# Chapter 1

# Overall introduction

## 1.1. Background

There is continual interest in the development of new techniques and optimisation of existing ones for the non-destructive analysis of chemical components. The techniques are expected to give unambiguous information on all chemical components and if possible, their relative amounts. Such techniques as described above could find application in the study of archaeological earthenware objects and iron oxides, among other studies in chemistry.

## 1.2. Rationale for the study

### 1.2.1. Earthenware objects

The earthenware objects (referred to here as low temperature fired clay pottery) are often African domestic accessories and artefacts. These are the types of pottery that were produced below temperatures required for the melting and fusion of the raw aluminosilicates (e.g. clays, feldspar and quartz) into a glassy material in a process called vitrification. Vitrification is an integral part of Chinese ceramics production.

The low temperature fired red-brown and black pottery is common to Africa. The pottery shards have a coarse texture with open sponge-like internal structures and are visibly heterogeneous. This is contrary to the Asian ceramics, which are often white in colour, smooth textured and homogeneous. The Chinese potters are known for processing the clay minerals before pottery making, e.g. to reduce the iron oxide level. The Asian potters fire their clay wares at temperatures well in excess of 1100 $^{o}$C [1]. The African pottery is not fired at high enough temperatures that are required for vitrification of the silicium and flux present in the clay [2]. No pre-treatment of clay minerals by African potters has been reported, but minerals were used as acquired [3]. Clay pots were used in cooking and in ritual context. In a settled culture, pottery became increasingly important for long-term storage of food and

liquids [4a]. The black coloured pottery without decorations was normally for daily use, e.g. cooking [2]. The decoration on pots can be ritualistic, cultural and reminders of etiquette of gender interactions [4b]. The brightly coloured (red and black) and most decorated pottery was used for storage and serving of food and drinks [2].

### 1.2.1.1.    The standard procedure for making African clay pottery

The knowledge and understanding of raw materials, additives, processing of clay, decorating procedure, fuel and firing conditions used in pottery making aid in the full characterisation of components observed in the clay pots.

The quarried clay (either from riverbanks or the foot of a mountain) was initially broken into small pieces by hand. It was then powdered with wooden sticks as water was added in small portions to achieve a satisfactory level of working plasticity. Vessels were formed by a combined technique of modelling and coiling. The body, neck and shoulder were finished, complete with decoration, before the base was begun. Therefore, the making of clay vessels is a two-stage process [2]. Once the surface of the vessel was smoothed by hand and water, the pot was left to dry until firm but still workable. The surfaces of most pots were burnished with a smooth rounded river pebble until lustrous to varying degrees.

Some vessels were polished with fine graphite powder and further decorated and coloured with red ochre. Pots were left to dry for several days (~3). Firing occurred in oxidising atmospheres in either an open bonfire or shallow pit. Fuel used included cattle dung, tree bark and wood fuel stacked around the pot. The firing process was complete in about 40 minutes. After cooling, the exterior surfaces of the vessels were orange-red in colour, sometimes with dark gray or black patches. The dark gray or black colours are due to insufficient oxidation [2].

**1.2.1.2.    The significance of chemical phases that constitute museum clay artefacts**

The information on chemical phase composition of valuable objects is even more relevant to the keepers and curators of clay items and artworks (e.g. of museum and private objects), because the origin, history, properties and full description of objects are closely linked to the chemical compositions.

Museums are the repositories of history, heritage, technology, culture, etc. Therefore, full characterisation of museum objects is essential to facilitate conservation, reconstruction, dating, discrimination and authentication, but the objects cannot be destroyed in the process. Objects of historical importance need to be preserved for the coming generations. Acceptable methods of preservation require full knowledge of the constituents of the preserved object. Reconstruction work is an integral part of every museum with clay products. For reconstruction of pottery the knowledge of the following is essential: raw materials (e.g. different types of clays), firing temperature, atmosphere of processing (i.e. oxidative or reductive atmosphere), special material applied to give the clay product unique properties and function of the product. For the museum record all objects are normally recorded with full description of shape, origin, size, markings, colours and decorations. The chemical compositions could provide an alternative and more reliable way of recording and characterising museum artefacts. Authentication is essential for discrimination between the genuine artefacts and imitations.

Most literature studies on earthenware objects (low temperature fired clay pottery) were of archaeological nature and concerned with the determination of various chemical species and their corresponding amounts. For instance, in provenance studies the assumption is often made that a link exists between the raw materials and the final clay products. The link is based on specific chemical species and their corresponding amounts. The results on chemical species obtained from the clay products are then compared with those obtained from the raw materials in the same area where the objects were found. The techniques often

used include neutron activation analysis (NAA), proton induced X-ray excitation (PIXE), petrography, infrared reflectance, X-ray fluorescence (XRF), etc [5, 6]. These techniques are used in conjunction with statistical clustering methods for grouping based on the amounts of chemical species. The results obtained are then used to define different groups of pottery, to identify foreign objects and to further retrace interactions and trade relations between different ancient communities. The techniques previously used to analyse these types of clay products are either destructive and/or give only elemental results. The valuable objects and those kept in museums cannot be analysed using the above techniques. Therefore, there is a need for a non-destructive technique that will give information on the chemical composition.

