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VITRIFICATION AND NEOMINERALISATION OF BENTONITIC AND KAOLINITIC CLAYS FOR POSSIBLE CERAMIC APPLICATIONS

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ABSTRACT

The bulk mineralogy of selected raw and fired bentonitic and kaolinitic clays from Botswana, Mozambique, Pakistan, Senegal, South Africa and the United States of America was determined by X-ray powder diffraction (XRPD) technique. each sample was fired at 950 °C, and 1250 °C, for 35 minutes in order to study the effects of firing on them. It was noticed that the samples vitrified, and neomineralization was realised. These processes are found to be similar to those of transformation of sedimentary rocks into metamorphic and/or igneous rocks. Resultant fired mineral phases depicted mineral compositions of ceramic bodies, and the study suggested that these clays could be gainfully utilized in the making of ceramic wares, subject to selected beneficiation processes.

KEYWORDS: Kaolin; bentonite; vitrification; neomineralization; ceramic; firing

INTRODUCTION

Bentonitic and kaolinitic clay deposits are exploited for a wide variety of industrial applications, one of which is the ceramic industry (Patterson and Murray, 1983). These clays are used for ceramic applications to make claybodies, slips and glazes of different chemical and mineral compositions. However, their usage in ceramic production is accompanied by significant problems at different stages of manufacturing: raw clay mining, processing, claybody formulation, drying, glazing, firing, and cooling of finished products.

Firing starts with the final drying of the claybody with slow heating. Fast heating at this stage may cause cracks that may encourage failure at later stages of the product development. Organics need to be burnt off firstly, under very favorable oxidizing conditions, or else the color of the finished product may be darkened. Clays rich in organics may cause bloating. With increasing temperatures, all water is removed from the claybody, enabling intimate contact between particles as well as the formation of chemical bonds, a stage known as clay sintering. Decomposition of minerals follows the sintering stage. Vitrification and neomineralization, which are reactions that occur at very high temperatures, wrap up the firing process.

Firing leads to the transformation of smectite, kaolinite and associated minerals to new mineral phases, and to the disappearance of these clay minerals. The physical, chemical, mineralogical and ceramic properties of the resulting ceramic products are determined by the properties of the original minerals in the raw clays. The composition and properties of the new mineral phases are controlled by protore raw materials, and type and amount of clay minerals, grain size distribution of clay minerals, their crystallinity and firing atmosphere (Dubois *et.al.*, 1995), firing temperature and rate of firing.

An understanding of the mineralogy of the associated mineral phases in the raw clay materials utilized in the ceramic industry is essential. It is imperative to have an insight of the mineralogical properties resulting from the transformation of the raw clay to the desired finished product (Konta and Kühnel, 1997). This paper attempts to improve the understanding of the mineralogical transformation of bentonite-rich and kaolin-rich claybodies, which could possibly find gainful applications in the ceramic industry.

METHODS AND ANALYTICAL TECHNIQUES

Samples and sample preparation

Analysed samples in this study came from Botswana, Mozambique, Pakistan, Senegal, South Africa, and United States of America (USA). They were numbered from 1 to 17 (Table 1).

Moisture-free clay samples for firing were prepared in a proportion of 65 wt % solid and 35 wt % water, mixed with 1 wt % deflocculating agent. Rectangular test pieces were made with approximately 50 mm X 10 mm X 10 mm, in dimension. Free water content was eliminated by heating in an oven at 100 °C for 12 hours.

For XRD analyses of disoriented powders, dried clay samples were gently crushed in an agate mortar to reach a fine texture. The powdered samples were then mounted on the sample holder with very little pressure, by using a blade to minimize any preferred orientation of specifically the kaolinite particles (Hughes and Brown, 1979), and later scanned in the diffractometer. Montmorillonite was distinguished from chlorite and vermiculite groups by rendering the clay homoionic with preferably Mg^{2+}, solvating with glycerol (under-estimation of smectite content) and ethylene glycol (over-estimation of smectite content) and by observing shifts of the (001) spacings (Bühmann *et. al.*, 1985).

Firing of raw clay samples

Clay samples were fired at 950 °C and 1250 °C for 35 minutes in a muffle furnace, and allowed to cool overnight. These temperatures were within the range applicable in industrial ceramics (Jordan *et. al.*, 1999).

