containing Mg, \(\text{Mg(NH}_4\text{)}_2\text{AlF}_6\) precipitated. Its effect on kaolinite and halloysite, especially the latter, is probably due to an attack on exposed OH groups and the complexing of Al and Fe. The solution as prepared (section 3.5.7) is buffered at pH 5.0. Al and Fe are complexed by fluoride at this pH.

The apparent increase in mica could, at least in part, be a case
of mistaken identity. The solution used contained NH$_4$Cl. Kaolinite, halloysite, dicktite and nacrite are known to form ~10Å complexes with NH$_4$Cl (Wada, 1964) and could possibly be mistaken in XRD for a dioctahedral mica type mineral. However, changes in the IR spectra could possibly identify such complexes. Wada (1964) found the OH stretch bands were displaced downwards by 50-80cm$^{-1}$ and the OH deformation peaks shifted from 930—→970 while, with the exception of the 3700cm$^{-1}$ band which decreased, the OH bands increased in intensity. All this indicates Cl$^-$ enters the interlayer and forms some sort of OH-Cl bond.

Similarly, 2:1 type layer silicates will be attacked along the lines described in Appendix 1, forming vermiculite. Ammonium saturated vermiculite has a 10Å XRD reflection that is also equivalent to a mica.

Also, in addition to the solution's ability to dissolve layer silicates, Rich reported that XRD evidence suggested dissolution of quartz. SiO$_2$ is normally insoluble in acid conditions - in which case this must be due to the complexing ability of fluoride ions.

2.4.8 Hydrochloric Acid HCl

HCl has been used in some of the treatments already described, eg Mitchell and Mackenzie (1954) used it to remove iron sulphide that precipitated during their dithionite extraction.

Hence HCl was one of the iron extraction treatments used in Warnham clay in trials to remove iron sulphides. However, its effect on clay minerals, at least in low pH solutions, is likely to be equivalent to the weathering reactions described in Appendix 1. The H$^+$ will displace ions in the octahedral layer, which may or may not dissolve in solution, depending on their solubility or the complexing
ability of the solution. It has long been known that dilute HCl will
dissolve chlorite by attacking the octahedral layer (Brindley & Yowell
1951). Mitchell and Mackenzie (1954) noted a decrease in the CEC of
illite and kaolinite after treatment with 0.05M HCl. This decrease can
probably be explained by H+ substitution into vacant sites, with the
displaced ion becoming fixed as a hydroxy ion in an exchange site.

It is also probably worth mentioning that Steger (1953) recorded
that HCl will dissolve kaolinite as well as chlorite if it is preheated
to its dehydroxylation temperature first.

2.4.9 Oxalate

Numerous extraction techniques have appeared in the literature
over the years, based on acid oxalate solutions, for removing 'free'
amorphous iron and aluminium oxides. Some have even been used on a
quantitative basis for amorphous Fe estimation.

The earliest technique was that of Tamm (1922), who used ammonium
oxalate buffered to pH 3.25 with oxalic acid to dissolve free oxides of
Si, Al and Fe. Tamm's technique was investigated by Deb (1950) who
found it dissolved only small quantities of crystalline oxides
(goethite and hematite). An increase in the CEC of the treated clays
was interpreted as removal of fixed exchange iron and aluminium. It
was also suspected of removing Al(OH)\text{2+} from the outer edges of the
layer silicate lattice, especially in the case of kaolinite.

Deb (1950) also described a modified technique, namely the
reduction of iron by using an acid oxalate solution in sunlight.
(Certain oxalate solutions are photosensitive and while the exact
nature of the photochemical reactions that occur is not known, it seems
as though the dominant ionic species and therefore the oxidation
potential of an oxalate solution are to an extent dependent on the degree of illumination.) Investigating the photochemical reaction over a small range of pH and molarity, Deb concluded that the optimum treatment was to subject 0.25-1.0g of clay to a series of extractions in sunlight, using 35-40ml of a solution composed of a 4:1 ratio of 0.2M ammonium oxalate and 0.2M oxalic acid - this solution having a pH of 3.8 - with extractions continuing until no 'straw yellow' colour develops in the aliquot. Complete extraction, according to Deb, usually required 10-12 hours of bright sunlight. The extraction was found to be faster at lower pH (ie 3.4 at a 2:1 ratio) and quite slow at higher pH (4.2 at an 8:1 ratio). The standard 4:1 pH 3.8 solution had the effect of decreasing the CEC slightly while at lower pH it increased. It was also found to be capable of dissolving crystalline oxides, in contrast to Tamm's solution.

Mitchell and Mackenzie (1954) produced a variant of Deb's technique by treating clays for four weeks in bright sunlight with only one change of solution. They noted that extraction in darkness was not as 'effective' and that artificial UV is not a suitable alternative. Their variation was found to remove more Fe than their variation of the dithionite technique, and they rightly suspected that prolonged extraction with such an acid solution could attack layer silicates.

Yet another variant is that of Schwertmann (1964), who reported that one extraction with acid ammonium oxalate (pH 3.0) carried out in darkness dissolves only XRD amorphous oxides. The Canadian National Soil Survey (1965 & 68) later recommended this procedure as a standard classification technique for soils. This resulted in its quite widespread adoption for the quantitative estimation of amorphous iron of dithionite which gives amorphous plus crystalline iron oxide.

Some researchers, however, have reported 'side effects' of this
treatment and have questioned its unreserved use. Baril and Bitton (1969), for example, have found that this technique resulted in the partial dissolution of magnetite. This led Arshad et al (1972) to study the effects of this treatment (pH 3) compared to DCB (pH 7.3) and potassium pyrophosphate (pH 10) on crystalline materials. They found that with the exception of DCB on illite, oxalate extracted the maximum amount of Fe, Al and Mg in all instances. Given that it is known that DCB can dissolve crystalline material, (McKeague & Day, 1966 etc), they interpreted the results as indicating this technique dissolved crystalline material.

These authors believed trioctahedral minerals were more susceptible to dissolution than dioctahedral ones. They based this idea partly on the theoretical consideration of the similarity between the trioctahedral structure and that of chlorite (known to be soluble in acid) and partly on the lower amount of Fe, Al and Mg extracted by oxalate from illite. This latter result could well be due to their use of freshly ground macroscopic trioctahedral minerals, in contrast to Fithian illite - the soil illite possibly being already partly leached. Their theoretical postulation does not seem well founded either, at least in the case of non Mg minerals, so their belief may well be unjustified.

Pawluck (1972) also investigated the relative effects of DCB and oxalate extraction. He noted that repeat extraction with acid oxalate removed more Fe than did DCB but at a slower rate. XRD indicated that crystalline oxides, eg lepidocrocite and goethite, were completely removed by the third extraction. All crystalline oxides were removed by the twelfth. (Schwertmann (1973) found lepidocrocite is more soluble than goethite.) Pawluck (1972) noticed a decrease in XRD intensity which indicated that prolonged extraction resulted in attack on the layer silicates. (An increase in the 14Å region not mentioned
Fey and Le Roux (1975) treated 50mg of clay with 10ml of 0.2M ammonium oxalate (pH 3.0) for two hours in darkness with constant agitation (almost the same as Scwertmann). They found that this treatment could result in the total dissolution of synthetic aluminosilicate gels while gibbsite was relatively insoluble. They concluded that aluminous goethite was also relatively stable.

They found that in some cases oxalate extracted more Al from clays following DCB treatment than prior to it, which they attributed to increased particle dispersion due to prior removal of some amorphous material. As in no case was the Al removed markedly lower than with the untreated material, they suggested the Al removed by DCB belongs essentially to the crystalline phases and is removed primarily as a result of Fe dissolution rather than citrate complexation. They also suggest the complexing power of oxalate for Al is greater than that of citrate.

2.4.10 Hydrogen Peroxide

It is obligatory in order to perform some tests on clay minerals and eg DTA and IR, to remove organic matter. One of the common methods of doing this is with hydrogen peroxide. Indeed the pretreatment of clay samples, either before or after dispersion with H₂O₂, is often routine. It is also occasionally used to disaggregate clay material.

Numerous studies indicate that it is not always totally effective at removing organic matter and some of the constituents of the carbon containing residue have been identified, eg calcium oxalate (Martin, 1954).
Farmer and Mitchell (1963), in studying the effects of peroxidation, have shown that significant amounts of chelated oxalate ion may be formed by $\text{H}_2\text{O}_2$ treatment if the organic matter content is high. Most of it was present as soluble oxalato aluminates—minor formation of soluble ammonium and sulphate ion were also recorded. In the clays studied by Farmer and Mitchell, the complexes were shown by IR to be oxalato aluminates. No oxalato ferrates were identified. Not all the oxalate found was soluble, some was presumed to be complexed to $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ ions attached to clay surfaces. This oxalate plus calcium oxalate and incompletely oxidised organic matter was interpreted as contributing to the residual carbon content.

Calcium oxalate is insoluble and so is a potential contaminant of any treated Ca-rich clay, eg WOC. Farmer and Mitchell found prewashing clay with $\text{NH}_4$ reduced residual calcium oxalate but generally increased the chelated oxalate content.

The presence of chelated oxalate can be recognised by its distinctive IR absorption band at 7.75$\mu$m—it's strongest band at 5.9$\mu$m overlaps sorbed water at 6.1$\mu$m and a strong band at about 7$\mu$m is near where carbonate and ammonium ions also absorb. Hence its presence can interfere with some IR studies. Unchelated oxalate, when present, absorbs about 12.8–13.0$\mu$m. In DTA tests chelated oxalate gives thermal effects in the same region as amorphous and crystalline hydrated iron and aluminium oxides (Taylor, 1959).

Farmer and Mitchell noted an increase in solution of both Al and Fe in peroxised samples. While some of the Al and Fe in the soluble oxalato complexes may have come from the original organic matter, it seems likely that a portion will have come from the clay minerals. It is known that the pH during peroxidation can be quite acid.

Douglas and Fiessinger (1971) found that the pH change on $\text{H}_2\text{O}_2$ treatment in organic matter free clays was negligible. However, in the
clay mineral plus sucrose mixtures they made, the solution became very acid. $H_2O_2$ treatment of expanding lattice clay:sucrose mixtures was found to result in a significant decrease in the clay's XRD intensity - so indicating structural damage.

The effects of $H_2O_2$ treatment could well be considered to be similar to an oxalate extraction under ill-defined conditions. Their results seem to justify the view that $H_2O_2$ should not be used as a matter of routine and should be avoided where possible. Where its use is necessary, it would seem expedient to follow the suggestion of Farmer and Mitchell (1963) and to monitor pH and use a buffer to prevent strongly acid conditions. (Though in their case the use of 1N Na acetate did not stop damage, only reduced it.)

It seems that in clays with a high organic content, and hence a larger need to get rid of it, there is a larger danger of clay mineral breakdown due to the increased oxalate production and lower pH. Also the use of $H_2O_2$ to disaggregate a clay or before dispersion, is more likely to cause damage than after dispersion and fractionation as the amount of organic matter will probably be greater then.

One point that must be remembered is that $H_2O_2$ is a powerful oxidising agent (hence its use) and it is quite likely that it will oxidise any multivalent ion in a clay up to its higher state, eg $Fe^{2+} \rightarrow Fe^{3+}$. This could affect the layer silicates, causing a change not only in the CEC but also in their crystal structure, for example by changing the layer charge.

Farmer et al (1971) observed that the oxidation of Fe$^{2+}$ in vermiculitised biotite by $H_2O_2$ or bromine water was compensated for first by a reversible loss of protons and subsequently by an irreversible loss of octahedral iron and an increase in the number of vacant dioctahedral sites present. The loss of interlayer cations
appeared to play little or no part in any compensatory mechanism.

Electron microscopy and XRD revealed that the ejected iron formed amorphous interlayer oxides when H$_2$O$_2$ was used as the oxidant. However, orientated crystals of α-FeOOH developed on the surface of the flakes when bromine water was used.

The possibility of structural damage to clay minerals as a result of H$_2$O$_2$ treatment therefore ought to be taken as a serious possibility.

Note: Insoluble oxalates can be removed by saturating the clay with neutral ammonium acetate - this forms ammonium oxalate complexes which ought to be removed by washing with water.
Given that Al and Fe are now accepted as present in clays as a continuum of amorphous to crystalline oxides and oxyhydroxides which has a close association with the Fe and Al oxide/hydroxide groups bonded onto the peripheral portions of layer silicates and in their interlayer regions, it ought to be self evident from the material presented, that selective dissolution techniques cannot give a sharp differentiation.

The degree of crystallinity is not the only factor affecting solubility. No sharp difference in solubility exists between say, amorphous and crystalline iron oxide or between amorphous surface coatings and interlayer material or even essentially fixed octahedral Fe. The extracted material represents a portion of the continuum between readily extractable iron and aluminium and essentially fixed non-extractable material. Exactly which part of the continuum is extracted depends on the composition of the starting material and the severity of extraction - that is, the precise extraction conditions, eg time, temperature, pH etc.

One potentially interesting approach to the problem of quantitatively determining easily extractable constituents from those representing attack on crystalline or layer silicates has been used by Segalen (1968). The basis of such an approach is to extract material repeatedly using an appropriate extraction method and to plot the amount removed against the number of extractions and then to extrapolate back to zero extractions to obtain a correction for crystalline material attacked in the extraction series (amorphous component = x see figure 2.4.11.1).
The aim of this differential dissolution work was not primarily for quantitative analysis, but to produce material for use in firing trials, to help simplify the study of the reaction series giving rise to colour development. In this context it would now seem to be a less appropriate approach than initial investigation suggested.

All the treatments described are either known or are suspected of producing structural and chemical changes in layer silicates. For example it is apparent from the foregoing section that oxidising or reducing agents are likely to oxidise or reduce any suitable multivalent ion in the treated material, not just those one wishes to oxidise or reduce. This in turn can result in structural and chemical changes in the layer silicates. Since the thermal reactions of clays are known to be sensitive to relatively small changes in structure and chemical impurities, chemical pretreatment is probably not such an appropriate approach as at first thought.
3.1.1 X-Ray Diffractometry

X-ray diffraction traces were obtained with Ni filtered Cu radiation using a Philips Norelco diffractometer fitted with a crystal monochromator. The X-ray generator was run at 46kV and 37mA for all traces used.

Unorientated clay samples were prepared by carefully packing dried clay powder into an appropriate Al holder. Attempts to produce unorientated samples by utilising the 'chain' forming characteristics of fumed silica in liquids (Blount et al, 1979) were not very successful. The fumed silica tended to increase the background in the 2θ=15-20° region. It also proved difficult to produce a clay:silica:corn oil mixture with a suitable consistency to permit reliable flat 'smears' to be made.

Orientated samples were prepared by smearing a clay:water paste onto a glass slide, forming a uniformly thick layer and leaving to dry. Occasionally deposition from aqueous suspensions (ie gravity settling) onto glass slides was used, but only where sample fractionation was not important (see later).

The samples were run over the range 2θ=5-90°. For routine traces speeds of 1° per minute were used, while for accurate cell determination, speeds of 1/4° or 1/2° of 2θ were used (with silicon powder added to the sample as an internal standard). A silicon disc was used as a standard reference for calibration purposes.

Fired material was ground to <10μ diameter in a αAl₂O₃ ball mill and packed into an Al holder. Routine samples were run over the range 2θ=70-10° at 1° per minute. Preliminary trials suggested that the optimum chart settings for the fired material was a range of 3x10² with
a 10 second time constant. The range was dictated by the low signal, probably due to the low crystallinity of the new phases, while the high time constant was necessary to reduce the excess 'noise'. Such settings were used for all routine investigations.

Unit cell determinations were, however, run at 1/4° of 2θ per minute, with appropriately adjusted range and time constants. Silicon powder was used as an internal standard.

Attempts at quantitative XRD by the known addition method (see later) were abandoned when TEM revealed that the main phases of interest were changing in crystallinity, particle size and composition with firing temperature. An appropriate range of standards was not available, while the choice of one for use over the whole range seemed somewhat arbitrary and of limited accuracy. It was evident from the few traces done that an inappropriate standard gave results not consistent with TEM data. Quantitative analysis was in addition being hindered by the use of Cu radiation - Cu fluoresces Fe and ought not to be used for Fe minerals, eg hematite (and iron rich mullite). It was a multi-user machine so it was not possible to change to Co or Mo.

3.1.2 Quantitative XRD

Numerous attempts to extend the use of XRD from a qualitative to a quantitative technique for clay mineral analysis have been made. Detailed considerations of the general approach to quantitative XRD are to be found in the literature, eg Cullity (1978). Natural clay sediments however, present the investigator with a significant range of problems not normally encountered in simple systems, eg mixtures of oxides or silicates.
All of the techniques developed so far for clay minerals have, at best, been only semiquantitative. At present no recognised 'standard' technique exists. Given the nature of clay sediments it is unlikely one perfect standard technique will ever be developed. However, until a standard procedure is adopted, one has to try to develop a technique that takes all the possible sources of variability - error into account and suits one's own set of circumstances. To do this one has to be aware of likely causes of variability/error in quantitative XRD estimates. Some of the more important factors encountered so far are listed below:

1. Orientation
   a) degree of orientation
   b) reproductivity of mounting technique

2. Crystallite size

3. Crystallinity
   a) polytype
   b) mixed layered clay structure

4. Isomorphous substitution
   chemical composition

5. Interlayer cation
   a) hydration
   b) humidity

6. Equipment conditions

7. Methods used to calculate relative amounts
   a) 'internal' standard
   b) added 'standard'
   c) reflection chosen

Most methods of sample preparation are directed towards attaining either a completely random distribution of particles or towards complete preferred orientations. Deviations from either will cause errors in resultant percentages.

Stokke & Carson (1973) studied the effect of mounting techniques and found that techniques which employ gravitational settling of particles in suspension give neither true nor consistent results.

If a size difference exists between the mineral components, then
for thinner mountings the small size makes it difficult for that mineral to achieve a sufficient degree of orientation of preferred basal orientation at very low concentration, therefore it is underestimated. If too thick, then one obtains an excessively high value for the fine fraction due to its concentration in the surface layer.

Suction onto a porous ceramic tile or smearing a clay paste onto a glass slide are the most reproducible orientation techniques. Sedimentation onto a glass slide either in a dish or pipetting the suspension onto the slide and allowing it to dry should NOT be used, but both commonly are.

Mossman et al (1967) found that illites in an artificial mixture tended not to orientate themselves to the same degree as kaolinite at high illite concentrations, though the relative degree of orientation between samples was reproducible. This is a possible case of size affecting orientation.

The crystalite size effects observed in clays are similar to those observed in other materials. Very small size leads to peak broadening, perhaps even to the extent where it is lost, while too large a size (>~10\(\mu\)) results in a low reproducibility of XRD data (in diffractometer traces/equivalent to spotty ring on film). The size of a crystal can affect its intensity. Brindley and Udagawa (1960) noted quartz intensity increased with decreasing size up to ~10\(\mu\). It is thus best to use the <2\(\mu\) fraction of clay sediments for XRD investigation.

Crystallinity is more problematic, as in clays it is not an easy factor to quantify. Bates et al (1955) established a method for
evaluating the crystallinity of kaolinite, founded on the non basal reflections, classifying them as either poor (fireclay type), intermediate or well crystallised (china clay type). However, in many natural clays where kaolinite is a minor component, non basal reflections are often not easily discernible so it is not often easily achieved. Schultz (1959) adopted an index founded on the shape and broadness of basal reflections that is the ratio of area:height. Broad peaks with high ratio (>1.7) were poorly crystalline while sharp peaks with a low ratio (1.1-1.3) were taken as well crystallised.

The relative intensity of kaolinite varies from good to poor crystallinity. Schultz (1959) found that for artificial (50:50) mixtures, well crystallised kaolinite gave a 7Å peak with twice the area of the illite, while the area of the poorly crystalline kaolinite was on average slightly less than the 10Å reflection.

A crystallinity index (eg Schultz type) versus relative intensity correction should, if possible, be employed in quantitative XRD work. An allowance for changes in the difference of relative intensity ought to be made irrespective of whether or not the 'standard' is internal, eg illite, or added, eg CaF or Zn(OH)$_2$ (see later).

It ought to be remembered that illite, like many other minerals, exists as various polytypes (fig. 3.4.6.8), so this is also a potential factor. Mossman et al (1967) found that 2M muscovite had a sharper 10Å peak than 1Md illite but its integrated intensity was slightly smaller. Therefore muscovite ought not to be used as a 'pure illite' in the production of standards, as is occasionally done. The appropriate polytype mineral ought to be used.

In the case of mixed layered clays, eg illite and especially montmorillonite, and vermiculite type expanding lattice clays, the nature and degree of the mixed layering is an additional factor and is
difficult, if indeed possible, to account for.

Isomorphous substitution is also known to affect peak intensities. Brown (1955) has shown that such substitution has a significant effect on low angle (001) intensities, due to changes in atomic scattering factors of the different atoms. Methods based on relative (001) intensities have been suggested for determining octahedral compositions (fig. 3.4.6.9). Graff & Peterson (1961) noted that I /I of less than 3-4 indicates illite is of dioctahedral type rather than trioctahedral.

Interlayer cations can also have an appreciable effect in expanding lattice clays. The variability in position and broadness of the (001) reflection (c parameter) and changes in b parameter (Leonard and Weed, 1967) with changes in the interlayer cation are well known. Cations affect the degree of hydration. Ca, for example, has two associated water layers compared with K which has one. Sayegh (1965) has shown that one ought to control not just the interlayer cation but also the humidity at which the sample is run, as both affect the degree of hydration.

It must also be appreciated that changes in machine conditions can also affect peak shape and relative areas and that the changes can be non-uniform. Changes in time constant or scanning speed will affect relative peak sizes if the peaks being compared have notably different shapes. An increase in time constant would tend to reduce the apparent size of say, a 7Å peak, from well crystallised kaolinite in a kaolinite:illite mixture compared to that observed at a lower time constant. In contrast, the relatively broad peaks of a poorly crystalline kaolinite would probably not be affected as it would probably have a similar shape to that of the 10Å illite peak.

As already mentioned, no really accurate method exists to
calculate relative compositions from peak intensities. All methods try
to relate peak intensity to concentration but this is often a non
linear relationship, eg due to differences in absorption coefficient.
With a binary system a working curve of relative
intensities:concentration can be prepared by producing a standard
series composed of systematically varied artificial mixtures of the two
components. With more than two components it becomes increasingly
impractical to attempt to duplicate all the possible combinations. In
the case of clays where crystallinity, size, degree of mixed layering
etc have to be taken into account in most instances, suitable pure
standards simply do not exist. This lack of suitable standards hinders
all such approaches. (If they are not found such systems do not work.)

In relatively simple systems the normal 'solution' to account for
the variable absorption coefficient of the matrix in a mixture is to
add a fixed amount of an internal standard. Reflections of the
standard are absorbed by the matrix to the same extent - the intensity
ratio is therefore independent of matrix absorption. But again
calibration is done by comparison with an artificial standard:mineral
mixture series. An additional potential problem may be encountered.
Standards suitable in other systems because of their non platy
morphology become ineffective in clays unless a reproducible degree of
orientation is possible (not easy). One possible answer is to use a
platy standard that orients to the same degree as clay minerals thus
preserving the relative intensity. Mossman et al (1967) investigated
such an approach and suggested the use of Zn(OH)_2 (N.B. it decomposes
above 300°C) or pyrophyllite.

A similar variation is the known addition method where a known
weight (Wt) of a pure component is added to a sample containing this
component and measuring the reflected intensity before and after
addition, determining \( I_1 \) and \( I_2 \) respectively. One can then determine the approximate weight proportion of that component.

\[
W_p = \frac{W_t (I_1/I_2)}{1 + W_t - (I_1/I_2)}
\]

But the ratio of the mean absorption coefficients before and after addition must be about 1. If \( \bar{\mu}_2/\bar{\mu}_1 > 1 \), then \( W_p \) is too small, or conversely, too large if \( > 1 \). The absorption effect can be eliminated by using several values of \( W_t \) and extrapolating to \( W_t=0 \). The usefulness of this method depends considerably on the substances involved and on their proportions. If they have similar values of absorption coefficient, then further small additions of any one of them will have relatively little effect on the mean absorption coefficient for the sample. Quartz, kaolinite and illite are of this type (table 3.1.2.1) and changes in intensity must be accurately recorded. If a component is present in small quantities the reflections will be weak and the \( I_1/I_2 \) ratio will probably not be measured very accurately so the percentage accuracy of \( W_p \) will be low. The choice/availability of the standard for addition is still of major importance.

In the few cases where suitable standards do exist, working curves of peak area of mineral x to a standard either internal, eg illite or added, eg \( \text{Zn(OH)}_2 \) ought to be produced. Such curves have an advantage over a fixed ratio as they can for example cope with a non linearity of intensity in cases where one component stops orientating to the same extent as the others (eg Mossman et al, 1967).

The factor most likely to affect the result is the position chosen for the base line for intensity measurement or perhaps the method chosen for calculating the relative proportions (Pierce & Siegel,
1969).

Probably the best approach for expanding lattice clay mineral assemblage of the Warnham clay type is similar to that of Austin & Leninger (1976). They based their estimate on the expanding lattice component on the difference in intensity of the 10Å peak after treatment with ethylene glycol (when vermiculite and montmorillonite are 14.6Å & 17.0Å respectively) and that on subsequent heating. The change was assumed to be due to the collapse of the expanding layer clays. They found that the optimum temperature for treatment was 375 ± 20°C. Cooling in a dessicator allowed some rehydration, therefore the sample had to be run while still above 100°C. They assumed the intensity of the 10Å peak of both phases is equivalent, though it is probably best to test this (eg working curve).

<table>
<thead>
<tr>
<th>Material</th>
<th>cm/gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>35.0</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>34.4</td>
</tr>
<tr>
<td>Metakaolinite</td>
<td>33.5</td>
</tr>
<tr>
<td>Muscovite</td>
<td>42.8</td>
</tr>
<tr>
<td>Illite (Fithian)</td>
<td>53.6</td>
</tr>
<tr>
<td>Mullite</td>
<td>32.7</td>
</tr>
</tbody>
</table>

Table 3.1.2.1
Typical Mass Absorption Coefficients
(After Brindley & Udagawa, 1960)
Warnham clay proved to be less than amenable to quantitative XRD analysis. Qualitative XRD revealed low crystallinity kaolinite, halloysite and an illite:vermiculite mixed layer material as the main components. This particular combination of minerals presented significant problems.

Attempts to locate suitable pure mineral standards were unsuccessful, so analysis methods requiring them were not possible. The Austin and Leninger (1976) approach was not really feasible either. The 14Å vermiculite component did not expand on glycol treatment and was relatively stable on heating. The possibility of using chemical treatments to remove interlayer material, so permitting the material to expand, was considered. However, the different treatments have different extractive powers and leave the significance of the result very much an open question (see sections 2.4 & 3.5). (Alexiades & Jackson (1965) proposed a quantitative test for vermiculite based on a clay's cation exchange capacity after chemical treatment, which is dubious for exactly the same reason.) Estimations based directly on the 14Å peak are dubious due to the unknown relative intensity of this type of dioctahedral vermiculite component of a mixed layered clay.

The 10Å peak also provided a problem. This peak was dominantly due to the illitic component of the mixed layered clay, though one could possibly regard some as collapsed vermiculite. Perhaps more importantly, the appearance on prolonged drying of a 7.56Å peak interpreted as metahalloysite, suggests that some of the 10Å peak could be due to 10Å hydrated halloysite. On heating, the 10Å halloysite should change to about 7.5Å. Thus the change in the 10Å peak on heating is due to the combined effect of collapsing vermiculite and halloysite and so is not directly attributable to the vermiculite.
Some samples used in this investigation were orientated using gravity sedimentation techniques. These samples revealed that the illite present has a smaller mean particle size than the kaolin (ie different apparent I:K ratios). The particle size effects mentioned previously were therefore active in this case.

The relatively sharp 7.5Å peak taken to represent metahalloysite was generally absent in fresh samples, probably because the metahalloysite was ordinarily present as the 10Å variety and its presence was not revealed until its partial dehydration. The overlap of both peaks either in whole or in part with those of illite and kaolinite hindered analysis.

Electron microscopy indicated that the halloysite present is not the typical tubular variety. Use of the normal pure form of this mineral for a standard would therefore seem inappropriate.

The 7Å kaolinite peak, apart from the partial overlap of halloysite, is, in contrast to the others, relatively straightforward. It could be estimated using the approach of Schultz (1959), if the other components were amenable - it cannot really be estimated in isolation.

Quantitative estimates of the constituents of Warnham clays are unavoidably crude. In a simple system, if all the precautions are taken, an accuracy of ±10% is attainable for major components - minor ones will have greater errors. In the case of Warnham clay the percentage error must be considerably more that 10%, especially as out of the four main components, only one is at all amenable to anything like accurate measurement.
3.2.1 Transmission Electron Microscopy

Transmission electron microscopy (TEM) and electron diffraction have been used extensively during this research project. As TEM and electron diffraction are now commonly used techniques and are very adequately described in the literature, both in terms of theory and practice, it seems unnecessary to go into any great detail here.

Therefore only design features specific to the microscope used, a Philips EM 400T and not found on other microscopes, that have facilitated or have a bearing on this study will be mentioned.

3.2.1.1 TEM Optical Systems

The basic lens arrangement for 'conventional' TEM (CTEM) and selected area diffraction (SAD) are shown in figure 3.2.1.1, while figure 3.2.1.2 shows the arrangement in the EM 400T. A modification as yet unique to this instrument is the use of a 'twin' objective lens. The symmetrical objective lens is combined with an auxiliary lens which provides for conventional operation of the illumination in TEM mode.

This innovation has a significant advantage when the microscope is being used for microanalysis. Normally microanalysis with TEM is limited by a minimum spot size of 100-200nm. The twin objective lens makes possible a 'unique' nanoprobe mode providing beam spot diameters down to 4nm, with the image still on the phosphor screen. This obviates the need to switch to other imaging techniques, eg STEM, to obtain such spot sizes, with the associated inconvenience of having to reidentify the area of interest under different contrast conditions and magnification. (In practice it was found that the STEM image of these
samples was very poor and most, if not all of the fine detail seen in the accompanying photographs was not visible in STEM.) This modification allowed relatively fast operation during X-ray analysis which could be achieved simply by condensing the beam to a point located in the area of interest. This could be done in either CTEM (microprobe) or nanoprobe mode. The range of spot sizes achievable is shown in table 3.2.1.1. The choice of spot size used depended on the size of crystal to be analysed and was a balance between the need for a small spot size (ie volume to be analysed - see figure 3.2.3.2) and a reasonable count rate. Small spot sizes generally meant low count rates - hence poor statistics and an associated decrease in accuracy. This could be combatted only by increasing analysis time. Spot sizes of 40-10nm were most generally used. A 4nm diameter spot was rarely used as the image was too faint to be easily seen and it generally gave a very low count rate.

<table>
<thead>
<tr>
<th>Magnification Ranges</th>
<th>Spot Size</th>
<th>LM</th>
<th>M &amp; SA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>10μ</td>
<td>2μ</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5μ</td>
<td>1μ</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2μ</td>
<td>400nm</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1μ</td>
<td>200nm</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>500nm</td>
<td>100nm</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>200nm</td>
<td>40nm</td>
</tr>
</tbody>
</table>

Table 3.2.1.1

EM 400T Beam (spot) diameters
Fig. 3.2.1.1 Conventional TEM Optical System
Fig. 3.2.1.2 EM400T electron 'optical' system.

Fig. 3.2.1.3 EM400T X-ray detector geometry.
Selected area diffraction (SAD) was possible in CTEM mode with a minimum area on the sample of about 1 μ in diameter. 'Micromicrodiffraction' was possible in nanoprobe mode. In this mode the area was selected by means of the lenses positioning the beam – a diffraction aperture was not required.

<table>
<thead>
<tr>
<th>Condenser apertures</th>
<th>30</th>
<th>50 top hat</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffraction (Pt)</td>
<td>800</td>
<td>150</td>
<td>30</td>
</tr>
<tr>
<td>Selected area on specimen</td>
<td>5</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Objective apertures (Pt)</td>
<td>150</td>
<td>50</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 3.2.1.2
Aperture Sizes (microns)

3.2.1.2 X-ray Microanalysis

The geometry of the X-ray detector system is important in the consideration of microanalysis (section 3.2.1.3).

Since the X-ray signal is relatively small, it means that the detector should have as large a detection area as possible and be as close as possible to the specimen, but at the same time not restrict specimen movement. The detector has a collection angle of about 0.13 Sr.

As seen in figure 3.2.1.3, the 'take off angle' in the 400T is 20°. This allows analysis of untilted samples using the single tilt low background (Be) holder. This means that the backscattered
electrons emitted from the specimen surface are unlikely to return and strike the specimen or holder giving rise to spurious peaks. The only spurious peaks were Cu peaks ($K_a$ & $K_b$) eg. fig. 4.4.7.3, probably due to backscattered electrons exciting atoms in the brass objective pole piece. (It is just possible that they originated from the Cu slot grid used to support the sample, though this is unlikely.)

\[ A_a = \text{Atomic weight of element A} \]
\[ B = \text{Backscatter coefficient} \]
\[ C_a = \text{Concentration of element A} \]
\[ E_0 = \text{Electron beam energy} \]
\[ E = \text{Energy of X-ray} \]
\[ I_c = \text{Measured characteristic X-ray intensity from element A} \]
\[ K_{AB} = \text{Ratio method correction factor} \]
\[ N = \text{Avogadro's number} \]
\[ Q = \text{Ionisation cross section} \]
\[ t = \text{Specimen thickness} \]
\[ Z = \text{Atomic number} \]
\[ \mu_A^t = \text{Mass absorption coefficient} \]
\[ \rho = \text{Density} \]
\[ \omega = \text{Fluorescence yield} \]

Table 3.2.1.3 Notation for RTS Derivation

3.2.1.3 Quantitative Microanalysis: Ratio Thin Section Approach (RTS)

'Characteristic' X-rays arising from each element result from internal electron transitions within the atom after an inner shell electron has been ejected by a primary electron. Each primary electron loses an increment of energy at each collision and so its efficiency at exciting further inner shell electrons changes - hence it changes with depth/thickness.
In the thin films observed in TEM, the transmitted electrons lose only slight amounts of energy; the characteristic intensity generated per incident electron can therefore be expressed as (Goodhew & Chescoe, 1980):

\[ I_{oA} = \rho BN C_A/A_B \omega_K Q_t \]  

(1)

By assuming that the probability of an electron ejecting a particular inner shell electron (ionization cross section = Q) is constant throughout the specimen thickness ( - the thin film criterion), Green and Cosslett (1961) derived the following formula for ionisation cross section Q:

\[ Q = 7.92 \times 10^{-18} \ln \left( \frac{E}{E_0} \right) m^2 \]  

(2)

Hence the characteristic intensity for element A per incident electron is:

\[ I_A = C_A \frac{\rho BN}{A_A} \omega_K \frac{7.92 \times 10^{-18}}{E/E_0} \ln \left( \frac{E}{E_0} \right) t \]  

(3)

Cliff and Lorimer (1972) pointed out that it is possible to eliminate many of the unknown parameters and even to a first approximation specimen thickness if one compares intensities of different elements from the same spectrum.

In practice it has been found that at the Bragg positions, the X-ray intensity can be significantly enhanced compared with orientations not diffracting strongly, hence equation (3) ought to have an orientation dependent term (Cherns et al, 1973). (The effect is at
a maximum when the beam is parallel.) The effect is removed however, by ratioing.