### 1.2.2. Iron oxides

The iron oxides are the largest sector of the inorganic pigment industry (including paint, ink, construction materials, etc), which are produced both chemically and from natural sources [7]. Pigments are fine powders used for colouring media and other powdery materials, e.g. metallic powders showing magnetic or anticorrosive properties that are intentionally dispersed (not dissolved) into media to increase value and to impart some special properties [8a]. The proportion of iron oxides as pigments will continue to rise as the construction activities increase and new markets are found as concern grows over the use of heavy metal pigments. The continually increasing importance of iron oxides is also based on their non-toxicity, chemical stability, durability, wide variety of colours and low costs. Therefore new and simple cost-effective methods for the preparation of iron oxides are required in order to meet the demands. With the development of new and cost-effective methods (including methods that use cheaper raw materials) arises the need for specific and sensitive techniques to maintain the required standard and quality levels.

As an additional work to the present study some of the pure iron oxides (namely, magnetite ($Fe_3O_4$, black), hematite ($\alpha\text{-}Fe_2O_3$, red), maghemite ($\gamma\text{-}Fe_2O_3$, brown), goethite ($\alpha\text{-FeOOH}$, yellow), and ferroxyhite ($\delta\text{-FeOOH}$, dark brown)) were prepared and characterised (by Raman spectroscopy and X-ray diffraction) for use as standards during a separate study

involving the *in situ* micro-Raman spectroscopic analysis of the composition of passivation film on iron metal [9].

### 1.2.2.1. Theoretical background on inorganic pigments

The value of pigments results from their physical-optical properties. These are primarily determined by the pigment physical characteristics (crystal structure, particle size and distribution, particle shape, agglomeration, etc) and chemical properties (chemical composition, purity, stability, etc).

The two most important physical-optical assets of pigments are the ability to colour the environment in which they are dispersed and to make it opaque. Opacity of pigments prevents transmission of light and obscures the subject on which it is applied. The opacity of the pigment is a function of the pigment particle size and the difference between the pigment refractive index and that of the medium in which pigment particles are dispersed [8b]. Any agglomeration of pigment particles can affect their opacity. At a certain pigment loading/thickness the substrate becomes completely hidden and the pigment determines its colour [8b].

The most commonly measured pigment properties are elemental analysis, impurity content, crystal structure, particle size and distribution, shape, density and surface area. These parameters are measured so that pigment producers can better control production and set up meaningful physical and chemical pigment specifications.

The measured pigment colouristic properties include, colour, colour strength, opacity, lightfastness, weathering, heat stability, chemical stability and rheological properties [8b] and many of them are determined also by the dispersing media and processing conditions. The particle size and distributions affect the colour, colour strength, hiding power (the ability of a coating to hide the substrate [8c]) and rheological properties (related to the deformation and flow of dispersed pigment under the influence of applied stress) [10]. For inorganic pigments to be useful in most applications, they must have an average particle size between 0.1 and

10 µm [8d]. However, for smaller particles the granulating agents are added for intentional agglomeration (to form granules) in order to prevent powder dusting and make handling easier.

The surface area and porosity of the pigment affect its oil absorption ability, such that the higher the surface area the greater the oil absorption [8d].

Different shades are controlled primarily by the oxide particle size, shape and surface properties [8e]. If the surface area value is higher than expected (e.g. higher than that of literature and commercial product) then the particle surfaces are porous [11]. Uniformity of particle shape is essential, if quality hiding power is to be achieved [12]. Hiding power of a uniform coating is expressed as the area of substrate that can be hidden by unit volume of coating ($m^2$/L). It is expressed through the Lorentz-Lorenz equation:

$$HP = 0.16 \, (n_p - n_m)^2$$

where $n_p$ and $n_m$ are the refractive indices of the pigment and medium, respectively [8c]. The ability of a pigment to change the colour of an opaque film is known as its tinting strength. Tinting strength is related to particle size, such that the increase in particle size results in decreases in tinting strength. The darker and more saturated colours yield deeper tints [13]. Elemental analysis, impurity content and stoichiometry are determined by chemical or instrumental analysis. Chemical analysis of principal components is carried out to determine pigment stoichiometry. The presence of undesirable elements, such as heavy metals, even in small amounts can make the pigment unusable for environmental reasons. A single-compound pigment can exist in several crystal structures not all of which have equal colouristic properties. A good pigment contains a colourant as a principal phase. Secondary phases determined by X-ray diffractometry might be present only to reduce colouristic properties [8c].

Many pigments can get darker, change their shade or lose colour saturation when exposed to high intensity light such as direct sunlight or UV lamp. Inorganic pigments, particularly

those containing ions that exist in several oxidation states, e.g. Fe, Pb, etc, usually get darker [8c]. Some colour changes can be reversible, while others are permanent. Lightfastness is measured by exposing pigment film to an artificial or natural light for a predetermined time [8f].

Weathering is the ability of the coloured system, i.e. coating, paint, etc, not the pigment alone, to resist light and environmental conditions. Colour and gloss changes are the main factors evaluated in weathering tests [8f].

Heat stability is expressed as the maximum temperature at which the colour of the system does not change. Chemical resistance can be determined by measuring colour changes of pigmented binder surfaces after exposure to various chemicals such as water-sulphur dioxide or water-sodium chloride systems [8f]. These systems imitate the environment to which the coloured articles could become exposed.

For more details on inorganic pigments, see reference [8].

## 1.2.2.2.    Synthesis of iron oxides

In developing new methods (including the use of alternative starting materials) for the preparation of the desired products, a full investigation is often required in order to understand the processes taking place. The common aim of such an investigation is the determination of the reaction mechanism. The most important step in the investigation of the reaction mechanism involves the identification of as many reaction products as possible (irrespective of their amounts). The understanding of the reaction mechanism allows one to modify, control and optimise the process. The characterisation technique should be specific and sensitive enough to detect as many components present as possible.