X-Ray Powder Diffraction (XRPD) technique

The XRPD analyses were performed on the raw and fired clay samples in order to identify the constituent mineral phases. A Philips PW 3710 XRPD system operated at 40kV and 45 mA, with Cu-K_{α} radiation and a graphite monochromator was used for the analysis. A PW 1877 Automated Powder Diffraction,

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Table 1: Sample code and identification of clayey materials

Sample number	Sample identification
1	Bentonite, Mozambique
2	Bentonite MD 100#, South Africa
3	Bentonite 3%, South Africa
4	Bentonite HV 100#, South Africa
5	Topi clay, Pakistan
6	Sample 1, USA
7	Sample 2, USA
8	Sample 3, Senegal
9	Sample 4, Senegal
10	Sample 5, South Africa
11	Sample 6, South Africa
12	Sample 7, South Africa
13	Sample 8, South Africa
14	Sample 9, South Africa
15	Sample 10, South Africa
16	Makoro kaolin, Botswana
17	Kgwakgwe kaolin, Botswana

Table 2: Mineralogy of raw clay samples as determined by XRPD

Sample No	Chlorite	Montmorillonite	Beidellite	Nontronite	Illite-montmorillonite	Lepidolite	kaolinite	Dickite	Nacrite	Pyrophyllite	Muscovite	Illite	Cristobalite	Cordierite	Augite	Calcite	Quartz	Microcline	Ilmenite
1		++	+										+				++		
2		++			+								+				++		
3		++														+	++		
4		++	+													+	++		
5	+			+							+		+	+			++	+	
6	+											++	+				++		
7	+	++			+							+		+			++		+
8	+						+++								+		++		
9	+						+++										++	+	
10	+	+					+++			+		+					++		
11							+++	+				+					++		
12							+++	+		+	+	+					++		
13						+	+++					+					++		
14		++				+		+		+		+					+++		
15	+	++							+	+		+					++		
16		+					+++										++		
17							+++				+						+++		

(Note: + = trace; ++ = minor; +++ = major)

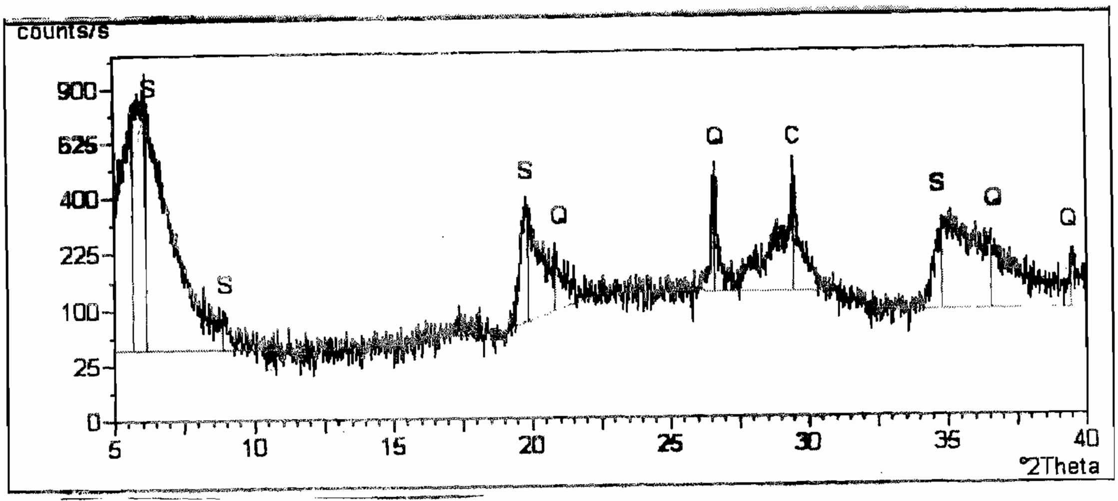

Figure 1: X-ray powder diffractogram of sample 3 (S is smectite, Q is quartz, and C is calcite).