In this as in many other studies, only the $K_\alpha$ peaks have been used for analysis and so equation (3) ought to be modified by $K_\alpha/(K_\alpha + K_B)$. However, if one uses only the ratio of intensities of two $K$ peaks, eg $A$ & $B$, then this factor will cancel out, along with others, eg path length, leaving

$$\frac{I_A}{I_B} = \frac{C_A}{C_B} \left[ \frac{A_B}{A_A} \frac{\rho_A}{\rho_B} \omega_{KA} \frac{E_B}{E_A} \ln \left( \frac{E_0/E_A}{E_0/E_B} \right) \right]$$

(4)

So for a given beam current, if the thin film criterion is obeyed, ie infinitely thin so the matrix effects of absorption and fluorescence effects can be ignored and the intensity of the beam leaving the foil is identical to the incoming beam, all the terms in the square brackets should be constant and so could be rewritten as

$$\frac{I_A}{I_B} = K_{AB} \frac{C_A}{C_B}$$

(5)

The $K_{AB}$ values can be determined empirically by measurement on thin film standards of known composition. If however, all the ratios are taken with respect to a single element, then the $K_{AB}$ values can be regarded as elemental sensitivity factors. Silicon is often used as the standard and was adopted in this study as it occurred in all samples.

The factor for element $x$ then becomes $K_{xs}$ and the equation can be rewritten as
If the intensities of several elements are measured, their relative intensities are given by

\[ \frac{C_A}{C_B} : \frac{C_C}{C_D} = \frac{K_{AS_A}}{K_{BS_B}} : \frac{I_A}{I_B} : \frac{K_{CS_C}}{K_{DS_D}} : \frac{I_C}{I_D} \]  

(7)

If all elements are measured and then normalised to 100\%, then atomic percent concentrations can be calculated.

If a standard foil is used to determine \( K_{XSi} \), the observed intensity from the foil may well be attenuated by internal absorption. Hence an absorption correction is necessary to correct the apparent \( K_{XSi} \) value to the value it would be if no absorption occurred.

\[ K_{XSi} = \frac{C_x \ Area \ Si}{C_{Si} \ Area \ X} \frac{1}{(Abs.corrn)_x} \]  

(8)

The absorption correction entails assuming complete knowledge of the composition and thickness of the sample and is considered in detail by Goldstein et al, 1977. Assuming \( Q \) is constant throughout the sample, then it is defined as

\[ \left( \frac{K_{\rho}}{\rho} \right)_X \left( 1 - \exp \left[ - \left( \frac{K_{\rho}}{\rho} \right)_{Si} pt \ \cosec (\psi) \right] \right) \left( \frac{K_{\rho}}{\rho} \right)_{Si} \left( 1 - \exp \left[ - \left( \frac{K_{\rho}}{\rho} \right)_X pt \ \cosec (\psi) \right] \right) \]  

(9)

where \( \left( \frac{K_{\rho}}{\rho} \right) \) is the mean mass absorption coefficient for radiation from element \( x \) and \( \psi \) is the 'take off angle'. Absorption in the specimen varies with take off angle even though the characteristic X-rays are emitted virtually isotropically.

It has been known for some time that carbon contamination deposited during analysis, and the carbon conducting layer can strongly absorb characteristic X-rays of low atomic number elements (McKinley et
al, 1966). It can be corrected for by adding a second exponential to equation 9, i.e. $e^{-F}$, where

$$F = \left\{ \frac{(\mu/\rho)_{Bk}}{\rho_{Carbon}} - \frac{(\mu/\rho)_{Ak}}{\rho_{Carbon}} \right\} \rho X \eqno(10)$$

where $X$=path length through carbon.

Bender et al (1980) however, found that in ceramic materials, oxygen (not detected by EDS) significantly affected the total mass absorption coefficient of Mg and Al in oxide systems. They found they could correct for it by using the following correction:

$$\frac{\mu}{\rho}_{spec} X = \frac{\mu}{\rho} X_k C_x + \frac{\mu}{\rho} Y_k C_y + \frac{\mu}{\rho} O_k C_o \eqno(11)$$

where $C_x$ is the weight fraction of element $x$ and oxygen etc.

In order to correct data from a sample of unknown composition, a computer aided iterative approach is often adopted since specimen values are a function of the composition. The values are changed until the corrected concentrations converge.

In order to perform the absorption correction a knowledge of sample thickness is necessary. This is often estimated from parallax between contamination spots or convergent beam diffraction. Also, if the composition is unknown, it is likely that density is also unknown.

It is often very difficult to estimate thickness and density but it is possible for the effective mass path length to be determined directly from the data using one of two methods.

1). Measuring the intensity of two characteristic lines from one element and from the knowledge of the appropriate $K_{\alpha}$ factors adopting a value of path length that would give concentration ratio $C_A$(line 1) $\div C_A$(line 2) of unity.

This method requires at least one element in reasonable
concentration to have detectable K & L lines (in practice Z>27), the absorption coefficients of which are sufficiently different to enable accurate path lengths to be determined. This precludes the use of \( K_\alpha \) and \( K_\beta \) lines, therefore no lower Z. This technique has the advantage that geometry of the sample is not important and irregularly shaped particles may be analysed.

2). A second approach involves obtaining a series of spectra from precisely the same area at different known tilts, so producing a series of data with known relative path lengths. A best fit approach can then be adopted.

This approach does not have the atomic number limitations but requires a sample of known geometry and also several analyses with accurate repositioning of the beam. Absorption due to contamination is also a potential problem.

Provision does exist for calculating a theoretical \( K_{XSi} \) value using the equation

\[
K_{XSi} = \frac{A_x}{A_{Si}} \frac{\omega_{Si}}{\omega_x} \frac{Q_{Si}}{Q_x}
\]  

However, errors exist in estimates of \( Q \) and \( W \) and experimental values show a large scatter for low Z elements. Calculated values for \( Z < 22 \) elements are not necessarily very accurate. The efficiency term apparently dominates the \( K_{XSi} \) value at low energies and may also play a part (J.P., 1980).
Diffraction based techniques for measuring specimen thickness can unfortunately be applied only to single crystal specimens - which we do not have in this study. Estimates based in the parallax of contamination spots also were not viable due to the general absence of contamination. The EM 400T system was essentially contaminant free. In any case, such a technique has a tendency to overestimate thickness. Methods based on X-ray intensities rely, amongst other factors, on calibration to one of the two previous methods.

Parallax using some feature visible on both surfaces (eg grain boundary) could, in theory, be made, though cases where the same feature was visible on both surfaces were not common. It still relied on the assumption that the thickness at the point of interest was the same as at the point measured - rather dubious. Hence in most instances a measurement of specimen thickness was not possible, certainly not as a routine.

In addition, accurate estimates of effective mass path length were not viable using either of the two direct measurement methods described. In the first instance because no element with Z>27 was generally present; in the second because sample geometry was uncertain. The electron transparent areas were often on 'protuberances' which usually projected above or below the mean sample plane. So while that was known, the precise attitude of the area of interest generally was not. Changing the tilt angle also altered the diffraction conditions with many particles becoming effectively invisible at some tilts, so hindering accurate relocation.
The approach adopted therefore was to rely on statistics. A large number of analyses were made of a standard(s), in this case a mica sample, at various points and hence a range of thicknesses similar to the sample range. A mean analysis was calculated which was used to calculate a 'mean' correction value.

This mean value could then be applied to individual sample analyses which were then plotted as in figure 4.4.5.1. The analyses quoted in the text are the mean of these individual analyses.

Thus it is hoped that any slight inaccuracy in the data is allowed for. The scatter in the data points in figures 4.4.5-9.1 etc represents the true chemical variability of the materials combined with slight inaccuracies due to a non perfect correction value for that analysis.

Correction values were checked against a second 'standard' which consisted of a sample of 'Jordan' kaolinite deposited on a formvar film on a 100 mesh Cu grid. The carbon coat, thickness and analysis conditions were the same as for the other samples.

The mica standard consisted of an electron transparent sliver of muscovite produced by repeated cleaving of the mica sheet. (Both this muscovite and the Jordan kaolin were used as reference materials elsewhere in this study: eg table 4.2.6, figure 3.4.6.2). The mica was mounted on the same type of slot grid used for the fired clay samples. The analysis conditions were the same as for the samples.

All the microanalyses were made, unless otherwise stated, using the Philips EM 400T at 100kV equipped with a Link Systems 860 EDS system. The latter was not equipped with a quantitative analysis program and provided only net and gross integrated counts for each element. All additional calculations were done 'manually'. Analysis time was 100 seconds or occasionally multiples thereof. The objective
aperture was always removed for analysis and the condenser aperture used was either 150 or 50μ 'top hat' type as appropriate.

One final consideration to be mentioned is spatial resolution - that is, where precisely in the specimen the X-rays come from. It is clear that scattering of the electrons within the specimen will give rise to some sort of beam spreading (see fig. 3.2.3.1). As yet no agreement has been reached on defining the term either in terms of the emergent beam diameter $d_2$ or mid plane $d_1$ or even the size of the statistical envelope (i.e., % of electrons) to be used.

Spreading, be it defined as $(d_2-d_0)$ or $(d_1-d_0)$ is, however, known to decrease as (a) $E$ is decreased (b) $Z$ is decreased and (c) $t$ is decreased.

Fig. 3.2.3.1 Schematic definitions of the beam diameter at the specimen entry surface ($d_0$), at the midplane ($d_1$) and at the exit surface ($d_2$). In practice the envelope of electron trajectories would not necessarily be perfectly conical.

Specimen geometry is also relevant and figure 3.2.3.2 shows some fairly typical configurations. In figure 3.2.3.2 a and b, the particles are smaller than specimen thickness and larger than incident beam diameter. If the particle contains only the same elements as the matrix, one can learn nothing further about it. If it is say, pure B (figure 3.2.3.2b) then a change in the A:B ratio may indicate, but
cannot prove it is a pure phase. If the particle contains an additional element C, which is not in the matrix, we could probably calculate the B:C ratio. If a particle does not extend through the specimen we could not be certain whether or not it contained matrix element A - without extraction. Figure 3.2.3.2f shows a particle whose dimensions apparently exceed beam diameter but yet may still scatter electrons into the matrix and so excite A and B X-rays, whatever its composition. As all these scenarios are not uncommonly encountered in these clay ceramics samples, (especially the last one), and in reality are not always recognised/diagnosed with certainty, no one analysis was credited with undue significance.

![Diagram of configurations](image)

Fig. 3.2.3.2 Six of the many possible configurations which it is desirable to be able to analyse. Most quantitative procedures assume the homogeneous distribution of elements throughout analysed volume, as implied in (d). (After Goodhew & Chescoe, 1980)
3.2.4 TEM Sample Preparation

Two basic sample preparation techniques were used:

Type 1. In such cases as the unfired hydrocycloned Warnham Silty Clay (WSC-H, see sections 3.4.1-2) and Jordan kaolinite and the WSC-H fired to 800°C, the samples consisted of approximately clay grade (<5μ) particles.

A small quantity was added to analar grade ethanol and shaken to obtain a very fine suspension. A small quantity of this suspension was pipetted onto a Cu mesh grid covered with a formvar film and allowed to dry. This produced a dispersion of fine particles on the film, many of which were electron transparent. The samples were carbon coated in the conventional manner for non-conducting samples.

Type 2 The second technique was developed to cope with WSC-H samples fired to above about 950°C, as in these samples vitrification has occurred and the fused material cannot be easily dispersed.

These samples were fabricated and fired as described in section 3.6.1, the fired sample being in the form of a hard compact cylinder. These had to be sectioned, mechanically lapped and finally ion beam thinned to produce suitable EM samples.

3.2.4.1 Mechanical Stages

The samples were first sectioned into ~2.0mm thick discs using a slow speed diamond saw lubricated with parafin. The discs were washed in acetone to remove any oil, grease or other contaminant picked up in the cutting process.

Conventional cutting oil was avoided as a lubricant during this
and subsequent stages because in addition to handling difficulties (i.e., it is very dirty), it was found that the MoS additive it contained was adsorbed by the sample and was detected during EDS analysis (e.g., 4.4.15.2).

There then followed a series of grinding or lapping stages done using a Logitech PM2A lapping machine fitted with a cast iron lapping plate and using 1200 grade (mean 3μm diameter) SiC powder as a water-based slurry. Synthetic water-soluble cutting fluid was added to inhibit corrosion of the cast iron plate etc.

Both the first and second stages of the lapping process required the production of optically flat glass microscope slides. These were produced by grinding the slides flat in the conventional manner having first ensured that the surfaces of the sample holding jig and the lapping plate were coplanar during operation (by mutual grinding).

Both glass slide and sample disc were first washed with acetone and/or ethyl acetate and allowed to dry. The sample was then stuck to the slide using either commercial Durafix glue (cellulose acetate) or more usually with an adhesive made by dissolving polymethylmethacrilate in ethyl acetate. Care was taken to ensure no air bubbles were trapped between the sample and the slide. This could usually be achieved by moving the sample in a circular motion while pressing down on it. This done, the sample/slide was put into a mounting jig - this was used to ensure as far as possible an evenly thick glue layer was obtained and that the lower sample surface was as far as possible parallel to the slide surface. The glue was allowed to harden for at least 24 hours.

The choice of glue is important for such fragile material and had to be found by experimentation. The adhesive must be strong enough to
withstand the mechanical demands imposed during lapping yet still be capable of allowing the sample to be detached at a later stage.

Both the above glues had just enough mechanical strength to prevent the sample lifting off during lapping and being destroyed, and yet both were soluble in organic solvents. The matt surface of the lapped glass slide aided the bond and it was necessary to ensure both glass and ceramic surfaces were clean. Other adhesives were tried. Epoxy resins had the mechanical strength but were not easily removed. Cyanoacrilates proved to be of too low a viscosity for the porous samples, while thermomelting plastics, eg Lakeside 70, though quite adequate for the initial stages when the sample was thick, were found to be a little too viscous for the very thin samples. These tended to break up during the final removal of the sample from the slide. Lakeside 70 also left a residue on the sample, and contrary to some reports, it was found to be only partially 'soluble' in acetone and/or chloroform and decomposed rather than dissolved. Water soluble adhesives would dissolve in the grinding slurry.

Once a sample disc had been successfully stuck to a glass slide, it was carefully mechanically lapped until a flat, scratch-free surface parallel to the glass side was obtained.

It was then removed from the slide by dissolving the glue layer. The sample, after thorough washing, was inverted (ie lapped surface down) and stuck to a new ground glass slide, again making sure the glue layer was of even thickness and air bubble free.

After allowing 24 hours plus for the adhesive to harden, the sample was carefully lapped down as thin as possible. The amount removed was continuously monitored using a micrometer dial guage attached to the sample holding jig and by periodic manual inspection of
the specimen, the latter becoming more frequent as the sample became thinner.

With geological type materials thin sections of 30μ are routinely made by a very similar process and with care 7-10μ thickness can be achieved. The thinner the sample can be lapped, the less ion thinning that is required and the quicker it can be done. In this instance, however, it was found that the samples were quite porous and lacked the mechanical strength to remain intact at these sorts of thicknesses. In general lapping ceased when the sample was about 50-70μ thick - the precise thickness was determined individually for each sample and was judged by 'experience'.

The argon fired samples were much more porous than the others and lapping had to stop when they were 100-150μ thick. Some samples were so porous that it was not possible to produce specimens by this technique. Vacuum impregnation with an appropriate resin was necessary - but trials were only partly successful. These samples were beyond the temperature range of main interest and so were 'abandoned'.

Once the minimum practicable thickness was achieved, the sample was removed from the slide by dissolving the glue. The sample was handled using a fine paint brush, since tweezers broke it. The brush was used wet (ethanol) and surface tension was used to hold the sample.

3.2.4.2 Ion Thinning - Argon Ion Bombardment

A fragment of 3.0-3.5mm diameter was cut out of the sample wafer using a sharp scalpel or a razor blade. This fragment was then mounted in the sample holder of an ion Tech ion beam thinner. The sample was stuck in position on the lower Ta sheet over the hole by means of a
Polyisobutylene:xylene adhesive.

The samples were ion beam thinned at 3.5-7.5kV and 250-550mA for 10-30 hours depending on their thickness.

The sample thinned in the centre; usually a hole was produced, the thinned areas being supported by their thicker unthinned margins. The thinned sample was very carefully cut into 3 segments and each was mounted by gluing (polyisobutylene:xylene) the thick end of each wedge to a Cu slot grid. The sample was then carbon coated in the conventional manner for non-conducting specimens. The carbon coat thickness was monitored to an accuracy of about 25Å by means of the interference colours produced on a polished brass surface, table 3.2.4.1 (Kerrick et al, 1973). The interference colours are generally greatly enhanced by placing a small silicon oil droplet on the brass surface before evaporation. The film thickness was generally kept in the range of 200Å ± 50Å.

<table>
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<th>Approximate Thickness (Å)</th>
<th>Interference Colour</th>
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<tr>
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<tr>
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<tr>
<td>450</td>
<td>silver gold</td>
</tr>
</tbody>
</table>

Table 3.2.4.1
Carbon Coat Thickness
3.3 Infrared Spectroscopy

3.3.1 Preparation Techniques

All IR spectra were recorded using a Perkin Elmar model 937 spectrophotometer. Prior to preparation the materials were dried at 60°C and then stored in a vacuum dessicator. KBr discs were used throughout with a 1mg sample to 200mg KBr ratio. The samples plus KBr were carefully weighed out then transferred to an agate mortar and carefully dry ground to ensure thorough mixing. The mixtures were pressed into 13mm diameter discs in a vacuum die at a pressure of ~10,000kg. The spectrum was then run immediately.

The spectra were standardised by employing 10 minute runs with slit size 3 and the gain adjusted to about 8%. The base line was standardised by adjusting to 98% transmission at 2500cm⁻¹.

Differential IR traces were obtained by placing one sample in the analyser beam and the second in the reference beam.

3.3.2 Clay:Organic Complexes - Bipyridyl

Chester and Enderfield (1970) found that some expanding lattice clays formed complexes with 2-2 bipyridyl which had sufficiently distinctive spectral features in the 1650-1400cm⁻¹ region for them to be potentially useful in qualitative analysis. For reasons described on 3.4.6, a viability study and tests in Warnham clays were performed.

The technique was modified slightly with respect to that used by Chester and Enderfield (1970). Three series of tests were made, one, using pure clay minerals, another artificial 10% mixtures of various
clays in a kaolinite base and the third on Warnham clays. 10ml of 10% bipyridyl solution in chloroform was added to 0.25g of clay sample in a glass test tube. The tube was sealed, shaken and left to stand at room temperature for 48 hours - with intermittent shaking. The suspension was then centrifuged, the solution decanted and the residue washed three times with 10ml of chloroform. The suspension was separated each time by centrifuging. The residue was then dried (and stored) in a vacuum desiccator.

Control experiments were performed using CH₃Cl alone to see if clay:chloroform complexes were formed - these tests were negative. Bipyridyl is known to complex Fe²⁺ so absorption bands due to Fe²⁺ complexes are a possibility (though Chester & Enderfield (1970) found no absorption with chamosite, a Fe chlorite). Tests on FeCl₂ saturated kaolinite showed a negative result.
3.4.1 Materials

Bulk samples of Weald Clay were obtained from the Redland Brick Company's pit at Warnham, West Sussex. The two samples chosen for the study represented the two main lithologies at that site: (a) silty clay (b) ostracod clay.

Approximately 30 kg of each material was collected, the ostracod clay from a bed 0-20 cm above the top of the Cyrena limestone (a local marker horizon) and the silty clay from a bed 80-100 cm above the limestone.

3.4.2 Mineralogical Analysis

A mineralogical analysis of a similar sample was carried out by Hall (1978). The analysis was repeated in case there were any differences between the samples. A number were indeed found.

The bulk chemical analyses are given in tables 3.4.2.1 - 3. The two clays are essentially similar, the main difference being the CaO and SiO₂ content. The ostracod clay is much richer in calcium carbonate (calcite), while the silty clay contains more SiO₂ (quartz). Sulphur also seems to be more abundant in the ostracod clay.

The bulk clay samples were first air dried. They were then disaggregated in distilled water. The larger fragments broke down quite quickly of their own accord, under the slaking action of water (ie disrupted by high sheer forces between grains, produced by the capillary action of water in the small pores between the clay). Further disaggregation was achieved by stirring with a magnetic
The dispersed clay suspension was then separated into fractions coarser and finer than 300 mesh (53 μm) by wet sieving in distilled water. The sand fractions were dried at 60°C. Both clays proved to be very fine grained, with only about 1.4% of sand fraction in WOC and 1.6% 'sand' in WSC. A significant proportion of the sand fraction in each case was aggregated particles of quartz cemented clay/silt, and in the case of WOC, ostracods and shell fragments. The sand fraction of each clay was subjected to optical, SEM and electron microprobe analysis, as described later.

The silty clay fraction <300 mesh was concentrated by evaporation at 60°C. After stirring, a representative sample was dried at 60°C, the rest was stored and used as a thick paste. Some of this was subsequently further fractionated by means of a laboratory hydrocyclone at the Geology Department of Kings College, London. The operating conditions were adjusted to achieve a separation of particles with equivalent spherical diameters of above and below about 5 μm, the sharpness of the separation being improved by recycling the underflow (coarse fraction). Again this material was split, with some being dried at 60°C, with the remainder stored and used as a slurry. The dried clays, both hydrocycloned and non-hydrocycloned, were very, very carefully dry-ground in a mortar, to turn the material into a fine powder for use in the firing trials. Grinding was kept to an absolute minimum to avoid, as far as possible, any induced damage to the crystal lattice of the clay minerals.
3.4.3 Soluble Constituents

The water soluble constituents of the clays are given in table 4.2.5. The Ca\(^{2+}\) and SO\(_4^{2-}\) found in the aqueous extract of the ostracod clay suggests the presence of the mineral gypsum in the clay. There is however, slightly less soluble Ca\(^{2+}\) than required by the amount of soluble SO\(_4^{2-}\) for gypsum to be the only source of sulphate ions. Another source, such as another sulphate or simply sulphate ions existing in interstitial water must also be present. Should it, however, represent all the gypsum being dissolved, then ostracod clay contains 0.81% and silty clay 0.07% gypsum.

3.4.4 Sand Fraction

The constituents of the sand fraction were identified principally by optical and scanning electron microscopy and electron probe microanalysis. The mineralogical constituents of the sand fraction, in order of relative abundance are as follows (% are approximate):

Ostracod Clay: - (50%) Calcite - fossil shell fragments and ostracods

(15-25%) Quartz rich aggregates of clay material
(15-21%) Quartz crystals of fine sand grade
(4%) Clay particles cemented by calcite
(4%) Pyrite-usually as framboids, though also replacing calcite shells, eg ostracods
(3%) Phosphates - Apatite fossil fish remains
(1%) White granular aggregates of silt grade quartz
(<1%) Black organic particles
(<1%) Rare earth phosphates
Silty Clay:  
(60%) Green-grey aggregates of clay material with quartz cement  
(30%) Clay aggregates with quartz cement containing small siderite concretions  
(4%) Siderite nodules 3mm→50μ  
(3%) White granular aggregates of silt size quartz  
(2%) Pyrite mainly in cylindrical form or as irregular aggregates  
Rounded quartz grains of sand grade 3mm→100μ some showing an orange-brown iron-rich surface coating

Bromoform density separations were carried out on samples of the sand fractions. This succeeded in separating out the sulphide nodules which X-ray diffraction indicated were pyrite. SEM examination indicated the pyrite was of biological origin (iron reducing bacteria). The pyrite nodules in the two clays were slightly different with the typical form from WOC being spherical frambooids (photographs 11-12 and 15-16), while that from the silty clays was often a cylindrical shape (Phs. 13-14). (Pseudomorphed after a worm burrow.) In WOC the pyrite was also commonly found replacing calcite with some fossils, eg. ostracods being partially, and occasionally completely preserved in pyrite (Phs. 9-10, fig.3.4.4.2).

XRD indicated the sulphide present to be pyrite but the electron probe analyses suggested a significant variability in the stoichiometry of the sulphide nodules even within adjacent subgrains of the same particle, eg Phs. 15-16 and figure 3.4.4.3. Pyrite should have a more or less precise stoichiometry. (Fe_{1-x}S) - variable stoichiometry is usually indicative of pyrrhotite, another polymorph of iron sulphide. This variability suggests that the estimation of the sulphide content of the clays, based on sulphur content of the bulk clay, would be
difficult because one usually assumes a standard composition.

The 'heavy mineral' fraction of WOC also contained significant quantities of fossil fish fragments, eg scales and bone fragments. Electron microprobe and infrared analysis showed that they were composed of apatite-calcium phosphate (Phs. 17-18, fig.3.4.4.4).

Both clays were also found to contain a few large grains of a rare earth phosphate. Electron microprobe analysis identified the following elements: Cerium, lanthanum, neodymium and europium (Ph. 20, fig. 3.4.4.6).

Rounded grains of clear quartz with an orange-brown iron-rich surface coating were also found in the WSC sand fraction, see Ph. 19 and figure 3.4.4.5.

Also identified in the sand fraction of WSC was siderite (FeCO$_3$). This occurred as single nodules seen in undisaggregated clay particles (Phs. 23-24). The material was identified as siderite by electron microprobe and infrared analysis (fig. 3.4.4.9). The former showed that some of the nodules contained Ca, as well as traces of manganese (figs. 3.4.4.7 -8). These indicate moderate concentrations of a potentially important phase not reported by Hall (1978).

3.4.5 Clay and Silt Fraction

Identification of the minerals in the clay and silt fraction (<53μ) was performed principally by XRD using standard procedures for clay mineral analysis (section 3.1.1).

The ostracod clay material was found to be composed of clay minerals, calcite and quartz, while the silty clay fraction contained
only clay minerals and quartz. The proportion of quartz was greater in the silty clay, as would be expected (fig. 3.4.6.10).

The clay minerals present in the two phases were the same; a mixture of kaolinite (7Å), illite (10Å), a 14Å mineral identified by Hall (1978) as Fe vermiculite and a previously unreported material with a 7.56Å d spacing. The last two minerals could not be identified positively by comparison with the standard XRD data. Both were only detected in orientated samples.

The high background at low angles on the diffractometer traces could be due, in part, to poor orientation (SEM shows it is not perfect, Phs. 2-5), or to the presence of mixed-layered material or probably both. The low angle tail on the illite 10Å peak shows that it contains a mixed-layered component.

3.4.6 Clay Minerals

Detailed identification of the clay phases was undertaken, using hydrocycloned clay - ie clay fraction material (<5μ) only. The material was examined using a combination of XRD, SEM, TEM, microchemical analysis and infrared analysis.

3.4.6.1

Orientated and unorientated clay samples were run on the diffractometer as before, and very similar results were obtained (See figs. 3.4.6.10-11).
The 7.56Å material was again found in nearly all the orientated samples, while weak reflections at about 7.56Å were occasionally seen in unorientated samples.

The 7.56Å phase could easily be mistaken for gypsum in an XRD trace. The XRD signature for this phase is very like that of gypsum. While some gypsum is thought to be present (see 3.4.3), a quantitative discrepancy does appear to exist. The chemical analysis (table 3.4.2.2) shows that the calcium content of the silty clay is only 0.86% which, even attributing all the calcium to gypsum, would appear too low to be consistent with such a strong XRD reflection. Also the IR spectra, eg figure 3.4.6.2, show no sign of any spectral features attributable to gypsum. The same is true for the ostracod clay. Furthermore, no calcium sulphate was detected during electron microprobe or TEM microanalysis of Warnham clays (section 4.4.1).

As previously mentioned, gypsum is relatively soluble and one could reasonably expect a significant proportion of the gypsum present to dissolve during disaggregation and hydrocycloning. The water-soluble fraction of Warnham clays is given in table 4.2.5 and reveals that a small quantity of gypsum is in fact probably present.

(Likewise the chemical treatments used (section 4.2) should reduce the gypsum, if not totally remove it. Most, if anything increase the 7.56Å phase - especially the dithionite-treated ostracod clay. One could argue that this effect is due to increased oxidation of the pyrite present (DCB and HNO₃Treatments are oxidising) but this is likely to be of relatively minor significance as DCB at least, does not significantly reduce the pyrite content - so while the 7.56Å phase increases, the pyrite content (eg 2-4) seems unaffected.)
So though the XRD signature suggests the possible presence of significant quantities of gypsum, the IR spectra and bulk chemical analyses etc do not support this attribution.

After a thorough literature search, it was found that a dehydrated halloysite with similar, though not identical, d spacings had been reported (Grim, 1968, pg.138). Both WSC and WOC apparently normally contain some halloysite, probably with its normal d spacing - about 10Å. The presence of this phase is therefore masked by the 10Å illite peak - it is only on prolonged drying that dehydration occurs and the phase manifests itself as a 7.56Å metahalloysite reflection.

Halloysite normally occurs as tubular particles. SEM examination revealed no such material in either clay. Similar extensive TEM examination revealed only one or two crystals showing a tubular habit. It is probable therefore that the halloysite occurs either as discrete flakes or laths (like the kaolin) or possibly as an 'interlayer component' in some of the kaolin present - with the former being more likely.

The 14Å material had been identified by Hall (1978) as an unusually iron-rich ( trioctahedral) vermiculite. The iron-rich suggestion is probably due to the fact that the presence of siderite was not recognised. Vermiculite is an expanding layer silicate and can incorporate organic molecules and aqueous cations into its interlayer space, giving a characteristic change in d spacings of the (001) reflections.

Orientated samples of WSC and WOC were treated in the standard manner with both ethylene glycol and glycerol vapour at 60°C, prior to XRD. Neither produced a significant change in the d spacing of the 14Å phase.
Aqueous suspensions of WSC and WOC were treated with solutions containing Li, K, Na and Mg cations. Again the d spacing proved to be stable.

Both series of tests showed it to be stable - neither significantly expanding nor collapsing. This indicated that it could perhaps be some other 14Å mineral such as chlorite which is a non-expanding silicate.

A thorough literature search revealed XRD data of an iron-rich chlorite (chamosite) with d spacings near those observed (Shirozu, 1958). However, in the presence of kaolin and illite, it is not possible on XRD data alone to distinguish between a 14Å 'soil' vermiculite and an iron-rich chlorite because the peaks overlap. XRD data could not identify this phase with certainty.

Chlorite is normally thought to be soluble in HCl. WSC and WOC treated with 1M and 5M HCl still contained this 14Å phase - if anything in increased amount. (Mg chlorite was known to be soluble in HCl but there was no data for Fe chlorite so it was not certain if this was soluble or not.)

3.4.6.2 Infrared Investigation

While infrared analysis is not normally used in clay mineral identification, it was thought that it might prove useful in this instance. The infrared spectral features of many layer silicates are known. There are, for example, distinct differences between vermiculite and chlorite and it is theoretically possible to differentiate between them on this basis.

The infrared spectra were run as described in section 3.3.1. The
results obtained for both clays are shown in figure 3.4.6.2. It can be seen that the clay contains a kaolin-type phase and a 2M muscovite-type phase, in this case illite. (Note 2M has a double peak, while 1M has only one. In the case of Warnham clay, one peak is masked by the quartz peak at 795cm⁻¹.) Traces of absorbed water can be seen as well as interlayer OH (and could well represent the vermiculite modification of illite). No traces of either chlorite or trioctahedral vermiculite spectral features are seen.

The literature search revealed that montmorillonite, another expanding lattice clay, is capable of forming a complex with the organic dye 2-2' Bipyridyl, that has a characteristic absorption peak at about 1440cm⁻¹. Experiments (section 4.1) were made to see if the 14Å phase in WSC formed a similar absorption peak when treated with 2-2' Bipyridyl. It did - as can be seen in figure 4.1.1. Control experiments described in section 4.1 proved this is characteristic of expanding lattice clays only. This suggests that the 14Å phase is dioctahedral vermiculite and not chamosite.

Dioctahedral vermiculite tends to be stable to both lattice expansion and contraction, so the lack of variability in (001) reflections with cation exchange and organic complex formation is not unusual. Precisely why the vermiculite forms a detectable organic complex with bipyridyl and not with either ethylene glycol or glycerol, is unclear.

As explained in Appendix 1, if the vermiculite component formed from illite, it could be expected to be present as an interlayer component in some of the illite. The illite and vermiculite are therefore probably combined as a mixed-layered clay and not present as distinct crystal particles.

The clay minerals present are, in order of abundance:
Illite (~45%) / illite:vermiculite (~10%) > Kaolinite (~40%) > Halloysite (~15%)

Attempts made to quantify the phases using XRD gave unreliable results because not even a semi-satisfactory method could be devised for quantitative XRD analysis of Warnham clays (see section 3.1.3). It was decided, therefore, that apparent relative abundance would have to be used.

3.4.6.3 TEM Investigation

The detailed results of this investigation are given in section 4.4.1, only a summary of the general results will be included here.

Kaolinite was found to be the more perfectly crystalline clay mineral and often showed indications of a hexagonal plate-like habit. However, the XRD data suggested the bulk of the kaolin was of a relatively disordered fireclay type. Kaolinite material could be distinguished from illite:vermiculite by its lower K and Fe content. While pure kaolin does not contain significant Fe (ie <1%), microchemical analysis did show that these kaolin particles contained significant Fe (tables 4.4.1.1 -4). Some of the iron is likely to represent octahedral iron, but most is probably present as an oxyhydroxide surface coating - a feature often reported in soil clays.

Halloysite showing 'typical' tubular habit is rare. Most halloysite must have either a plate-like or lath-like form and so is not easily distinguishable from a disordered kaolin.

The illite-illite:vermiculite intergrade material could be
distinguished from kaolinitic material by electron diffraction as well as microchemical analysis. The illitic material was generally far from perfectly crystalline. Most particles proved to be aggregates of yet smaller platelets. Though one stacking orientation was dominant in any one particle, a significant amount of misorientation in the 'c' direction occurred. This manifested itself as 'powder rings' in the hk0 diffraction pattern (Ph.57). Electron diffraction patterns were sometimes observed to have a second set of reflections with the same orientation as the main set of reflections, but with a slightly larger d spacing (ie the spots appeared split). This could possibly be due to simple mismatch in stacking or it could represent two very similar phases in the same particle; such as that due to regular isomorphous substitution or changes in interlayer material. If it is the latter, it supports the view that vermiculite is a modified illite and is intimately intermixed with it.

The chemical composition varied from particle to particle (tables 4.4.1.1-4). The K and Fe content of the illitic material probably reflects the amount of vermiculitic phase present in the particle. The iron content of the illite-illite:vermiculite material could be present in three main sites. Some is probably substituted for Al in the octahedral layer (structural iron, fig. 3.4.6.4), while some represents part of the oxyhydroxide interlayer material (vermiculite) and the rest is part of an amorphous iron:aluminium oxyhydroxide coating on the clay particle.

The presence of an iron-containing coating on the particles was indicated by the higher Fe content of the kaolinite crystals and its presence on many of the quartz grains in both sand and clay fractions of Warnham clay. Its presence was also indicated by XPS (see 3.8.).
The difference in the two Warnham clays lies essentially in the increased material of biological origin in the ostracod clay as opposed to the relative abundance of silt grade detrital quartz in the silty clay. WOC contains considerably more calcium carbonate from fossil shells and calcium phosphate from fossil fish bones than does WSC. It also contains significantly more FeS. Its apparently higher gypsum content is associated with the higher sulphide content as the sulphate ion can form by the oxidation/weathering of sulphide. The sulphate could then react with calcite to form gypsum.