Natural and synthetic iron oxides consist of well-defined compounds with known crystal structures [14, 15]. Chemically, these are oxides and oxyhydroxide compounds of iron. There are seven polymorphs of iron oxides with varying properties, namely, magnetite

($Fe_3O_4$, black), hematite ($\alpha$-$Fe_2O_3$, red), maghemite ($\gamma$-$Fe_2O_3$, brown), goethite ($\alpha$-FeOOH, yellow), akaganeite ($\beta$-FeOOH, brown), lepidocrocite ($\gamma$-FeOOH, light brown) and ferroxyhite ($\delta$-FeOOH, dark brown) [16, 17, 18]. Iron oxides are important compounds for pigments, catalysis, magnetic devices, adsorbents, batteries and corrosion of iron and steel [19, 20, 21].

The iron oxides can be prepared by either thermal treatment and/or precipitation from aqueous media. Hematite is the only thermally stable polymorph prepared by oxidative thermal treatment of iron salts [22, 23]. Magnetite is one of the most thermally unstable iron oxides. It turns first into maghemite around 200 $^{o}$C, and then to hematite around 400 $^{o}$C [24]. Therefore, hematite is a common contaminant of any iron oxide polymorph prepared under heat.

All the iron oxides can be prepared by precipitation methods. The precipitation of one iron oxide is often preceded by the formation of another, e.g. the hematite particles are formed from the akaganeite particles via dissolution/reprecipitation [25]. Depending on the reaction conditions several compounds may be formed as the final products, thus influencing the purity and properties of the desired products. The chemical phase composition and properties of the precipitate depend on the type of starting material, e.g. hydrolysis of $FeCl_3$ results in the formation of akaganeite and hematite only [16]. The presence of organic molecules (e.g. citrates), inorganic ions (e.g. phosphate, sulphate) or transition metal ions (e.g. $Zn^{2+}$, $Cu^{2+}$) in the precipitation medium influences the reaction mechanism and properties (e.g., colour, particle shapes and sizes) of the products [26, 27, 28].

The use of iron wastes as the starting material in the preparation of iron oxides has previously rendered the processes cost-effective [22, 23, 29]. However, the waste materials often contain the active substance together with some other undesired substances.

It is clear from the above information that the preparation of iron oxides either from pure starting materials or waste materials is often accompanied by contamination (including other iron oxide phases). The presence of undesired compounds may alter the phase of the

product and influence the reaction conditions (e.g. pH), mechanism and the properties of the desired product. The properties of iron oxides that are often influenced include the colour, crystallinity, particle characteristics, etc. These properties determine the use of iron oxides. Therefore, the preparation of iron oxides should be accompanied by the use of an analytical technique that could identify as many possible contaminants as possible, even in their amorphous form.

### 1.2.3. Raman spectroscopy

The literature shows that Raman spectroscopy has been studied extensively and applied widely. The unique properties of this technique involve non-destructive nature, no sample preparation, reliability, specificity and sensitivity [30, 31]. It is also amenable to *in situ* analysis [17, 32, 33]. Raman spectroscopy has been found to be particularly sensitive to coloured molecules [34]. This technique is most effective in structural characterisation, identification and detection [34]. Therefore, Raman spectroscopy can distinguish between structural forms of the same compounds, even in their amorphous form.

From the comparison of the properties of Raman spectroscopy (as given above) and those required by the types of samples under investigation, Raman spectroscopy appears to be the potential analytical technique required for the analysis of both low temperature fired clay pottery and iron oxides.

### 1.3. Aims and objectives

The chemical phase study of valuable clay products (e.g. ancient ceramic pottery) and iron oxides requires the application of a technique, which is amenable to *in situ* analysis, non-destructive, sensitive, specific and gives chemical phase results.

Raman spectroscopy seems to be an appropriate technique for the types of samples mentioned above (clay products and iron oxides). This technique can detect crystalline and amorphous chemical phases and can be connected to a microscope thus making it possible

to detect phases in micrometre scale while reducing fluorescence. It has been found to be sensitive and specific. It is also amenable to *in situ* and non-destructive analysis. The measurement times could be short.

The overall aims and objectives of the current study are to demonstrate the effectiveness of dispersive Raman spectroscopy as applied to the chemical phase determination of clay products and iron oxides. These have been previously difficult to analyse by this and other techniques. Two main studies were chosen for this purpose: a) the determination of the chemical composition of low temperature fired clay pottery (earthenware) and b) the evaluation of synthetic iron oxides.

## 1.4.  Outline of the remaining chapters

The current study is divided into two major sections: a) the analysis of the low temperature fired clay pottery shards, and b) the preparation of iron oxides from mill scale iron waste.

Chapter 2 contains a literature review of the two major sections included in this study. This chapter outlines the developments and prospects in each section.

In Chapter 3 Raman spectroscopic theory and instrumentation are presented. Since this technique is applied in all the subsequent sections of the current study, it is appropriate that it be presented and described fully at this early stage. The theory of Raman spectroscopy, description of the different components and their uses and the operational parameters are outlined.

The main purpose of Chapter 4 was to determine the chemical components that constitute low temperature fired clay pottery using Raman spectroscopy. In this section a selected number of clay pottery shards from different locations in South Africa were analysed by Raman spectroscopy. The results were then compared with and complemented by those obtained when the same samples were analysed by X-ray diffractometry (XRD), FT-IR spectroscopy and X-ray fluorescence (XRF).