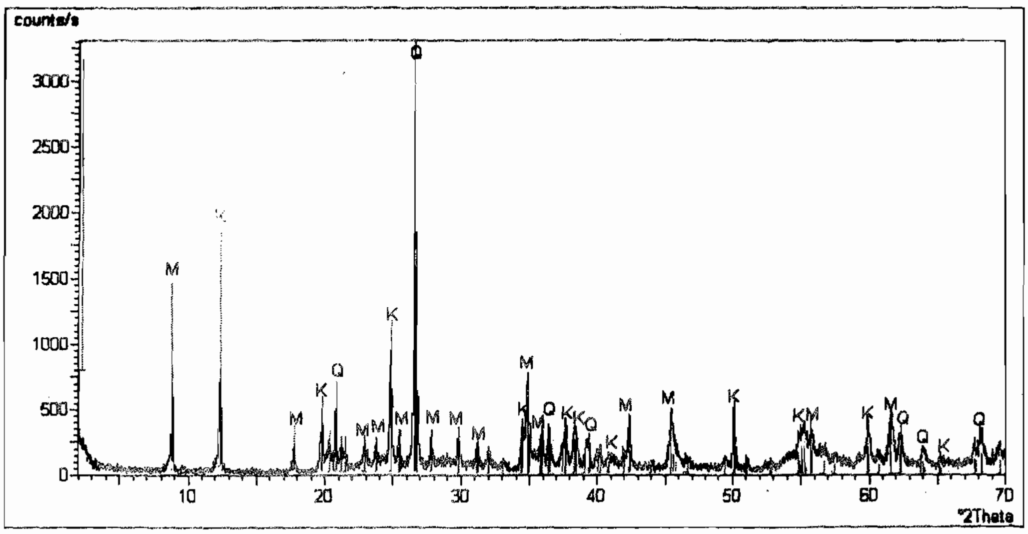

Figure 2: X-ray powder diffractogram of sample 17 (M is muscovite; K is kaolinite; and Q is quartz).

X'PERT Data Collector software package was employed to capture raw data, and a Philips X'PERT Graphics & Identify software package was used for the qualitative identification of the minerals from both the data and patterns obtained by scanning at a speed of 1°2θ / min. The interpreted results were compared with data and patterns available in the Mineral Powder Diffraction File, Data Book and the Search Manual issued by the International Center for Powder Diffraction Data (1986) for confirmation.

RESULTS

In ceramics, bulk clay samples are normally used. therefore the XRPD analysis used mostly the bulk samples. Moreover a textural classification of the samples was related to silty clays, with no sand component present (Ekosse *et. al.*, 2001), making them suitable for XRPD analysis.

Mineralogy of the raw bulk clay samples

A summary of minerals contained in the various raw clay samples identified by XRPD analysis is given in Table 2. The clay minerals which were identified in the samples included chlorite, montmorillonite, beidellite, nontronite, illite-montmorillonite, lepidolite, kaolinite, dickite, nacrite, pyrophyllite, muscovite and illite. Other minerals were cristobalite, cordierite, augite, tourmaline, calcite, quartz, microcline and ilmenite. Smectite and montmorillonite have been used interchangeably. Two representative diffractograms of the raw clay samples are given in Figures 1 and 2.

Mineralogy of clay samples fired at 950 °C

The results of XRPD analyses of fired clay samples at 950 °C are shown in Table 3. The following mineral phases were identified in the samples: cristobalite, amorphous phase, spinel, quartz, cordierite, hematite, kalsilite ($KAlSiO_4$), mullite, maghemite (γ-Fe_2O_3) and lepidolite. It should be noted that maghemite belongs to the spinel group. Spinel, as a member of the group, could be a spinel ($MgAl_2O_4$), a ferrian spinel {$(MgAl,Fe)_2O_4$}, hercynite $FeAl_2O_4$, or magnesioferrite ($MgFe_2O_4$). Three representative diffractograms of the raw clay samples are given in Figures 3, 4 and 5.

Mineralogy of clay samples fired at 1250 °C

At 1250 °C, as shown in Table 4, the following mineral phases were identified in the fired clay samples: cristobalite, amorphous phase, spinel, quartz, cordierite, hematite,

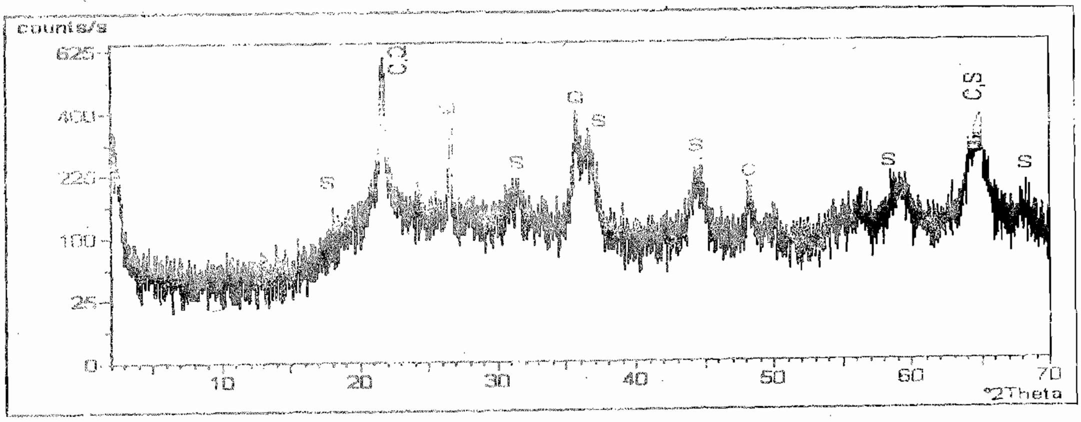

Figure 3: X-ray powder diffractogram of sample 2 fired at 950 °C (S is spinel, Q is quartz and C is cristobalite).