Siderite, with its iron-rich ankerite-type carbonate subsidiary component, was the only mineral found in the silty clay not observed in WOC. It is a potentially important mineral(s) not previously reported.

The mineralogical composition of the two clays are;-

Ostracod clay:

- Illite:vermiculite
- Kaolinite
- Halloysite
- Calcite
- Quartz
- Pyrite - Pyrrhotite
- Apatite
- Fe-Al oxyhydroxide coatings
- Organic material
- Rutile
- Rare earth phosphates
- Zircon
Silty Clay:

Illite:vermiculite
Kaolinite
Halloysite
Quartz
Siderite
Pyrite - Pyrrhotite
Fe-Al oxyhydroxide coatings
Rutile
Rare earth phosphates
Zircon

The main iron-containing phases are;-

Illite:vermiculite
Pyrite
Siderite-ankerite
Amorphous Fe-Al oxide oxyhydroxide coatings
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<td>H₂O⁺</td>
<td>6.61</td>
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<td>H₂O⁻</td>
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<tr>
<td>Others *</td>
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<tr>
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<td>- O = S</td>
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</table>

Table 3.4.2.1

Warnham Clay Composition
(After Hall, 1978)

* ignition loss = ? organic material
<table>
<thead>
<tr>
<th></th>
<th>WSC-H</th>
<th>*</th>
<th>*</th>
<th>*</th>
<th>ĸ</th>
<th>WSC</th>
<th>*</th>
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<tr>
<td>SiO₂</td>
<td>50.36</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
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<td>61.91</td>
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<td>1.52</td>
<td>1.54</td>
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<td>197</td>
<td>193</td>
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<td></td>
<td>99.57</td>
<td></td>
<td>102.93</td>
<td>103.02</td>
</tr>
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</table>

Table 3.4.2.2
Silty Clay Composition

* dispersed in distilled water, therefore has lost soluble components
(see table 4.2.5).

stå = mean value   nd = not determined   WSC-H = Hydrocycloned Fraction
WSC = Unfractionated samples
<table>
<thead>
<tr>
<th>Element</th>
<th>WOC</th>
<th>WOC *</th>
<th>WOC*</th>
<th>( \bar{x} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
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<td>59.49</td>
<td>nd</td>
<td>55.69</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>24.00</td>
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<td>7.65</td>
</tr>
<tr>
<td>MgO</td>
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<td>1.72</td>
<td>1.76</td>
<td>1.75</td>
</tr>
<tr>
<td>CaO</td>
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<td>4.22</td>
<td>3.04</td>
<td>5.42</td>
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<td>0.32</td>
<td>0.33</td>
</tr>
<tr>
<td>K(_2)O</td>
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<td>3.98</td>
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<td>4.25</td>
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<td>P(_2)O(_5)</td>
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</tr>
<tr>
<td>Total</td>
<td>99.69</td>
<td>104.75</td>
<td>-</td>
<td>101.20</td>
</tr>
</tbody>
</table>

Table 3.4.2.3
Ostracod Clay Composition

* dispersed in distilled water, therefore lost water-soluble constituents (see table 4.2.5)

\( \bar{x} \) = mean value  \( \text{nd} \) = not determined
SEM photographs of orientated Warnham Ostracod Clay

SEM photographs of orientated HCl-HNO₃ treated Ostracod Clay
Fig. 3.4.4.2 EDXS analysis of pyritised ostracod
Note - Al, Si & K due to clay minerals present on the surface
Fig. 3.4.4.3 EDXS analyses of pyrite frambooid note variable composition between 'sub grains'
Fig. 3.4.4.4 EDXS analysis of fragments of fish bone (Ph.18)
Fig. 3.4.4.5 EDXS analysis of quartz grain. Note Al & Fe content probably derived from a surface coating.

Fig. 3.4.4.6 EDXS analysis of rare earth phosphate grain.
Fig. 3.4.4.7 EDXS analysis of siderite nodule. Note the variable composition of some grains - suggesting some ankerite type material.
Fig. 3.4.4.8 EDXS analysis of siderite granules - again note indication of ankerite type component. Al, Si & K from adjacent clay minerals.
Fig. 3.4.4.9 Infra red spectrum of a siderite nodule.
Fig. 3.4.6.1 Schematic summary of the assignments of the infrared-absorption bands of layer-lattice silicates containing basically Al\(^{3+}\), Mg\(^{2+}\), Fe\(^{3+}\), or Fe\(^{2+}\) in the octahedral site. Relative intensities of the bands are described as vs = very strong, s = strong, m = medium, and w = weak. (After Stubic.)

Fig. 3.4.6.2 IR Traces of Hydrocycloned Silty & Ostracod Clay Showing Similarity to Muscovite & Kaolinite Samples.
Fig. 3-4-6-3 Diagrammatic sketch of the structure of the kaolinite layer. (After Gruner.)

Fig. 3-4-6-4 Diagrammatic sketch of the structure of muscovite.
Exchangeable cations
\( nH_2O \)

Fig. 3-4-6-5 Diagrammatic sketch of the structure of smectite according to Hofmann, Endell, and Wilm, Marshall, and Hendricks.

Fig. 3-4-6-6 Diagrammatic sketch of the vermiculite structure, showing layers of water. (After Hendricks and Jefferson.)
Fig. 3.4.6.7 Diagrammatic sketch of a portion of the halloysite 4H2O structure, showing a single layer of water molecules with the configuration suggested by Hendricks and Jefferson.4

| C   | Calcite         | Ca CO₃       |
| I   | Illite          | (K₃H₃O)₂₋ₓ Al₄₋ₓ Feₓ [Si₆₋ₓ Al₂₋ₓ O₂₋ₓ] OH₄ |
| K   | Kaolinite       | Al₄ Si₄ O₁₀ (OH)₈ |
| Mh  | Metahalloysite  | ~Al₄ Si₄ O₁₀ (OH)₈ n |
| Py  | Pyrite          | Fe S₂        |
| Q   | Quartz          | Si O₂        |
| R   | Rutile          | Ti O₂        |
| V   | Vermiculite     | ~ Illite     |
|     | (dioctahedral)  |             |

Table 3.4.6.1 Abbreviations used to annotate the XRD traces in sections 3.4 and 3.5. There are indications in the traces that both 2M and IM illite polymorphs are present (see fig. 3.4.6.8).
Fig. 3.4.6.8 X ray powder data for micas  
(after Bradley & Grim)

Fig. 3.4.6.9 Graph showing the change in intensities of the (00l) reflections with varying composition of the octahedral layer for a dioctahedral mica.  
(After Grim, Bradley, and Brown,\textsuperscript{13})
Figure 3.4.6.10  Unorientated WSC and WOC
Three grades of chemically untreated clays were used in the firing trials. The first two were described briefly in section 3.4.2.

The first designated WSC-H and WOC-H, for silty and ostracod respectively, was the hydrocycloned material and represented the clay grade fraction of Warnham clays, that is, the sub 2\(\mu\) diameter material. By simply removing the coarser grade material, this material was effectively enriched in clay minerals and contained only minor quantities of quartz, calcite, pyrite etc (see fig. 3.4.6.10).

The second, designated either WSC or WOC, was that section of the clay that was disaggregated in distilled water and wet sieved to pass 300 mesh (< 53\(\mu\)). This represented the clay and silt fraction of the clays.

The third was the 'homogenised' material prepared for use in the firing trials and designated by the suffix x-2. It is essentially the same as the second grade described but was not sieved and so retained undisaggregated fragments.

It was prepared at Redland Technology using the following procedure (Aston, 1978). A 5kg sample of clay was added to 225 litres of deionised water in a 350 litre polythene tank. The suspension was stirred by means of a large electric stainless steel paddle mixer (twin 3-blade 8" paddles) and two pneumatically driven Silverson mixers. After sufficient disaggregation the slip was allowed to settle and the bulk of the water was removed by siphoning. Further dewatering was done with the aid of a small filter press.
3.5.2 Chemical Treatments - Basis of

The initial mineralogical analysis of Warnham clay (Hall, 1978) suggested that it would be possible to use a number of chemical treatments to remove selectively some of the iron rich minerals from Warnham clay.

The main treatments used and the components it was designed to remove are summarised in table 3.5.2.1. The following sections outline the relevant experimental procedures. A number of trials with other extraction techniques were done (eg K pyrophosphate, NaOH, Na₂CO₃) but were not considered suitable for firing trial experiments and so are omitted here.

<table>
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<th>Vermiculite</th>
<th>Pyrite</th>
<th>Illite</th>
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<td>-</td>
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Table 3.5.2.1
Proposed Action of Chemical Treatments

Silty clay x = 1   Ostracod clay x = 2
D = dissolved

Note 1) Siderite Fe CO₃ was not identified in the initial mineralogical analysis and so did not feature when these experiments were designed.

2) Fluoride treatment was 'supposed' to enrich illite and vermiculite and dissolve other phases.

3) Homogenised material was treated with water only - so only water-soluble salts are likely to have been extracted and so this material is essentially 'untreated'.

3.5.3 Tiron

This extraction technique was based on Biermans and Baert (1977), who suggested using an approximately 0.1M tiron solution buffered at pH 10.5 with 1N Na₂CO₃ solution to remove amorphous iron oxides (see section 2.4.3).

Preliminary tests showed that 0.1M tiron solution is quite acid and that the desired pH could not be attained using 1N Na₂CO₃ solution without complete loss of tiron molarity.

The procedure was therefore adapted to give the parameters suggested. A 0.1M tiron solution was made with distilled water, solid Na₂CO₃ being added to this until the pH reached 10.5 (the optimum determined by Biermans and Baert). This required a not inconsiderable amount. Extraction was then carried out at a temperature of 80°C for 1 hour at a solid:solution ratio of 25mg:100ml as in Biermans and Baert.

Tiron treated material was only used in small scale tests. No bulk clay treatment was undertaken.

3.5.4 Dithionite - Citrate - Bicarbonate

The procedure recommended by Mehra and Jackson (1960) was used for all small scale trials. 40ml of 0.3M sodium citrate solution and 5ml of 1M NaHCO₃ were added to 1g of clay (ie a sample containing less than 0.5g of extractable iron oxide). The suspension was then heated to 80°C on a water bath and 1g of solid Na₂S₂O₄ was added and the mixture stirred for about 15 minutes. At the end of this treatment the suspension was allowed to cool and settle. The liquid was decanted off and the residue washed with distilled water. When samples larger than
1g were required, simple multiples of the ingredients were used.

Bulk DCB treatment of clay for use in the main firing trails was done at Redland Technology's laboratories. Again scaled up quantities were used (Aston, 1978).

5kg of clay was disaggregated in 225 l of deionised water in a 350 l polythene tank. The tank was heated by two 2kW immersion heaters to 78°C at which point an equilibrium between heat input and loss was attained. 5.19kg of sodium citrate and 2.10kg of sodium bicarbonate were added, followed after a short interval of vigorous stirring by 5kg of sodium dithionite. Slow stirring was maintained for 30 minutes. The heaters were then turned off and ice added to inhibit further reaction. Once the suspension settled, the liquid was siphoned off. The clay was washed twice with 160 l of water. After the second washing the clay did not settle out (3 days) and in order to floculate it, 0.5 l of glacial acetic acid was added.

It was appreciated that the citrate ion can complex Si and is known to be capable of inducing chemical attack on glass, so glass containers etc were avoided.

3.5.5 Nitric Acid:Hydrochloric Acid Extraction

The laboratory scale extraction procedure adopted for small scale tests was as follows: 25g of disaggregated clay was dispersed in 400ml of distilled water and 400ml of a solution of 10% HCl and 20% HNO₃ was added. The suspension was heated to 70°C in a water bath and was maintained at this temperature for 1.5 hours with occasional stirring.
The suspension was allowed to cool and once the clay settled, the liquid was removed by decanting. The residue was then washed with distilled water.

Bulk material preparation for the firing trials was carried out at Redland Technology using the same extraction procedure scaled up (Aston, 1978).

5 kg of disaggregated clay in 150 l of deionised water in a polythene tank was heated to approximately 70°C by means of immersion heaters. 9 l of concentrated HCl and 18 l of concentrated HNO₃ were added. The suspension was maintained at 70±1°C for 1.5 hours, during which time it was continually stirred.

Rapid corrosion of the stainless steel paddle stirrer and immersion heater sheaths was expected. This was minimised by suspending an inert carbon electrode in the suspension connected to them and applying a potential to the cell thus established to oppose the corrosion reaction. The potential applied was adjusted to maintain minimum current flow through the circuit (minimum was about 0.6 mA).

After 1.5 hours the stirrer and heaters were removed and ice added to the suspension. The clay settled out and the liquid was siphoned off. The clay was washed three times with deionised water. Final dewatering was carried out with the aid of a filter press.

3.5.6 Hydrochloric Acid Extraction

The same procedure was used as in the previous extraction, except that HCl alone was used in the place of the nitric:hydrochloric acid mixture.
3.5.7 Fluoride Extraction

The fluoride extraction treatment used is a very slightly modified version of that of Rich (1966). The same 'F' solution was used, that is a 0.4N NH₄F, 0.1N HCl, 0.1N NH₄Cl solution. It was prepared by dissolving 14.8g of NH₄F, 100ml of 1M HCl and 54.3g of NH₄Cl in 1 litre of distilled water. The solution as prepared is buffered at pH 5.0.

The clay:solution ratio was modified in order to reduce liquid volume to manageable laboratory scale quantities. Rich used 10ml per 10mg - this was changed to the equivalent of 10ml for 200mg. 50g of WSC-H clay was washed salt free using 500ml of 2M NH₄Cl to prevent precipitation of insoluble fluorides. The clay was then treated by stirring it with the aid of a magnetic stirrer with 2.5 l of the 'F' solution at room temperature for 24 hours. The suspension was allowed to settle and the liquid decanted. The clay was thoroughly washed with water and then methanol.

Plastic beakers etc were used throughout as the fluoride solution is capable of inducing minor chemical attack on glass.

3.5.8 Oxalate Extraction

The oxalate extraction used was essentially that of Fey and Leroux (1975). A 0.2M ammonium oxalate solution buffered at pH 3.0 with oxalic acid was used. The 50mg per 10ml of solution ratio was maintained by treating 5g of WSC-H with 1 litre of solution. Extraction was carried out for 2 hours in darkness at room temperature. The suspension was stirred with a magnetic stirrer throughout, and again plastic beakers were used.
It was necessary to obtain some 'organic' free Warnham clay for TEM, XPS and IR experiments.

The following procedure was adopted in case low pH values were attained during extraction, further contributing to potential damage to the layer silicates. 5g samples of WSC-H and WOC-H were added to 25ml of distilled water in two beakers. The pH of the resultant suspensions was measured using a pH meter which was previously calibrated against two buffer solutions (pH 7 & 9.4). 25ml of a 30% analar H₂O₂ was added to each suspension and the beakers placed in a water bath at about 80°C. The mixtures were stirred and the pH monitored at intervals for a period of two hours, during which no appreciable pH change was noted.

As no change occurred (see table 3.5.9.1), the use of a buffer seemed unnecessary (see 2.4.10). It was thought that the minimal change in pH indicated that the hydrocycloned clays contained little organic matter - this was later supported by XPS data.

<table>
<thead>
<tr>
<th>Solutions/Suspensions</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>4.75 ± 0.05</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>4.80</td>
</tr>
<tr>
<td>WSC-H + H₂O</td>
<td>6.45</td>
</tr>
<tr>
<td>WSC-H + H₂O + H₂O₂ (2 hrs)</td>
<td>6.57</td>
</tr>
<tr>
<td>WOC-H + H₂O</td>
<td>6.54 ± 0.02</td>
</tr>
<tr>
<td>WOC-H + H₂O₂ + H₂O (2 hrs)</td>
<td>6.49</td>
</tr>
</tbody>
</table>

Table 3.5.9.1
3.6.1 Firing Trials - Procedures

A Stanton Redcroft muffle furnace was used for all the firing runs in air. The heating rate, 'soak' and cooling rate were controlled by means of a Eurotherm programmer. The temperature was independently monitored using a Pt:Rh thermocouple and recorded on a chart recorder.

All the gas (non-air atmosphere) firings were done in a conventional Carbolite tube furnace - again controlled by a Eurotherm programmer and the temperature monitored with a Pt:Rh thermocouple. The vacuum experiment was done in a Torvac/Edwards vacuum furnace.

A standard heating cycle similar to that used in commercial brick production was adopted. The samples were heated at a rate of 1°/minute to a top temperature, held there for three hours and allowed to furnace cool. A one-hour hold at 575°C was used in the heating ramp to allow for quartz inversion. In controlled atmosphere firings the gas was kept running through the furnace until the temperature was down to about 100°C, at which point samples were removed and air cooled.

Table 3.6.1.1 shows the combination of material, atmosphere and temperatures used. Intermediate firings were done at 50°C intervals.

Samples were prepared in one of three ways:

a) Wet clay paste was pressed into 1"x1.5" cylindrical plastic moulds and dried at 60°C.
b) Dry clay cylinders were prepared by compressing about 15g of dry clay powder in a 25mm diameter stainless steel die at about 750kg/cm . A stearic acid-acetone solution was used as a lubricant - this resulted in some surface contamination but it was burnt off during firing.
c) Dried clay powder in a platinum lined crucible was also used.

A small series of firings were performed where the samples were either air quenched or cooled at a specific slow rate, i.e. heated during cooling. Pure minerals were also included in some of the firings for use as comparisons/controls.

<table>
<thead>
<tr>
<th></th>
<th>Air</th>
<th>Argon</th>
<th>Nitrogen</th>
<th>N₂/H₂</th>
<th>Vacuum</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSC/WOC (wet)</td>
<td>800-1300</td>
<td>1050</td>
<td>1000-1100</td>
<td>-</td>
<td>1050</td>
</tr>
<tr>
<td>WSC/WOC (dry)</td>
<td>900-1300</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WSC-H WOC-H (wet)</td>
<td>800-1400</td>
<td>900-1200</td>
<td>1000-1100</td>
<td>1050</td>
<td>1050</td>
</tr>
<tr>
<td>WSC-H WOC-H (dry)</td>
<td>800-1400</td>
<td>900-1200</td>
<td>1000-1100</td>
<td>1050</td>
<td>1050</td>
</tr>
<tr>
<td>WSC-H (powder)</td>
<td>300-1000</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chemically treated³</td>
<td>900-1300</td>
<td>1050</td>
<td>-</td>
<td>-</td>
<td>1050</td>
</tr>
<tr>
<td>Kaolin 'Jordan'</td>
<td>800-1300</td>
<td></td>
<td>1000-1200</td>
<td></td>
<td>1050</td>
</tr>
<tr>
<td>Kaolin BDH</td>
<td>800-1300</td>
<td></td>
<td>1000-1200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolin St Austel</td>
<td>900-1200</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Muscovite (2M)</td>
<td>900-1050</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vmriculite</td>
<td>900-1050</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>900-1050</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.6.1.1
Clay:Atmosphere Combinations

1. Forming Gas (5% H₂)
2. Maintained at 1x10⁻³ torr by dynamic pumping
3. Includes 1-2, 1-3, 1-4, 2-2, 2-3, 2-4, 2-5, oxalate and fluoride
3.7 Bulk Chemical Analysis.

Inductively Coupled Plasma Atomic Emission spectroscopic analysis was done at Kings College, London, by Mr D. Smith, using standard techniques.

3.7.1 Lithium Metaborate Fusion Procedure

Approximately 2g of clay powder was fired to 900°C for 4 hours in a platinum lined ceramic crucible. 0.5g of the fired material was weighed accurately into a platinum crucible. Exactly 0.5g of spectroflux 106 and approximately 1g of spectroflux 100B (Lithium Metaborate) were added. The powders were mixed and carefully fused over a bunsen flame for 30 minutes. After cooling the crucible was placed upright into a polythene beaker containing 200ml of nitric acid (5% v/v) - the solution level being above the top of the crucible. The fusion bead was dissolved with the aid of a magnetic stirrer. When dissolved, the contents were washed into a 250ml volumetric flask and diluted to volume. The solutions were stored in polythene bottles.

3.7.2 Trace Element

0.5g of fired sample was accurately weighed into a platinum crucible. 4ml of perchloric acid were added using a safety pipette along with about 15ml of hydrofluoric acid. Once the sample had dissolved, the solution was evaporated to dryness in a sand bath. After cooling, 2ml of perchloric acid were added and evaporation repeated. Then on cooling, 4ml of perchloric acid were added and the crucible half filled with distilled water. The salts were dissolved, using a water bath where necessary. The cold solution was transferred quantitatively to a 50ml volumetric flask and diluted to volume. The solutions were stored in polythene bottles.
X-ray Photoelectron Spectroscopy is a surface analysis technique based on the phenomenon of incident X rays inducing the emission of photoelectrons from the top few tens of Angstroms of a material. The energy of a given photoelectron is characteristic not only of the element from which it originated but also the orbital. In addition, variations in oxidation state and crystal structure can result in small shifts in energy of a peak from an element in, say an oxide or silicate, to the same peak from the pure element. The technique therefore offers the potential of providing crystallographic information on the constituents of both fired and unfired clays.

The detailed theory behind XPS is well covered in the literature and will not be included here (see Carlson, 1975 or Briggs, 1977). Only details relevant to XPS investigation of silicates need be included.

The surface information available from conventional Si XPS is limited because only the 2p and 2s core level peaks are observed and both are relatively weak and at the low binding energy end of the spectrum (Castle & West, 1980).

Another problem associated with silicates is that they are insulators - charging causes the ejected photoelectrons to be retarded by an undefined amount. This problem can be eliminated by combining the positions of the KLL Auger and 2p core levels for each element to form an Auger parameter (α*) which is independent of charging but strongly dependent on crystalline structure (Castle & West, 1980).
\[ \alpha^* = E_K \text{KLL} + E_B (2p) - \hbar \nu \]

or

\[ \alpha^* = E_K \text{KLL} - E_K (2p) \]

Changes in \( \alpha^* \) represent site differences and differences in electronegativity of adjacent atoms.

The XPS spectra were run on a 'Vacuum Generators Ltd' ESCA 3 Photoelectron Spectrometer using a Mg K\( \alpha \) X ray source with the help of Mr J. Watts.

Samples were produced by pressing carefully freshly ground powdered clay (or brick powders) into indium foil (Castle et al, 1978) and mounting on a conventional sample holder with double sided tape.

Wide scans were run together with individual 2p analyses for Si, Al K, Fe, O and C - an extended analysis period was used to permit sufficient peak to background ratios to be obtained for both the Al and Si Bremsstrahlung induced KLL Auger peaks (Castle & West, 1980). A Mg source was used because the Al KLL peak induced by Al Bremsstrahlung radiation gives a peak at 100eV and so distorts the Si 2p peak (Castle & West, 1980), while the use of a more suitable Zr La radiation was prevented by machine failure (of ESCA 2).

Two basic experimental series were conducted. One attempted to utilise XPS sensitivity to surface features to investigate the oxyhydroxide coatings on the clay minerals in Warnham clay and to look at the Al\( \alpha^* \) parameter. (Generally relatively little variation is seen in the \( \alpha_{si}^* \) for layer silicates - probably because of relatively open crystal structure (Castle & West, 1980), so it was not investigated in detail.) The second series involved an attempt to follow changes in the oxidation and coordination state of iron on firing.
The results of the XPS investigation of the unfired Warnham clays suggested there was no truly marked difference between any of the samples. Figure 3.8.1.1 shows the results obtained from WSC-H and provides an example of the type of results obtained. The differences observed between samples could generally be attributed directly to the relevant chemical pretreatment given to them. For example, figure 3.8.1.2 shows that both the untreated and DCB treated silty clay had low levels of iron on the surface and that while DCB treatment does marginally reduce the quantity of iron present in the surface layer, it does not totally remove it. This suggests DCB treatment is not fully effective at removing oxide and oxyhydroxide surface coating present on clay minerals. Furthermore, it introduced sodium and increased the carbon contamination.

Other chemical treatments employing organic agents also apparently increased the surface carbon contamination, suggesting the organic ions 'adhered' to the clay surface. The carbon content of the hydrocycloned clay (fig. 3.8.1.1) was in contrast, relatively low, suggesting only minor quantities of natural 'organic' materials in Warnham clay.

Attempts to follow any changes in coordination and oxidation state of the iron during firing were not particularly successful. As seen in figure 3.8.2.1, the iron peaks were typically of low intensity. As the peak to background resolution was poor, the results were inconclusive. Measurements of $a^{*}_{Al}$ were made to see if changes in Al coordination on firing could be detected (table 3.8.1), but
surprisingly little variation was observed. The only significant variation was that shown by the magnetic fraction (see 4.3.15), which suggested that the Al in this fraction is dominantly in an octahedral coordination site (cf tetrahedral or mixed oct. and tet. - supporting the idea of octahedral Al coordination in this defect Fd₃m iron oxide structure, see 5.1-2).

The apparent uniformity of α⁺ᵦ between fired and unfired hydrocycloned silty clay contrasts with the results obtained by M. Edgell (1982) for α⁺ᵦ variations in Jordan kaolinite (see table 4.2.6). A marked change occurred between the unfired material and that fired to 900°C, which suggested a change from octahedral to tetrahedral coordination.

In both cases, however, α⁺ᵦ values for material fired to above 900°C remained constant, suggesting no further change in coordination, except for the fractionated material.

It should however, be noted that the initial α⁺ᵦ value for WSC-H is rather lower than one might expect for octahedral coordination (Edgell, 1982). This may be due to the fact that WSC-H contains both impure kaolinite and illite, both of which are likely to have an oxyhydroxide surface coating which contains Al. The Al peak is thus likely to be a composite one and this may well be responsible for a low α⁺ᵦ value.

<table>
<thead>
<tr>
<th></th>
<th>Si 2p BE</th>
<th>Si KLL KE</th>
<th>Si_α⁺ (eV)</th>
<th>Al 2p BE</th>
<th>Al KLL KE</th>
<th>Al_α⁺ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin</td>
<td>105.2</td>
<td>1607.2</td>
<td>458.8</td>
<td>76.8</td>
<td>1386.2</td>
<td>209.4</td>
</tr>
<tr>
<td>Kaolin 900°C</td>
<td>104.4</td>
<td>1607.6</td>
<td>458.4</td>
<td>76.2</td>
<td>1385.6</td>
<td>208.2</td>
</tr>
<tr>
<td>Kaolin 1000°C</td>
<td>104.8</td>
<td>1607.4</td>
<td>458.6</td>
<td>76.6</td>
<td>1384.8</td>
<td>207.8</td>
</tr>
<tr>
<td>Kaolin 1050°C</td>
<td>104.2</td>
<td>1607.4</td>
<td>458.0</td>
<td>76.2</td>
<td>1385.2</td>
<td>207.8</td>
</tr>
<tr>
<td>Kaolin 1100°C</td>
<td>104.2</td>
<td>1607.8</td>
<td>458.4</td>
<td>76.0</td>
<td>1385.6</td>
<td>208.0</td>
</tr>
<tr>
<td>WSC-H</td>
<td></td>
<td></td>
<td></td>
<td>76.0</td>
<td>1385.2</td>
<td>207.6</td>
</tr>
<tr>
<td>Magnetic</td>
<td></td>
<td></td>
<td></td>
<td>75.1</td>
<td>1386.9</td>
<td>208.4</td>
</tr>
<tr>
<td>Fraction (1050°C)</td>
<td></td>
<td></td>
<td></td>
<td>75.7</td>
<td>1385.6</td>
<td>207.7</td>
</tr>
<tr>
<td>WSC-H 1050°C</td>
<td></td>
<td></td>
<td></td>
<td>75.3</td>
<td>1386.0</td>
<td>207.7</td>
</tr>
</tbody>
</table>

Table 3.8.1 XPS 2p core level and Bremsstrahlung induced KLL Auger peaks using Mg Kα radiation (after Edgell, 1982).
Fig. 3.8.1.1a Full XPS spectrum of WSC-H.

Fig. 3.8.1.1b XPS Silicon peak WSC-H.
Fig. 3.8.1.1c Details of the XPS spectrum of WSC-H.
Fig. 3.8.1.2 DCB and untreated Silty clay. Note that both show signs of iron compounds on the surface.
Fig. 3.8.2.1 XPS 2p iron peaks.
Fig. 3.8.2.2 XPS spectra for WSC-H 1050°C.
Fig. 3.8.2.3 Alα⁺ spectra for WSC-H magnetic fraction and WSC-H 1100°C
4. Results

4.1 Clay Analysis - Infra Red Tests

As described in section 3.4.6, the 14Å phase in Warnham clay proved difficult to identify using conventional analysis procedures.

The literature search revealed that montmorillonite, an expanding lattice clay, was capable of forming a complex with the organic dye 2-2′ bipyridil, that has a characteristic absorption peak at about 1440 cm⁻¹. Experiments were undertaken to see if this behaviour could be utilised as an identification aid for expanding lattice clays.

A number of test runs were made with standard layer silicates, to establish that the bipyridil gave the characteristic peak only with known expanding layer silicates. This it did (figs. 4.1.2 - 3).

Additional tests showed that it could detect expanding lattice material in concentrations down to at least 10% (fig. 4.1.4).

As can be seen in figure 4.1.1, Warnham silty clay did form a weak absorption peak at about 1440 cm⁻¹, thus indicating the presence of an expanding lattice clay. This suggests that the 14Å material is probably dioctahedral vermiculite, and not chamosite.
4.2 Chemical Dissolution Treatments

These treatments were adopted with the aim of producing material with a simplified mineralogy for use in firing trials, in the belief that they would permit the effects of the various iron-rich components to be determined individually. The initial mineralogical analysis (Hall, 1978) had suggested that it was possible to use a number of chemical treatments, devised primarily for soil analysis, to remove selected iron-rich minerals from Warnham clay. This would permit the role of various iron constituents during firing to be more easily determined.

At a fairly advanced stage in the firing trials (see 4.3) a number of important facts became apparent, that have reduced, but not totally removed the validity of this approach to the problem. The mineralogical analysis of the material collected for this study (see 3.4) revealed that there were small but important differences between it and the previous estimates - the most notable being the presence of siderite and the different nature of the vermiculite component. The net result of these changes is that it is now known that some of the conclusions of Hall (1978) are not totally justified, for example the proposed action of the chemical extractions; table 3.5.2.1 contrasts somewhat with the present estimation of their activity, table 4.2.1.

It is now apparent that the precise action of many of the treatments used is uncertain (see 2.4) and it is unwise to attribute too much importance to the results of such extractions. For example, estimates of constituents, eg amorphous iron oxyhydroxides based on oxalate extraction, are considered not particularly worthwhile, partly for the reasons outlined in section 2.4 and partly because it was found that often not all the water-soluble constituents were removed by the
(often extensive) washing treatments which followed extraction. The concentration of some components is therefore perhaps higher than it ought to be, so leading to wrong estimates.

As mentioned previously, these extraction techniques were devised originally for mineralogical/soil analysis; they were not devised to produce clay material for firing trials. It has become evident that some of the side effects of these treatments, while quite probably totally irrelevant for soil analysis applications, can significantly affect the course of the high temperature reactions. The important mineralogical changes produced by the chemical treatments will be outlined in the following sections.

4.2.1 DCB-Treated Silty Clay (Code 1-3)

This treatment was devised to remove crystalline and amorphous oxides and hydroxides. The chemical composition of the DCB-treated silty clay is shown in table 4.2.2. While the treatment has extracted about 18.5% of the iron present (8.0 cf 9.9%), it has also altered the potassium, sodium, and calcium contents. The potassium content is up marginally from about 3.31% in the untreated clay to 3.65%. The sodium content is up 200% from about 0.21 to 0.63%, while the calcium content is down from about 0.62 to 0.35%. Sodium and potassium act as fluxes and so a change in the temperature at which reactions occur and an increase in the amorphous content of fired material is likely, due to their increase.

The XRD trace of DCB-treated clay (fig.4.2.0.1) reveals only a very faint trace of a 14Å vermiculite component, but an apparent increase in the 10Å component relative to the 7.1Å material is evident compared to the untreated clay. Metahalloysite (7.56Å) can also be identified - at
least in orientated samples. As mentioned in section 3.4., the metahalloysite component could easily be mistaken for gypsum in XRD traces; again the Ca content would appear too low to give such a strong XRD reflection. Similarly, the IR spectrum, figure 4.2.1.0, reveals no sign of gypsum.

The spectrum of DCB-treated clay is also shown in figure 4.2.1.1. - the spectrum contains features characteristic of citrates (1730 & 1385cm⁻¹) and acetic acid (1290cm⁻¹). (Note: acetic acid was used to floculate the clay - see 3.5.4). A weak spectral feature at about 1460cm⁻¹ is in a similar region to the organic complex absorption features described in section 4.1. This may indicate that the vermiculite component has formed a complex with one of the organic agents used. If so, it should be noted that such organic material has been reported to be capable of affecting the course of high temperature reactions (See 2.3.2). However DCB treatment ought not to remove totally the siderite present, so it could represent a poorly resolved siderite absorption feature normally seen at 1430cm⁻¹.

(Features at 2965, 2930 & 2870cm⁻¹ are attributed to contamination of the sample with oil from the vacuum pump used in KBr disc production.)

4.2.2 HNO₃-HCl Treated Silty Clay (Code 1-4)

The original proposed extraction capability of this technique is shown in table 3.5.2.1 while the present estimate is given in table 4.2.1.

The actual chemical composition of this material is given in table 4.2.2. The iron content has been reduced by about 66.5% from 9.9 to 3.3%. The manganese and calcium content have decreased by 0.4 to 0.2%
and 0.62 to 0.38% respectively, primarily because of acid attack on the carbonates present (e.g., ankerite-type material, see 3.4.4). The attack on the carbonates is partly responsible for the decrease in the iron content. This treatment should also be expected to attack severely the (Al-Fe)O OH coatings and pyrite, which would again reduce the iron content.

The reduction in Mg content from 1.54 to 1.01 could be partly due to attack on the carbonates present but is most likely indicative of at least partial attack on the octahedral cations of the clays (see appendix 1 etc.). Such an attack would also be partly responsible for the lower iron content. The small increase in K+ from 3.31 to 3.45% may simply be due to the 'closed' nature of the system. (If one component is removed, then the remaining ones apparently increase in concentration.) However, it could also represent K+ fixation which is often associated with acid weathering (see appendix 1). This too would then be consistent with at least partial attack on interlayer and octahedral components of the clay minerals.

The XRD trace is shown in fig. 4.2.0.1. Note that no 14Å vermiculite phase is evident. This would suggest the removal of 'fixed' interlayer oxyhydroxides from the vermiculite phase and could suggest that any expanding layer silicate that formed as a result of acid attack on the layer silicates has in fact collapsed again, e.g., due to K+ fixation. The 7.57Å phase is still present - if it did represent gypsum and not metahalloysite, one would have expected this treatment to remove it.

The IR spectrum of this clay is shown in figure 4.2.1.0. It is seen to be very similar to the untreated hydrocycloned clay; most of the differences that do exist can be attributed to the relative clay:quartz content of the two samples. One should note that the slight absorption at 1430 cm⁻¹ in the untreated clay is not seen in this
material - this would be consistent with the removal of carbonate minerals.

4.2.3 Acid Oxalate Treated Hydrocycloned Silty Clay (Code 1-6)

The original proposed extraction capability of this treatment and the present estimate of its action are given in tables 3.5.2.1 and 4.2.1 respectively.