In Chapter 5 the results obtained when the chemical components in the low temperature clay pottery shards and clay pot of Chinese origin were analysed non-destructively using Raman spectroscopy are discussed.

The results obtained when iron waste materials were used in the preparation of various iron oxides are presented in Chapter 6. In this study magnetite, goethite, maghemite and hematite for pigment purposes were prepared from mill scale (iron waste). Magnetite and goethite were prepared directly from mill scale. Maghemite and hematite were then derived from thermal treatment of magnetite and goethite, respectively. The primary characterisation technique was Raman spectroscopy, while complementary techniques involved X-ray diffractometry (XRD), scanning electron microscopy (SEM) and surface area determinations.

The overall conclusions of the current study are then presented in Chapter 7. Finally, the Appendix section outlines the status of the core chapters (chapters 4 – 6) in the international peer review journals.

## 1.5.   References

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# Chapter 2

## Literature review

The literature presented in this section involves the studies related to the chemical components of clay products (including earthenware objects) and preparation of a selected number of iron oxides

### 2.1. Clay products

The literature covered in this section highlights the studies done on characterisation and investigation of thermal decomposition of clay minerals and related compounds often present in clay products. Furthermore, the clay compounds and some inorganic minerals (essential to the chemical characterisation of clay pottery) analysed by Raman spectroscopy are outlined.

### 2.1.1. Origin of clays

Clays are secondary minerals formed by weathering or hydrothermal alteration of rocks [1]. They are often found in rocks undergoing alterations. Therefore, clays often occur as several types mixed together and composed of rock-forming minerals such as carbonates, phosphates, feldspar, oxides, sulphates, etc. Types of clay minerals include smectite $(Mg_3(Si,Al)_4(OH)_2.4.5H_2O[Mg]_{0.35})$, mica $(KAl_2(AlSi_3O_{10})(OH)_2)$, kaolins $(Al_2Si_2O_5(OH)_4)$, etc. Kaolin clay minerals include kaolinite, halloysite, nacrite and dickite [2]. They all have the same chemical formula $Al_2Si_2O_5(OH)_4$, but different structures [3]. Clays high in kaolinite content are suitable for earthenware pottery and binders in refractory material production [4]. Clays are often medium to brownish gray [1]. Mica gives a yellowish-brown colour to many other clay minerals [4]. Clay products result from the firing of clays and related compound at high temperatures. An example of the group of smectite clays is montmorillonite, which is one of the common clays often identified in the clay mixtures used in earthenware objects [1,2].

**2.1.2. Types of clay ceramics**

There are three major types of ceramics: porcelains, earthenware and stoneware. Earthenware objects are clay products manufactured at lower temperatures ($\leq 900\ ^oC$). They are often red, brown, gray or black in colour. They are commonly African domestic pottery, but are also found in other parts of the world (e.g. China and Europe). The raw materials of earthenware objects are often not processed but are used as acquired [5]. Raman studies of earthenware objects are very rare.

Porcelain is characterised by a very low porosity (2% open porosity). It is white in colour (due to low iron content) and shows signs of a well-developed reaction between components [6a]. They are clay products (ceramics), which are prepared at higher temperatures ($\sim 1200\ ^oC$). The raw materials used in making porcelain are often similar to those used in making earthenware objects. Porcelains are widely studied by Raman spectroscopy. The application of Raman spectroscopy in archaelogical porcelain samples often included the analysis of pigments [7]. The majority of porcelain studies by Raman spectroscopy involves the use of FT-Raman [3, 8, 9] or higher laser excitation [10, 11].

Stoneware objects are made under similar conditions (e.g. higher temperature) as porcelains. They are much denser with low porosity and often occur in various colours other than white [6b].

**2.1.3. Thermal evolution of clay minerals**

The knowledge of the decomposition products of the clay minerals and raw material mixtures used in pottery making is important for chemical characterisation of objects, determination of raw materials and processing conditions (e.g. temperature). Materials identified in archaeological artefacts can be classified as primary minerals, firing minerals and secondary minerals [12]. Primary minerals are those present in raw materials, like quartz, which do not undergo reaction over a wide range of temperatures. Firing minerals, like rutile ($TiO_2$), are the products of thermally induced reactions, i.e. they are formed during firing. Secondary

minerals are those formed after production of wares (for instance, during use and burial) as a result of transformation of metastable firing minerals or infiltration of any solution [13]. The chemical components of clays are often analysed by X-ray diffractometry (XRD) in combination with other analytical techniques such as infrared (IR), thermogravimetry (TG) and X-ray fluorescence (XRF) [12, 14, 15]. However, these techniques have shown some drawbacks such as long analysis time, inability to give information on amorphous phases and are destructive.

During the firing of clay minerals and accompanying minerals such as quartz, feldspar, calcite, limestone, hematite, etc, a series of transformations occur which determine the final properties of the ceramic products [16, 17]. These crystalline structures gradually decompose and simultaneously others are formed [18]. For example, the thermal decomposition of kaolinite mineral has shown the formation of metakaolin ($Al_2O_3.4SiO_2$) at 550 $^o$C, spinel-type phase ($Al_2O_3.3SiO_2$) at 950 $^o$C, mullite-like phase ($Al_2O_3.2SiO_2$) at 1100 $^o$C and mullite ($Al_2O_3.\frac{4}{3}SiO_2$) at 1400 $^o$C [19, 6b].