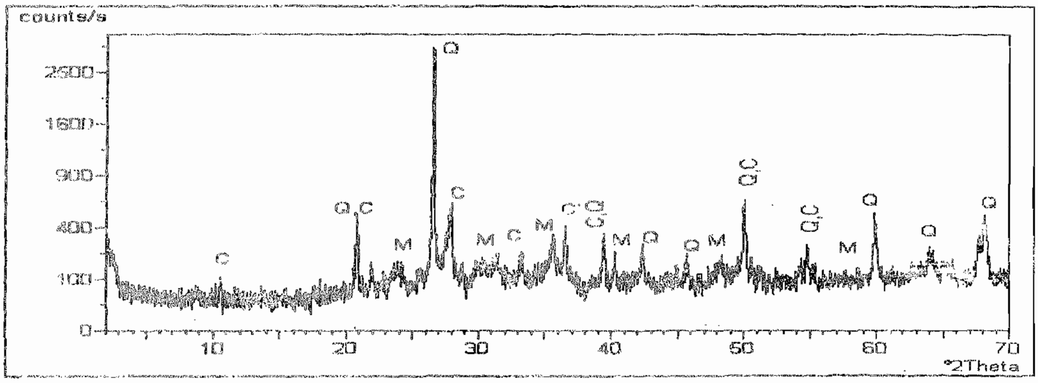

Figure 4: X-ray powder diffractogram of sample 5 fired at 950 °C (C is cordierite, Q is quartz and M is mullite).

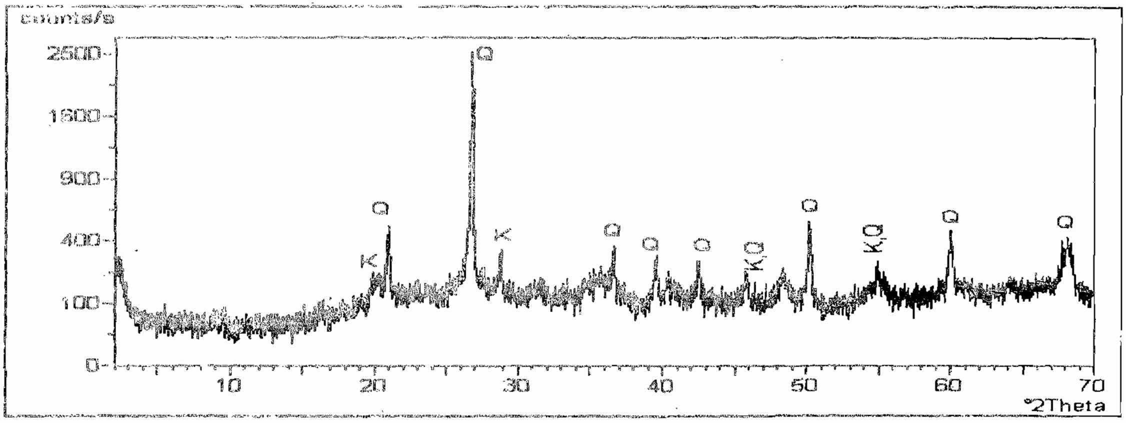

Figure 5: X-ray powder diffractogram of sample 11 fired at 950 °C (K is kalsilite and Q is quartz).

tridymite and mullite. Spinel, could again be a spinel ($MgAl_2O_4$), a ferrian spinel {$(MgAl,Fe)_2O_4$}, hercynite $FeAl_2O_4$, magnesioferrite ($MgFe_2O_4$). Three representative diffractograms of the raw clay samples are given in Figures 6, 7 and 8

DISCUSSION

Mineralogy of raw clay samples

Based on mineralogical analyses carried out for the raw clay samples, they could be distributed into four sub classes depending on the active mineral component occurring in them. Samples 1, 2, 3, 4 and 5 were predominantly made of smectitic clayey material. Samples 6 and 7 consisted of

Table 3: Mineralogy of clay samples fired at 950 °C

Sample No	Cristobalite	Amorphos phase	Spinel	Quartz	Cordierite	Hematite	Kaisilite	Mullite	Maghemite	Lepidolite
1	+	++								
2	+	++	++	+						
3		++	++	++						
4		++	++	+						
5		++		+	+			++		
6	+	+++					+			
7	+	++	+							
8	+	+++							+	
9	+	++							+	
10			++	+		+				
11		+++		+			+			
12		++		++			+			
13		++		++					+	
14			+	++						+
15		++	+	++						
16		+		++					+	
17		++		++					+	

(Note: + = trace; ++ = minor; +++ = major)

chloritic/illitic clays. Samples 8 to 13, 16 and 17 had a kaolin mineral as the main clay mineral in them. Sample 15 had a strong blend of chlorite and smectite.