The actual chemical composition of this material is given in table 4.2.2. The iron 'oxide' content is seen to have decreased by 75%, from 8.77 to 2.19%. The decrease in Mn and Ca from 0.3 to 0.01 and 0.71 to 0.48% respectively is again due to acid attack on the carbonate components, as is part of the decrease in iron content.

The decrease in Mg content of 62% (1.52-0.58%) is indicative of attack on the octahedral layers of the clay minerals present and this too would be expected to be partly responsible for the reduced iron content. The decrease in K could be expected to be associated with a synthetic vermiculitization process of the type described in appendix 1.

The IR spectrum of this material (fig. 4.2.3.1) shows an increase in adsorbed water relative to the untreated material, as could be expected if the potassium reduction is associated with synthetic vermiculitization. The spectral features at 1400 and 1320cm⁻¹ indicate the formation of insoluble chelated oxalates, eg calcium oxalate. (Note: the CaO content is not reduced to the same extent by this acid treatment compared to the others.)

This chemical treatment completely defloculated the clay. The XRD samples for this material were produced by slow sedimentation and
evaporation - not suction. This resulted in very well orientated samples, in which the upper surface was enriched in the very fine clay fraction. The marked decrease in the background at low angles (fig. 4.2.0.3) suggests that this feature in the other samples is associated with only partial orientation. The main XRD feature of these samples is the absence of vermiculite and metahalloysite. This may be due to the fractionation that has occurred (see 3.1.2). In the case of vermiculite, with all the above indications of a synthetic vermiculitization process, one would have expected it to have been present in increased amount - and not absent. The reason for the absence of both phases is unclear - it may be that both materials have been converted to 10\AA phases, vermiculite by taking NH\textsubscript{4} ions into its interlayers (see 2.4.7), and metahalloysite by hydrating to 10\AA halloysite.

4.2.4 'Fluoride' Treated Hydrocycloned Silty Clay (Code 1-7)

The proposed action of this extraction technique is shown in table 3.5.2.1, while the present estimate of its action is given in table 4.2.1.

The bulk chemical composition is shown in table 4.2.2. The iron content is found to be reduced by 42\% compared to the untreated material (5.0 cf 8.7\%). The decrease in calcium from 0.71 to 0.36\% reflects the removal of the carbonates - this again is partly responsible for the drop in iron content. The Mg content remains at about the same level, indicating a lower level of attack on the octahedral layers of the clay components than with the other acid treatments. There is a slight change in K from 4.01 to 4.3\% which may reflect K\textsuperscript{+} fixation and/or clay mineral concentration. This change and
the large drop in iron content suggest the removal of oxyhydroxide coating and interlayer material.

The IR spectra, figure 4.2.4.1, show the development of new absorption features at 1405 and 3150 cm⁻¹ - due to residual fluoride. The absence of an absorption band at 1430 cm⁻¹ seen in the untreated clay is consistent with the removal of carbonate materials by this treatment. The different spectra indicate a decrease in structural OH⁻, indicating an attack on the octahedral or perhaps more probably on the interlayer material.

The XRD trace of this material is shown in fig. 4.2.0.3. As with the previous acid treatment, no 7.56Å metahalloysite phase is evident. The reason for this is unclear, but it could be for the same reasons suggested for the previous material.

4.2.5 DCB-Treated Ostracod Clay (Code 2-3)

The chemical composition of this treated material is given in table 4.2.3. As can be seen, it differs from the homogenised ostracod clay in a number of important ways. The silica content is lower (47.5 cf 53%) and the aluminium content is higher (32.8 cf 24.8%). This probably represents a relative decrease in quartz content and increased clay mineral content. The slight increases in Na and K could also be due to a relative increase in clay minerals. The Ca content is noticeably lower (2.4 cf 7.8%) as is the Mn content (0.07 cf 0.14%). The treatment thus appears to have caused the partial removal of calcite and associated carbonate materials.

Surprisingly, the iron content is similar to that of the homogenised material - 7.0 cf 7.8, a change of about 10%. This suggests a removal of mainly the (Fe-Al)O-OH coating material, in
addition to the carbonates. The slight decrease in Mg from 1.76 to 1.44%, however, could represent partial attack on the octahedral clay layers. On the other hand, it could be due to loss of carbonate material, or both.

The IR spectrum (fig. 4.2.5.1) again shows the presence of citrate ions (as with 1-3). The almost complete elimination of carbonate absorption at 1430cm⁻¹ is evident.

The XRD trace of this clay is shown in fig.4.2.0.4 The reason for the very marked apparent increase in the 7.56Å metahalloysite component in this material is not known.

4.2.6 HNO₃-HCl Treated Ostracod Clay (Code 2-4)

The chemical composition is shown in table 4.2.3. There is significant enrichment in Al₂O₃ relative to the starting material. The fairly large decrease in calcium and manganese reflects the removal of carbonates. The major change in iron content is due to the removal of pyrite, (Fe-Al)O OH coatings - interlayer material, along with carbonate extraction and a partial attack on the octahedral clay cations. The last two of these are also probably associated with the reduction in Mg content. The Na and K contents show a slight increase and this is probably associated with the partial concentration of clay minerals and, in the case of Na, some material derived from the extraction solutions (eg cation exchange). This acid treatment also appears to have attacked the phosphate components, which are also down slightly.

The IR spectrum, figure 4.2.5.1, shows the elimination of carbonate absorption at about 1430cm⁻¹. A slight increase in sorbed water is also evident, relative to the untreated clay and indicates
probable attack on the octahedral and interlayer components of the clay minerals. See figure 4.2.0.4 for the XRD trace.

4.2.7 HCl-Treated Ostracod Clay (Code 2-5)

The bulk chemical analysis is given in table 4.2.3. The notable change in Ca and Mn reflects the removal of carbonate material. The marked decrease in Fe and Mg is due in part to the removal of carbonates, but mainly to the partial attack on the octahedral and interlayer components of the clays. This extraction technique does not seriously attack the pyrite, but it does reduce the phosphate content.

The IR spectrum, figure 4.2.5.1, shows very little in the way of a carbonate absorption feature. A slight shoulder in the background at about 1400 cm⁻¹ may indicate a residual carbonate presence. As with the previous material, a slight increase in sorbed water relative to untreated material is evident, which indicates at least a partial attack on the octahedral and interlayer components of the clays.

4.2.8 Hydrogen Peroxide Treated Clay

As described in section 3.5.9, tests were made to investigate any possible side effects, eg oxalate formation and/or acid attack on the clays, as a result of organic matter extraction with hydrogen peroxide. Details of the pH changes are given in table 3.5.9.1. Figure 4.2.7.1 shows the spectra of the two treated clays, compared to the starting material. Very little difference is detectable and there is no sign of oxalate absorption in either clay.
<table>
<thead>
<tr>
<th>Treatment Code</th>
<th>Amorphous Oxides and Hydroxides</th>
<th>Crystalline Oxides and Hydroxides</th>
<th>Vermiculite</th>
<th>Pyrite</th>
<th>Illite</th>
<th>Siderite</th>
<th>% Fe dissolved from WSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tiron x-8</td>
<td>D</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>5.67</td>
</tr>
<tr>
<td>DCB x-3</td>
<td>D</td>
<td>D</td>
<td>a</td>
<td>-</td>
<td>a</td>
<td>-</td>
<td>18.54</td>
</tr>
<tr>
<td>Fluoride x-7</td>
<td>D</td>
<td>D</td>
<td>A</td>
<td>N</td>
<td>A</td>
<td>D</td>
<td>42.41*</td>
</tr>
<tr>
<td>HCl x-5</td>
<td>D</td>
<td>D</td>
<td>A</td>
<td>a</td>
<td>A</td>
<td>D</td>
<td>-</td>
</tr>
<tr>
<td>HCl-HNO₃ x-4</td>
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<td>D</td>
<td>A</td>
<td>D</td>
<td>A</td>
<td>D</td>
<td>66.46</td>
</tr>
<tr>
<td>Oxalate x-6</td>
<td>D</td>
<td>D</td>
<td>A</td>
<td>N</td>
<td>A</td>
<td>D</td>
<td>75.03*</td>
</tr>
</tbody>
</table>

*WSC-H used in these experiments, not WSC, therefore N = none present in start material.

D = dissolved   A = attacked   a = probable minor attack

Table 4.2.1 The Actual Action Of Chemical Extractions on Warnham Silty Clay

- x-1 As collected
- x-2 Homogenised
- x-3 Dithionite Citrate Bicarbonate (DCB)
- x-4 HCl-HNO₃
- x-5 HCl
- x-6 Acid oxalate
- x-7 Fluoride
- x-8 Tiron

- x=1 Silty clay (WSC)
- x=2 Ostracod clay (WOC)

WSC-H Hydrocycloned silty clay
WOC-H Hydrocycloned ostracod clay
<p>| | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>50.36</td>
<td>61.91</td>
<td>62.63</td>
<td>62.12</td>
<td>67.06</td>
<td>52.66</td>
<td>52.48</td>
<td>61.98</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>32.25</td>
<td>23.92</td>
<td>23.59</td>
<td>25.62</td>
<td>23.11</td>
<td>33.83</td>
<td>33.05</td>
<td>24.43</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.77</td>
<td>9.61</td>
<td>9.87</td>
<td>8.04</td>
<td>3.31</td>
<td>2.19</td>
<td>5.05</td>
<td>9.31</td>
</tr>
<tr>
<td>Mg O</td>
<td>1.52</td>
<td>1.59</td>
<td>1.59</td>
<td>1.54</td>
<td>1.01</td>
<td>0.58</td>
<td>1.54</td>
<td>1.54</td>
</tr>
<tr>
<td>Ca O</td>
<td>0.71</td>
<td>0.81</td>
<td>0.62</td>
<td>0.35</td>
<td>0.38</td>
<td>0.48</td>
<td>0.36</td>
<td>0.86</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.31</td>
<td>0.28</td>
<td>0.21</td>
<td>0.63</td>
<td>0.25</td>
<td>0.14</td>
<td>0.31</td>
<td>0.30</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.01</td>
<td>3.39</td>
<td>3.31</td>
<td>3.64</td>
<td>3.45</td>
<td>2.08</td>
<td>4.30</td>
<td>3.29</td>
</tr>
<tr>
<td>TiO₂</td>
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<td>1.16</td>
<td>1.17</td>
<td>1.13</td>
<td>1.17</td>
<td>0.73</td>
<td>1.43</td>
<td>1.24</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.38</td>
<td>0.21</td>
<td>0.17</td>
<td>0.15</td>
<td>1.11</td>
<td>0.05</td>
<td>0.29</td>
<td>0.23</td>
</tr>
<tr>
<td>Mn O</td>
<td>0.03</td>
<td>0.05</td>
<td>0.04</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
</tr>
</tbody>
</table>

| Ba  | 601  | 471  | 474  | 458  | 491  | 364  | 667  |
| Ce | 117  | 124  | 140  | 105  | 91   | 63   | 128  |
| Co | 25   | 30   | 28   | 21   | 13   | 13   | 15   |
| Cr | 119  | 126  | 99   | 121  | 168  | 38   | 119  |
| Cu | 400  | 44   | 49   | 35   | 7    | 23   | 130  |
| La | 68   | 66   | 75   | 55   | 55   | 39   | 74   |
| Li | 123  | 98   | 102  | 95   | 104  | 59   | 130  |
| Nb | 33   | 83   | 78   | 84   | 88   | 21   | 34   |
| Ni | 101  | 91   | 87   | 69   | 53   | 46   | 69   |
| Sc | 26   | 20   | 21   | 19   | 17   | 12   | 24   |
| Sr | 179  | 162  | 152  | 105  | 102  | 103  | 148  |
| V  | 183  | 192  | 182  | 197  | 169  | 87   | 187  |
| Y  | 29   | 32   | 27   | 23   | 19   | 12   | 38   |
| Zn | 200  | 93   | 92   | 94   | 63   | 59   | 110  |
| Zr | 92   | 244  | 235  | 223  | 264  | 97   | 95   |

**Total** | 99.65 | 102.93 | 103.2 | 103.25 | 99.97 | 92.7 | 98.83 | 103.21 |

**Table 4.2.2**

Chemical components of Silty Clay materials
<table>
<thead>
<tr>
<th>Major elements - as oxides</th>
<th>ppm</th>
<th>ppm</th>
<th>ppm</th>
<th>ppm</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
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<td>52.92</td>
<td>47.52</td>
<td>63.11</td>
<td>59.91</td>
</tr>
<tr>
<td>Al₂O₃</td>
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<td>24.85</td>
<td>32.85</td>
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<td>27.27</td>
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<tr>
<td>Fe₂O₃</td>
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<td>7.83</td>
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<td>5.89</td>
</tr>
<tr>
<td>Mg O</td>
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<td>1.76</td>
<td>1.44</td>
<td>1.28</td>
<td>1.25</td>
</tr>
<tr>
<td>Ca O</td>
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<td>7.40</td>
<td>2.40</td>
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<td>0.31</td>
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<tr>
<td>Na₂O</td>
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<td>0.26</td>
<td>0.37</td>
<td>0.34</td>
<td>0.31</td>
</tr>
<tr>
<td>K₂O</td>
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<td>3.92</td>
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<td>4.67</td>
<td>4.26</td>
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<tr>
<td>TiO₂</td>
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<td>0.95</td>
<td>0.93</td>
</tr>
<tr>
<td>P₂O₅</td>
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<td>0.20</td>
<td>0.23</td>
<td>0.15</td>
<td>0.13</td>
</tr>
<tr>
<td>Mn O</td>
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<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Trace elements ppm</td>
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<td></td>
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<tr>
<td>Ba</td>
<td>561</td>
<td>560</td>
<td>737</td>
<td>601</td>
<td>471</td>
</tr>
<tr>
<td>Ce</td>
<td>96</td>
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<td>82</td>
<td>86</td>
<td>124</td>
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<td>Co</td>
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<td>28</td>
<td>21</td>
<td>13</td>
<td>30</td>
</tr>
<tr>
<td>Cr</td>
<td>94</td>
<td>118</td>
<td>100</td>
<td>178</td>
<td>126</td>
</tr>
<tr>
<td>Cu</td>
<td>33</td>
<td>32</td>
<td>47</td>
<td>8</td>
<td>44</td>
</tr>
<tr>
<td>La</td>
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<td>46</td>
<td>51</td>
<td>46</td>
<td>66</td>
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<td>Li</td>
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<td>83</td>
</tr>
<tr>
<td>Ni</td>
<td>86</td>
<td>93</td>
<td>91</td>
<td>70</td>
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</tr>
<tr>
<td>Sc</td>
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<td>22</td>
<td>23</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
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<td>317</td>
<td>169</td>
<td>109</td>
<td>162</td>
</tr>
<tr>
<td>V</td>
<td>169</td>
<td>178</td>
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<td>198</td>
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</tr>
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<td>Zn</td>
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<td>156</td>
<td>73</td>
<td>93</td>
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<tr>
<td>Zr</td>
<td>169</td>
<td>163</td>
<td>72</td>
<td>208</td>
<td>201</td>
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<td>Total</td>
<td>99.69</td>
<td>100.3</td>
<td>97.22</td>
<td>102.97</td>
<td>100.30</td>
</tr>
</tbody>
</table>

Table 4.2.3

Chemical composition of Ostracod Clay materials
### Table 4.2.4
Constituents removed by chemical treatments - expressed as % of whole rock.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>WSC</th>
<th>WOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Soluble</td>
<td>Cation Exchange</td>
<td>Δ</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>CaO</td>
<td>0.02</td>
<td>0.32</td>
</tr>
<tr>
<td>MgO</td>
<td>0.01</td>
<td>0.09</td>
</tr>
<tr>
<td>Cl</td>
<td>nil</td>
<td>nd</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.04</td>
<td>nd</td>
</tr>
</tbody>
</table>

### Table 4.2.5
Water-soluble and Exchangeable Cations

Constituents expressed as % of whole rock. Exchangeable cations were removed by treating with 1N Ammonium Acetate solution.
<table>
<thead>
<tr>
<th>Elements</th>
<th>St. Austel</th>
<th>BDH</th>
<th>'Japanese'</th>
<th>'Australian'</th>
<th>'Jordan'</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>50.05</td>
<td>46.75</td>
<td>47.7</td>
<td>45.7</td>
<td>44.8</td>
</tr>
<tr>
<td>Al₂O₃</td>
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<td>53.40</td>
<td>37.49</td>
<td>35.6</td>
<td>38.9</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.64</td>
<td>1.08</td>
<td>1.41</td>
<td>1.27</td>
<td>0.17</td>
</tr>
<tr>
<td>MgO</td>
<td>0.09</td>
<td>0.16</td>
<td>0.54</td>
<td>0.54</td>
<td>0.08</td>
</tr>
<tr>
<td>CaO</td>
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<td>0.07</td>
<td>0.07</td>
<td>&lt;0.01*</td>
<td>0.06</td>
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<tr>
<td>Na₂O</td>
<td>0.25</td>
<td>0.11</td>
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<tr>
<td>K₂O</td>
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<tr>
<td>TiO₂</td>
<td>0.02</td>
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<td>P₂O₅</td>
<td>0.39</td>
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<td>nd</td>
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<tr>
<td>MnO</td>
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<td>0.01</td>
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<td>98.91</td>
<td>99.75</td>
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<tr>
<td>Loss on Ignition (H₂O)</td>
<td>5.35%</td>
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Table 4.2.6
Chemical composition of the 'standard' clay minerals used in this study.

* below detection limit

BCRA = British Ceramic Research Association

▲ = Wet chemical analysis, English China Clays PLC
Fig. 4.2.0.1 Unorientated Warnham Silty Clay
Fig. 4.2.0.2  Orientated chemically treated Silty clays.
Fig. 4.2.0.3 Orientated chemically treated Silty clays.
Fig. 4.2.0.4 Unorientated Warnham Ostracod Clay
Fig. 4.2.1.0  IR Traces of Treated Silty Clay

Fig. 4.2.1.1  IR Spectra Show DCB Treated Material Retains Organic Molecules Despite Washing – Adsorbed or Complexed?
Fig. 4.2.3.1 Oxalate Treated Clay Also Retains Organic Material Despite Washing

Fig. 4.2.4.1 Fluoride Treated Clay - Note new Absorption peaks, due to (?)
Fig. 4.2.5.1  IR Traces of Ostracod Clay – Note the Reduction in the Carbonate Absorption After All Treatments

Fig. 4.2.7.1  Hydrogen Peroxide Treatment Produces no Significant Change in IR Spectra eg. no Oxalate Formation
4.3 Results of Firing Trials

4.3.1 Homogenised Silty Clay (Code 1-2) 800-1300°C.

The appearance of the bulk samples is shown in Ph.25. A progressive darkening from orange to brown associated with an increase in the top firing temperature is obvious.

Optical microscopy revealed that these materials were composed of what can best be described as a microcrystalline matrix. In contrast to normal geological-type specimens, these ceramic materials had virtually no readily identifiable discrete crystals - the only resolvable ones being scattered quartz grains.

XRD (fig.4.3.1.1) revealed that significant quantities of crystalline material were present, and that the amorphous component was relatively minor. The inference is that the crystals are in the main below the resolution of the optical microscope. An increase in the amorphous content does occur with increase in temperature (note change in the background level 2θ=15-30°), but this was not obvious under the optical microscope. Glass, being an isotropic material, does not rotate polarised light so that under crossed polarisers, in reflected light, the reflectivity ought to remain constant as the stage is rotated. With an isotropic material (eg non-cubic crystals) it varies slightly. Such changes, though slight, could be distinguished and suggested crystalline material was present.

Photographs 29-32 show typical areas. Orange-brown regions representing undisaggregated clay fragments set in a lighter yellow-orange matrix proved to be the dominant textural features. Some of these undisaggregated fragments contained dark red - reddish black spots (Phs. 29 & 31). Similar spots were also encountered in the
matrix. Aggregations of circular red - reddish black spots (Ph. 33) were also fairly numerous as were diffuse, bright red regions (Ph. 30).

Investigations using high-power oil immersion lenses revealed these red spots as polycrystalline. It was just possible to resolve very small crystalline particles. By inference the diffuse red regions, and probably the matrix colour, were derived from dispersed submicroscopic crystals. It was apparent that electron microscopy would be necessary to resolve these crystals.

It proved possible to produce features identical to the concretions of spots seen in Ph. 32 by firing iron sulphide nodules, extracted from ostracod clay and set in a kaolinite matrix, to the same temperatures (Ph. 36). This indicated that iron sulphides do not contribute significantly to the bulk colour - rather the oxide that is derived from them remains as discrete concretions of very small particles. The concretions are visible to the naked eye as dark red specks. The iron showed no significant evidence of reacting with the adjacent matrix - at least over the temperature range studied.

A similar test with siderite nodules extracted from silty clay gave similar results, suggesting the other type of dark red-black features (eg in Phs. 29 & 31), are derived from siderite. The nodules thermally oxidise on heating, forming hematite, but again the iron did not apparently react with the matrix.

The infrared spectra of fired silty clay are shown in figure 4.3.1.2. The spectrum at 950°C exhibits spectral features typical of quartz - and little else. With increasing temperature a progressive degradation occurs, with the spectra tending to become similar to those of fused silica. Little in the way of a mullite spectrum is evident.
The decrease in quartz and increase in amorphous material with increased firing temperature is evident in both IR and XRD traces.

4.3.2 Homogenised Ostracod Clay (Code 2-2) 800-1300°C

Bulk samples (Ph. 26) are generally similar to the silty clay ones, though they are slightly darker. Optical microscopy reveals a similar range of inhomogeneity and of microscopic features, eg red spots, diffuse red regions etc. Red spots derived from pyrite are more numerous than in the silty clay, as was to be expected. Occasional small yellow crystals were encountered but no such crystals were seen in the silty clay.

White areas, not seen in the silty clay, and presumably derived from calcite, are frequent (Phs. 37 & 38). It was noted that while the bulk samples looked darker than their corresponding silty clay ones, the matrix of disaggregated material seen during optical microscopy usually looked lighter in colour than the silty clay material. The reason for this apparent contradictory situation is not known.

Figure 4.3.2.1 shows the XRD traces of the fired ostracod clay, while figure 4.3.2.2 shows the corresponding infrared spectra. The IR spectra are slightly different to those of fired silty clay. In the case of silty clay, increasing temperature was associated with a general degradation of spectral features. In this case a progressive loss of quartz is accompanied by the development of new spectral features. These features are associated with the development of an anorthite-type phase, which appears in the XRD traces.
It did not prove possible to characterise accurately this new phase beyond anorthite-type triclinic feldspar because of the composite nature of many of the XRD reflections. It was evident, however, that while the basic structure was of anorthic type, discrepancies occurred between the reflection intensities of this phase and the JCPD index anorthites, along with minor differences in d values.

Anhydrite is also seen to be present in the lower temperature samples. This phase is presumably formed by the reaction of sulphurous gases, derived from the pyrite, with calcium oxide derived from calcite.

Firing trials using chemically treated samples of Warnham clays were well advanced before the results and implications of sections 2.4 and 4.2 were known. As the precise actions of these chemical treatments are uncertain and the existence of some side effects could be seen, it became apparent that the results of the extensive investigations planned for these materials would not be as useful as at first thought, so only the basic firing schedules were completed.

Despite the uncertain nature of the chemical extractions, a number of useful general points can be obtained by studying these fired samples. Basic results will therefore be included.
<table>
<thead>
<tr>
<th>I</th>
<th>Illite</th>
<th>(K,(H_3O))<em>{2-x} \ Al</em>{4-y} \ Fe_y \ \left[ \text{Si}<em>{6+y} \ \text{Al}</em>{2-x} \ \text{O}_{20} \right] \ \text{OH}_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>Kaolinite</td>
<td>\ Al_4 Si_4 O_{10} (OH)_8</td>
</tr>
<tr>
<td>Q</td>
<td>Quartz</td>
<td>SiO_2</td>
</tr>
<tr>
<td>C</td>
<td>Cristobalite</td>
<td>SiO_2</td>
</tr>
<tr>
<td>R</td>
<td>Rutile</td>
<td>TiO_2</td>
</tr>
<tr>
<td>P</td>
<td>Pseudobrookite</td>
<td>Fe_2 Ti O_5</td>
</tr>
<tr>
<td>S</td>
<td>Spinel type material</td>
<td>(Al-Fe-Si) O_4</td>
</tr>
<tr>
<td>M</td>
<td>Mullite</td>
<td>Al_6 Si_2 O_{13}</td>
</tr>
<tr>
<td>H</td>
<td>Hematite</td>
<td>αFe_2 O_3</td>
</tr>
<tr>
<td>An</td>
<td>Anhydrite</td>
<td>Ca SO_4</td>
</tr>
<tr>
<td>A</td>
<td>Anorthite</td>
<td>Ca Al_2 Si_2 O_8</td>
</tr>
<tr>
<td>T</td>
<td>Troilite</td>
<td>Fe S</td>
</tr>
<tr>
<td>Hr</td>
<td>Hercynite</td>
<td>Fe Al_2 O_4</td>
</tr>
<tr>
<td>F</td>
<td>Ferrocordierite</td>
<td>Fe_2 Al_4 Si_5 O_{18}</td>
</tr>
<tr>
<td>α</td>
<td>Corundum (contaminant)</td>
<td>αAl_2 O_3</td>
</tr>
<tr>
<td>?</td>
<td>Unassigned</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>γ Iron</td>
<td>γ Fe</td>
</tr>
</tbody>
</table>

Table 4.3.1

Abbreviations used to annotate the XRD traces in section 4.2

(Note: I and K will be in the dehydrated phase and will have lost almost all their water)
Figure 4.3.1.1  XRD traces of Fired Silty Clay (1-2)
Figure 4.3.2.1  Fired Ostracod Clay (2-2)
Fig. 4.3.1.2 Warnham Ostracod Clay - Note Spectral Development of Amorphous Silica Type Spectrum

Absorption features, in contrast to WSC (anorthite type)

Fig. 4.3.2.2 Warnham Silty Clay - Note Spectral Show Development of New Absorption Features
4.3.3 Dithionite Citrate Bicarbonate Treated Silty Clay (Code 1-3) 900-1300°C

The appearance of the bulk samples can be seen in Ph. 25. They are generally quite similar to ordinary silty clay (1-2) but up until about 1000°C they tend to be lighter in colour. Similarly, optical microscopy revealed a range of features, eg hematite derived from pyrite and carbonate nodules, Ph. 33. The matrix tended on average to be slightly lighter in colour than the untreated clay, Ph. 34.

The corresponding XRD traces can be seen in fig. 4.3.3.1. It is seen to be very similar to the untreated silty clay (fig.4.3.1.1), the same phases are present in both in similar quantities - even the unidentified material in the 1100°C sample.

4.3.4 Hydrochloric and Nitric Acid Treated Silty Clay (Code 1-4) 900-1300°C

The bulk samples are shown in Ph. 25. There is a general progression from off-white at 900°C to pale buff at 1300°C. An above average increase in this trend is perceptable between 1000 and 1050°C.

Below about 1000°C, optical microscopy revealed a white - pale yellow microcrystalline matrix which, with increasing temperature, became yellow until 1050°then gradually lost its yellow colour, becoming pale buff at 1300°C. Virtually the only features are fragments of undisaggregated clay, which tend to be slightly darker than the matrix (Ph. 35). Rare iron oxide concretions derived from pyrite nodules were seen.

The XRD traces (fig.4.3.4.1) reveal no hematite, unlike the previous materials. They also show that the increase in colour at
about 1050°C corresponds to the development of mullite and the final disappearance of the spinel type phase. The buff colour is probably due to Fe substituting into the mullite. Chemical analysis shows 3.31% iron oxide is present (table 4.2.2) and XRD shows mullite is virtually the only new crystalline phase present. Iron substitution is known to be common and to produce buff-coloured mullite (section 2.3.1.7).

The sample fired was found to contain cristobalite in addition to mullite - this was the only instance when this material was observed in fired Warnham clays. One additional difference between this sample and the others is the more marked development of amorphous material. The increase in background level between 2θ=15-30° is much more marked than in untreated silty clay fired to the same temperature.

Photograph 26 illustrates the bulk samples and their corresponding XRD traces are shown in fig.4.3.5.1. It seems as though the increased sodium content, due to the chemical treatment (0.33 cf 0.26%) combined with the lower calcium content, has significantly affected the high temperature phases that develop. As can be seen in Ph.26, material fired to 1300°C has undergone significant vitrification - it has 'melted' and this is probably associated with the increased sodium content. Sodium acts as a 'flux'.

In the untreated material an anhydrite-type material appears at about 950°C and progressively increases, reaching maximum development at about 1100°C before disappearing at about 1200°C. In this material no feldspar-like phase is evident until about 1150°C, when significant
and very rapid development occurs. It remains well developed up to at least 1500°C. Due to the composite nature of many of the XRD reflections and the possible presence of an additional unidentified phase, it has not proved possible to characterise this feldspar accurately, but it would appear to be a sodium-rich anorthite-type triclinic variety - no precise match with anything in the JCPDS index could be made.

4.3.6 Hydrochloric and Nitric Acid Treated Ostracod Clay (Code 2-4) 800-1300°C

The bulk samples are shown in Ph. 26 and the corresponding XRD trace in fig. 4.3.6.1. This material shows a similar reaction series to the corresponding silty clay version, (1-4). The chemical treatment has reduced the calcium content sufficiently to prevent anhydrite and anorthite formation. The only new crystalline phases that develop on firing are spinel and mullite. Optical microscopy revealed rare iron oxide concretions presumably derived from unextracted pyrite, Ph. 39.

4.3.7 Hydrochloric Acid Treated Ostracod Clay (Code 2-5) 900-1300°C

The colour of bulk samples can be seen in Ph. 26. Samples fired between 900-1000°C are a very pale pinkish-white colour. Between 1000 and 1050°C a dramatic colour change occurs and a pale brown colour develops that continues to darken up to about 1100°C. This is coincident with the appearance and disappearance of hematite in the XRD traces (fig. 4.3.7.1). Above 1100°C a sudden increase in porosity
occurs and the samples become slightly lighter in colour. The reason for the increase in porosity is not known, but it is probably an artifact of the chemical treatment. The bleaching is probably associated with iron dissolving in mullite.

Optical microscopy of samples fired below 1050°C reveals a yellowish matrix with occasional red-black spots derived from pyrite, Ph. 40. At 1050°C or above the matrix colour changes to brown. Porosity also increases.

As with the previous material, this acid treatment has reduced the calcium content sufficiently to prevent the formation of anhydrite and anorthite in the fired material.

Despite 'washing' this material still contains soluble iron compounds. These and other soluble salts tend to become concentrated at or near the surface during the drying stage of sample preparation. On firing this results in an iron oxide skin forming at the surface derived from the decomposed salts. This is just visible on the low temperature samples in Ph. 26. Soluble salt concentration is also a probable cause of the colour zoning seen in the sample fired to 1100°C (Ph. 26).

4.3.8 Fluoride Treated Hydrocycloned Silty Clay

A fluoride extraction technique (3.5.7) was used in trial experiments to see if it could enrich clay samples in illite and dioctahedral vermiculite. As described in section 2.4.7., it is in reality an artificial weathering process and it was thought it could have unwanted side effects when the material was fired. Preliminary firing trials appear to have confirmed this.
The XRD trace of fluoride-treated silty clay fired to 1050° is shown in fig. 4.3.8.1. Compared with the untreated sample it gives the appearance of being fired to a higher temperature (see fig. 4.3.15.3). It is seen to have a significantly lower quartz content than the untreated material and substantially more mullite. The amorphous content is also higher. The iron oxide content, however, is lower. While this is normally observed in material fired to higher temperatures in this case it is probably at least partially due to the removal of interlayer iron from the raw clays.

A number of small unidentified peaks are present in the XRD trace, suggesting at least one new phase not seen in the untreated material has developed. It did not prove possible to match conclusively any of the following peaks with any material in the JCPDS index:

<table>
<thead>
<tr>
<th>2θ</th>
<th>d (Å)</th>
</tr>
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<tbody>
<tr>
<td>18.28</td>
<td>4.853</td>
</tr>
<tr>
<td>19.00</td>
<td>4.671</td>
</tr>
<tr>
<td>19.72</td>
<td>4.502</td>
</tr>
<tr>
<td>37.42</td>
<td>2.403</td>
</tr>
<tr>
<td>44.33</td>
<td>2.043</td>
</tr>
</tbody>
</table>

4.3.9 Acid Ammonium Oxalate Treated Hydrocycloned Silty Clay

Figure 4.3.8.1 also shows the results obtained when material treated with a similar extraction technique - acid ammonium oxalate (3.5.8) is used. This extraction method is also capable of extracting interlayer material from the illite-vermiculite clay.

The results obtained in the preliminary trials were very similar to those obtained when fluoride was used. The decrease in quartz and
increase in mullite and amorphous content, compared to the untreated material was not so marked though. Surprisingly, as with the fluoride-treated material, a number of small unidentifiable peaks appeared, in similar positions. The values obtained in this case were the following:

<table>
<thead>
<tr>
<th>2θ</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.28</td>
<td>4.853</td>
</tr>
<tr>
<td>18.95</td>
<td>4.683</td>
</tr>
<tr>
<td>19.68</td>
<td>4.511</td>
</tr>
<tr>
<td>44.72</td>
<td>2.024</td>
</tr>
</tbody>
</table>
Figure 4.3.3.1  Fired D.C.B. Treated Silty Clay (1-3)
Figure 4.3.5.1  Fired D.C.B. Treated Ostracod Clay (2-3)
Figure 4.3.6.1
Fired HCl-HNO₃ Treated Clay (2-4)
Figure 4.3.7.1
Fired HCl Treated Ostracod Clay (2-5)
Figure 4.3.8.1  Treated Hydrocycloned Silty Clay Fired at 1050°C
Side effects associated with the chemical treatments were evident in most of the samples.

As mentioned in section 4.2, the sodium content of the DCB-treated clays (1-3) and (2-3) is significantly higher than that of the untreated clays (200% & 42% respectively). Sodium acts as a flux and tends to increase glass formation. The treated ostracod clay appears highly vitrified by 1300°C (Ph. 26) but surprisingly the XRD trace (fig.4.3.5.1) suggests only a moderate amorphous content, showing instead a high sodium-rich anorthite content. (See 4.2.5).

Water-soluble salts are still present in the treated materials. During the drying of wet moulded samples, they are concentrated at or near the surface of the samples. This gives rise to differences in colour. A surface skin of iron oxide developed on HCl treated ostracod clay samples—it was formed by the thermal oxidation of water-soluble iron salts.

Internal zoning effects were also encountered and are most marked in HCl-treated ostracod clay (Ph. 26). It is also evident to a lesser extent in DCB treated clays.

An effect which is probably related was seen during optical microscopic examination. A 'streaking' effect was often evident in DCB and HCl treated clays. Regions of matrix were observed with slightly different colours, which suggested uneven mixing of partially and fully treated material.
None of the previous specimens showed any sign of the black core seen in commercial bricks (Ph. 1). An intact sample of silty clay included with one of the batches fired to 1050°C, however, was found to contain a black core in some of the fragments (Ph. 41).

XRD revealed that the outer red material was similar to disaggregated silty clay (fig.4.3.1.1). The core, though, was found to be composed of a hercynite-type spinel (eg section 4.3.16), along with quartz and subsidiary mullite, similar to figure 4.3.16.1.

Bulk chemical analysis showed that both had normal silty clay bulk compositions. (eg Table 4.2.2). There was essentially no significant chemical difference between them. (Note: analysis technique does not distinguish between oxidation states.)