The decomposition of the kaolinite rich in calcium carbonate results in anorthite ($CaAl_2Si_2O_8$) at 200 $^o$C, gehlenite ($Ca_2Al_2SiO_7$) and plagioclase at higher temperatures in excess of 800 $^o$C [20, 21, 22]. Illite decomposes at 800 $^o$C to form spinel-type phase while $CaCO_3$ forms $CaO$ in the same temperature region [9, 15]. Alia et al. [9] observed the presence of albite at 900 $^o$C ($NaAlSi_3O_8$). Gehlenite and wollanstonite ($\alpha$-$CaSiO_3$) form when calcium oxide ($CaO$) reacts with quartz around 600 – 700 $^o$C. The decomposition of separate raw clays at 800 $^o$C revealed that chlorite and kaolinite structures were completely destroyed. When the temperature is raised further and the modification of tetrahedral layer of clay minerals occurs then the intensities of the Raman bands weaken until the bands disappear completely. Bhatnagar and Goel [23] studied the thermal evolution of clay mixtures, e.g. kandite/mica, muscovite/mica, during brick making, in the temperature range 700 – 1100 $^o$C. Dehydroxylation of clay mixtures was observed at 850 $^o$C. The skeletal structure of muscovite/mica was still observed at 900 $^o$C. Other compounds including spinel-type, e.g. olivine and enstatine, crystallise around 900 $^o$C from micaceous structures. The final collapse of the illite skeletal structure also occurs around 850 $^o$C – 900 $^o$C [23, 24]. At elevated

temperatures the strength development and reduction in porosity of the clay products were observed during enhanced vitrification ($\geq$ 1100 $^o$C) [6a]. Vitrification of clay minerals involves the dissolution of alumina, hematite and spinel and their reaction with fused silica to form mullite, which progressively increases both in quantity and crystallinity, and finally dissolves in the liquid phase in excess of 1400 $^o$C [6c]. The vitrification of illite and micaceous clays were observed around 1050 $^o$C [9].

Minerals that have been identified in ceramic objects using other techniques include quartz, feldspar, calcite, gypsum, clay minerals, hematite, etc [4, 25]. The decomposition of various clay minerals and related compounds, e.g. illite, kaolinite, smectite, etc have been studied by techniques such as XRD, FT-IR, XRF, SEM and TG and their decomposition products at different temperatures have been identified [4, 12, 19, 23].

### 2.1.4. Raman spectroscopic analysis of clay minerals

There is a scarcity of data relating to the Raman spectroscopic study of chemical molecules that constitute low temperature fired ceramics (earthenware). For a chemical substance to give a Raman spectrum, the vibrations of its bonds and angles have to result in polarisability change. The aluminosilicates that form an integral part of clay pottery are composed mainly of Si-O and Si=O bands [26]. The polarisability changes in the above bonds are negligible. These compounds also have low scattering cross-section and therefore result in weak Raman bands. The Raman spectra of clays and related products are often accompanied by fluorescence and give broad bands due to the presence of amorphous aluminosilicates. The fluorescence in clay minerals is often due to organic substances that occur in soil and the presence of $Fe(OH)_3$ [14].

Clay minerals have also been studied by Raman spectroscopy using Fourier transform (FT) spectral acquisition and high wavelength excitation lasers (e.g. 632.8 nm). The clay minerals studied include kaolin clays (kaolinite, halloysite, nacrite and dickite) [3, 27], montmorillonite [28, 29], illite [9, 30], etc. Kaolinite appears to be the most studied of all clay minerals by Raman spectroscopy. Despite the use of FT-Raman spectroscopy, long recording times were

required [3, 31]. Therefore, the Raman spectra and the assignments of the above clay minerals and related compounds (quartz, rutile, anatase, mullite, etc) are known and available in the literature for reference [14].

The Raman spectroscopic characterisation of clay products is not possible without the full Raman characterisation of inorganic minerals (e.g. sulphates, carbonates and phosphates). A comprehensive Raman study on various inorganic minerals is beneficial for the complete characterisation of clay products [26, 32, 33]. The spectra of these minerals give intense and well-defined Raman bands due to the presence of high polarisability groups with substantial M-O $\pi$-bonding, where M is a metal ion [7, 26, 34].

### 2.1.5. Conclusion

Typical components that constitute raw materials of clay products and the processed objects have been identified using various destructive but robust techniques, such as XRD, FT-IR, SEM, etc. The thermal evolution of clay minerals and related compounds has also been studied. Studies show that there is often a gradual distortion from the original crystalline structure to some other amorphous forms (e.g. metakaolin) before a new phase (e.g. mullite) crystallises. Furthermore, clay minerals and other inorganic minerals common in nature have been characterised separately by Raman spectroscopy. Some clay objects are valuable pieces of art or have been manufactured in ancient times, therefore are kept in museums as heritage. These objects however, cannot be characterised on the basis of their chemical or mineralogical components because the analytical techniques applied at present are often destructive or cannot detect components of poor crystallinity. Therefore, there is a need for the application of a non-destructive technique to the clay products, which is sensitive, specific and amenable to *in situ* analysis.

### 2.2.   Synthesis of iron oxides

The literature on iron oxides in this section deals with the preparation of hematite, magnetite, goethite and maghemite for pigment purposes, because these are the focus of the current study. The pigment properties are determined by the chemical phases and particle

morphology. Therefore, the synthesis methods presented are those concerned with the structure, particle shape or size.

It has long been known that varying colours of iron oxides are determined by average particle size rather than by variation in the chemical structure [35]. Heating temperature duration and atmosphere affect the iron particle characteristics, namely size, shape, specific gravity, sintering and surface area. The pigment properties influenced by the above characteristics are colour, tinting strength, hiding power and oil absorption [36].