Vitrification

Vitrification is a process that develops in claybodies during firing. Some claybodies may vitrify over a wide range of temperatures whereas others do so suddenly. Certain ceramic products, such as earthenwares and low-temperature whitewares are incompletely vitrified because they [illegible] sufficiently.

In the vitrification process, silica changes to different mineral species due to changes in temperature. Quartz, tridymite and cristobalite are three different silica minerals, which can exist in either the *α*- or *β*- form (Tan, 1998) depending on environmental temperature. Whereas the *α*- form of the minerals is prevalent in low temperature environments, the *β*- form exists at high temperature conditions as illustrated below.

α- Quartz (trigonal) *α*- tridymite (hexagonal) *α*-cristobalite (tetragonal)

↑↓573 °C ↑↓117 °C ↑↓220-280 °C

β- Quartz (hexagonal)→ *β*- tridymite (hexagonal) → *β*-cristobalite (cubic)

← ←

870 °C 1470 °C

Table 4: Mineralogy of clay samples fired at 1250 °C

Sample No	Cristobalite	Amorphos phase	Spinel	Quartz	Cordierite	Hematite	Tridymite	Mullite
1	++	+	+					
2	++	+	++					
3		+					+	++
4		++			+		+	
5		+					+	++
6		+	+					++
7		+					+	++
8		+					+	++
9		++					+	+
10				+				++
11				+				++
12		+						++
13				+		+		++
14		++					+	++
15		++	+					
16		++		+				++
17				+				+++

(Note: + = trace; ++ = minor; +++ = major)

Quartz conversion is an important factor to be considered when having to optimize fired properties, and quartz inversions must be taken into account during firing in order to prevent loss resulting from crack development. Quartz inversion occurs quickly at 573 °C with α-quartz becoming inverted into β- quartz with a lattice expansion of 1 vol %. Cristobalite inversion occurs at 220-280 °C, with a change of 2.5 vol %. These changes affect dense claybodies that do not fire to full vitrification.

Vitrification of claybodies is realized when there is a sharp increase in porosity and a decrease of bulk density (Fentaw and Mengistu, 1998). The products of incomplete vitrification usually show cooling cracks, a status which must definitely be avoided. Chemically, Al_2O_3 acts as a skeleton for SiO_2 moving into a liquid state, with further stabilization of the clay mass during the vitrification process. Any new formed mineral phases are indicative of the level of vitrification.

With increase of firing temperatures, the crystalline structures of the mineral phases of the raw material partially change, whereas at the same time neomineralization occurs (Jordan *et. al.*, 1999). From the firing and vitrification of a claybody containing quartz (SiO_2), chlorite $(Mg,Al,Fe)_{12}[Si,Al)_8O_{20}](OH)_{16}$, illite $K_{1-1.5}Al_4[Si_{7-6.5}O_{20}](OH)_4$, and kaolinite $Al_2SiO_2O_5(OH)_4$, and small amounts of dolomite $CaMg(CO_3)_2$, hematite α-Fe_2O_3 and plagioclase $(Na,Ca)Al_{1-2}Si_{3-2}O_8$, neomineralization occurs leading to the formation of enstatite $(Mg,Fe^{+2})[SiO_3]$, gehlenite $Ca_2[Al_2SiO_7]$, hercynite $Fe^{+2}Al_2O_4$, mullite and abundant vitreous phase (Jordan *et. al.*, 1999).

Neomineralization

Neomineralization is a process that develops in claybodies during and after firing. A number of factors determine the extent of neomineralization in terms of new mineral phases, whether crystalline or not. These factors depend on::

1. The mineral association in raw claybodies
2. The rates of firing and cooling
3. The temperatures to which the clayey material is heated.
4. The type of furnace/kiln, and whether the reaction develops in oxidation or reduction conditions.
5. The pressure and deviatoric stress under which the claybody is fired. Pressure is a uniform stress affecting the rock in all directions. Fluid phases and load create pressure on a given clayey material. Deviatoric stresses are specific stresses that act along particular direction, giving to the rocks their foliation.