Optical microscopy revealed the outer red material to be very similar to the homogenised clay. There was none of the features caused by the contrast between dispersed clay and undisaggregated material, of course, but other features, such as a microcrystalline matrix and polycrystalline iron oxide concretions derived from siderite and pyrite, were seen. The black core was significantly different. It consisted of an almost clear optically isotropic material. It gave what was later found to be a false impression of containing significant numbers of small but resolvable crystals. (See 4.3.16). The core was also much more porous. Both regions were found to have small quartz grains.

The transition between the two types was somewhat variable. As in Ph. 42 it was sometimes relatively sharp and was marked by a thin zone in which the normal orange-red microcrystalline material changed first to brown and then to black before rapidly becoming essentially
colourless. The 'colourless' material in fact had a slight greyish cast. Pores in the core, especially near the transition zone often had a black rim. In other cases the brown-black transition zone could be quite broad. In some regions there was no black material at all, the colourless material apparently changing to brownish-orange.

In this region, as in others, one gained the impression that the brown-orange colour was exsolving/precipitating out of the colourless material. In many cases, material was seen that had replaced its slightly grey cast with a brown one. Such translucent brown-orange material is seen in Ph. 43. Moving towards the outer edge of the zone, the brown-orange material gave way to the more normal orange-red matrix.

The use of oil-immersion lenses suggested that very small crystals, presumably iron oxide, were precipitating within the clear spinel-rich material. The iron in the spinel was Fe$^{2+}$, while the oxide was Fe$^{3+}$. Therefore the change is associated with an oxidation process.

4.3.12 Argon Atmosphere Firings

The results obtained from the previous sample indicated that the black core of commercial bricks is in some way associated with non-oxidation (of Fe$^{2+}$) during the firing process. Firing trials in an inert atmosphere were undertaken to establish what the course of chemical reactions would be if oxygen were excluded.
Samples of Warnham silty clay and some of its chemically treated versions were fired in an atmosphere of pure argon (see 3.6.1). Photograph 28 shows the appearance of the bulk samples, while figure 4.3.12.1 shows the corresponding XRD traces.

The untreated silty clay can be seen to contain quartz and a small quantity of mullite. Significant development of a cubic hercynite-type Al-Fe spinel is also evident. The (400) reflection gives a d value of 2.0294Å. This is equivalent to a unit cell size of a=8.118Å. (The other peaks are composite ones - they overlap with other phases and are therefore unsuitable for unit cell calculations.) Hercynite has a unit cell range of about a=8.113-8.119Å and like all spinel solid solutions it varies slightly with composition.

One small peak at 32.50°, equivalent to d=2.755Å, could not be positively attributed to any known phase.

The DCB-treated silty clay (1-3) proved to have a very similar mineralogical composition to the untreated material, virtually the only differences being the slightly higher 'amorphous' background. The unidentified peak was not seen in this case.

The hydrochloric and nitric acid treated silty clay (1-4) was, surprisingly, also black in colour. When fired in air its low iron content generated a cream, rather than red colour.

XRD revealed that it contained slightly more quartz and mullite than the untreated clay, while the amorphous content, as indicated by the background level between 2θ=15-30° is noticeably higher. Perhaps most significantly, reflections consistent with a moderate development
of a cubic phase are again evident. The only clear, strong, non-composite peak from this phase is at 44.65°, which would correspond to a unit cell of \( a = 8.117 \text{Å} \). This again would be consistent with an Al-Fe spinel (hercynite=8.113-8.119Å).

One significant difference between this material and the hercynite-type spinel found in the untreated clays is that normally the (311) reflection at about 36.20° is the strongest reflection, while the (400) is of moderate strength. In this case the situation appears to be reversed, the (400) appearing as the main reflection. This would suggest a fairly important crystallographic difference between the two, eg cations or vacancy distribution differences or perhaps even different composition, though one would expect the latter to be associated with changes in unit cell size as well.

### 4.3.12.2 Argon Fired Silty Clays Refired in Air

Samples of the above materials were refired to 1000°C in air, in order to study the effect of subsequent oxidation. Photograph 28 shows their appearance. As expected, the untreated material was converted to a state not vastly different from the normal air-fired material. The HCl-HNO₃ treated material (1-4), though, unexpectedly developed a pink-red surface colour. The bulk of iron present apparently did not dissolve in the mullite as occurred when this material was fired solely in air. Rather, when the spinel phase broke down, it crystallised as \( \alpha \text{Fe}_2\text{O}_3 \).
4.3.13.1 Argon-Fired Ostracod Clays

The mineral assemblage in argon-fired homogenised ostracod clay (2-2) is relatively similar to that in the air-fired samples (fig. 4.3.13.1). Quartz, anorthite and mullite are the main crystalline components. There is some evidence for minor anhydrite development. The bulk of the pyrite, though, appears to have been converted to troilite - another iron sulphide phase.

As with the HCl-HNO₃-treated silty clay, a cubic spinel phase with (400) as the major reflection is evident. The (400) reflection in this case suggests a unit cell size of a = 8.109Å for the cubic phase - again the multiple component nature of the sample precludes any truly accurate unit cell measurement.

The DCB-treated material (2-3) gives a significantly different mineral assemblage from the untreated ostracod clay. The chemical treatment has reduced the calcium content, so no significant development of either anorthite or anhydrite is possible. The pyrite has in consequence given rise to troilite, and not anhydrite and iron oxide.

Significant development of a cubic phase has again occurred, and unlike the untreated clay, the reflection intensities are closer to 'conventional' Al-Fe spinel - though minor discrepancies in d values and intensity do still exist. Its reflections however, have a different character to all the other instances of spinel development. The peaks (listed below) are generally sharper and a (111) reflection is seen for the first time. The (400) reflection at 44.7° has a distinct shoulder (45.05°) which suggests that this peak may in fact be a composite one - ie an additional phase is present.
The HCl-HNO₃ treated ostracod clay (2-4) is found to contain noticeably greater quantities of quartz, mullite and amorphous material than the untreated ostracod clay. Again a cubic phase is seen with a strong (400) reflection and broader, weaker (311) and (220) ones.

In addition, one unidentified peak at 43.4°, equivalent to d=2.084 is seen. This peak could be due to either troilite or contaminating αAl₂O₃, but the other peaks for both phases are not sufficiently developed for positive identification. The quartz peak at 45.63° (d=1.998Å) is slightly out of position and is stronger than expected. This indicates that another unidentified reflection is present. It is not known if these two unattributed reflections belong to the same phase or not.

The argon-fired HCl treated ostracod clay (2-5) contains mostly quartz and mullite. This chemical treatment removed calcite but not pyrite from the unfired clay. As a consequence, neither anorthite nor anhydrite is formed on firing. The pyrite again changes to troilite.
As before, a cubic phase with a strong, sharp (400) reflection and weaker, broader (220) and (311) reflections is found.

<table>
<thead>
<tr>
<th>$\theta^\circ$</th>
<th>d(Å)</th>
<th>hkl</th>
<th>a(Å)</th>
</tr>
</thead>
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<td>7.99</td>
</tr>
<tr>
<td>37.30</td>
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<td>7.99</td>
</tr>
<tr>
<td>44.70</td>
<td>2.027</td>
<td>400</td>
<td>8.11</td>
</tr>
</tbody>
</table>

4.3.13.2 Argon-Fired Ostracod Clay Refired in Air

As with the silty clay, samples of the above materials were refired in air to 1000°C in order to see the effect of subsequent oxidation. Photograph 28 shows their appearance.

Again, most were converted to a state not vastly different from their air-fired counterparts. Sample 2-4, like sample 1-4, developed a pink colour and did not revert to the normal cream colour. The iron present did not dissolve in mullite as it did during normal firing, but precipitated out as $\alpha$Fe$_2$O$_3$.

4.3.14 Vacuum-Fired Clay

A similar experiment to that of 4.3.13 was undertaken, this time firing the samples in a vacuum furnace, to 1050°C at a dynamic pressure of $1 \times 10^{-3}$ torr.

The appearance of the samples and those subsequently refired to 1000°C can be seen in Ph. 28. Figures 4.3.14.1 - 2 give the
Chemically Treated Silty Clay Fired in Argon at 1050°C
Figure 4.3.13.1  Chemically Treated Ostracod Clay Fired in Argon at 1050°C
Figure 4.3.14.1 Chemically Treated Silty Clay Fired in a Vacuum (1x10^{-3}torr) at 1050°C
Figure 4.3.14.2 Chemically Treated Ostracod Clay Fired in a Vacuum (1x10^{-3} torr) at 1050°C
corresponding XRD traces. It is seen that the results are almost identical to those of the argon firing trial. Virtually the only detectable difference is that the unidentified peak found in the argon-fired homogenised silty clay is not found in the corresponding vacuum-fired material.

4.3.15 WSC-H (Dry Pressed) Air 800-1300°C

These samples (Ph. 27) were produced primarily for TEM examination. Hydrocycloned material was used so as to concentrate the clay minerals and reduce the unwanted components such as quartz. They were dry pressed in an attempt to reduce porosity.

Optical microscopy revealed only a microcrystalline matrix of the type described in section 4.3.1. No features due to undisaggregated clay fragments of siderite nodules were seen, as these had been removed by the hydrocyclone. (Ph. 44)

Figures 4.3.15.1 - 3 show the corresponding XRD traces. The trend is very similar to that in homogenised silty clay - the main difference being the lower quartz content. Crystal lattice parameters of the mullite in the 1200°C material were measured to act as a check for TEM microchemical analysis results (section 4.4.12). The (041), (401), (331), (002), (250), and (520) reflections were used along with the standard orthorhombic formula:

\[ 1 = \frac{h}{a} + \frac{k}{b} + \frac{l}{c} \]

Initial estimates were made using (002) for c and (041) and (401)
for a and b. Refined estimates of a and b were made using (250) and (520). Average values of a and b were then used with (331) to give a value for c. Two separate runs were made and the following mean values obtained:

Mullite 1200°C

\begin{align*}
a & = 7.5710 \pm 0.0006\text{Å} \\
b & = 7.7247 \pm 0.0006\text{Å} \\
c & = 2.9889 \pm 0.00005\text{Å}
\end{align*}

Detailed comparison of the iron oxide peaks were also made. The change in height and broadness (fig.4.3.15.4) was consistent with either an increase in quantity or in crystalline size or both. (Note - XRD is relatively insensitive to crystallite size changes between 100-1000nm, being most effective for 5-100nm changes.)

It was evident from the results of the TEM investigation that a significant proportion of the Fe₂O₃ was the γ rather than the normal α form (section 4.4.4) The XRD traces, however, do not reveal the presence of γFe₂O₃ - some of the major reflections of the two forms are quite similar but the characteristic γ peaks (eg 220=2.95Å) were absent. See figures 4.3.15.1 - 3.

Maghemite - γFe₂O₃ is ferrimagnetic. It proved possible to concentrate a ferrimagnetic fraction from fired hydrocycloned silty clay by causing a suspension of finely ground material to settle/sediment through a magnetic field.

Figure 4.3.15.5 illustrates the XRD trace of this ferrimagnetic fraction, compared to the normal starting material. The relevant d
values are shown in table 4.3.15.1. The fraction is enriched in αFe₂O₃. Though some peaks could have 'contributions' from γ reflections, the characteristic γ peaks still cannot be seen, even though it must be present, as the fraction is ferrimagnetic and αFe₂O₃ is not. It did not prove possible to identify positively let alone obtain any crystal lattice dimensions for γFe₂O₃ using XRD. It must be assumed that despite its frequent appearance in TEM, the γ form is not sufficiently developed to give strong XRD reflections.

One point of interest is the presence of reflections at 37.20° and 43.20°. Reflections with similar values (37.82=2.379Å / 43.40=2.085Å) are seen in many of the other traces and can generally be assigned to minor contamination with αAl₂O₃ derived from the ball mill used to prepare the XRD powders. In this case though, initial contamination is probable; it could reasonably be expected that it should have been removed by the separation technique used. Whilst it is possible that αAl₂O₃ is a genuine reaction product of fired Warnham clays, it is unlikely, for corundum does not usually form in the presence of free silica. It should be noted that there is also a slight difference in values between these peaks and αAl₂O₃. One must consider that the 43.20°reflection could be due to an above average intensity (202) αFe₂O₃ peak, possibly with a contribution from a γ(400) reflection. (As shown in table 4.3.15.1, some of the other peaks could have γ components.)

An interesting feature of the XRD trace of the magnetic fraction is that it has a lower background in the 2θ=20-30° region than the starting material. This indicates less amorphous-microcrystalline material is present and is probably a feature of the fractionation.
<table>
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<th>2θ</th>
<th>(Å)</th>
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<th>γFe₂O₃</th>
<th>Mullite (Tet.)</th>
<th>Mullite (Cubic)</th>
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<td>1.4531</td>
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<td>300</td>
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Table 4.3.15.1

Iron oxide reflections from the ferri-magnetic fraction.

Showing possible assignments and probable composite nature of the iron oxide reflections in fig.4.3.15.5. Note γFe₂O₃ can be tetragonal or cubic, hence a double set of hkl notations.
Figure 4.3.15.1  Fired Hydrocycloned Silty Clay (WSC-H)
Figure 4.3.15.2  Fired Hydrocycloned Silty Clay (WSC-H)
Figure 4.3.15.5

(X) Warnham Silty Clay (WSC-H) Fired at 1050°C
(Y) Magnetic Fraction Extracted From (X)
A set of dry pressed WSC-H samples identical to those in 4.3.15 were fired in an argon atmosphere to establish the nature of the reactions in the absence of oxygen. These too were intended mainly for TEM work.

The bulk samples are illustrated in Ph. 27, while the corresponding XRD traces are seen in figures 4.3.16.1 -2. Like the other non-oxidised material, the crystalline component of these samples consists mainly of a spinel-type phase and subsidiary mullite, with ferrocordierite appearing at higher temperatures. Both hernycite and ferrocordierite contain ferrous iron - it had not been oxidised to Fe\(^3+\) during firing.

Detailed crystal lattice measurements on the sample fired to 1050 °C using the techniques described in section 3.7 and standard analysis techniques for cubic materials, gave a value of

\[ a = 8.1349 \pm 0.0079 \text{Å} \]

for the cubic material. This corresponds closely with the Al-Fe spinel - hernycite. While the JCPDS index quotes values in the range \[ a = 8.113 - 8.119 \text{Å} \] for the unit cell size of hernycite, one major reference work, Deer et al.,(1968), gives a value of 8.135Å.

The admittedly rougher estimates done on the cubic phase obtained with homogenised and chemically treated silty clays consistently gave values near the JCPDS quoted values, while the values obtained using hydrocycloned clay (an enriched 'purer' fraction) consistently gave larger values - nearer that quoted by Deer et al.

It is worth noting that both ranges of values found in this study are very close to the two ranges quoted in the literature under the name of hercynite. It is probable that the difference reflects a
slight chemical compositional difference between the two types and perhaps a different structural ordering of cations and vacancies.

Photograph 44 shows the typical appearance under the optical microscope. The isotropic, almost colourless material at first sight appeared to contain relatively large 'crystals'. The TEM results, however, showed this to be a false impression - the apparent crystal grains are not true single crystals at all. They are composed of essentially colourless submicroscopic crystals in a colourless amorphous matrix. The slight grey cast these particles exhibit is probably due to submicroscopic coloured crystals. Occasional genuine small crystals with a silver metallic appearance were seen (Ph. 44).

4.3.17 Hydrocycloned Silty Clay – Oxygen Deficient Atmospheres

A series of dry pressed hydrocycloned silty clay samples identical to those in the previous experiments were fired in a range of oxygen deficient atmospheres, to ensure that the results obtained in 4.3.15 were related to the oxygen deficiency and not to any reaction with argon. The XRD traces of these specimens are shown in figure 4.3.17.1.

It can be seen that firing in nitrogen produced a composition identical to the corresponding argon sample. The sample fired in a vacuum exhibits a slightly lower quartz content than the corresponding argon samples. It also has a moderate ferrocordierite content. Both these features are found when the material is fired to a higher temperature in argon. Combined, they are indicative of a more advanced state of reaction, suggesting the reactions occur at a lower temperature when material is fired in a 1x10 torr vacuum.
The sample fired in forming gas reveals the compositions of the material if fired in a reducing atmosphere as opposed to a neutral or oxidising one. This sample was inadvertently fired to a slightly higher temperature than the others (ie 1080 cf 1050). This may be partially responsible for the decrease in crystalline silica. Overall, the mineralogical composition is similar to the other non-oxidised material.

Yet at least one 'new' phase is present, for otherwise unattributed peaks are found at $\theta = 43.60$ and 50.78°. No conclusive direct match with any materials in the JCPDS index could be made. However, it seems that the material in question is probably the high temperature form of iron - ie $\gamma$Fe. Barrett and Massalski (1980) give the unit for $\gamma$Fe as F.C.C. with $a=3.6468\,\text{Å}$. If this material is assumed to be F.C.C., as indicated in the following table, then the unit cell is $\approx 3.5956 \pm 0.0002\,\text{Å}$. This is slightly smaller than the quoted value but this attribution is supported by the fact that tests revealed the fired material does contain a small quantity of magnetic materials and the lines for other alternatives, such as $\alpha$Fe or Fe$_3$O$_4$ are absent. Precisely why the unit cell size in this instance appears a little low and why the phase did not invert to the normal $\alpha$ polymorph at 911°C is not known.

<table>
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<tr>
<th>$\theta$</th>
<th>$d,\text{Å}$</th>
<th>hkl</th>
<th>$a,\text{Å}$</th>
<th>$a \bar{x}$</th>
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</thead>
<tbody>
<tr>
<td>43.60</td>
<td>2.0758</td>
<td>111</td>
<td>3.5958</td>
<td>3.5956 ± 0.0002</td>
</tr>
<tr>
<td>50.78</td>
<td>1.7979</td>
<td>200</td>
<td>3.5954</td>
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</table>

The peak at $44.65^\circ d=2.0294\,\text{Å}$ is slightly stronger than would be expected for hercynite alone, suggesting that it may be a composite peak with a contribution coming from an additional unidentified phase. It is also possible that it could represent a similar cubic phase to that seen in some of the chemically treated argon fired clays, where the (400) reflection, not the (311) is the strongest.
Figure 4.3.16.1  Hydrocycloned Silty Clay Fired in Argon
Figure 4.3.16.2 Hydrocycloned Silty Clay Fired in Argon
Figure 4.3.17.1 Hydrocycloned Silty Clay Fired in N<sub>2</sub>, A and a Vacuum at 1050°C and in N<sub>2</sub>:H<sub>2</sub> at 1080°C
Firing trials in air and nitrogen, using hydrocycloned ostracod clay were undertaken. As can be seen in figure 4.3.18.1, the mineral assemblage is similar to the untreated ostracod clay (figs. 4.3.2.1 & 4.3.13.1), when allowance is made for the reduction in calcium, silica and iron sulphide content due to the partial removal of calcite, quartz and pyrite. This is manifested mainly as a lower anorthite and anhydrite content in the air fired material, and a lower anorthite and troilite content in the nitrogen fired material. The cubic phase in the nitrogen fired material is similar to that previously reported for the ostracod clay, again the composite nature of most of the peaks precludes accurate unit cell size measurements but the following measurements were obtained.

<table>
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<th>2θ°</th>
<th>d(Å)</th>
<th>hkl</th>
<th>a(Å)</th>
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<td>1.4266</td>
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<td>8.070</td>
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Despite the significant differences in mineralogy between this ostracod material and the silty clay, the colour of the bulk specimens is very similar. It was decided to direct the main TEM investigation at the simpler situation prevailing in the silty clay. As a consequence, the detailed description of these samples is not considered necessary beyond pointing out the similarity in colour, despite the mineralogical differences.
Figure 4.3.18.1  Hydrocycloned Ostracod Clay (WOC-H) Fired in Air, \( \text{N}_2 \) at 1050°C
Ph. 25  Results of firing trials on Warnham Silty clay, code as in Table 3.5.2.1

Ph. 26  Results of firing trials on Warnham Ostracod clay, code as in Table 3.5.2.1
Ph. 27  Results of firing trials on dry pressed hydrocycloned Warnham Silty Clay.

Ph. 28  Results of firing trials on 'wet moulded' Warnham Clay.
Vacuum = 1 x 10^{-3} torr, R1000 represents material refired in air to 1000°C.
See text for discussion - code as in Table 3.5.2.1
Illite was the dominant clay mineral in the TEM samples, though this could be due to the specimen preparation techniques used. XRD had revealed that the illite was generally of a smaller particle size than kaolin, so it may have become concentrated in the fraction of clay suspension used - i.e. from the mid depth of a sedimenting solution.

Examination of individual illite particles reveals some to be relatively well crystallised single crystals (Ph. 49). However, most appear to be composed of aggregates of yet smaller irregularly shaped platelets. Though the platelets often seem to be crystallographically similarly orientated, forming a dominant crystal orientation (entity) per particle, electron diffraction patterns from illite particles often have the appearance of a powder pattern (Ph. 47) indicating some mismatch. A typical illite particle seen in Ph. 51 is observed to show complex moire fringes when viewed in dark field, supporting this idea.

Due to the platy morphology of the crystals, the resultant orientation means that generally only hk0 reflections are obtained. The 'd' spacing values measured vary slightly from particle to particle as does chemical composition (Ph. 59, table 4.4.1.2). While some variation due to errors in measurement is to be expected, it seems probable that some of the variation in hk0 reflections is due to lattice variations, associated with impurities and isomorphous substitution. It is considered outside the range of this work to investigate this thoroughly.

The kaolinite is generally of moderately low crystallinity. Particles showing indications of hexagonal plate-like structures were
observed, some were single crystals while others were aggregates similar to the illitic ones. Again electron diffraction showed hk0 reflections only and again minor variations in d values were observed. Ph. 58 shows a typical kaolinite pattern.

Microchemical analysis of the clay particles indicated that they are all composed of Al, Si, K and Fe (tables 4.4.1.1 - 3). The Al and Si content of kaolinitic and illitic particles is apparently slightly different. The K content of kaolinite is lower, as expected. All analyses of kaolinitic particles revealed some iron. It was not possible to determine if it was present as an amorphous surface coating on the particles or was due to isomorphous substitution in the octahedral lattice sites.

Some particles indicated they were in fact aggregations of both kaolinitic and illitic materials. The selected area diffraction pattern obtained from some crystal had typical kaolinite d values. Microchemical analysis, however, indicated a moderately high K and Fe content, higher than would be expected for kaolinite and more like illite. Close examination of the bright field images revealed an indication of the presence of smaller platelets. So it appears that the kaolin particles are sometimes 'coated' with very thin illitic platelets. These platelets are apparently too thin to affect noticeably the diffraction pattern, but do affect the chemical analysis.

It would appear that very few of the particles observed were in fact true single crystals - particle disaggregation was not total. Microchemical analysis (table 4.4.1.3) suggests that kaolin and illitic materials were still often intimately intermixed.

XRD (fig.4.2.0.3) suggested a significant proportion of
metahalloysite was present in Warnham clay. Halloysite is typically tubular in habit, but tubular halloysite particles were very rare in the TEM samples. One can be seen in Ph. 48. There is a definite discrepancy between the amount of halloysite suggested by XRD and the number of 'typical' halloysite crystals seen. It is considered that the halloysite present is in a non-typical crystal habit. Non-tubular halloysite has been reported by Bates (1950) and it is possible, as suggested in section 3.4.6, that the halloysite present may represent an alteration product of the kaolin and thus have kaolin-type morphology.

Halloysite is chemically very similar to kaolinite, the main difference being H2O content, so it is not really possible to distinguish between them using microchemical analysis. Also, their hkO reflections are very similar and are not sufficiently characteristic. The halloysite and kaolinite present in Warnham clay are thus not readily differentiated in the TEM samples.

Other phases were seen in the unfired clay. The commonest was small grains of quartz (Phs. 45, 49, 55 & 59). Rutile was also relatively common (Ph. 57). Occasional crystals of calcium phosphate and a few rare earth phosphates were found. Rare yttrium-rich crystals were also observed (fig. 4.4.1.1). Surprisingly, however, no pyrite or siderite was encountered - the hydrocycloning and the sample preparation technique must have removed these components from these TEM samples.

The vacuum of the microscope apparently partially dehydrated the clay minerals, as expected, the associated changes in crystal structure producing minor changes in the a-b plane. Heat produced by electron bombardment during observation is likely to initiate further
dehydroxylation - the low thermal conductivity of these minerals prevents its dissipation.

Beam-induced damage is visible on the illite particle in Ph. 54. The spotty contrast is thought to indicate void formation - this is consistent with the dehydroxylation model described in section 2.3.1.1. The general mottled appearance of the clay particles may indicate very fine scale void formation caused by the vacuum - the voids formed in the beam-damaged regions may simply represent a 'more advanced development'.

Electron bombardment also has some other crystallographic effects, and often results in the redistribution of some strain fields and the initiation of new ones. In fact, care was necessary during observation because one frequently encountered the movement of dislocations and extinction contours.

Meandering extinction contours cut by dislocations can be seen in an illite particle in Ph. 49. (Diffraction conditions at the strain field around the dislocation line are different from those causing the extinction contour - hence the contour is cut and/or bent at the intersection. The complicated strain features in Ph. 57 are possibly due to aggregates of stacking faults.

THE SCALE BAR ON ALL THE TEM PHOTOGRAPHS IN THIS SECTION REPRESENTS 100NM.
Ph.45 Hydrocyloned Silty Clay
Ph.46 Kaolin Crystal plus illite
Ph.47 Typical Illite Diffraction Pattern
Note the Powder Type Rings
a=4.57  b=4.52  c=4.37Å

Ph.48 Tubular Halloysite
Ph.49 Well Crystallised Illite Crystal
Showing dislocations in lattice
Ph.50 Diffraction Pattern of the Illite Crystal
a=4.40  b=4.38  c=...
Note extinction contours interrupted by stacking faults in the kaolin crystal (1). Particle 2 is a rutile crystal.

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Table 4.4.1.1 Point analyses in Ph.57 (Wt% cation).

Ph.58  Kaolinite hko
from crystal 1.

a 4.590Å
b 4.537Å
c 4.434Å
Ph.59 Hydrocycloned clay on a formvar film.

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Table 4.4.1.2
Microchemical analyses in photograph 59.

N.B. Some analysis points are just off the photograph.
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Table 4.4.1.3.
Clay Particle Compositions (Wt% Cation)
FIG. 4.4.1.1 Unidentified Yttrium-rich crystal - ?decay product of radioactive heavy metal compound - Note Th etc.
Samples fired to 800°C still retain many of the characteristics of the unfired clay. The particles are similar in size and shape to those seen in the unfired material. As can be seen in Phs. 60-75, no vitrification has occurred. Kaolin crystals still maintain their hexagonal plate structure. Illite (Ph. 68) still has the irregular aggregate crystal habit seen in the unfired material. Even halloysite retains its tubular habit (Ph. 74).

Diffraction patterns correspond closely to the hk0 reflections of the unfired clays. Precise measurement of the d values, however, indicates that the a-b plane is slightly more distorted than in the unfired clay. The degree of distortion varies from particle to particle and no systematic trend could be identified.

Moiré fringes (in well-crystallised illite particles), due to the offset of the layers, are much more prevalent in this fired material than in the unfired material. Photographs 60-61 show a clear example - rotational moires are visible in both bright and dark field. The associated diffraction pattern (Ph. 62) reveals each spot to be associated with three orthogonal streaks due to the rotational displacement of successive crystal layers - i.e. disruption of c axis ordering. A less well developed and more typical example is seen in Phs. 64 & 65.

Some of the clay particles are beam-sensitive and still appear to be partially hydrated. As with the unfired material, beam damage seems to cause void formation. At high magnification (x 100k plus), indistinct contrast features suggest the widespread development of microvoids (~50Å diameter) as would be expected if dehydroxylation is associated with micropore formation.
Also just visible in the photographs is another form of speckled contrast features. Even after allowing for the fact that some of the mottled appearance of the particles and formvar film seen in the photographs is due to the amorphous carbon coating they were given, most of the particles seem to be more mottled than their unfired equivalents. This feature tends to be indistinct even at high magnification, yet it gives the appearance of being due to very small (<250Å) particles randomly distributed over the clay particles. They were too small for positive identification but microchemical analysis of groups of such particles showed a small increase in Fe content relative to adjacent points, indicating their probable cause is small microcrystallites of iron oxide derived from the oxyhydroxide coating.

The non-clay mineral components seen were unaffected by the firing. Photograph 73 shows a rutile crystal that still retains its original morphology and chemical composition. Quartz crystals were similarly unaffected.
Ph. 60 Well Crystallised Illite Showing Lattice Disruption

Ph. 61 Darkfield View

Ph. 62 Corresponding Diffraction Pattern
Note Streaks Corresponding to rotational moires.

Ph. 63 Rotational Moire Fringes Showing c axis Disruption in a 'well crystallised' Illite. Also note microparticles arrowed.

Ph. 64 Illite Showing c axis Disruption

Ph. 65 Corresponding Diffraction Pattern - Note Spots are Split
Ph.66  Kaolin Crystal Showing Hexagonal Morphology

Ph.67  Corresponding Diffraction Pattern - Still Shows Typical hk0 Pattern

Ph.68  Illite Particle Showing Typical Aggregate Structure. Also Note Microparticles arrowed.

Ph.69  Corresponding Diffraction Pattern. Shows Typical Illite hk0 Pattern though d values Indicate 'minor' changes due to dehydration
Ph. 70 "Illite" crystal
Al 18.78 Si 50.71 K 24.37 Fe 6.14

Ph. 71 Darkfield view. Note moire fringes showing c axis disruption.

Ph. 72 Corresponding diffraction pattern.

Ph. 73 Rutile Crystal (TiO₂)

Ph. 74 Halloysite Crystal plus Illite

Ph. 75 Corresponding Illite Pattern
Rings due to Aggregate Morphology.
4.4.3  800-950°C

Despite a number of attempts, it did not prove possible during the time allocated to produce TEM samples fired in this temperature range. No significant vitrification occurred in samples fired below 800°C. The material remained as discrete clay-sized fragments. Consequently such material could be dispersed onto a formvar film, producing a useful TEM sample. Material fired to 950°C or above underwent sufficient vitrification to fuse the material into a solid, though often highly porous, body, that had sufficient mechanical strength to be prepared as described in sections 3.2.4.1-2.

Between 800-950°C partial vitrification occurred, which resulted in clay crystals fusing into aggregates, producing slightly larger particles. These larger particles were generally electron opaque, and so little success was obtained with the dispersion TEM sample preparation technique. The powdery nature of the bulk sample precluded straight forward ion beam thinning as used for the more solid material.

Resin impregnation followed by ion beam thinning is the probable answer but was not perfected due to lack of time. The particles fell out of the thin resin foil during preparation.

4.4.4  950°C

Samples fired to 950°C had little mechanical strength. Consequently, TEM samples of this material were extremely fragile and difficult to prepare. It did not prove possible to undertake the same extensive examination given to the more robust, higher temperature material, as they tended to break up during routine handling and observation.
The microstructure of the 950°C material is very similar to that at 1000°C. Detailed description of new phase development is probably best done with reference to the 1000°C material, for which a more comprehensive range of examples is available. Only a brief description will be given here.

TEM examination revealed that structural breakdown of the clay minerals was almost complete at this temperature. Residual dehydrated clay minerals can be seen in Phs. 76 & 77. The bulk of the clay material appears to have broken down to a non-crystalline 'textured' phase.

One of the common new crystalline phases that has appeared takes the form of very small acicular crystals, or small rectangular crystals aligned end to end, forming needle-shaped structures (Phs. 76 & 79). The needles are commonly aligned subparallel, often over relatively large regions. Their orientation appears to have been derived from the original clay minerals.

As well as the dehydrated clays and the needle-like material, rectangular, hexagonal and irregularly-shaped crystals can be seen (Ph. 79). Relatively large crystals (ie 100nm plus) such as that seen in Ph. 79, proved to be Fe-Ti rich pseudobrookite type material (see later). Though sub 100nm crystals of this material were found, most of the smaller crystals, as seen in Ph. 79, were shown by microchemical analysis to be Ti poor Fe-Al compounds. This material had two common crystal habits: the smaller ones (<40nm) were generally hexagonal platelets; the larger ones tended to be rectangular or irregular in shape, though relatively large hexagonal ones were seen.
Ph.76 Residual Dehydrated Clay Minerals. Also New Acicular Spinel Development - arrowed

Ph.77 Residual Dehydrated Clay Minerals

Ph.78 Pseudobrookite (∼Fe₂ Ti O₅) Type Crystal With Smaller Fe-Al Oxides in Amorphous Matrix Al 6.0 Ti 40.1 Fe 53.9

Ph.79 Acicular Spinel Crystals and Fe-Al Oxides in Amorphous Matrix
The microstructure at 1000°C is much the same as that at 950°C, the main difference being that there are no residual dehydroxylated clay minerals. The crystalline phases that appeared at 950°C are present and are slightly better developed.

The main feature of the microstructure is the widespread development of subparallel orientated acicular crystals. They are typically <5nm in diameter and <75nm long. As seen in Ph. 81, the needles are found in what appears to be various stages of development; chains of very small rounded particles or small rectangular crystals are arranged end to end following the general trend of the main needle development. These structures appear to represent stages in the nucleation and growth of the acicular crystals. Though they appear to be nucleating out of a non-crystalline material, their orientation seems to be related to the orientation of the original clay minerals, suggesting that the non-crystalline material has a definite 'texture' if not a crystal structure. The increase in acicular crystals seen between the 950 and 1000°C samples is accompanied by a corresponding decrease in the non-crystalline matrix material.

Microchemical analysis of this phase was only partially successful. (It suggested, though could not prove, that they were Al-Si compounds with variable subsidiary K and Fe.) The acicular-rectangular crystals proved to be too small to be analysed individually without analysing adjacent material - even using a 4nm spot size.

Similarly, microdiffraction was only partially successful, with the crystals again being too small for diffraction experiments on individual crystals. Diffraction of groups of crystals generally produced powder type ring patterns as shown in Ph. 85. The d spacings
were compatible with a spinel type cubic crystal structure. Slightly larger cubic-rectangular shaped crystals (Ph. 84) were also found. Microdiffraction and microchemical analysis suggested they too were spinel type Al-Si compounds, possibly with subsidiary K and Fe. (They too were too small for definitive analysis.)

Microchemical analysis was more successful at identifying some of the other crystalline phases present. Analysis of small crystals of unknown composition set in a matrix of unknown composition poses significant problems (see section 3.2.3), especially when some at least of the elements present are likely to occur in both materials. One simply cannot distinguish between X rays generated in the crystal and those from the matrix. The problem was most easily overcome by deliberately introducing a selection bias during the microchemical investigations. Analyses done using a high voltage and small spot size were restricted, where possible, to relatively large crystals near the edge of the sample. It was recognised that this selection bias could lead to errors, if, for example, the large crystals had a different composition from the smaller ones. Such a situation was found to exist, but was identified.

Relatively large crystals (>100nm) such as that in Ph. 94 proved to be Fe-Ti rich material which was shown by selected area diffraction to give a pseudobrookite type crystal structure (Phs. 95-98). Other smaller examples are shown in Ph. 89. Relevant analyses are given in table 4.4.5.1 and fig. 4.4.5.4.