### 2.2.1. Red iron oxide (hematite, $\alpha$-Fe$_2$O$_3$)

The earlier workers were mainly concerned with the structural formation of the products and the applied aspects of the process. Therefore, most of the results brought forward have been documented inaccessibly in the patent literature [37- 42]. Hematite can be prepared by both thermal treatment of Fe (II) salts and precipitation from iron (III) salts in aqueous media.

### 2.2.1.1.     Synthesis using thermal methods

The most common starting material for thermal treatment is steel pickling chemical waste (97.3% FeSO$_4$.7H$_2$O, 1% free H$_2$SO$_4$, 1% water and 0.7% unidentifiable impurities referred to here as SPW), FeCl$_2$.H$_2$O, Fe$_3$O$_4$ and $\alpha$-FeOOH [43]. Hematite is the most thermally stable phase of all iron oxides. All other iron oxide phases turn into hematite under heat treatment. Due to the economic needs and environmental demands, SPW was used to prepare hematite. SPW is a waste formed during the final phase of steel manufacturing process called steel pickling. The decomposition of SPW in the temperature range 700 – 900 $^o$C gave hematite of particle sizes 0.61 – 1.29 µm [43] in air and oxygen (O$_2$) atmospheres. When the reaction was carried out under dry nitrogen (N$_2$) atmosphere the formation of $\alpha$-Fe$_2$O$_3$ of 1.76 – 3 µm began at 500 $^o$C [44]. The increase in temperature and the use of N$_2$ atmosphere resulted in the increase in particle size and loss of colour and consequently loss in tinting strength. The thermal decomposition of pure FeSO$_4$.7H$_2$O also results in red iron oxides [45]. High quality copperas reds are obtained by thermal decomposition of FeSO$_4$.7H$_2$O in a

multistage process that includes the reduction of sulphates with carbon-containing compounds [37]. Thermal decomposition of $FeCl_3$ in air at high temperatures yielded low quality iron oxide pigments [39]. Micaceous red iron oxides were obtained when iron (III) chlorides and iron metal react at 500 – 1000 $^oC$ in an oxidising atmosphere in a tubular reactor. Micaceous iron oxide is a crystalline plate-like compound [46].

Black, brown and yellow iron oxides have been calcined at low temperatures in oxidising atmosphere under counter current flow to produce a wide range of different red shades [47a]. For instance, hematite has been observed when goethite (yellow) and magnetite (black) were decomposed separately [48]. When maghemite (brown) was heated at 400 $^oC$ pure red iron oxide was formed [49]. The calcinations of other iron oxide phases result in pure red hematite of high tinting strength. Thermal decomposition of jarosite compounds (e.g. hydrogen jarosite, sodium jarosite) at 900 $^oC$ yielded red iron oxides of particle sizes 20 – 60 $\mu m$ [50, 51, 52]. Bye et al. [53] prepared acicular $\alpha$-$Fe_2O_3$ with high tinting power by heating goethite to 500 $^oC$. Yellow iron oxides (goethite) were acicular in shape.

### 2.2.1.2.    Synthesis using precipitation methods

The work of Matijevic and Scheiner [54] demonstrated that iron oxide and oxyhydroxide particles could be controlled using precise control of reaction environment. The precipitation methods are often used in order to control the chemical phase formed and the particle characteristics. For a powdery material to show good pigment properties 85% of the particles must have sizes < 10 $\mu m$, have regular shapes and be uniform [55].

One of the earliest methods for the preparation of hematite involved the slow precipitation from solution in the presence of oxygen and metallic iron powder [56, 57]. The starting material often used in the preparation of hematite was ferric chloride. Other ferric salts such as nitrates were also used. The precipitation of hematite involves the hydrolysis of ferric ion in the presence of an alkali (e.g. NaOH). Various particle shapes have been prepared.

A gel-sol method involving phase transformation starting from highly condensed ferric hydroxide gel with excess of ferric ions yielded 2 μm pseudocubic, ellipsoidal, peanut-like and plate-like hematite [58 - 61]. Spindle-type hematite of particle size 1.90 μm was prepared by ageing dilute solution of ferric chloride in the presence of phosphate ions [61, 62]. Spherical and pseudocubic particles of $\alpha$-$Fe_2O_3$ were prepared by ageing concentrated solution of ferric chloride at 100 $^o$C [63, 64]. Diamandescu et al. [65] prepared hematite powders with distinct morphology (acicular, polyhedra, plate-like, spherical, hexagonal, etc) and dimensions 0.1 – 3 μm by hydrothermal synthesis using goethite and ferric hydroxides.

Atkins et al. [66] aged solutions of ferric nitrate at 100 $^o$C for 18 days in the presence of NaOH to give hematite of particle size range 0.05 - 0.8 μm. The short time ageing using lower temperatures showed the presence of both goethite and hematite. The commonly proposed mechanism for the precipitation of hematite involves the formation of $Fe(OH)_3$, which then transforms into $\beta$-FeOOH. Hematite of particle size 0.25 – 2 μm results from dissolution and reprecipitation of the $\beta$-FeOOH [50, 67]. Uniform single crystal particles of $\alpha$-$Fe_2O_3$ in the crystalline form and particle size range 0.35 – 0.41 μm were prepared by a highly condensed suspension of $\beta$-FeOOH particles doped with $PO_4^{3-}$ ions in a solution of HCl and $NaNO_3$ [68]. Hydrous ferric oxide (HFO) was transformed into hematite in the presence of Zn (II) or Mn (II) at pH 6.5 and 65 $^o$C [69].