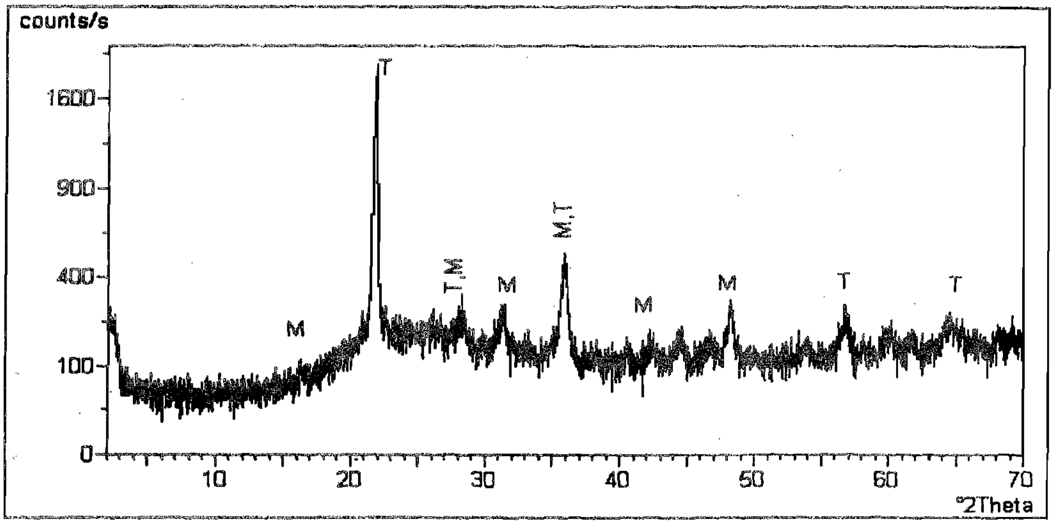

Figure 6: X-ray powder diffractogram of sample 3 fired at 1250 °C (M is mullite and T is tridymite).

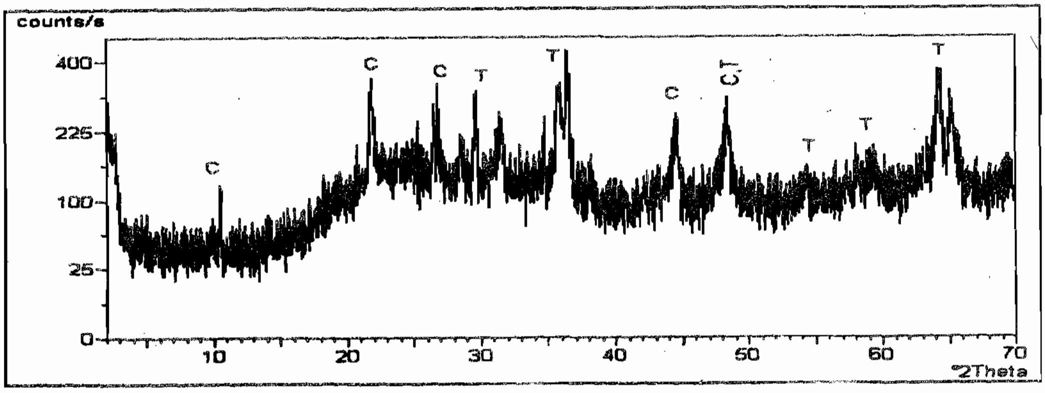

Figure 7: X-ray powder diffractogram of sample 4 fired at 1250 °C (C is cordierite and T is tridymite).

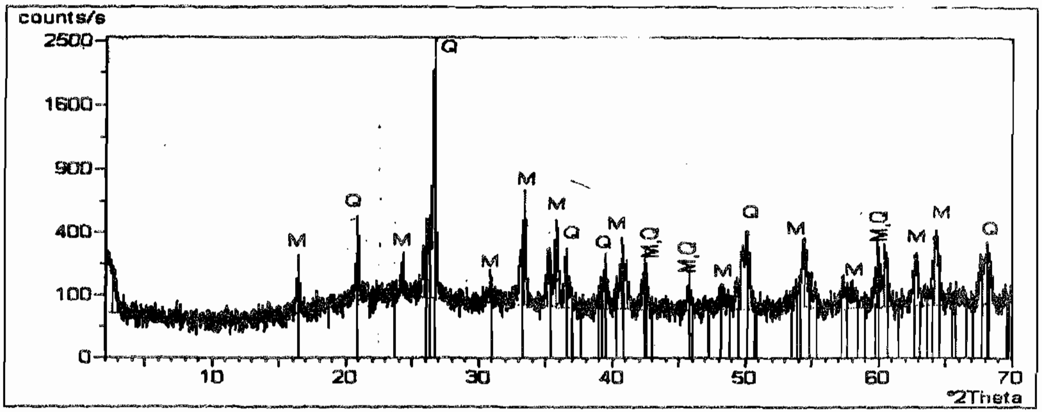

Figure 8: X-ray powder diffractogram of sample 10 fired at 1250 °C (M is mullite and Q is quartz).