Figure 4.4.5.1 shows the results of all the microchemical analyses of Fe-Ti-Al compounds for the 1000°C sample. Two distinct sets are easily identified. The Ti rich pseudobrookite type material, though generally of a larger crystallite size, was the rarer of the two. Crystals of the second, more numerous type rarely exceed 125nm in
diameter (Ph. 93). As can be seen in figure 4.4.5.1, the Ti content of this group was typically less than 5 Wt% cation. The Fe-Al content on the other hand was quite variable with a maximum range of 66.08 Wt% Al, 33.15 Wt% Fe to 0.96 Wt% Al , 95.47 Wt% Fe. Though there is a definite bias towards the iron-rich end, there is no obvious break in the sequence, indicating a fairly uniform gradation between the two. It resembles a solid solution series.

It was found that the Al-Fe ratio can vary significantly even within one crystal. The twinned crystal shown in Ph. 92 was found to have twins with significantly different Al and Fe contents (table 4.4.5.1 and figs. 4.4.5.3-4).

Crystallographically this 'group' proved to be somewhat more complex. Hexagonal plate-like crystals, eg Ph. 90, typically gave diffraction patterns with d values equivalent to Fe₂O₃ (hematite). Some of the rectangular iron-rich crystals could be indexed on a cubic system while others, such as the twinned crystal shown in Phs. 86-88 yielded diffraction patterns that suggested it is tetragonal with a cubic subcell. It is neither perfectly cubic nor perfectly tetragonal and appears to be intermediate - the angular arrangement of the spots is not quite compatible with either system. The material seems to be γFe₂O₃ (maghemite) - the d values are within the errors of measurement expected and this material is known to exist in cubic, tetragonal and intermediate forms (JCPDS card no.15-165). Some rectangular crystals with an αFe₂O₃ structure were also found.

Many of the iron oxide particles showed complex moire fringe patterns, indicating their internal structure is disrupted (Ph. 83). Diffraction patterns of such crystals are usually combined spot and ring patterns, and not infrequently d values corresponding to both α and γFe₂O₃ are found in the same pattern.
Visible in Ph. 82 is a region of orientated chain-like features described earlier. Also visible, superimposed on this structure, are three rather indistinct sets of large needle-like crystals 20nm in diameter and 150nm long. One weakly developed set lies subparallel to the trend of the finer chain-like structure, the other two sets can just be distinguished lying at 60° to each other and this set. No iron oxide crystals occur in this area. Comparison with specimens fired to a higher temperature (see following sections) suggests this represents the beginning of orientated mullite development from a kaolin crystal. Needle-shaped crystals slightly larger than those previously described can be seen in Ph. 94 and apparently represent the early stages of 'random' mullite crystallisation.

The only other phase present in significant quantities is quartz - an example of which can be seen in Ph. 94. Some vitrification appears to have taken place at the surface of the quartz crystal and the grain is now fused with the non-crystalline matrix.

Also visible in Ph. 94 is a crystal of calcium silicate (fig. 4.4.5.3). It was beam-sensitive and damage caused during microchemical analysis is visible in the photograph. Diffractional evidence was insufficient to identify the actual polymorph - only one d spacing (3.084Å) could be obtained (=dark field view, Ph. 98). One or two other minor components were also observed. Just visible in Phs. 94 & 98 is one of the few rutile crystals found in the fired material. The crystal was 'twinned' but only one of the apparent twins was pure TiO₂, the other being pseudobrookite (~Fe₂TiO₅).
Figure 4.4.5.1
Oxide Compositions for 1000°C (Wt% Cation)
Figure 4.4.5.2
Titanium Rich Oxides
- 1000°C (Wt% Cation)
Orientated 'spinel' crystals in amorphous matrix. Note pseudobrookite crystals and early Fe₂O₃ crystal development.

Early stages of irregular Fe₂O₃ growth - note irregular moiré fringes.

Orientated spinel crystals and preliminary development of mullite.
Ph.86 Twinned \( \{\text{Fe}_2\text{O}_3\} \) crystal similarly orientated to the 'spinel' crystals

Ph.87 Tetragonal with cubic subcell. Mean \( a = 8.368 \text{Å} \) \( \{310\} \) arrowed \( d=2.695 \text{Å} \)

Ph.88 Corresponding \( \{310\} \) darkfield view

Ph.89 Typical area showing orientated spinel and \( \text{Fe}_2\text{O}_3 \) crystals. See table 4,4,5,1
Ph.90  αFe₂O₃ crystal. Note moire fringes showing misaligned crystal structure

Ph.91  Corresponding diffraction pattern. Note split spots due to offset crystal lattice. 2.533Å = \{110\}  αFe₂O₃

Ph.92  Variable composition twinned γFe₂O₃ crystal. Analyses table 4.4.5.1

Ph.93  αFe₂O₃ crystals in amorphous matrix
Area showing subsidiary phases - SiO₂, pseudobrookite, rutile and calcium silicate.

Diffraction pattern of pseudobrookite
- a = 2.894Å [230]
- b = 10.044 {001}
- c = 3.497Å {220/101}

Darkfield view {001}

Diffraction pattern
- a = 2.076Å
- = 2°
- d = 3.518Å

Darkfield view of calcium silicate
Ph.99 Fe₂O₃, spinel and mullite crystal in amorphous matrix.

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Table 4.4.5.1
Microchemical analyses
(Wt% Cation)
Ph. 84
Orientated 'spinel' crystals.

Ph. 85
Diffraction pattern from 'spinel' crystals.

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f = faint rings from adjacent material, eg. \( \alpha \)SiO\(_2\), camera length = 794 \( \pm \) 15.9 hence SD. Unit cell size mean = 8.0885 \( \pm \) 0.0543 Å

Table 4.4.5.2
Fig. 4.4.5.3  

a-c show the variable Al-Fe composition within one twinned crystal (Ph. 92)  
d - the chemical analysis of the calcium silicate zone in Ph. 94  
(see table 4.4.5.1)
Fig. 4.4.5.4 Analyses reveal a range of 'oxide' compositions.
The very small acicular spinel crystals seen in the previous sample have declined greatly in number and only residual traces of them are left, eg Phs. 101 & 103. It should be noted that most of those that do remain are slightly larger than those seen in the previous sample.

Mullite development which was just starting in the previous sample can be seen to be well in progress, though the degree of crystallisation is variable from area to area (ie original clay flake to clay flake). The mullite seen in Phs. 130-2 is for example less well crystallised than that in Ph. 133. In both examples three sets of mullite can be distinguished, each at 60° to the others. They would appear to be more advanced stages in the development of orientated mullite first observed at 1000°C (Ph. 82). Diffractional evidence, eg Phs. 131 & 134, indicated that these crystals were normal mullite but microchemical analysis generally gave Si values significantly outside the solid solution range possible for mullite. A small number of analyses showing typical mullite compositions were obtained. The general inference given was that the crystals were still a little too small for accurate analysis and the evidence suggested that the mullite occurred in a Si-K rich amorphous matrix material which often contributed to the analysis results. It should be noted that in the areas showing pronounced development of orientated mullite, no other crystalline phases (eg iron oxides) were found.

Mullite crystals were also observed distributed randomly throughout the sample as shown in Phs. 100, 101 & 107. Most of the mullite in these samples occurred in an apparently random distribution.

Microchemical analysis indicated that the matrix material was Si
rich, with variable amounts of subsidiary K, Al and Fe. Microdiffraction gave weak diffuse rings - a little too diffuse to give meaningful approximate d spacings. Very close examination at very high magnification revealed a slightly mottled appearance and suggested the presence of micropores/voids a few angstroms in diameter. Slightly larger pores can often be seen in the amorphous matrix material, especially near the edges of thinned regions - it is possible however that these are an artifact caused by ion beam thinning (Phs. 103 & 118).

Fe-Al-Ti oxides proved to be the next most common crystalline phases. Microchemical analysis identified two main oxide groups. The main oxide group proved to be the relatively Ti poor Fe-Al oxides. As before, the crystal structure of this group was found to be variable. Hexagonal plate-like particles were one of the typical crystal habits observed (eg Ph. 118). These crystals gave diffraction spot patterns compatible with αFe₂O₃, though some exhibited complex moire patterns, suggesting considerable internal distortions/misaligned crystal structure and these usually gave a combined spot/ring pattern (Phs. 104-6).

Cubic-rectangular Fe-Al oxides were common and represented the other typical crystal habit (Ph. 107). They generally gave diffraction patterns that could be indexed on a cubic system. Microchemical analysis proved their Fe-Al content was variable - as with those for 1000°C, and that some contained traces of K. Twins forming one crystal were often found to have significantly different chemical compositions (Phs. 107-8, table 4.4.6.2).

Some of these cubic crystals were also observed with complex moiré patterns, indicating internal disorder, eg Phs. 104-5. Such crystals often gave combined spot-ring patterns. The dominant pattern was
usually cubic but fainter rings with d values equivalent to $\gamma$Fe$_2$O$_3$ were not infrequently seen.

A few examples of a phenomenon not seen in the previous samples were found - orientated iron oxide crystals. A large number of parallel acicular crystals can be seen in Ph. 109. The results of microchemical analyses (table 4.4.6.1) indicated that they were iron oxides with a variable Al content. Selected area diffraction indicated they had a cubic crystal structure suggesting they were $\gamma$Fe$_2$O$_3$ crystals. Two or more sets of reflections with identical orientation but different d spacings can be seen in the accompanying diffraction patterns. This would appear to relate to differences in unit cell size associated with variations in chemical compositions. Two subparallel crystals seen at 60° to the main set could represent a second crystal set.

Another example of orientated $\gamma$Fe$_2$O$_3$ crystals is shown in Phs. 116-7. In this instance three sets of acicular crytals are clearly seen at 60° to one another. These crystals too were found to have a slightly variable Al content with only traces of Ti (table 4.4.6.2).

As with the lower temperature materials, many of the larger iron containing crystals proved to be pseudobrookite, eg Phs. 1 4-6. A few rare TiO$_2$ crystals were found in the 'body' of the brick and two situated inside regions of pure SiO$_2$ - quartz Quartz was the only other crystalline phase identified. It appeared to be derived from original quartz grains present in the clay and frequently showed signs of partial vitrification at the edges of the crystal.
Figure 4.4.6.1
Oxide Compositions for 1050°C (Wt% Cation)
Figure 4.4.6.2
Titanium Rich Oxides
- 1050°C (Wt% Cation)
Ph.100  Orientated spinel in amorphous matrix.

Ph.101  Orientated spinel and early mullite development.

Ph.102  SiO₂ and orientated mullite.

Ph.103  Orientated spinel and early mullite development.
Ph.104  $\gamma$ and $\alpha$ Fe$_2$O$_3$ crystals in amorphous matrix. Note the long mullite crystals.

Ph.105  $\gamma$ & $\alpha$ Fe$_2$O$_3$ crystals. Note irregular moire fringes.

Ph.106  Diffraction pattern of $\alpha$ Fe$_2$O$_3$ 2.5326Å and mullite [110] 5.4

Ph.107  Fe$_2$O$_3$ and mullite crystals. See table 4.4.6.2

Ph.108  $\gamma$Fe$_2$O$_3$ crystals in amorphous matrix.
Ph.109 Orientated $\delta$Fe$_2$O$_3$ crystals.

Ph.110 Diffraction pattern. Note broad double sets of spots indicating differing unit cell size, eg. [311] = 8.195 & 8.464Å.

Ph.111 Corresponding darkfield v

Ph.112 $\delta$Fe$_2$O$_3$ diffraction patterns

Ph.113 Unit cells, giving $a = 8.225$, $b = 5.283$, $c = 8.492$ & $\alpha = \beta = \gamma = 90^\circ$.

Ph.114 Unit cells giving $a = 8.195$, $b = 5.283$, $c = 8.464$ & $\alpha = \beta = \gamma = 90^\circ$. 
Ph.115  Linearly orientated $\gamma$Fe$_2$O$_3$ crystals.

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Table 4.4.6.1
Microchemical analyses in photograph 115.
Three sets of orientated $\gamma Fe_2O_3$ crystals.

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Table 4.4.6.2
Ph.107 point 6A  Table 4.4.6.2

Ph.107 point 6B  Table 4.4.6.2

Fig. 4.4.6.3
Ph.118 Twinned αFe₂O₃. Al 3.8
    Ti 6.7  Fe 89.5

Ph.119 Diffraction pattern. Note double spots due to twins (024)
    d = 1.847, 1.755 Å.

Ph.120 Darkfield view (024)

Ph.121 Diffraction pattern
    a = 4.224  b = 3.270  c = 4.224

Ph.122 Diffraction pattern
    a = 2.146 & 2.247 = {113}

Ph.123 Darkfield view of {113}
Ph.124  Pseudobrookite. Note complicated strain and dislocation contrast.
Al 4.9  Ti 36.8  Fe 58.3

Ph.125  Corresponding diffraction pattern. Note streaking associated with the rutile-pseudobrookite transformation
a=3.477  b=2.967  c=2.243

Ph.126  Darkfield view. Note contrast to the shear transformation.

---

Ph.127  TiO$_2$ crystals.
Al 1.5  Ti 97.7  Fe 0.9

Ph.128  Diffraction pattern
a = 2.58Å  b = 1.33Å

Ph.129  Darkfield view
Ph.130  Orientated mullite.

Ph.131  Diffraction pattern 3.422Å  {120}

Ph.132  Darkfield view

Ph.133  Orientated mullite development

Ph.134  Selected area diffraction pattern
No traces of the spinel were found in these specimens. Mullite and iron oxides were the dominant crystalline phases. As can be seen in Figs. 136-140, the degree of mullite crystallisation, though variable, was greater than in previous lower-temperature materials. The size of the mullite crystals had increased sufficiently to permit accurate microanalysis of individual crystals. The circular contamination spots visible in Fig. 142 mark analysis points. The results of a typical analysis series are shown in Table 4.4.7.1. The results of all the mullite analyses are plotted in Figure 4.4.7.2.

Microchemical analysis again suggests the mullite crystals are developed in a Si-rich amorphous matrix. As seen in Fig. 142 and Table 4.4.7.1, analyses that fall slightly off a crystal generally have higher Si contents than those that do not and they usually have values above the maximum possible for mullite. Such analyses were considered invalid and not as a rule plotted in Figure 4.4.7.2.

The mullite shown in Figs. 136-139 is orientated in a similar fashion to that seen in the 1050°C material. Again, orientated mullite regions contained no other crystalline phase. As before, most of the mullite was not orientated and occurred alongside iron oxide crystals. Photograph 135 represents a typical area. Microdiffraction and microchemical analyses were performed on mullite from such regions. The results of these microchemical analyses are also included in Figure 4.4.7.2.

After mullite, iron oxide proved to be the next most prominent crystalline phase. The results of the microchemical analyses of the oxide particles are plotted in Figure 4.4.7.1. The Ti-rich, pseudobrookite type oxides are apparently much less numerous than in
previous samples and the Ti-poor oxides are obviously the dominant group. Various crystal habits were observed for this latter group. The hexagonal platelets shown in Ph. 149 gave diffraction patterns compatible with $\alpha Fe_2O_3$. The cubic/rectangular ones seen in Ph. 149 either gave an $\alpha Fe_2O_3$ pattern or $d$ values equivalent to $\gamma Fe_2O_3$, though not infrequently with the spots having an angular arrangement not truly compatible with either cubic or tetragonal systems. They apparently represented some intermediate structure. 'Octahedral' shaped crystals were also fairly common, eg Phs. 135 & 149. One axis was usually elongated and these crystals generally gave the appearance of representing rectangular crystals which had developed corner facets. These crystals gave either $\alpha$ or $\gamma Fe_2O_3$ patterns.

Acicular crystals were the fourth and least common crystal habit observed (Phs. 146-7). Electron diffraction yielded $d$ values indicative of $\gamma Fe_2O_3$. As in the lower temperature samples, the acicular crystals were often orientated, as seen in Ph. 146.

Not all the orientated oxide crystals were orientated linearly. The oxide particles in Ph. 148 surrounding a quartz region were orientated in a circular fashion. They were also found to have a very slightly different chemical composition from the norm, ie lower $Al$ and $Ti$. They probably represented the iron oxide coating seen on some unfired quartz grains (section 3.4.4).

A roughly orientated set of oxide crystals is shown in Ph. 143. Table 4.4.7.2 lists the results of a series of microchemical analyses of the area and shows clearly that they are iron oxides.

In addition to mullite crystals (a typical microanalysis of one of these is shown in fig. 4.4.7.3) one other phase was identified in this and a few other areas. The microchemical analysis identified a few small $Mg Fe$ aluminates. (Table 4.4.7.2 and figure 4.4.7.3.) The
composition appeared variable - ie probably a solid solution series. Unfortunately no clear selected area diffraction pattern could be obtained. Exactly why was unclear.

Unlike lower temperature materials, very few Ti-rich pseudobrookite crystals were observed. Photograph 150 shows one of the few that was. (Note the complex contrast features including precipitate induced contrast.)

The very strange structure seen in Ph. 151 is still only partially identified. Microchemical analysis (fig. 4.4.7.4) indicated that it is probably a thermally altered zircon particle. Weak Bragg contrast was observed so it was at least partially crystalline but selected area diffraction failed to produce a pattern - perhaps because the area was quite thick.
Figure 4.4.7.1
Oxide Compositions for 1100°C (Wt% cation)
Figure 4.4.7.2
Mullite Compositions for 1100°C (Wt% cation)
Ph.135  Iron oxide and mullite crystals in amorphous matrix.
Ph.136 Orientated mullite

Ph.137 Selected area diffraction pattern
a = 5.50Å  b = 5.55Å  c = 5.57Å

Ph.140 Orientated mullite. Note rud
acicular crystal habit.

Ph.138 Darkfield view [110]

Ph.139 Orientated mullite

Ph.141 Superimposed mullite diffra-
patterns showing d = 3.46Å
  d = 2.94Å
### Table 4.4.7.1
Microchemical analyses in photograph 142.

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**Ph.143** Orientated iron oxide crystals
Mullite Ph.143 (No. 14 Table 4.4.7.2)

Magnesium, iron aluminate Ph.143 (No. 8 Table 4.4.7.2)

Fig. 4.4.7.3
Ph.148 $\alpha$Fe$_2$O$_3$ crystals surrounding quartz crystal.

Ph.149 Fe$_2$O$_3$ and mullite crystals in amorphous matrix.

Ph.150 Pseudobrookite. Al 6.3 ± 0.3
Ti 30.5 ± 1.4 Fe 63.2 ± 1.7

Ph.151 Zirconium silicate
Fig. 4.4.7.4

Zirconium Silicate Ph.151
The microstructure and components found for this temperature are very similar to those observed in the 1100°C material. Photographs 152/158 show a typical area containing a few iron oxide crystals, while table 4.4.8.1 shows the results of a series of microchemical analyses. The round contamination spots (Ph. 158) indicate the analysis points. The diffraction patterns, Phs. 154, 156 etc, show the main crystal to be $\gamma$Fe$_2$O$_3$. The second smaller crystal (Ph. 155) is seen to be similarly orientated to the larger one, despite a fairly considerable distance separating them. Though roughly hexagonal in shape, suggesting $\alpha$Fe$_2$O$_3$, it has been found to be $\gamma$Fe$_2$O$_3$. A more typical $\gamma$Fe$_2$O$_3$ crystal is shown in Phs. 164-6. Though many $\gamma$Fe$_2$O$_3$ crystals are seen in this material, significant $\alpha$Fe$_2$O$_3$ is present.

Another typical area containing $\alpha$Fe$_2$O$_3$ and mullite is shown in Phs. 162-3 and accompanying analyses in table 4.4.8.2. The results of all the microchemical analyses of iron oxides are plotted in figure 4.4.8.1.

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Table 4.4.8.1  Microchemical analyses in photograph 159 (Wt% cation)
Figure 4.4.8.1
Oxide Compositions for 1150°C (Wt% cation)
Ph. 152 Two 'hexagonal' crystals of $\gamma$Fe$_2$O$_3$

Ph. 153 Darkfield view [440] - note similar orientation.

Ph. 154 Corresponding diffraction pattern
\[ a = 3.03\,\text{Å} \quad b = 3.00\,\text{Å} \quad c = 2.135\,\text{Å} \]

Ph. 155 Similar darkfield view [220]

Ph. 156 Corresponding diffraction pattern
\[ a = 4.96\,\text{Å} \quad b = 2.98\,\text{Å} \]
\[ c = 2.66\,\text{Å} \]

Ph. 157 $\gamma$Fe$_2$O$_3$ diffraction pattern
\[ a = 5.33\,\text{Å} \quad b = 4.98\,\text{Å} \quad c = 4.95\,\text{Å} \]
Ph. 158  Fe$_2$O$_3$ diffraction pattern
\[ a = 4.80\text{Å} \quad \{110\} \]
\[ b = 2.56\text{Å} \]
\[ c = 3.00\text{Å} \quad \{220\} \]

Ph. 159  Photograph depicting analysis points in table 4.4.8.1

Ph. 160  Darkfield view of mullite crystal
\[ \{110\} \]

Ph. 161  Corresponding mullite (and iron oxide) diffraction pattern.
\[ a = 5.53\text{Å} \quad \{110\} \]
\[ b = 1.94\text{Å} \]
\[ c = 1.25\text{Å} \]
Ph.162 Typical area showing well developed mullite and iron oxide crystals.

Ph.163 Analysis points in table 4.4.8.2. Note 'contamination' spots.

Ph.164 Irregular and acicular shape of Fe₂O₃ crystals and the indication of 'surface' reactions may indicate dissolution of iron oxide phase in matrix and/or mullite.

Ph.165 Diffraction pattern of elongate Fe₂O₃ crystal. 

\[
a = 4.89\text{Å} \quad \{113\} \quad b = 3.01\text{Å} \quad \{220\}
\]
Ph.167 Iron oxide and mullite crystals - the latter showing 3 sets of preferred orientation.

Ph.168 The iron oxide crystals show signs of a reaction rim which may indicate Fe₂O₃ dissolution by the amorphous matrix.

Ph.169 Typical area. Note the increased mullite crystal size and amorphous Si-rich matrix.

Ph.170 Same area showing unidentified, apparently tubular, structure.

Ph.171 Typical area showing mullite and Fe₂O₃ crystals. Thickness fringes arrowed.

Ph.172 Orientated mullite in amorphous matrix.
Table 4.4.8.2 Microchemical analyses in photograph 163

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<td>11.31</td>
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*Fig. 4.4.8.2 Mullite crystal Ph.163 (No.5 Table 4.4.8.2)*
The microstructure for this temperature is very similar to the previous two. Photographs 167-172 show some typical areas. Mullite and iron oxide are the dominant crystalline materials with the amorphous matrix being composed mainly of Si with variable subsidiary K, Al and Fe.

As with previous samples, both \( \alpha \) and \( \gamma \)FeO were recorded. Crystal morphology again was not a suitable reliable diagnostic aid. The large irregularly shaped oxide crystal in Ph. 168 exhibits one of the few observed instances of a crystal with reaction rim seen in the fired clay - indicating secondary growth. The fringes in the 'diamond' shaped crystal of Ph. 171 are thickness fringes. The results of all the microanalyses of the iron oxides are plotted in figure 4.4.9.1.

Mullite development at this temperature is more advanced than at lower temperatures. The mullite crystals seem to have increased progressively in size with increasing firing temperature, since they first appeared at about 1000°C. Attempts to quantify this encountered difficulty in defining a suitable measurable parameter for such acicular crystals and were not very successful. Differences in, say, length of the crystals between 1000 and 1200°C are obvious (Phs. 82 & 169) and show that crystal growth has occurred.

Oxide-free regions of orientated mullite were again observed (Ph. 172), though as before, most mullite occurred apparently randomly intermixed with iron oxide crystals. Photograph 168, however, shows one of the few instances where mullite intermixed with iron oxides showed some signs of being orientated. As with other instances of mullite orientation, three sets can be distinguished, each at 60° to the others. The results of all the microanalyses of mullite crystals
are plotted in figure 4.4.9.2.

One unusual and unidentified feature can be seen in Fhs. 169 & 170 (arrowed). Contrast indicates the structure to be a long thin tube. Microchemical analysis gave results indistinguishable from the adjacent Si rich matrix and probably bears little relationship to its actual composition.
Figure 4.4.9.1
Oxide Compositions for 1200°C (Wt% cation)
Figure 4.4.9.2
Mullite Compositions for 1200°C (Wt% cation)
The general increase in crystallinity with increase in top firing temperature seemed to be reflected in a change in size of the oxide crystals.

Measurements of the average diameter of the Ti-poor oxides revealed an almost linear increase in mean diameter with increased top firing temperature. The means plus standard deviations are plotted in figure 4.4.10.1.

The measurements were obtained from randomly selected photographs of typical areas, by measuring the maximum diameter of a crystal and that at 90° to it. A minimum of 200 particles per temperature interval were taken. It is acknowledged that this method does not give an absolute value for particle size but it is thought to give a useful measure of crystallite size. Determining the exact mean crystallite size would be a very difficult proposition, as the photographs one obtains represent semi-2D sections (2½ D projections) of variably orientated crystals that vary in shape between cubes, rectangular solids and hexagonal platelets.
Fig. 4.4.10.1 Particle size variations with firing temperature
(Bars show standard deviation of data sets)
Microchemical analysis revealed significant development of mixed Fe-Al-Ti oxides in all samples fired above 950°C. Apart from the Ti-rich Fe-Ti oxides apparently derived from rutile described in section 4.4.13, most of these oxides are Ti-poor containing <5 Wt% Ti. The Al content of these oxides for any one firing temperature is variable. If the analyses of the oxides from each temperature are treated as a series, a definite pattern emerges.

The results of all the microchemical analyses of these oxides can be seen in figures 4.4.5.1, 4.4.6.1, 4.4.7.1, 4.4.8.1, 4.4.9.1 and 4.4.10.1. If the compositional fields into which most of the oxides fall for each temperature are represented diagrammatically one can see a definite progressive change in compositional field, figure 4.4.11.2.

Table 4.4.11.1 and figure 4.1.11.1 give the mean oxide composition for each top firing temperature and the standard deviation. A decrease in aluminium content with increased temperature is obvious.

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<th>Temperature °C</th>
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<th>Ti</th>
<th>Fe</th>
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<td>1.92 ± 1.53</td>
<td>83.60 ± 12.63</td>
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<tr>
<td>1050</td>
<td>10.92 ± 10.30</td>
<td>1.90 ± 1.79</td>
<td>87.24 ± 10.10</td>
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<tr>
<td>1100</td>
<td>8.25 ± 4.63</td>
<td>2.81 ± 0.85</td>
<td>89.19 ± 4.43</td>
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<tr>
<td>1150</td>
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<td>3.82 ± 0.57</td>
<td>90.48 ± 2.44</td>
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<td>1200</td>
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<td>4.86 ± 0.83</td>
<td>89.37 ± 1.99</td>
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Table 4.4.11.1

Mean composition and standard deviations of the iron oxides for the different top firing temperatures (Wt % cation).
Fig. 4.4.11.1 The change in mean Al content of iron oxide crystals and the standard deviations with firing temperature
Fig. 4.4.11.2 Variation in Oxide Composition Fields with firing temperature (Wt% cation)
Mullite was observed in all the samples fired to 1000°C or above. The crystals increased in size with increased top firing temperature. They were not large enough for accurate microchemical analysis in samples fired below about 1100°C. In lower temperature samples one nearly always 'analysed' some of the adjacent matrix, and the analysis suggested a higher Si content than is feasible for a mullite type structure.

The results of a series of microchemical analyses of mullite crystals in samples fired to 1100 and 1200°C are shown in figures 4.4.7.2 and 4.4.9.2. A number of important facts can be seen in these results:

1) Contrary to much contemporary thinking there is no indication of a grouping of analyses around a 3:2 Al₂O₃:SiO₂ molar ratio in either set. Rather, there is an apparent solid solution range between about 72.33 Wt% Al 27.67 Wt% Si and 84.66 Wt% Al 15.33 Wt% Si, as suggested by Cameron (section 2.3.1.3). In fact the sum of the Al + Fe means for the two sets are 76.60 Wt% and 76.56 Wt% for 1100 and 1200°C respectively. These fall within the 60-66 mole % (75-78.3 Wt%) observed by Cameron to be typical of mullite formed in solid state reactions.

2) The mullite compositional field can be seen to change with temperature (fig. 4.4.12.1).

3) The mean iron content of both sets of analyses indicates that the mullite is iron saturated or very nearly so. The amount of iron capable of being dissolved varies with temperature. The measured
values (table 4.4.12.1) agree well with the maximum values
determined by Bronwell (fig. 2.3.1.12).

4) There was no apparent chemical difference in material derived from
kaolinite or illite-vermiculite clays. Analyses of crystals in
areas such as those in Ph. 135 which are derived from pure kaolin
crystals in Ph. 142 for example.

<table>
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<td>66.15</td>
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<td>1200⁺</td>
<td>67.09 ± 3.48</td>
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<td>1200⁻</td>
<td>67.28</td>
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Table 4.4.12.1

Mean composition of the mullite in the samples
fired to 1100 & 1200 °C

⁺ = Wt% cation
⁻ = weight % oxide
Fig. 4.4.12.1 Variation in mullite composition with top firing temperature (Wt% Cation)

1100°C

1200°C
Rutile crystals present in the unfired clay remain relatively unaffected by firing at temperatures up to about 800°C. They were found to be increasingly rare in samples fired above 950°C and were not observed at all in material fired above 1100°C. The disappearance of rutile crystals corresponded to the appearance and increase in Fe-Ti compounds of pseudobrookite type material (Fe₂TiO₅).

One can infer that iron is diffusing into the rutile crystals, altering them to pseudobrookite. Rutile is known to be capable of dissolving up to about 3 mole % iron before pseudobrookite precipitates. (Unlike αFe₂O₃ and ilmenite, no solid solution occurs between the two materials.) Initially it forms defects in the rutile structure and later orientated precipitates of pseudobrookite develop. The transformation of rutile to pseudobrookite is complex and has been studied by Bursil (1974). It was not studied in detail in this work because pseudobrookite is really only a minor phase. A zig-zag fault system of the type described by Bursil can be seen in Phs. 124 & 126 and is the probable cause of the streaking seen in the accompanying diffraction pattern.

As the rutile crystals in the unfired clay are relatively large (ie >200nm), the pseudobrookite derived from them is also of a similar size. In the 950 and 1000°C material there are few Fe-Al oxide crystals of a similar size and this results in a sampling bias towards pseudobrookite.

One semiconsciously preferentially selects larger crystals as it is easier to obtain accurate microchemical and diffractional information from them.
Figure 4.4.13.1
Titanium Rich Oxides
1000 & 1050°C (Wt% cation)
This sample, like the next two and unlike the previous samples, was fired in an argon atmosphere and not in air (see section 4.3.16). Like the one fired in air to the same temperature, this sample proved to have limited mechanical strength and was very fragile. Extensive examination was not possible due to lack of suitably thin areas - they fell off during handling.

Phs. 173-6 show some of the typical features of this material. As with the equivalent air fired sample (section 4.4.4), some relic dehydrated clay structures remain. The dominant crystalline features are the orientated acicular crystals and the small rectangular crystals that are aligned end to end, forming needle-like features (Phs. 173-4). These are similar to the spinel crystals seen in the 0-1000°C air fired material (section 4.4.5). Slightly larger rectangular spinel crystals can also be seen (Ph. 176). These will be described in greater detail in the next section.
Little if anything in the way of residual dehydrated clay minerals remain. The only possible example is the structure seen in Phs. 197-9. This area was very thin and the X-ray count during microanalysis was very low, even after prolonged analysis and so was inaccurate. It did indicate it was Si-Al rich material though. The diffractional evidence was also insufficient to aid positive identification - only one d value, of 3.526Å, was obtained (Ph. 198).

The small orientated acicular spinel crystals seen in argon 950°C have gone. The dominant crystalline features now are the cubic-rectangular crystals seen in Ph. 178. Their size is variable but does not generally exceed 200nm. Selected area diffraction proved they were all cubic and had patterns compatible with the spinel structure.

The results of microchemical analyses of these crystals are plotted in figure 4.4.15.1. The composition was found to be variable but within the solid solution range known for Al-Fe-Ti spinels. The Ti content was generally low if not zero while the Al-Fe content, though variable, was often near 60:40 Wt%. As is to be expected, the unit cell size of the crystals varied with composition, eg 66 Wt% Al = 8.25Å, (Ph. 188) and 97 Wt% Fe = 8.31Å (Ph. 185).

Some twinned crystals were found to show significantly different chemical compositions. The twinned crystal in Phs. 177-8 was found to have three distinct compositions (fig. 4.4.15.2).

Also shown in figure 4.4.15.2 is an analysis of the quartz crystal visible in Ph. 177. The analysis shows peaks for argon, tantalum and a combined molybdenum and sulphur peak in addition to the usual spurious copper peak. This gives a clear indication of the contamination sample preparation procedures can produce. The molybdenum
sulphide is probably derived from the oil used as a lubricant in the sectioning procedure. The argon is probably due to argon implantation during ion thinning - it is not due to the firing atmosphere as it was common in air-fired samples as well. The tantalum is due to sputtering from the supporting shields used during the ion thinning. The fragile nature of the sample asks for low angle ion beam thinning, but this increases the likelihood of the beam knocking Ta off the shield and onto the sample.

Mullite was the only other crystalline phase identified in this material, Phs. 194-6. The matrix, as with air-fired samples, appeared to be Si rich with variable K, Al and Fe - and amorphous.

4.4.16 Argon 1050°C

These samples were considerably more porous than the previous material and consequently were very fragile. Examination was again limited by the samples' propensity for disintegration.

The crystalline phases observed in this material were very similar to those seen in the previous one - though generally they were slightly larger in size. The dominant phase was again Al-Fe spinel though Al-Fe-Ti spinels were observed. As before, the unit cell size of the crystals was found to vary with chemical composition.

Mullite was the only other crystalline phase identified. The amorphous matrix was dominantly Si rich with subsidiary K, Al and Fe.
Figure 4.4.15.1
Aluminium, Iron, Titanium Spinels in Sample Fired in Argon to 1000°C (Wt% cation)
Ph.174 Orientated 'spinel' crystals in amorphous matrix.

Ph.173 Orientated 'spinel' crystals in amorphous matrix.

Ph.175 Residual dehydroxylated clay minerals plus Fe-Ti spinels in amorphous matrix.

Ph.176 Fe-Ti spinels in amorphous matrix.
Ph.177 Typical area showing SiO₂ region adjacent to area containing mixed Al-Si-Fe (small) and Al-Ti-Fe (large) spinels plus primary mullite development.