## 2.2.2.  Yellow iron oxide (goethite, $\alpha$-FeOOH)

### 2.2.2.1.      Synthesis using precipitation methods

Goethite is only prepared by precipitation methods. This compound shows only acicular and spindle-type (needle shaped) particle shapes [47b, 47c]. Atkins et al. [66] aged solution of ferric nitrate at room temperature for 24 hours to produce acicular goethite particles of 0.02 – 0.8 μm. Jang et al. [69] observed the formation of goethite in the presence of chloride. Yellow pigments have been prepared using oxidation of iron (II) hydroxide solution and oxidation of iron (II) salt solutions [70]. The oxidation of iron salt solutions is basically the Pennimann-Zoph process, which includes the use of metallic iron and FeOOH seed crystals to catalyse

oxyhydroxide formation [71]. Leskéla and Leskéla [45] and Tamaura [72] studied and prepared the yellow $\alpha$-FeOOH pigments from iron (II) sulphate solution by alkali precipitation and gas oxidation methods. High quality yellow pigments (goethite) have been prepared during the reduction of nitrobenzene with iron in the presence of aluminium chloride [40]. Gallagher and Phillips [73] prepared crystalline goethite by hydrolysis of ferric oxalate solution in the presence of $NaHCO_3$. Goethite can also be prepared by the hydrolysis of ferric chloride [74, 75].

### 2.2.3. Brown iron oxide (maghemite, $\gamma$-Fe$_2$O$_3$)

### 2.2.3.1. Synthesis using thermal methods

Maghemite can be prepared by both thermal and precipitation methods. Goto [49] has shown that maghemite forms around 200 $^o$C during the thermal treatment of magnetite. The single-phase brown maghemite has been prepared by the controlled oxidation of $Fe_3O_4$ at ca. 500 $^o$C [41]. The calcinations of organic iron salts like ferrous oxalate [76], ferrous hydrazine carboxylate [77] and ferrous acetate [78] yield maghemite in a single step. Narasimhan et al. [79] showed that the direct thermal decomposition of ferrous carbonate gives maghemite. The thermal decomposition of lepidocrocite ($\gamma$-FeOOH) also results in maghemite [48].

### 2.2.3.2. Synthesis using precipitation methods

Itoh and Sugimoto [68] carried out the oxidation in air stream at 240 $^o$C. The particle properties of the prepared maghemite can be controlled [80]. For instance, acicular gamma ferric oxide is prepared by first producing acicular particle of alpha ferric oxide (hematite) from alkali precipitation of ferrous salts followed by its tapotactic reduction to magnetite which is then oxidised under controlled conditions [81]. Jing and Wu [82] prepared acicular shaped $\gamma$-Fe$_2$O$_3$ particles using a molar ratio of lauric acid to iron nitrate of 2:1 at 300 – 400 $^o$C. The molar ratio determined the particle sizes and thermal stability of maghemite.

## 2.2.4.  Black iron oxide (magnetite, $Fe_3O_4$)

### 2.2.4.1.        Synthesis using thermal methods

Black iron oxide pigment with a high tinting strength can be prepared by thermal decomposition of iron salts under reducing conditions [47d]. However, this process is not often used because of the furnace gases. It has also been reported that the thermal decomposition of red iron oxides at temperatures in excess of 1200 $^o$C results in grayish black magnetite [11].

### 2.2.4.2.        Synthesis using precipitation methods

The earliest method of preparing magnetite is the Laux process. During this process an aromatic nitro-compound, e.g. nitrobenzene is reduced with antimony or iron in the presence of iron (II) chloride or aluminium chloride, sulphuric acid and phosphorous acid [40]. When iron (II) chloride is added during the reduction of nitrobenzene with iron, a black pigment (magnetite) with very high tinting strength is produced. The raw materials for the Laux process are mainly by-products from other industries, e.g. steel scrap obtained from deep drawing, grinding from cast iron, $FeCl_2$ from steel-pickling [47d].

Feitknecht [83] first reported the formation of $Fe_3O_4$ by air oxidation of $Fe(OH)_2$ suspension. Kiyama [84] indicated that $Fe_3O_4$ is formed readily from $Fe(OH)_2$ suspensions at temperatures above 60 $^o$C in the pH range 7 – 10. Tamaura et al. [85] showed that the reaction mixture of $\gamma$-FeOOH transforms into stoichiometric $Fe_3O_4$ at 25 $^o$C when the pH was raised from 5 to 9. Ueda et al. [86] developed a method for the preparation of crystalline $Fe_3O_4$ involving the ageing of a solution containing low concentration of $Fe^{2+}$ ions at room temperature. The particle sizes were less than 1 $\mu$m. Duboise et al. [87] prepared magnetite particles of fine octahedral morphology and 1 $\mu$m size by solvothermal method using FeOOH precursor and a mixture of water and ethanol (with reducing properties). The hydrolysis of $FeCl_3$ and $FeSO_4$ solutions containing urea at 90 – 95 $^o$C resulted in $Fe_3O_4$ nano disks with average diameters of 40 – 50 $\mu$m and lengths of up to 1 $\mu$m [88]. Itoh and Sugimoto [68]

prepared magnetite by reduction of hematite in a $H_2$ stream at 330 $^o$C. Magnetite particles grow from goethite when hydrous ferrous oxide is aged with Cu (II) and Fe (II) at pH 8.5 and room temperature [69].