6. The fluids involved at the melting state, which are usually affected by H_2O, and other components such as CO_2, CH_4, N_2, Cl, S, B, Na and K.

The thermal transformation of kaolinite through two intermediate phases (meta-kaolinite and γ-alumina) to mullite has been reported (Jordan *et. al.*, 1999; Galan *et. al.*, 1996, and ProdanoviĆ *et. al.*, 1997). Thermal transformation of bentonite is however not well documented because its main applications in ceramics have been limited to value added commodity, by enhancing both composite body plasticity and strength. However, montmorillonite affects topactic reactions and influences the type of high temperature mineral phases formed in a given reaction (Brindley and Lemaitre, 1987). Quartz transformation is complicated because of the several phases involved, from quartz to cristobalite to tridymite and also to both α and β, thereby constituting six possible phases (Tan, 1998). In addition to the six phases, a seventh silica phase is obtained which is characterized by a glassy/vitreous non crystalline amorphous material. In this study, amorphous silica was identified by XRPD in almost all the samples at higher temperatures.

Metamorphism under laboratory conditions

The transformation of clayey material to ceramic products for varied applications could be compared to geologic processes and changes in the classification of rocks resulting from neomineralization. Metamorphic changes, although occurring naturally could also be replicated in ceramics as indicated by changes of clays and clay minerals as demonstrated in this study. The changes are depicted schematically in Figure 9. The raw clayey materials had the following mineral phases typically found in argillaceous sedimentary rocks: smectite (montmorillonite, beidellite, nontronite), kaolinite, nacrite, dickite, quartz, illite, illite-montmorillonite, muscovite, chlorite, calcite and hematite. Some minerals like tourmaline, cristobalite, pyrophyllite and cordierite were found in some of the raw clay samples. It would be assumed that the clay samples, which contained them, were derived from a hydrothermal, magmatic or metamorphic source.

Cristobalite, microcline, spinel, ferrian spinel, mullite, chlorite, kalsilite, pyrophyllite, hematite, muscovite and lepidolite in the artificial metamorphic processes were similar to those found in contact metamorphic and hydrothermal terrains. The minerals of the igneous phase (orthoclase, anorthite, sanidine, albite, cristobalite, tridymite, ilmenite, leucite, tourmaline, forsterite and hematite) were similar to those constituting felsic, mafic or plutonic rocks.

At 950 °C, most of the samples were sintered, and vitrification was observed at 1250 °C. At both temperatures, the fired clay samples exhibited an amorphous phase, constituted by non-crystalline minerals. Cristobalite, spinel, quartz, cordierite, hematite and mullite were identified in the samples at both firing temperatures. At 950 °C, kalsilite, maghemite and lepidolite, and at 1250 °C, only tridymite, were the new mineral