Ph.178 Twinned 'spinel' crystal - with twins of very variable composition, fig. 4.4.15.2. Note also significant development of Al-Si-Fe hercynite type spinels and rarer mullite.
Ph. 179  Hercynite type spinel
1) Al 22.4 Ti 2.6 Fe 75.0
2) Al 24.2 Ti 0.5 Fe 75.3

Ph. 180  Typical Diffraction Pattern
Mean $a = 8.255 \pm 0.057 \text{ Å}$

Ph. 181  Corresponding darkfield
{$\{220\}$} = 2.88Å $\equiv a = 8$

Ph. 182  Hercynite type spinel
1) Al 58.0 Fe 42.0
2) Al 54.6 Fe 45.4

Ph. 183  Typical diffraction pattern

Ph. 184  Corresponding darkfield
{$\{331\}$} = 1.89Å $\equiv a =$
Ph. 185  Cubic iron oxide  Al 2.4  Fe 97.2

Ph. 186  Typical diffraction pattern
Mean $a = 8.309 \pm 0.046 \text{Å}$

Ph. 187  Corresponding darkfield view
$\{220\} = 2.953 \text{Å} \equiv 8.351 \text{Å}$

Ph. 188  Al-Fe spinel  1) Al 66.8  Fe 33.2
2) Al 62.2  Fe 37.8

Ph. 189  Typical diffraction pattern
Mean $a = 8.253 \pm 0.029 \text{Å}$

Ph. 190  Corresponding darkfield view
$\{220\} = 2.923 \equiv a = 8$. 
Ph. 191 Early stages of orientated mullite growth. 1) Al 43.4 Si 19.1 K 7.1 Fe 28.4

Ph. 192 Mullite diffraction pattern.
\[ d = 2.967 \text{Å} \]

Ph. 193 Corresponding darkfield view

Ph. 194 Mullite - larger crystal

Ph. 195 Diffraction pattern of larger crystal in Ph. 194.
\[ a = 3.497 \text{Å} \quad b = 2.635 \text{Å} \]
\[ c = 2.746 \text{Å} \]

Ph. 196 Darkfield view
1) Al 52.3 Si 30.9 K 5.3
2) Al 49.9 Si 29.1 K 5.5
Ph. 197  Unidentified structure.  Dehydrated clay mineral?

Ph. 198  Diffraction pattern plus superimposed spinel pattern.  \( a = 3.526 \text{Å} \)

Ph. 199  Darkfield view

Ph. 200  Well developed acicular mullite crystal plus small Al-Fe-Si crystals in amorphous matrix.

Ph. 201  Mullite diffraction pattern  
\[ d = 5.555 \text{Å} = \{110\} \]

Ph. 202  Darkfield view
Ph. 203 Al Fe 'spinel' crystals
1) Al 65.4 Fe 34.6
2) Al 61.4 Fe 38.6

Ph. 204 Ph. 204 Diffraction pattern
d = 2.054 \equiv \{400\} \equiv a = 8.205 \text{Å}

Ph. 205 Darkfield view \{400\}

Ph. 206 Al-Ti-Fe spinel. Al 49.1 Ti 1.4
Fe 49.6

Ph. 207 Diffraction pattern
d = 2.909 \equiv \{220\} \equiv a = 8.178 \text{Å}

Ph. 208 Darkfield view \{220\}
5. Discussion

5.1.1 Firing Trials—Chemically Treated Clays

Samples of Warnham clays subjected to selective chemical extraction treatments (3.5.3-9) were used in the firing trials (3.6.1). However, as there is some uncertainty concerning the degree of selectivity of these treatments (2.4.0-11 & 4.2.1-8) and on the precise nature of observed side effects, it is thought inappropriate to give undue significance to the results of these firing trials. That said, a number of useful general points can be obtained by studying these fired samples.

Perhaps the most significant result is illustrated by the dramatic colour change between HCl treated ostracod clay fired to 1000 and that fired to 1050°C. Though an above average colour change can be seen in all the other samples sets at about this temperature interval, it is not this obvious (Ph. 26). Usually it is only discernible as a slightly larger step in the general progressive darkening observed with increasing firing temperature.

This strongly indicates that there are two stages of colour development and presumably two sources. One source is probably the iron-rich oxyhydroxide coating that is present on the clay particles which is removed by the HCl treatment (fig. 4.2.1). This treatment is thought not to attack/extract clay lattice iron significantly.

Thus if the typical orange-red colour of clay fired below 970°C is due to the thermal oxidation of this Fe-Al oxyhydroxide material, as described in 5.1.2, its removal would account for the light cream colour of samples fired below about 950°C. Above about 950-1000°C clay lattice breakdown should liberate iron which could then react in such a
way as to produce the almost typical brown colour of untreated clays.

If DCB extraction removed the iron-rich oxyhydroxide surface coating as it was supposed to, then if, as suggested, the light orange-brown colour that is seen below about 970°C is derived from this coating then these materials ought to have relatively little colour.

They were slightly lighter in colour below about 1000°C than the untreated material and this is therefore not inconsistent with this idea if one assumes that the DCB extraction was only partially successful at removing the surface coating - which from the evidence is quite likely.

It can be seen that the fired HCl-HNO₃ treated clays are essentially very light in colour (Ph.25). This treatment is thought to remove the oxyhydroxide coating completely and result in an attack on the clay lattice. These clays still contain approximately 33% of the original iron content - presumably derived mostly from Fe not extracted from the clay lattice. The removal of the oxyhydroxide coating and the partial extraction of clay lattice iron has reduced the iron content to below that which can be dissolved in the mullite present (2.3.1.7).

Note that the yellow colour which appears quite sharply between 1000 and 1050° is gradually lost at higher temperatures. Mullite can dissolve more iron at higher temperatures than at low. Therefore it is just possible that the iron that is liberated when the clay lattice decomposes gives rise to very very small widely dispersed oxide crystals, which in an off-white mullite/glass matrix give the bulk sample a yellow colour. As firing temperature is increased, more iron can dissolve in mullite, thus reducing the yellow colour and giving the typical buff of iron-rich mullite.

The iron content of treated materials compared to their untreated equivalents indicates that only a relatively small amount of iron is
active in forming the orange-red colour of fired bricks.

Most if not all of the iron in the HCl-HNO₃ treated clays is derived from the clay lattice and their light colour could therefore be wrongly interpreted as suggesting clay lattice iron is not responsible for any significant colour development. The red-brown colour of HCl treated ostracod clay fired above 1000°C however discredits this idea and shows that, if unattacked, clay lattice iron is responsible for the second phase of colour development.

5.1.2 Chemical Treated Clays - Conclusions

The chemical treatments therefore show that colour development occurs in two stages and that each has a separate source of iron. The first phase is due to the thermo oxidation of the amorphous oxyhydroxide coating to form dispersed iron oxide microcrystallites.

The second phase follows clay mineral breakdown when the iron released reacts to give the second phase of oxide development.

The clay mineral analysis (3.4.6) revealed four basic clay mineral types; kaolinite, halloysite, illite and dioctahedral vermiculite. Of these, only the last two are commonly acknowledged to contain significant amounts of lattice iron. These results indicate that the bulk of the second phase of colour development is due to the iron derived from the breakdown of the illite-illite:vermiculite intergrade material. The presence of kaolinite and halloysite should only have a secondary effect on the colour. They should generate mullite when fired (2.3.1) which would be capable of dissolving some of the iron liberated by the illitic material, so reducing the amount of iron free to generate the main coloured component (ie oxide).
5.2.1 High Temperature Reactions of Illite - Predicted Topotactic Thermo Oxidation Transitions

The XRD results (4.3.1-18) indicate that on firing illite gives rise, apparently via a disordered spinel type intermediary structure to mullite and hematite in addition to amorphous silica.

An analogy can be drawn with the kaolinite → mullite transition suggesting the octahedral layer gives rise to the mullite and hematite and the silica tetrahedral layer contributes to the mullite and the amorphous component.

The kaolinite → mullite transition is commonly accepted as being a topotactic transition. A topotactic Fe rich spinel → hematite transition mechanism has been described and will be outlined shortly. It thus appears possible that virtually the whole thermal reaction series could involve a series of topotactic transitions based on a relatively rigid and stable oxygen lattice and one in which diffusion based processes play only a secondary role.

As described in section 2.3.1, when kaolin is heated, the Al from the octahedral layer gives rise to the transitory spinel structure. The octahedral layer of illite contains both Al and Fe and so the formation of an Al-Fe spinel would be a directly analogous structure. Most of the iron in illite is in the ferrous state so if oxygen is not present during firing it remains as Fe$^{2+}$. Hercynite - an Al-Fe spinel - was found to be a major constituent of illitic clay fired in the absence of oxygen (4.3.12). It is apparent from the samples fired in an oxygen deficient atmosphere that the presence of oxygen significantly affects the course of the reactions. It must be remembered that the 'normal' thermal reaction sequences involved in the high temperature reaction of illitic clays involves an element of thermal oxidation. The intermediary spinel structure proved to be much
more stable and persistent in low $pO_2$ environments than it was in air.

This apparently is not to be unexpected. Phase equilibrium studies in the system Fe-Al-O (Richards & White, 1954, Turnock & Engster, 1962 and Meyers et al 1980) have shown that though hercynite and related Al-Fe spinels are stable over a wide range of temperature, cations concentrations and oxygen potentials, they are thermodynamically unstable except at low $pO_2$. Meyers et al (1980) found for example that hercynite and magnetite are completely miscible above 860°C, although not all the solid solution series existed at any specific $pO_2$. Below 860°C the solid solution separates into Al-rich and Fe-rich spinels. (The immiscibility dome is symmetric about $55\pm3$ mol% FeAl$_2$O$_4$ in Fe$_3$O$_4$. ) The widest range of oxygen pressures in which it was stable was in the magnetite field - increases in Al content shifted the phase field to lower oxygen pressures and narrowed its range of magnitudes.

Since an Al-Fe spinel is likely to be at best metastable when heated in air it is not surprising that the Al-Fe spinel that develops from illite should turn out to be a poorly developed and transient phase. There could be an additional complicating factor with this spinel, for if the analogy with the kaolinite → mullite transition is accurate it is likely to contain Si as well as Al and Fe, at least when it first develops. If this spinel behaves similarly to the FeAl$_2$O$_4$ - Fe$_3$O$_4$ system described above, it could perhaps exsolve into Al-rich and Fe-rich spinels. The Al( Si) rich spinel - probably with minor Fe - could then go on to form mullite in much the same way as that described for kaolin in section 2.3.1, leaving the Fe spinel to react separately. The precise nature of this Fe spinel, on hypothetical grounds, must be open to question but there would appear to be two main possibilities, both iron oxides with an inverse spinel structure - magnetite Fe$_3$O$_4$ and
maghemite $\gamma$Fe$_2$O$_3$. Considering the reactions are taking place in air, since $\gamma$Fe$_2$O$_3$ is the more oxidised of the two, it would appear to be the most likely.

As described in 4.3.15 a ferrimagnetic iron oxide fraction was observed and isolated from air fired clay. Unfortunately neither XRD nor IR could identify the magnetic phase positively as $\gamma$Fe$_2$O$_3$. Electron diffraction results (4.4.5) however, confirmed the presence of cubic-tetragonal $\gamma$Fe$_2$O$_3$ in the fired clay; so it is known to be present.

$\gamma$Fe$_2$O$_3$ is itself normally considered to be metastable as it usually transforms irreversibly to $\alpha$Fe$_2$O$_3$ at a rapid rate above about 300°C. Bernal et al (1957) and Kachi et al (1963) observed that the transformation involves a change in the close packed oxygen layers from cubic to hcp such that

\[ (111)_\gamma \parallel (0001)_\alpha \equiv (\bar{1}10)_\gamma \parallel (112)_\alpha \quad \text{Rh} \]

\[ [1\bar{1}0]_\gamma \parallel [01\bar{1}0]_\alpha \equiv (\bar{1}13)_\gamma \parallel (101)_\alpha \quad \text{Rh} \]

with the $\alpha$ product having either a basal or (0110) twin plane. Kachi et al (1963) suggested a transformation involving a restacking of the close packed oxygen layers and the synchronous displacement of Fe$^{3+}$ ions at the interstices of the oxygen.

$\gamma$Fe$_2$O$_3$ is essentially a cation deficient inverse spinel type structure (Fd$_{3m}$) with about $2\frac{2}{3}$ vacancies per unit cell, mostly on octahedral sites, ie Fe$^{3+}_{21}\frac{1}{3}\square_{2}\frac{2}{3}O_{32}$. Ordering of the vacancies can result in a superstructure that approximates to a tetragonal unit cell (Kachi et al, 1963).

Looked at along (111) the spinel structure can be seen as built up of layers of close packed oxygen anions stacked in the order

A,B,C,A,B,C,.....

with metal ions in the interstices. Looked at along $\langle 111 \rangle$, two
alternating 2D metal lattices can be distinguished (fig. 5.1.3.1).

1) a 'kagome' layer in which all the cations are octahedral sites.
2) a 'mixed trigonal layer' consisting of both tetrahedral and octahedral sites.

\( \alpha \text{Fe}_2\text{O}_3 \) is rhombohedral/trigonal with \( a_r=5.4271\text{Å} \) and \( \alpha=55^\circ 17' \) but it is often considered for convenience to be hexagonal with \( a_h=5.0345\text{Å} \) \( c_h=13.749\text{Å}. \) This lattice can be envisaged as cph oxygen layers stacked in the sequence \( A,C,A,C,... \) with the metal ions located in the interstices. In this case only octahedral sites exist which form a honey comb structure, fig. 5.1.3.2, with \( M-M\ 2.9\text{Å}. \) The \( \gamma \rightarrow \alpha \) transition described by Kachi et al (1963) involves a change in stacking sequence of \( \text{ABBABC} \rightarrow \text{ACAC} \) and as such is very similar to the isothermal martensitic transition from fcc to hcp seen in metallic cobalt (Christian, 1951 & Seeger, 1956).

Kachi et al suggest the transition involves a \( 19^\circ \) shear in the \( [112]_\gamma \) direction with every two close packed oxygen layers either side of a kagome layer locked together. Thus each set of two layers moves \( \frac{1}{\sqrt{3}}a \) with respect to the adjacent pairs (\( a=0-0 \) distance in these layers, \( \approx 2.97\text{Å} \)). As proposed by Seeger, the transformation occurs by the movement of a sweeping partial dislocation around a pole screw dislocation with a Burgers vector twice that of the \( 0-0 \) distance along the \( \langle111\rangle_\gamma \) direction.

The shear should occur along the mixed trigonal layer because the metallic ions in the tetrahedral sites are more weakly bonded to the adjacent oxygen layers than are octahedral ions. eg. \( M-O \) distance = 1.8Å cf \( M-O(\text{oct}) = 1.2\text{Å}. \) If a metal ion in the 'mixed trigonal layer' is bonded to 3 oxygens in the adjacent layer then it will be dragged towards \( [112]_\gamma \) by that layer. Metallic ions in octahedral sites move in a \( [\bar{1}21]_\gamma \) or a \( [2\bar{1}0]_\gamma \) direction in synchrony with \( a/\sqrt{3} \) \( [112] \).
Fig. 5.1.3.2
'Honey comb' lattice of $\alpha$Fe$_2$O$_3$

Fig. 5.1.3.1 Plane trigonal lattices
in spinel. a) 'kagome' lattice
b) 'mixed trigonal' lattice

Fig. 5.1.3.3 Relation between 'kagome'
lattice and 'honey comb' lattice.
Meshes of solid lines represent
'honey comb' lattice and those of
circles represent 'kagome' lattice.

Fig. 5.1.3.4 Cooperative migration of ferric ions
around irregularly distributed vacancies and
resulting twin structure. The lattice points shown
by $\bigcirc$, $\bigodot$ and $\bigotimes$ represent a 'kagome' lattice and
meshes of solid lines represent 'honey comb'
lattice. Dotted arrows represent the displacements
of ferric ions to the neighbouring sites.
displacement of the overlying oxygen layer. The original mixed trigonal layer will gradually change to a kagome lattice (ie totally octahedral). It is presumed the original kagome layer moved with the pair of oxygen layers without changing its configuration.

If the kagome lattice is compared to the a honeycomb lattice it is seen that 75% of the sites correspond. In an 'ideal' $\gamma$Fe$_2$O$_3$ crystal $1/6$ of the cation sites are vacant. If the vacancies exist in a random fashion in the kagome lattice an unsymmetrical distribution of ionic charge around the vacancies will exist and they are likely to migrate in a fashion similar to that shown in fig.5.1.3.4, producing an $\alpha$ structure with the twin on $[01\overline{1}0]$. The basal plane twin could be produced by the occasional non-synchronous shear resulting in disorder of the metal lattice. Both twin types could be expected to be removed by annealing as was observed by Kachi et al (1963).

Barker and Whelan (1968) and Tighe & Swan (1976) found a very similar structural relationship between $\gamma$Fe$_2$O$_3$ R$_{3c}$ structure and an Fd$_{3m}$ spinel structure. They studied almost the reverse reaction, ie the reduction of $\gamma$Fe$_2$O$_3$ to Fe$_3$O$_4$ and found the reverse fcc $\rightarrow$ hcp lattice transition, namely

$$\{111\}m \ // \ {0001}h$$

with $\pm \langle1\overline{1}0\rangle_m \ // \ \langle01\overline{1}0\rangle_h$

Tighe & Swan noted the similarity between this $R_{3c} \rightarrow Fd_{3m}$ transitions and the hcp $\rightarrow$ fcc (isothermal) martensitic transitions in Cobalt - ie a shear mechanism accomplished by glide of dislocations lying in the magnetite-hematite interface and moving with it.

Thus the whole thermo oxidative reaction that transforms ilite to mullite, hematite and amorphous silica can be postulated as:
The illite anhydride should transform into the defect Al-Fe-Si spinel in a manner similar to the formation of Al-Si spinel from metakaolin (2.3.1). The Fe$^{2+}$ will be oxidised to Fe$^{3+}$ and as such will become harder to accommodate in a spinel type lattice, even a high defect one. This, combined with the tendency of Al-Fe spinels to exsolve at about 860°C should result in the exsolution of a γFe$_2$O$_3$ type material which could then transform topotactically into αFe$_2$O$_3$ while the Al-rich spinel should transform into mullite as in the case of kaolinite.

There is at least one other apparent example of a topotactic thermo oxidation of a ferrous silicate system to αFe$_2$O$_3$ via a spinel type intermediary.

Champness (1970) found that the low temperature oxidation (200-800°C) of fayalite (iron-rich olivine - used in refractories) gave rise to well orientated hematite- and magnetite- like precipitates together with amorphous silica. In the early stages of the reaction an iron-rich spinel type material precipitated with

$$a_{01} \parallel [111]_{sp}; b_{01} \parallel \pm [\bar{1}12]_{sp}; c_{01} \parallel \pm [1\bar{1}0]_{sp}$$

while at higher temperatures a 'hematite like phase' was found in twinned orientation with respect to olivine such that

$$a_{01} \parallel c; b_{01} \parallel \pm h; c_{01} \parallel \pm [210]_h$$
Olivine is an orthosilicate (ie individual SiO₄ tetrahedra) in which the oxygen ions (hcp) lie parallel to (100) while the Mg/Fe cations in six-fold coordination (ie oct) occupy about half the available sites forming zig-zag chains along [001] while Si occupies about 1/3 of the available tetrahedral sites.

Spinel consists of close packed oxygen ions parallel to {111} which alternate with alternating 'kagome' and 'mixed trigonal' cation sublattices (as described earlier).

Hematite consists of cph oxygen ions parallel to (0001) while Fe³⁺ occupies 2/3 of the octahedral sites in each cation layer parallel to (0001). Therefore a change from olivine to spinel is equivalent to hcp → fcc and spinel to hematite fcc → hcp. The reaction is cellular; thin needles of oxide, separated by regions of amorphous silica about 50-100Å wide, grow into the matrix. Nucleation of the spherical colonies of iron oxide and silica occurs on dislocations. Although αFe₂O₃ and Fe₃O₄ always show the same crystallographic relationship with the matrix, the direction in which the needle like plates grow is determined by the orientation of the nucleating dislocation.

One interesting feature of this topotactic transition not observed in the kaolinite → mullite transition is the development of orientated silica. At low temperature the silica is usually amorphous. At higher temperatures it was seen to crystallise partly as a cristobalite type phase such that

$$(100)_{\text{si}} // (111)_{\text{crist}} ; b_{\text{si}} // [\hat{1}10]_{\text{crist}}$$

or occasionally

$$(110)_{\text{si}} // (111)_{\text{crist}} ; b_{\text{si}} // [\hat{1}12]_{\text{crist}}$$

Despite the oxygen in cristobalite not being close packed, the stacking along [111] to some extent resembles hcp and both [110] and
[112] are structurally similar to [010]0, hence the orientation (Champness, 1970).

5.2.2 Diffusion in Spinel Systems - Relevance to Topotactic Transitions

The kaolinite → mullite and muscovite → mullite transitions (2.3.1 & 2.3.2.2 respectively) are now commonly accepted as topotactic in nature. It could be predicted therefore that illite should transform in a similar fashion. The existence of a topotactic thermo oxidation process of a ferrous silicate such as olivine and a topotactic iron rich spinel → hematite transition further supports a fully topotactic transition series.

However this does not mean that it is necessarily the only or even the main transition mechanism involved. While there is significant crystallographic evidence to support a diffusionless martensitic topotactic \( \gamma \rightarrow \alpha \text{Fe}_2\text{O}_3 \) (Fd\(_{3m} = R_3c\) ) transition, some researchers have suggested a nucleation and diffusion fed growth based process is active.

Ridge et al (1969) for instance, have suggested that trigonal nuclei form on crystallites and that they grow by surface diffusion - the temperature being too low for volume diffusion. (Note - Hayes, 1980, reported surface diffusion as the main mass transport system active in the sintering of \( \alpha \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \) powders between 300-500°C.) Alternatively, the transition could be initiated at the surface by diffusion to give nuclei, which then initiates the diffusionless transition of the crystallite. If the transition takes place by nucleation and diffusion fed growth, nucleation is likely to be heterogeneous and could result in a non-orientated product. However, a diffusional mechanism does not necessarily preclude precipitated
particles from inheriting their orientation from the phase in which they form, resulting in the new and old phase having structurally related orientations.

In the illite → mullite and hematite transition we are in all probability looking not at a pure $\gamma \rightarrow \alpha \text{Fe}_2\text{O}_3$ transition, but at the combined exsolution of Al-rich and Fe-rich spinels from a defect Al-Fe-Si spinel and the almost simultaneous structural transition and oxidation of the Fe-rich fraction into $\alpha \text{Fe}_2\text{O}_3$. It is self evident that these combined processes must involve some diffusional component. As already mentioned, Al-Fe spinels tend to exsolve into Al and Fe rich components at low temperatures. Vacancies and associated defects should therefore play an important role in any diffusional process active during exsolution or the spinel $\rightarrow \alpha \text{Fe}_2\text{O}_3$ transformation.

If it is assumed as seems probable (for high temperatures at least - Halloran & Bowen, 1981), that cation distribution will be effectively randomised in Al-Fe spinels, then a significant proportion of the Fe should be expected in both tetrahedral (A) and octahedral (B) sublattices. Therefore at least four basic diffusional paths are possible, two interstitial and two vacancy:

1) Interstitial Fe can diffuse via octahedral interstices - normally unoccupied octahedral sites in the cation sublattice separated by $\sqrt{2a_o/4}$ ($a_o = $ lattice parameter).

2) Via tetrahedral interstices which are separated by $a_o/4$, or even a jump from tetrahedral to octahedral is possible.

3) A vacancy on an A site will be surrounded by 4 neighbouring A sites, each at a distance of $\sqrt{3a_o/4}$.
4) A vacancy on a B site has 6 similar sites at a distance of $\sqrt{2}a_0/4$. A vacancy jump between sublattices is also possible.

Halloran & Bowen (1980) found that Fe diffusion in Fe$_3$O$_4$ and Fe(Fe$_{1.5}$Al$_{0.49}$)O$_4$ (at high temperature) occurs via an interstitial mechanism at low p$_{O_2}$ and a vacancy mechanism at high p$_{O_2}$ ($<<10^{-4}$ and $10^{-6}$ respectively). They observed a similar interstitial:vacancy change during cooling Fe$_3$O$_4$ and Fe(Fe$_{1.5}$Al$_{0.49}$)O$_4$ at constant p$_{O_2}$ (eg $10^{-6}$) resulting in minimum D$_{Fe}$ values at 1200 and 1240°C respectively. Diffusion was faster at lower temperatures, for the enthalpy of vacancy diffusion was lower than for vacancy formation via oxidation of the Fe$^{2+}$ ion. At constant p$_{O_2}$ magnetite is oxidised to Fe$_2$O$_3$ with decreasing temperature and reduced to FeO with increasing temperature. Since an increase in T at constant p$_{O_2}$ has the effect of reducing the spinel, the vacancy concentration at constant p$_{O_2}$ will decrease with increasing temperature.

Halloran and Bowen concluded that diffusion of Fe in higher Al spinels was by a vacancy mechanism except perhaps for the 'end member' hercynite itself. At constant temperature and p$_{O_2}$ the vacancy concentration apparently increases with Al content (ie Al decreases vacancy concentration's dependance on p$_{O_2}$), while for a constant cation ratio, vacancy concentration decreases with increasing temperature at constant p$_{O_2}$ (ie effectively reducing the spinel).

Halloran & Bowen determined the following activation energies for Fe diffusion:
Fe$_{1.5}$Al$_{0.49}$O$_4$ (1400°C) interstitial diffusion, apparent activation energy = 62.16 kcal/mol.
Fe$_{1.5}$Al$_{0.49}$O$_4$ (1480°C) vacancy diffusion, apparent activation energy = 65.0 kcal/mol.
Fe₃O₄ vacancy diffusion, apparent activation energy = 40.7 kcal/mol
Fe₃O₄ interstitial diffusion, apparent activation energy = 70.1 kcal/mol

The migration of Fe and Al cations by a vacancy mechanism in Al-Fe spinels is supported by Petuskey & Bowen (1981). They claim that the thermal segregation (demixing) of Al-Fe spinels under a temperature gradient is due to the development of a vacancy flux with the correlated movement of cations. They report that the self diffusion of Fe is within a factor of five faster than that of Al for most temperatures and pO₂ - also the enthalpies of motion for Al and Fe by a vacancy mechanism are:

\[ \Delta H_m(\text{Al}) \approx 2 \Delta H_m(\text{Fe}) = 280 \text{kJ/mol} (=66.6 \text{kcal}) \]

Petuskey & Bowen observed that Al-Fe spinels (like Fe-rich magnetite type spinels) tend to become cation deficient at high pO₂ and that the cation vacancy concentration at constant pO₂ decreases with increasing temperature, since a large cation vacancy corresponds to a small concentration of oxygen vacancies and interstitial cations. They suggested this indicates that the creation and anihilation of vacancies must involve the exchange of oxygen with the atmosphere via the reaction:

\[ 3\text{Fe}^{3+} + \frac{2}{3} \text{O}_2 + \text{V}_c \rightarrow 2\text{Fe}^{3+} + \frac{1}{3} \text{Fe}_3\text{O}_4 (\text{s}) \]

(c refers to cation sites)

It is generally assumed that the spinel oxygen lattice is stable and rigid - indeed the topotactic transition of γ → αFe₂O₃ or Al₂O₃ is based on this assumption. This however suggests that some oxygen ions at least are mobile within the lattice. Similarly Tighe & Swan (1976) noted that the reduction of αFe₂O₃ to Fe₃O₄ even with its apparent topotactic mechanism must involve some fairly rapid oxygen
diffusion, if only for the reason that magnetite has a lower oxygen content than Fe$_2$O$_3$ and so must diffuse out of αFe$_2$O$_3$ during the transition. Reddey & Cooper (1981) reported that the activation energies of $415 \pm 15$ kJ/mol (=98.8±3.5 kcal/mol) and $360$ kJ/mol (=85.7 kcal/mol) for the self diffusion of oxygen and aluminium in a MgAl$_2$O$_4$ spinel. They also noted that oxygen diffusivity in Al-rich non-stoichiometric MgAl$_2$O$_4$ spinel is higher than in stoichiometric material and suggested it could be explained by assuming oxygen diffused by an interstitial mechanism. Since an increase in Al over stoichiometry is accommodated by producing Al vacancies according to

$$4\text{Al}_2\text{O}_3 \rightarrow 3\text{Al}_2\text{M}_2^{\text{III}} + \text{V}_{\text{Al}}^{\text{III}} + 5\text{Al}^\text{X} + 12\text{O}_0^\text{X}$$

an increase in Al vacancy concentration should result in a decrease in oxygen vacancy concentration, which in turn will increase the oxygen interstitial concentration. Hence the increased oxygen diffusivity, if one assumes it occurs by an interstitial mechanism.

### 5.2.3 Summary of Diffusion in Spinel Systems

Thus diffusion studies on similar spinel systems have revealed a number of significant facts which are likely to affect the exsolution stage of the Al-Fe-Si spinel $\rightarrow$ hematite transition at least. The general points can be summarised as follows:

i) Diffusion mechanism (ie interstitial or vacancy) can be influenced by

a) composition

b) oxygen partial pressure

c) temperature

ii) Activation energy of iron diffusion varies with

a) mechanism

b) composition
iii) Oxygen diffusion can and probably does occur.

Of these, the possibility of oxygen diffusion is likely to be the most significant - for the basis of any of the proposed topotactic transitions involved is that the oxygen lattice is rigid and relatively stable. This would appear to be at variance with the notion of oxygen ion diffusion. It is significant that the activation energy for oxygen diffusion in Al-rich non stoichiometric material is lower, suggesting oxygen diffusion is more likely in such material and could therefore be expected in an Al-rich Al-Fe-Si defect spinel.

It should also be noted that iron diffusion is faster than Al (and has lower activation energies) and so it is probable that iron does most of the movement during the Al-Fe exsolution stage. It would appear that Fe diffusion in Al-rich Al-Fe spinels occurs by a vacancy mechanism while oxygen diffusion is by an interstitial path.
The kaolinite in Warnham clay transformed to mullite by means of the predicted 'topotactic' route described in section 2.3.1. Only relatively minor deviations were observed.

Microchemical analysis indicated that the mullite showed no preference for a 3:2 composition (see later) and that the actual compositional range varied apparently uniformly with firing temperature. Brindley and Nakahira's original model postulated a varying mullite composition - however, they thought the change was somewhat discontinuous, while this study suggests it varies relatively uniformly. The gradual change in mullite composition is slightly at variance with the postulation of Chakraborty and Gosh (1978) that the Al-Si spinel has the same composition as mullite (ie 3:2) and that all the Si exsolved in the transition is exsolved at the metakaolinite - spinel transition. The small crystallite size prevented definitive measurement of the spinel composition, so preventing the degree of chemical similarity between spinel and primary mullite being checked. The TEM data did however suggest that the bulk of the Si exsolved in the kaolinite - mullite transition is 'lost' at the metakaolinite - spinel transition - subsequent changes are not great.

One possibly unexpected result was that microchemical analysis revealed no discernible difference in the mullite composition of material derived from kaolinite or illite - despite for example, the higher Fe content of illite.

When mullite from both sources was plotted out into the same 'compositional field', both apparently attained identical 'equilibrium' compositions for each temperature. These analyses revealed that the mullite crystals, irrespective of source, were at or close to the point of Fe saturation for that temperature.
As previously described (2.3.2 & 5.2.1), extrapolation of known, apparently analogous transitions predicts a topotactic mechanism for the transformation of illite to mullite, hematite and 'glass'.

While the XRD investigation (4.3.15) indicated that illite gave rise to mullite and hematite, it did not offer any evidence of the mechanisms involved. TEM in contrast, did shed some light on the mechanisms involved in the transition.

If the thermal transitions of illite are topotactic, one could expect mullite and hematite and the intermediary phases to be orientated with respect to one another and to the original clay lattice. While TEM revealed a few clear instances of orientated oxide particles and one of illite derived mullite, such examples seemed far too few for an entirely topotactic process to be the main one involved.

It is difficult to envisage how a fully topotactic transition could give rise to the non-orientated reaction products frequently found (see Ph.149). So despite the strong predictive 'evidence' from apparently analogous systems, the high temperature products of illite are NOT (fully) TOPOTACTIC.

Microdiffraction and Dark Field work (4.4.1.) showed that the oxygen lattice of illite is reasonably good (eg. Phs.52 & 55). It is sufficiently regular that if a rigid oxygen lattice is the main factor governing the transition, it ought to follow a topotactic route; but it does not.

As explained in 2.3.3 & 5.2.2, oxygen diffusivity is not as low as previously thought and so the idea of a stable, rigid oxygen lattice looks a little suspect. It could be that the apparent steering of the
thermal transitions in some layer silicates by their oxygen lattices is something of an 'illusion'.

If, as suggested in 2.3.3, oxygen ions are relatively mobile but cations such as Al and Si are not, then cation immobility could produce the subsequent orientation effects (cf anion immobility) by restricting nucleation and growth of the new phases.

Mackenzie (1969) (see 2.3.3.5) reported that impurity cations could act as nucleating sites. If this is the case, then the combined effects of 'cation nucleation' and 'cation immobility' could significantly affect the transition. The distribution of nucleation-promoting cations should affect the eventual crystallite distribution. (See also precipitate coarsening, section 5.7.1).

Minerals like kaolinite and muscovite typically have regular cation distributions and low cation impurity concentrations as well as a regular oxygen lattice, and this provides an at least equally feasible explanation for the regular orientated reaction products. Note that Comer (1960) reported orientation effects were more pronounced in purer, well crystallised kaolinite than in the ones in which impurity levels and isomorphous substitution were higher (see 2.3.1). In illite, cation distribution is relatively random and isomorphous substitution and impurity levels are high - hence relatively random product orientation.

The 'spinel' and related phases that nucleate from the 'amorphous' material that forms when the illite anhydride breaks down, precipitate in an apparently semi-structured and orientated way, often over relatively large regions (see Ph. 81). The fact that the spinel forms in this semi-ordered way suggests that the amorphous material, while not crystalline, must have some form of relatively uniform texture.

However, the scarcity of orientated high temperature products
reveals that as 'crystallisation' and 'grain growth' progress, the orientation effect is lost. Thus the topotactic type of transition of Brindley and Nakahira (1959) only appears to occur in illite up to about the nucleation of the spinel phase - as subsequent crystallisation, growth and later, transformations occur, it apparently ceases to follow any such mechanism on a large scale.

However, as isolated examples of orientated products are seen, a topotactic mechanism, or at least something that mimics it, is not totally inappropriate. Photograph 116 shows γFe₂O₃ crystallites orientated in a way similar to that one could predict for a topotactic transition.

If cation distribution and relative cation immobility do affect the transition process as suggested, then the orientation effects seen in Ph.116 could be produced by a significant (almost total) degree of Fe for Al substitution in the octahedral clay sites over a small region/crystal. This localised, ordered substitution could then give rise to well orientated γFe₂O₃ crystals via a crystal chemical dominated transition as described. Likewise, the orientated mullite crystals seen in Ph.167 that have also apparently been formed from illite could be explained by the illite having a relatively regular cation distribution and low impurity level. This would leave Al and Si free to dominate the mullite orientation. Note that in this region the iron oxides show 'reaction rims' - indicating secondary growth. It is suggested in section 5.7.1 that oxide crystallite growth processes could involve the preferential growth of earlier formed crystals (eg. derived from the oxyhydroxide coating) at the expense of new crystals which form when the clay minerals break down. Such a process could cause the final oxide distribution to show no or only limited orientation relative to the 'contemporary' mullite components.
Photograph 167 may represent an example of such a case and explain why the mullite is relatively well orientated and the iron oxide is not.

While specific examples of various features can be provided by individual samples (eg. possible structural inheritance), some features of the reactions only become apparent when the measurements obtained are viewed as a series.

Mullite, for example, first definitely appears in material fired to about 1000°C. As the firing temperature increases, there is a progressive increase in particle size eg. Ph.82 of Ph.169. Likewise, microchemical analysis reveals that the mullite shows a progressive change in mean composition, eg. Table 4.4.12.1 and fig. 4.4.12.1. The relative Fe and Al contents increase and Si decreases - this could represent Si exsolution or Al and Fe uptake or a combination of the two. Either way, the change is apparently gradual - that is, for example, Si is not 'exsolved' at one or more precise temperatures, but there is a uniform progressive change with increasing firing temperature.