### 2.2.5. Conclusion

The literature on the synthesis of certain iron oxides has been presented. Magnetite, hematite, goethite and maghemite of different particle sizes and shapes can be prepared by either thermal treatment of iron salts or precipitation from iron salts in aqueous media. The chemical phase and properties of the final products strongly depend on the reaction environment. Furthermore, the raw materials (type of iron salts) determine the product phase and particle characteristics. The resulting product often retains the particle characteristics. Iron oxides of various particle shapes (cubic, spherical, spindle-type, ellipsoidal, etc) and small sizes (< 1 µm) have been prepared. Therefore, iron oxides of particular properties can be tailor-made for a specific application. Many procedures showed that the preparation of one iron oxide phase might first involve the formation or phase transformation of another. Therefore, there is a possibility of contamination of one iron oxide phase by another. The presence of contaminants affects the properties of the products (e.g. colour, crystallinity). The preparation of iron oxides requires the use of analytical techniques that are sensitive to various structures, specific and able to detect amorphous compounds. However, most techniques used cannot detect amorphous compounds or compounds at very low levels, e.g. XRD. The preparation methods available are costly because they make use of pure starting materials, involve many complicated steps or give pigments of poor quality. Therefore, there is a need for simple, yet effective methods that may use cheaper raw materials (iron wastes) and analytical techniques that are sensitive to various structures, specific and capable of detecting amorphous compounds.

## 2.3.    Raman spectroscopic analysis of iron oxides

The iron oxide polymorphs (including oxyhydroxides) occur as corrosion products and pigments, while they also find use in archaeological objects, novel/specialised materials (e.g. magnetic materials) and catalysis, among other applications.

The iron oxides, main products of iron corrosion, strongly absorb infrared radiation but are usually poor light scatterers [89]. Pure $Fe_3O_4$, FeO, $Fe(OH)_3$, $Fe(OH)_2$, $\alpha$-$Fe_2O_3$, $\gamma$-$Fe_2O_3$, $\alpha$-FeOOH, $\gamma$-FeOOH, $\beta$-FeOOH and $\delta$-FeOOH, for use as reference materials in the study of iron corrosion, have been characterised by Raman spectroscopy and their spectra assigned [90 - 97]. Raman spectroscopy has further been used to confirm the presence of all the above-mentioned iron oxide polymorphs in samples obtained from the corrosion (under various conditions) of iron metal [90, 98, 99, 100].

The Raman spectra of natural iron oxide pigments such as haematite, Mars yellow ($\alpha$-FeOOH), and Mars red ($\alpha$-$Fe_2O_3$) have been recorded and assigned [10, 101, 102]. The Raman spectroscopic studies of the composition of archaeological objects (ceramics and other clay pottery) revealed that $\alpha$-$Fe_2O_3$, $Fe_3O_4$, FeO and $\alpha$-FeOOH were commonly used as pigments [10, 102, 103, 104, 105, 106].

The unique Raman spectrum of each iron oxide polymorph facilitates easy identification in mixtures and in the presence of other compounds, such as catalysts ($\alpha$-$Fe_2O_3$, $\gamma$-$Fe_2O_3$) and novel/specialised materials ($\alpha$-$Fe_2O_3$) [107,108].

The iron oxides and oxyhydroxides have been widely studied by Raman spectroscopy and their spectra fully assigned (see Table 2.1).

**Table 2.1:** Raman wavenumbers of all iron oxide polymorphs and their assignments as obtained from literature.

| COMPOUND | WAVENUMBER ($cm^{-1}$) | ASSIGNMENT | REFERENCES |
|---|---|---|---|
| Magnetite | 298<br>319<br>540<br>668 | $t_{2g}$ (Fe-O asym. bend)<br>$e_g$ (Fe-O sym. bend)<br>$t_{2g}$ (Fe-o asym. bend)<br>$a_{1g}$ (Fe-O sym. str) | 90, 97, 98, 99,<br>104 |
| Goethite | 299<br>400<br>550<br>1003 | Fe-O sym. bending<br>Fe-O-Fe / -OH sym. str<br>Fe-OH asym. str<br>Fe-OH asym. str | 90, 91, 93, 98 |
| Hematite | 225<br>247<br>293<br>412<br>498<br>613 | $a_{1g}$ (Fe-O sym. str)<br>$e_g$ (Fe-O sym. bend)<br>$e_g$ and $e_g$ (Fe-O sym.bend)<br>$e_g$ (Fe-O sym. bend)<br>$a_{1g}$ (Fe-O sym. str)<br>$e_g$ (Fe-O sym. bend) | 94, 106, 107 |
| Maghemite | 344<br>390<br>507<br>665<br>721 | $e_g$ (Fe-O sym. str)<br>$t_{2g}$ (Fe-O asym. bend)<br>$t_{2g}$ (Fe-O asym. bend)<br>$a_{1g}$ (Fe-O sym. str)<br>$a_{1g}$ (Fe-O sym. str) | 90, 94, 100, 105,<br>108 |
| Akaganeite | 300<br>415<br>745 | Fe-O sym. bend<br>Fe-O-Fe / -OH sym. str<br>Fe-OH asym. str | 90, 91, 94 |
| Lepidocrocite | 252<br>380<br>527<br>650<br>1307 | Fe-O sym. bend<br>Fe-O-Fe /-OH sym. str<br>Fe-O asym. bend<br>Fe-OH asym. str.<br>Fe-OH asym. str. | 90, 91, 94, 98 |
| Feroxyhite | 400<br>663<br>1322 | Fe-O-Fe /-OH sym. str<br>Fe-OH asym. str<br>Fe-OH asym str | 90, 91, 94 |

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