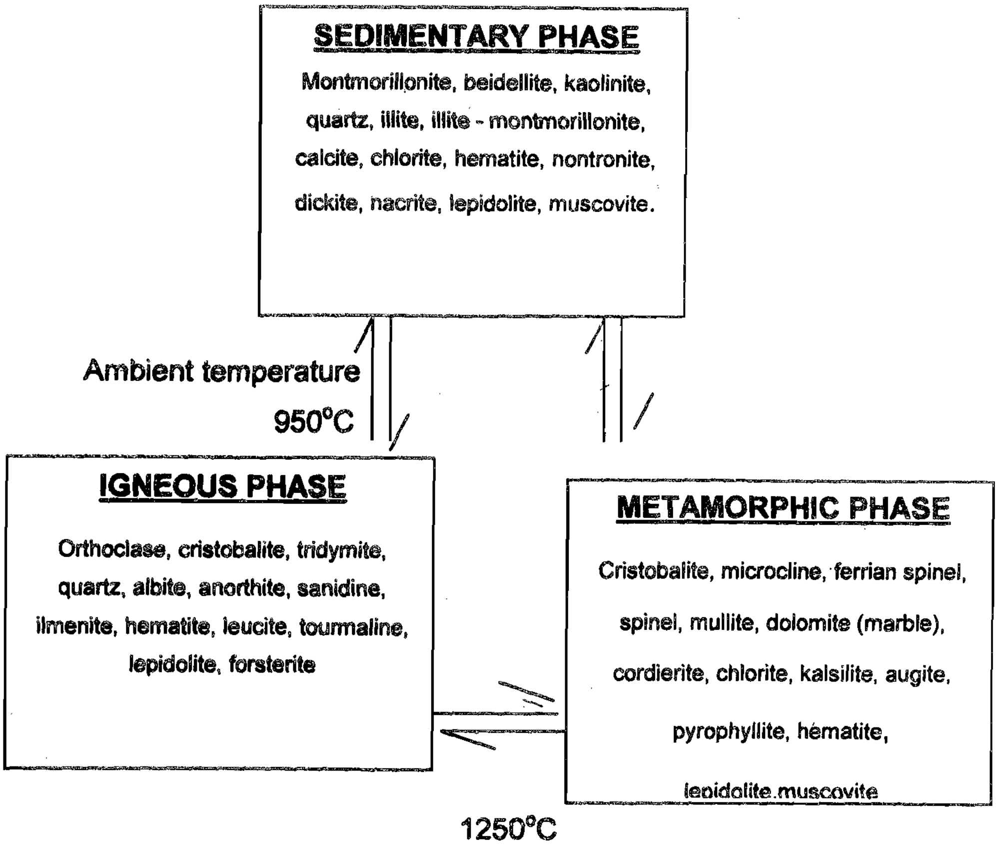

Figure 9: Changes in mineral and rock class phases of the studied samples with increase in temperature (Compiled from Tables 2, 3 and 4, and from Brindley and Lemaitre, 1987; Dubois *et. al.*, 1995; Grim and Kulbicki, 1961; Jordan *et. al.*, 1999).

phases. In the thermo-mineralogical reactions, the amorphous phase yielded high temperature minerals, which are associated with metamorphic and igneous terrains in nature.

Ceramic applications

The mineral assemblages contained in the raw clay samples have been found to be similar to those contained in clays currently used in ceramics industry. In ceramics, bentonites are used as plasticizers: they increase the drying and firing strengths and reduce the degree of absorption. They are also used as additives in refractory ceramics. Bentonites are equally added in glazes where they function as suspension agents and are also used, in ceramics, to improve the strength of the fired vessel, and serve as a source of fluxing agent.

Kaolins are used quite extensively in the manufacturing of different types of ceramic products. Due to its purity, it has a high fusion temperature and is used in refractory ceramics. In a separate study (Ekosse, 2000; 2001), kaolins from Botswana have been recommended for ceramics. Kaolins as ball clays provide good working properties and a green strength to ceramic bodies. They have the required casting property, plasticity and dry strength to produce a final ceramic body.

Samples 1 to 4, being identified as bentonitic clays could be conveniently utilized in any of the cited functions. The other samples, consisting of kaolinitic minerals, could be gainfully used in the ceramic industry to fulfil any of the functions mentioned in this text. However, the samples will have to be tailored towards specific applications.

For their application in the ceramic industry, the studied clays will have to be beneficiated so as to avoid process-generated problems such as black coring, bloating, crawling, crazing, exploding, peeling, pinholing, shivering and warping. These problems ensue from claybody formulations, glaze applications, rate of firing, and temperature of firing. Failure to eliminate these deficiencies makes the final product of a low quality and unattractive. A lot of vessels will be discarded, and the economic venture becomes a loss. A further study should therefore be carried out for identifying suitable glazes to be applied on the fired clays.

The studied clay materials have not been found suitable for use in industrial ceramics. This indication could be attributed to their thermo-mineralogical behavior as they change to metamorphic and igneous mineral phases at temperatures below 1300 °C. Industrial ceramic materials should be able to withstand temperatures above 1300 °C during production. They should have very high thermal shock absorption capacities, as well as very high refractory properties.

CONCLUSIONS

This study focused on changes in mineral phases of raw clays when subjected to laboratory controlled firing at 950 °C and 1250 °C. The work has mainly examined the mineralogy of the raw and fired bentonitic and kaolinitic clay samples, and indicated the changes of argillaceous sedimentary rocks to contact metamorphism. Indeed, the mineralogy of the fired products is quite similar to the mineral constituents from metamorphic and igneous rocks.

The demand for clays, especially kaolin, in the ceramic industry remains on the increase. Increasing demands focus on the improvement of the clay mineral quality for ceramics (Bloodworth *et. al.*, 1993). Process technology is not only required to purify the mineral, but to modify it to become suitable for tailor-guided applications. Market demands and consumer needs dictate techniques of producing finished, beautiful and highly desired ceramic vessels.

Other decisive factors, which may also influence the use of the studied clayey materials, could be market variations. Whereas the demand for certain ceramic products has remained constant, others have declined in favor of novel designs. Innovative process technologies at small, medium and large scales such as fast firing, wet grinding, spray drying, and use of environmentally friendly glazes have led to drastic modifications in body designs.

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