Likewise TEM revealed that iron oxide, which also began to develop significantly at about 1000°C, undergoes a series of systematic changes in size, composition, crystallinity and polymorphism which correlate with the samples' maximum firing temperature. These changes will be discussed shortly.

5.4.2 Iron Oxide Particle Size Variation

Measurements of particle size revealed a precipitate coarsening type effect in which the mean size and size range increased with increasing temperature (fig. 4.4.10.1). If one treats the change in oxide crystallite size as a linear grain coarsening effect and projects
it back to a diameter of zero, it is found to cut the temperature axis at about 970°C (fig. 4.4.10.1). This temperature corresponds very closely to the 'peak' in the illite anhydrite →spinel transition (ie main exotherm on the DTA trace). This suggests the main phase of oxide growth begins as soon as the illite crystal lattice finally breaks down and Fe and Al are 'released'.

5.4.3 Iron Oxide Compositional Trends

Microchemical analysis of the iron oxides revealed that the composition field narrows and shifts to lower Al contents with increasing firing temperature (figs. 4.4.11.1-2). This trend is the reverse of what one might expect.

Al$^{3+}$ is known to be soluble in Fe$_2$O$_3$ and the maximum solubility is usually found to increase with increasing temperature. Mayers et al (1981) for example, report that αFe$_2$O$_3$ dissolves 21 wt% Al$_2$O$_3$ ($\xi_{Fe} = 0.745$) at 1380°C and 18 wt% ($\xi_{Fe} = 0.7$) at 1280°C. Why Al solubility in these oxide materials should decrease with increasing firing temperature is unclear. Al exsolution from a cubic-tetragonalγ form could be explained for low temperature material, but as the temperature is increased, Al$^{3+}$ solubility ought to increase irrespective of oxide polymorph.

It must be favorable for the Al to 'transfer' to one of the other phases present - probably mullite.

5.4.4 Iron Oxide Crystallinity and Polymorphism

Microdiffraction indicated that both γ and α Fe$_2$O$_3$ and distorted (apparently) intermediary forms occurred in the fired clays.
Oxide particles frequently gave diffraction patterns indicating that both the \( \gamma \) and \( \alpha \) structures existed in the same particle. Microdiffraction often resulted in patterns in which the geometrical arrangement did not totally correspond to a standard format, yet the 'd' values obtained were equivalent to known \( \gamma \) and/or \( \alpha \) values. The hkl reflections indicated by these values often suggested combinations that ought not occur in the same section through the reciprocal lattice. These features were interpreted as indicating two or more sections were being taken simultaneously - as would occur if the particle was made up of two or more zones of differently orientated material of one or two different phases. Such an explanation would also account for the 'random' moire patterns exhibited by many of the particles which indicated the frequent occurrence of highly complex irregular crystal lattice mismatch.

If, as seems likely, the \( \gamma Fe_2O_3 \) phase forms first and this then transforms to \( \alpha \) (\( \alpha \) would not change to \( \gamma \)) then such a situation could be generated by the formation and independent growth of a number of \( \alpha \) nuclei on a \( \gamma \) crystal. This could give rise to a situation as depicted in fig.5.4.4.1, where one particle contains some remnant of \( \gamma \) phase and partially mismatched regions of \( \alpha \). Moire patterns and superimposed diffraction patterns were seen in 'pure' \( \alpha \) crystallites and indicated that the mismatch may persist for a while after the \( \gamma \) phase has transformed.

Figure 5.4.4.1
It did not prove possible to confirm (or disprove) the topotactic nature of the $\gamma \rightarrow \alpha$ transition outlined in section 5.2.1. The diffraction patterns obtained for the combined $\gamma - \alpha$ crystals were typically poor and contained only a few low order reflections and could not give positive confirmation of orientation effects. However, some indications of the described orientation effects were seen.

5.4.5 $\gamma Fe_2O_3$ Stability

Microdiffraction (section 4.4) revealed that cubic-tetragonal $\gamma Fe_2O_3$ crystallites existed in material fired to between 1000-1150°C. This is considerably above the maximum temperature at which it is considered 'stable'. $\gamma Fe_2O_3$ is normally found to transform irreversibly into $\alpha Fe_2O_3$ at a significant rate at temperatures above 350°C. The maximum temperature it has previously been recorded to have reached before total transition is 650-700°C. So while the TEM data suggests it is only metastable, for it to exist at all and prevent 'instantaneous' transformation to $\alpha$ requires something to have stabilised the structure.

Lichtner & Szalck (1968) observed that the $\gamma \rightarrow \alpha$ transition is "remarkably" shifted to higher temperatures by increasing $K_2O$ contents. De Boer & Selwood (1954) noted that $\gamma$ doped with various ions was affected such that ions larger than $Fe^{3+}$ destabilised the structure (eg La), ones the same size (Ga) left it unaffected, while smaller ions, eg $Al^{3+}$, stabilised the structure and increased the activation energy necessary for the transition, eg:

\[
\begin{array}{ccc}
\text{Fe, Al}_y & \gamma & \text{kcal/mol} \\
0.0 & 18.3 \pm 2.4 \\
0.078 & 60.5 \\
\end{array}
\]
X-ray microanalysis of the oxides (eg. table 4.4.5.1) revealed that both Al and K were often present in small variable amounts and so could be responsible for stabilising the γ structure. It is interesting to note that the apparent stabilisation of γFe₂O₃ by impurity cations is sensitive to cation size (and charge) effects. Ridge et al (1967) and Renshaw & Roscoe (1969) report that the γ→α transition is catalysed by H₂O vapour. This again suggests crystal chemical factors such as those in 2.3.3 may be relevant.

5.4.6 Titanium 'Transitions'

The TEM investigation of unfired WSC-H (4.4.1) revealed that the clay contained traces of rutile (TiO₂), while the microchemical analysis of the clay minerals themselves showed that none contained detectable levels of Ti.

These observations combine to show that the bulk of the Ti detected in the bulk chemical analyses of the hydrocycloned clay (table 3.4.2.2) is present in the form of small rutile crystals. It is however possible and probable that some Ti may be substituting for Si and Al in the clay lattices, but that such substitution is likely to be occurring at such low levels that it is well below the detection limit for microchemical analysis (~0.5 - 1.0%).

TEM revealed that rutile existed unchanged in material fired to 800°C. It was also seen in material fired to 950°C but rutile crystals became increasingly rare in material fired to above about 1000°C. Minor pseudobrookite development was recorded at 950°C. As described in section 4.4.13, microchemical analysis revealed that a significant number of the larger 'oxide' grains detected in material fired to
temperatures between 1000-1050°C had pseudobrookite type compositions. By 1100°C, however, such crystals were rare and above this they appeared non-existent. Ilmenite (Fe Ti O₃) was never recorded.

This sequence suggests that on firing, rutile crystals (ie Ti) act initially as nucleation sites - attracting iron into the structure which then transforms to pseudobrookite. Rutile can only dissolve about 3 mole % Fe₂O₃ before pseudobrookite formation occurs (Bursil, 1974). The mechanism by which rutile is transformed into pseudobrookite is complex and involves a systematic variation in crystal shear structures that is both composition and temperature dependent. It is well described elsewhere in the literature, eg. Bursil (1974), Hyde (1976) and will not be described here. In this case pseudobrookite occurs primarily in the temperature range 1000-1050°C; below this the original rutile crystals remain relatively unaltered while above this the pseudobrookite is itself replaced by one or more other phases. Significant mullite development begins at about 1050°C and both Fe and Ti are soluble in mullite so they could dissolve into the mullite - especially since the amount of mullite present and the solubility of Fe and Ti increase with increasing firing temperature. Ti is also 'soluble' in αFe₂O₃ and so some could dissolve in the hematite that also begins its major development at about 1000-1050°C.

The precise high temperature reactions of Ti are still rather enigmatic, for while some could be expected to dissolve into the mullite, microchemical analysis of the mullite revealed little or no significant Ti content. The Ti could be dissolving in the mullite provided it is doing so more or less uniformly and at a low level, for only occasionally does it exceed the detection limit.

Microchemical analysis of the iron oxide crystallites revealed
they contain a low, though consistent Ti content that appeared to increase slightly at higher temperatures (see table 4.4.11.1). Thus it appears that the pseudobrookite 'dissolves' at elevated temperatures with the bulk of the Ti becoming distributed fairly uniformly in the α-Fe₂O₃ phase.
Given the nature of the fired materials, the most convenient 'quantitative' analytical technique for iron oxide estimation could appear to be XRD.

As described in 4.4.10, measurements of iron oxide crystallite diameters revealed a mean particle size which varied with temperature. The TEM data also revealed that the crystallinity of the oxides as a whole increased with top firing temperature; for example the degree of structural disorder indicated by the complex random moire fringes seen within 'single' crystals became less prevalent in higher temperature materials. Microanalysis, eg. fig 4.4.11.2, revealed a progressive change in oxide composition with firing temperature. So the iron oxide crystals are seen to increase in size and crystallinity and vary slightly in composition and change polymorph with increasing temperature. This could be significant when one looks at the changes in XRD traces for the same materials.

If one looks in detail at the iron oxide reflections, eg. figs. 4.3.15.1-3, one can see a progressive change in the height:width ratio. This could be interpreted as an increase in quantity of the oxide present. However, since significant changes in particle size, crystallinity and composition are occurring, it could be due, at least in part, to such changes. The use of XRD for quantitative estimation of this oxides phase must therefore be of suspect validity. (As explained in 3.1.2, such techniques presume composition, crystallite size and crystallinity are constant - and identical with the standard used.)

Similar 'arguments' would apply to mullite estimation as well - though perhaps to a slightly lesser extent as the change in crystallinity does not appear so great.
Fig. 5.5.1.1
a) Variation in Hematite XRD Reflections with firing temperature
b) Change in Oxide Particle Diameter with Firing temperature
5.6.1 Colour Generating Mechanisms

Now that the three main crystalline phases present in fired Warnham clay have been identified, with the advantage of hindsight one can obtain the details of the subatomic causes of the colour-generating processes from the literature. The important features can thus be identified.

5.6.2 Mullite - Optical Absorption Characteristics

No detailed information concerning the optical absorption properties of mullite could be located in the literature. However, as explained in section 2.3.1.3, mullite and sillimanite have very similar crystal structures, and data for sillimanite does exist. So whilst it cannot be certain the optical features of the two are identical, sillimanite is likely to provide a very close analogy for mullite.

Sillimanite is commonly yellow or brown in colour - it is known to vary with iron content. As can be seen in Phs.25 & 26, Warnham clays (1-4 & 2-4) which have had sufficient iron extracted to prevent oxide formation yield a yellow mullite-rich material on firing.

The main optical absorption features for yellow sillimanite, as determined by Rossman et al 1982, are absorption bands at;

- 462, 440, 412 nm in $\alpha$ (E//a)
- 616, 474, 438 nm in $\gamma$ (E//c)
- 361 nm in $\alpha$ & $\gamma$

A typical spectra series is shown in fig. 5.6.2.1.

As shown in fig. 5.6.2.2, Rossman et al found absorption intensity correlated to Fe$_2$O$_3$ content. These authors concluded that the main absorption features in the visible region were due to Fe$^{3+}$ in
Fig. 5.6.3.1 The optical absorption coefficient versus the photon energy for hercynite. Corrections for reflection losses have been made. The dashed curve indicates that the absorption between 0.4 and 0.8 eV was too large to be measured (estimated behaviour is shown). The main absorption peaks at 0.45 and 0.61 eV are caused by tetrahedral Fe. (After Slack, 1964)

---

**Fig. 5-6-2-1** Optical absorption spectrum of yellow sillimanite from Reinbolt Hills. Thickness: 5.0 mm, $E||a = \alpha = $ dots; $E||b = \beta =$ dash; $E||c = \gamma =$ solid line.

**Fig. 5-6-2-2** Correlation of the intensities of the optical absorption bands of yellow sillimanites with average Fe$_2$O$_3$ concentration. Bands at 361, 390, 410, and 440 nm in $\alpha$ and at 390, 410, and 440 nm in $\gamma$ follow trends which generally parallel these illustrated for 361 nm ($\gamma$) and 460 nm ($\alpha$). Absorption in the 620 nm region includes both the 616 nm and the Cr$^{3+}$ bands.
tetrahedral coordination. This was of special interest for Mossbauer spectroscopy revealed that 80% of the iron present was in octahedral coordination and only 20% in tetrahedral. The octahedral iron content of sillimanite and possibly mullite is apparently of little significance to the visible colour. Rossman et al also noted that the low absorption intensities of the 412, 440 and 361 nm absorption bands are indicative of spin forbidden Fe$^{3+}$ crystal field transitions (see 2.2.2).

Brown sillimanite is also quite common but Rossman et al found that data for such material suggested they contained exsolved acicular iron oxide crystals parallel to the c axis of the sillimanite (probably with dimensions close to the wavelength of visible light). This is an apparent analogy of the exsolution of hematite from mullite as observed by Bronwell (1958) (see 2.3.1.7) or even iron oxide precipitation in illitic brick clays.

Blue sillimanite has also been recorded and is thought to be due to Fe$^{2+} \rightarrow$ Ti$^{4+}$ charge transfer processes (see 2.2.3.1). Should a similar situation prevail in mullite, such a process could contribute to the blue-grey colour of non-oxidised fired brick clay (Ph. 1). It should be noted that ferrous iron is not easily accommodated in the mullite lattice and so significant Fe$^{2+}$ solution does not occur. However, Rossman et al noted blue sillimanites typically had a low Fe$^{2+}$ content. As mentioned in section 2.2.3.1, charge transfer processes have high absorption intensities - so small concentrations can still result in significant absorption features.

5.6.3 Hercynite - Optical Absorption Characteristics

Despite the significant interest in the optical absorption
characteristics of the 'gem' spinel systems, little appears to have been published on hercynite-type material, probably because natural hercynite is an 'uninteresting' dark green to black colour.

The only even semiquantitative study found is that of Slack (1964). Slack performed reflectivity measurements on an opaque synthetic single crystal - unfortunately the measurements were taken at about 30° to the normal and so are only approximate. He observed the following reflectivity maxima:

\begin{center}
\begin{tabular}{lcc}
$hv$ (eV) & $\% R$ & \\
0.038 & ~50 & small peak \\
0.061 & ~70 & broad peak \\
0.068 & ~50 & weak shoulder \\
0.086 & ~80 & peak \\
0.099 & ~40 & shoulder \\
0.180 & low & \\
\end{tabular}
\end{center}

From such measurements Slack calculated the optical absorption coefficient using standard procedures and then plotted absorption coefficient against photon energy, as shown in fig. 5.6.3.1, thereby illustrating absorption spectral features.

Slack attributed the strong double peaked absorption band between 0.4-0.8eV to the $3d^6 \, 5E(5D) \rightarrow 5T_2(5D)$ tetrahedral $Fe^{2+}$ Crystal Field Transition and believed the broad peaks at 1.23-5 and 1.65eV were due to the $5T_2(5D) \rightarrow 5E(5D)$ crystal field transition of octahedral $Fe^{2+}$. He attributed the small sharp peak at 0.176eV to lattice vibration. It was suspected the hercynite might not be fully reduced ($Fe^{3+}$ in Wustite can never be fully reduced to $Fe^{2+}$) in which case the absorption at 2.25, 2.40 and 2.65eV could be due to tetrahedral $Fe^{3+}$, while a 'hump' seen in some spinels at about 1.35eV was thought to represent $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer on tetrahedral sites.
It is evident from sections 4.3-4 that the Al-Fe spinels that can be derived from Warnham clay are of variable nature - eg. XRD reflections, fig. 4.3.13.1, reveal variable hkl intensities. Though the hercynite lattice is essentially cubic it is possible that variations in cation distribution, isomorphous substitution or cation and anion vacancies could locally distort the lattice and so alter the absorption energy and intensity of crystal field transitions. So slight differences in colour due to such effects ought to be expected. However, the colour observed in the bulk samples of the fired clay (eg. Ph.28) are not significantly different, indicating such effects are not great.

5.6.4 Hematite - Optical Absorption Characteristics

The structure of hematite is shown in fig. 5.1.3.2. In αFe₂O₃, Fe³⁺ is located in edge and face shared octahedral sites - adjacent sites being bridged by oxygen.

The absorption spectrum of hematite is shown in fig. 5.6.4.1. Crystal Field absorption features are seen at 850 and 660nm (11800 and 15200cm⁻¹) but the dominant spectral feature is the 0²⁻→Fe³⁺ Charge Transfer tail that extends from the UV into the edge of the near infrared (Bell et al, 1975). Thus the colour of hematite is due to a small transmission window in the visible at about 750nm, between the CTT and CFT absorption in the UV → visible/IR and the IR respectively. If this transmission is reduced the material should become opaque.

The TEM investigation revealed that some of the iron oxide present in the fired clays is the cubic form maghemite (γFe₂O₃). It is metastable and is in the process of transforming into the normal α form (hematite) described above. As explained in section 2.2.1, the precise
position and intensity of Crystal Field and Charge Transfer absorption bands depends on such things as crystallographic environment, e.g. site symmetry and M-O bond length etc. There will therefore be a difference between the absorption spectra of the Fe₂O₃ material from Warnham clay and 'standard' αFe₂O₃. However, as the associated shifts in absorption peaks will be outside the visible spectrum, only slight changes in the absorption tail that extends into the visible would be expected. Such changes are therefore likely to be of relatively little importance. Likewise, microchemical analysis revealed Al substituting for Fe and this too could affect the detailed spectrum, but again the main effect would be outside the visible.

<table>
<thead>
<tr>
<th>Peak Position</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>λmax (μm)</td>
<td>v_max (cm⁻¹)</td>
</tr>
<tr>
<td>860</td>
<td>11630</td>
</tr>
<tr>
<td>465</td>
<td>21500</td>
</tr>
<tr>
<td>350</td>
<td>28570</td>
</tr>
<tr>
<td>290</td>
<td>34480</td>
</tr>
<tr>
<td>231</td>
<td>43290</td>
</tr>
</tbody>
</table>

Table 5.6.4.1 Diffuse Reflectance Spectra of Ferric Oxide. (After Tandon & Gupta, 1970 (8μ particle size)

C.T.T. = Charge Transfer Transition. Note: Crystal Field (C.F.) Transitions are 'spin forbidden' and therefore of low intensity.

(A) ⁶A₁g → ¹T₁g (t₂g)⁴ (e₉)
(B) ⁶A₁g → ⁴E₉ (t₂g)³ (e₉)²

⁴A₁g (t₂g)³ (e₉)²
Fig. 5.6.4.2  Diffuse Reflectance Spectra of Oxides

(After Bell et al, 1975)

Fig. 5.6.4.1  Hematite Absorption Spectrum

(After Bell et al, 1975)
The previous sections outline the absorption characteristics of the main coloured components of fired bricks. In addition to the combined absorption of the various components the colour of such ceramics is sensitive to additional 'physical optical' parameters.

Most surfaces in ceramic systems are not perfectly smooth and consequently there is considerable diffuse reflection from the surface. Fig. 5.6.5.1 shows the amount of energy reflected from a surface by a single incident beam for various surface textures. Only in the case of metallic reflection does (nearly) all the light come from the surface layer. In most instances, such as with ceramics, some light penetrates below the surface and is scattered and reflected out again - but in the process some parts of the spectrum are absorbed - hence the object appears coloured (see fig. 5.6.5.3). The fraction of light specularly reflected from the surface determines the 'gloss' while that diffusely reflected from the near surface layers 'generates' the colour. The observed colour of a multiphase system is strongly influenced by the light scattering and absorption properties of both matrix and included particles.

The absorption characteristics of the main phases have already been described. The main factors determining the scattering coefficient are the particle size, refractive index and the volume of the second phase present. The relationship between particle size and scattering is well known - maximum scattering occurs at a size equivalent to the wavelength of the incident light. For smaller sizes $K$ increases with particle size and is inversely proportional to $\lambda^4$ while it reaches a constant value for sizes substantially larger than $\lambda$. Likewise scattering increases with increasing difference in
Fig. 5.6.5.1 Polar diagrams of reflection from surfaces of increasing roughness.

Fig. 5.6.5.2 Reflections from a rough surface.
Refractive Index (n) between particle and the matrix (Kingery et al, 1976). Approximate Refractive Indices of the main phases of interest are given in table 5.6.5.1.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Approx. Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass Phase (Kaolinite/porcelain)</td>
<td>( n_0 = 1.5 )</td>
</tr>
<tr>
<td>Mullite</td>
<td>( n_0 = 1.64 )</td>
</tr>
<tr>
<td>Quartz</td>
<td>( n_0 = 1.55 )</td>
</tr>
<tr>
<td>Hematite</td>
<td>( n_0 = 2.9-3.2 )</td>
</tr>
<tr>
<td>Hercynite</td>
<td>( n_0 = 1.84 )</td>
</tr>
</tbody>
</table>

Table 5.6.5.1 Refractive Indices

In the case of hematite the particle size affects the colour not only through scattering effects but also via absorption effects. \( \alpha Fe_2O_3 \) has relatively high absorption coefficient and reflectivity values, and these affect the way in which particles of various sizes absorb and/or reflect light.

Light is absorbed in an exponential fashion. One can visualise this phenomenon by considering light entering an absorbing medium that is divided into layers of equal thickness. On entering the top layer, the light has an intensity \( I_0 \); on leaving it has intensity \( I_o \) and at each successive layer the same proportional reduction takes place.

\[
\begin{align*}
I_0 & \rightarrow I_R \\
I_{o1} & \rightarrow I_{o1} \\
I_{o2} & \rightarrow I_{o2} \\
I_{om} & \rightarrow I_{om} \\
T_o & \rightarrow T_o
\end{align*}
\]

eg. for 10% absorption
\[
\begin{align*}
I_o & = 100 - I_R \\
I_{o1} & = (90 - I_R)\% \\
I_{o2} & = (81 - I_R)\% \\
I_{om} & = (72.9 - I_R)\% \\
T_o & = (65.6 - I_R)\%
\end{align*}
\]
Hence \[ I = e^{-\mu t} = e^{-4\pi \frac{k^t}{\lambda}} \]

where: 
\[ \mu = \text{logarithmic decrease factor} \]
\[ t = \text{thickness} \]
\[ k = \text{absorption coeff. decrease factor in air, ie } \lambda_0 = \text{vacuum} \]
\[ K = \text{absorption index } (k=nK) \]

As the absorption coefficient increases, the thickness through which say, 50% of the incident light can be transmitted decreases. Thus in materials with high absorption coefficients like hematite, significant transmission can occur only through very thin crystallites. As the thickness increases, so does the amount of absorption - hence the change in colour for crystallite size. As previously mentioned, transmission in hematite occurs only through a window at \( \sim 750\text{nm} \). If this is removed by increased absorption, the material becomes opaque. Note that for large crystals, little in the way of diffuse reflectance occurs and the high reflectivity gives the crystal a metallic silver appearance.

No accurate absorption coefficient figures for hematite could be found in the literature. Attempts to calculate them by measuring reflectivity values of a pure hematite single crystal yielded unreliable values, so attempts to quantify the differing absorption effects for the different particle size ranges encountered in the fired Warnham clays were unsuccessful. Accurate values of Absorption Coefficients are needed.

5.7.1 Iron Oxide Grain Growth

Iron oxide particle size is probably the single most important
factor governing the development of colour in fired bricks (see 5.6.5). As previously outlined, the size varies with firing temperature. The mechanism behind the growth process is therefore relevant and though while not understood, some of the features of the mechanism can be estimated.

There is a tendency for small particles with some solubility in the matrix in which they occur to dissolve and the material in them to precipitate on the larger particles, causing their growth. The driving force is derived from the consequent reduction of total interfacial energy.

Two general mechanistic models have been postulated (Greenwood, 1968).

a) Diffusion controlled - Diffusion through the matrix is the rate controlling step.

b) Interface controlled - When the ability of an atom to enter solution is the rate controlling step.

Relatively simple mathematical models have been constructed to cover these situations and have succeeded in producing a theory capable of predicting such things as growth rates and particle size distribution curves. However, these 'simple' growth equations do not appear to fit cases where the matrix is unstable, e.g. recrystallising, as in this instance and the theory has yet to be extended to such cases. The limitations of the theoretical approach can be seen in that so far only diffusion controlled processes have been identified experimentally - no authenticated case of an interface controlled coarsening has been reported.

Diffusion controlled processes seem more generally applicable to cases with a condensed (crystalline) matrix material. In contrast fired clays have an amorphous: microcrystalline matrix through which
diffusion is likely to be relatively rapid. Particles with contaminated surfaces growing in a liquid phase through which solute diffusion is rapid (e.g., iron oxide crystallites in a Si K amorphous 'glass' phase) could well fit an interface model. The firing trials produced samples with BOTH different times and temperatures, so it was not possible from the data to ascertain if the process was diffusion or interface controlled.

As described in section 2.3.3, crystal chemical factors could be affecting diffusion and so limit growth. So a diffusion controlled growth/coarsening process is feasible.

If a diffusion controlled process is assumed, though no detailed predictions can be made due to the discrepancy between idealised boundary conditions (see Greenwood, 1968) and reality, a few relevant general features of such a process can be stated. In diffusion controlled processes, crystallite growth ought to proceed such that the cube of the mean particle radius \( r \) increases linearly with firing time, while the precise rate increases with temperature. Also theory predicts that the maximum particle size ought to be of the order of 1.5-2 times the mean radius. Particles below \( \bar{r} \) ought to be dissolving at increasing rates as \( r \) decreases; if \( r=\bar{r} \) then it ought to be static, while if \( r>\bar{r} \) then the particles ought to be growing with 1.5-2\( \bar{r} \) showing maximum growth rate. This process causes a narrow particle size spread to broaden with time.

One potentially very interesting extrapolation from the basic model (Greenwood, 1968) postulates that coherent precipitates, because of their associated strain energy, must always have a higher solubility than a non-coherent precipitate of the same phase.

If the spinel-oxide microcrystallites that nucleate shortly after the clay lattice finally breaks down are 'coherent' with the
'amorphous' matrix, as seems possible in the case of a topotactic type transition, then this might accentuate the tendency of these micro-crystallites to start dissolving and the material to reprecipitate on any larger crystal - for example those oxide crystals derived from the decomposition of the oxyhydroxide coating. If such a 'recrystallisation' process is active then the final oxide particle distribution need not show any coherence/orientation effects with the rest of the material derived from the clay lattice, even if the illitic material transformed via an essentially topotactic transition.
6 Conclusions

Powders of air fired WSC subjected to alkali extraction procedures of the type described in section 2.4 showed no significant change in colour even in the case of severe repeated extraction. As no colour change was observed and XRD indicated a reduction in the amorphous SiO₂ content, it was concluded that the amorphous phase contributed little to the colour.

This implied that the colour was generated by the crystalline components. XRD revealed that mullite and iron oxide were the main crystalline phases present. As described in section 5.6.2, mullite is typically a cream-buff colour - the precise colour depending on the iron content. Microchemical analysis and XRD measurement of unit cell dimensions revealed that the iron content of the mullite present varied with top firing temperature, therefore so too should its colour. The yellow - buff colour range of fired HCl-HNO₃ treated clay is consistent with this observation, and supports the notion that mullite is not responsible for the orange-brown colour of fired Warnham clay. The 'elimination' of mullite leaves only iron oxide and hematite is typically a reddish colour.

The TEM investigation plus the results of the firing trials with chemically treated clays revealed that oxide growth occurs in two stages. The first occurs between about 350-900°C when the thermo oxidation of the amorphous Fe-Al oxyhydroxide 'coating' produces sub 250Å Fe₂O₃ crystallites. Transmisssion in the 750nm region is relatively high for such small crystallites - hence the fairly bright reddish-orange colour of such materials.

The second phase of oxide growth began at about 950-970°C when the iron 'released' during the breakdown of the clay minerals reacted to
form Fe$_2$O$_3$. TEM revealed that the mean crystallite diameter increased relatively uniformly with increasing firing temperature in material fired above 950°C. As described in section 5.6.5, the colour of α Fe$_2$O$_3$ varies significantly with variations in particle size due to systematic variations in transmission/absorption in the 750nm region.

Hence iron oxide Fe$_2$O$_3$ is responsible for the 'red' colour of fired Warnham clay - while the orange-brown temperature-dependent colour sequence correlates primarily with changes in mean particle size.

A significant proportion of the iron oxide present in material fired to the temperature range used for commercial bricks is derived from the clay minerals. In Warnham clay most of the iron comes from the illite - illite:vermiculite component - kaolinite and halloysite do not have a substantial iron content.

The mechanisms behind the high temperature reaction of the illitic and kaolinite type components are therefore of interest as they are important in determining the reactions of the clay mineral derived iron. The relatively complex mineralogy of Warnham clay has precluded any investigation in this study of the mechanisms, for such a study requires a pure, single mineral starting material. (In the case of illite such material is very rare - and arguably may not actually exist.)

The entire process of new mineral formation in Warnham clay can best be considered as a sequential process in which dehydroxylation, structural collapse, new crystallite formation and fusion with the ultimate formation of a glassy phase all take place in an overlapping fashion for each of the clay minerals in the mix.

TEM reveals there is no sign of spinodal decomposition (ie essentially a diffusion controlled process only) during the structural
collapse of the clay minerals and new crystallite formation. Rather, the transition shows signs of heterogeneous nucleation and precipitation followed by crystallite growth/precipitate coarsening.

The literature survey of apparently comparable pure well-crystallised phases, eg kaolinite and muscovite, suggests the transition series is topotactic and is based on ordered transformations of a stable, rigid, close-packed oxygen lattice with complimentary cation diffusion yielding orientated reaction products. Detailed study of the literature reveals a number of apparent inconsistencies between the observed reactions and the proposed mechanism - for example, why is the formation of mullite catalysed by H₂O vapour and certain cations?

The TEM investigation revealed that some of the kaolinite present in Warnham clay followed a transition sequence similar to that described in the literature survey. It followed a topotactic route in so far as it ultimately gave rise, via an orientated cubic intermediary, to three sets of orientated mullite in an amorphous silica-rich matrix. The illitic component, however, did not precisely follow the predicted topotactic route. The reaction products were indeed those predicted (see fig. 6.1.1) but there was little evidence in the way of orientated final reaction products of a true topotactic transition despite what appeared to be a reasonably regular oxygen lattice in much of the starting material.

The degree of orientation seen in the reaction products of kaolinite is known to be susceptible to variations in kaolinite crystallinity and impurity content. Muscovite, the structural equivalent of 'pure, well-crystallised illite' gives rise to orientated reaction products whereas illite, like impure kaolinite, does not. In the case of muscovite and illite the main difference between them is in
the nature and the distribution of the cations.

It appears, as described in sections 2.3.3 and 5.4.1, that the nucleation of new phases is more dependent of the cations present and the cation lattice than on the oxygen lattice. If so, then in reality pure kaolinite and muscovite mimic a topotactic transition due to their 'untypical' regular, impurity-free cation lattice. Their apparent topotactic transition series would therefore, as such, represent the exception rather than the rule.
Appendix One

Vermiculite: its origin and relationship to Illite

It is now reasonably well established that expanding layer silicates can be formed by natural and artificial weathering of other non-expanding layer silicates such as muscovite or biotite. Jackson and Sherman (1953) noted that the loss of K+ changed micas into expanding layer silicates. Since then, numerous accounts have appeared in the literature of studies of both natural and artificial weathering and a number of mechanisms have been proposed to explain the reactions.

Basically, natural weathering is now envisaged as a loss of K+ and an uptake of water as a result of leaching by acid ground waters, the acidity coming from dissolved CO₂ or organic soil acids. Numerous accounts of studies of weathering profiles and such like appear in the literature. In one such study of a Norwegian Pleistocene marine clay, Jorgensen (1965) noticed that with progressive weathering, dioctahedral illite changed first to an irregularly mixed layered illite:vermiculite and then to an illite:vermiculite with a regular alternation of the two layers. The first change observed is the development of a 'tail' on the low angle side of the 10Å XRD reflection, which probably indicates some water has entered the interlayer positions. (See XRD trace of WSC, fig.4.2.0.3).

The apparent mode of action is that H+ ions enter the vacant octahedral positions in the dioctahedral structure, thus obviating the need for interlayer K+ to balance the net layer charge, and so these are simultaneously lost. The contemporary uptake of water and slight lattice expansion ('tail') are probably the result of a decrease in bonding between the layers.
Laboratory weathering experiments have shed some light not only on the process of illite development but also on the reason for its low Cation Exchange Capacity and apparent stability (Section 3.4.6).

Rich and Cook (1963) treated samples of mica with sodium citrate solutions and succeeded in producing the dioctahedral analogue of vermiculite. They also reported that the rate of forming expanded layer silicates could be increased by substituting sodium chloride for the citrate. These salt treatments however, not only extract K+ and to an extent replace it by Na+, but they also attack the octahedral layer, releasing Al\(^{3+}\) ions - with the former occurring at a faster rate. (Vincente et al (1977) observed that K+ was extracted about 40% faster while the following extraction order was observed for octahedral cations: Mg > Fe > Al > Si . This order may be reversed for inorganic acids (Huang and Keller, 1972)). The Al\(^{3+}\) released by this weathering was capable of becoming fixed as hydroxy groups in the interlayer, so inhibiting collapse and also accounting for the low CEC and lattice stability seen in the 14Å product.

In the process of natural weathering of micas, hydroxy Al&Fe
groups accumulate in the interlayer space. These groups occupy exchange sites and inhibit the contraction of the mineral on K+ saturation or heating and restrict expansion due to liquid absorption. The process of interlayer filling can be reversed when natural chelating agents (organic matter) are abundant. The interlayer can be removed in the laboratory with complexing agents such as citrate or fluoride.

Two techniques described in section 2.4, namely acid oxalate extraction and fluoride solution, though devised respectively to remove free iron sesquioxides and to 'concentrate' dioctahedral mica and vermiculite, are in effect artificial weathering techniques as both agents are capable of complexing Al$^{3+}$.

In fact, a general study of the appropriate literature suggests that any acid (eg acetic, hydrochloric etc) - is potentially capable of, and almost certainly will cause artificial weathering if used at pH 2.5-5 (Vincente et al, 1977). Below about pH 2.5 significant mineral destruction occurs.

The fact that it is not reported more often is probably due to the great affinity of weathered dioctahedral mica for K+. It is capable of removing K+ from solutions of 'pure' NaCl and Na citrate etc. It is possible that >10ppm K+ in solution blocks weathering due to an equilibrium being set up with the reverse reaction.

\[ \text{Mica} \rightleftharpoons \text{Vermiculite} + K^+ \]

Rich and Black (1964) noted loss of K+ from solution of an impure salt containing 100ppm K to a vermiculite soil. Vermiculite will try to absorb K+ and collapse. It is only prevented/inhibited from doing so if interlayer Al:Fe material blocks both sites and prevents collapse.

While organic acids are known to be capable of extracting K+ and
causing vermiculite formation, some researchers have found that certain other complexing agents eg sodium tetraphenylboron (Tomita and Dozono 1972), can remove interlayer K, indicating that other naturally-occurring ones could too. Newman and Brown (1966) report significant oxidation by air in biotite during K+ extraction with sodium tetraphenyl boron. Farmer et al (1971) observed laboratory oxidation of vermiculitised biotite could involve a loss of octahedral iron and an increase in dioctahedral type vacancies. Wilson (1970) presented IR evidence for an increase in octahedral vacancies during natural oxidative weathering and suggested that natural complexing agents in the soil may remove interlayer iron.
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