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Mineral Thermochemistry of Bentonite and Kaolin Related to Their Possible Application in the Ceramic Industry

¹Georges-Ivo E. Ekosse and ²Antoine F. Mulaba-Bafibiandi

¹Geology, Mining and Minerals Programs, School of Physical and Mineral Sciences, University of Limpopo, P/Bag X1106, Sovenga 0727, South Africa

²Department of Extraction Metallurgy, Faculty of Engineering and the Built Environment, University of Johannesburg, P.O. Box 526, Wits 2050, Johannesburg, South Africa

Abstract: X-Ray Powder Diffraction (XRPD) analyses were carried out on the raw and fired clays for identification and study of mineral phases and their changes contained in the samples. The raw clays consisted of smectite, beidellite, kaolinite, dickite, illite, cristobalite, quartz and calcite. Clays fired at 950°C reflected the following mineral phases: cristobalite, spinel, quartz and kasilite. Upon further firing to 1250°C, spinel, cordierite, hematite, tridymite and mullite. Indistinguishable amorphous phases were also present in the fired clay samples. Equations of thermochemical reactions were advanced to support mineral phase transformations of the studied clays. The findings of the study confirm that despite the similarity of clays, when fired their end products are different due to their raw clay chemical and mineralogical compositions. The results further support the suitability of the studied clays for use in the ceramic industry.

Key words: Kaolinite, mullite, spinel, smectite, x-ray diffraction, firing

INTRODUCTION

Bentonitic and kaolinitic clay deposits are exploited for very wide varieties of industrial applications, one of which is the ceramic industry (Ekosse, 2000, 2001; Murray, 1999; Patterson and Murray, 1983). These clays are used to make claybodies, slips and glazes of different chemical and mineral compositions for ceramic applications (Dubois *et al.*, 1995). However, not much is known regarding the artificial metamorphic processes which bring into play new mineral phases upon firing (Prodanović *et al.*, 1997).

In ceramics, two or more clays of completely different physical properties may have similar chemistry and two or more clays from radically different chemistry may have similar physical and fired properties (Ceramic Technology, 2000). Different thermochemical reactions occur yielding different mineral phases (Balek and Mu, 1996). These reactions are dependent on the type and composition of raw clay materials.

An understanding of the mineralogy and associated mineral phases of raw clay materials utilized in the ceramic industry is beneficial to the production of high grade finished ceramicwares. It is therefore imperative to have an insight of the mineralogical properties resulting from the transformations of the raw claybody to the desired

finished product as explained by Chandrasekhar and Ramaswamy (2002), Konta and Kuhnelt (1997) and Kakali *et al.* (2001). This study focused on understanding the mineralogical transformation phases of bentonite-rich and kaolin-rich claybodies, which could possibly find gainful applications in the ceramic industry.

MATERIALS AND METHODS

Two bentonitic and two kaolinitic clay samples were used in this study. Because in ceramics, bulk clay samples are used, the XRPD study focused on the analyses of the bulk samples. The second reason was also because the textural classification of the samples was mainly silty clay, with no sand component present (Ekosse, 2001), making them fine particles for XRPD analysis.

Moisture-free, dry weight 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 of approximately 50×10×10 mm and free water content eliminated through heating in an oven at 100°C for 12 h. The rectangular clay samples were fired at 950 and 1250°C, for 35 min in a muffle furnace and allowed to cool overnight. These temperatures were within the range applicable in industrial ceramics (Jordan *et al.*, 1999, 2001).

Corresponding Author: Georges-Ivo E. Ekosse, Geology, Mining and Minerals Programs, School of Physical and Mineral Sciences, University of Limpopo, P/Bag X1106, Sovenga 0727, South Africa
Tel: +27 15 268 2451 Fax: +27 15 268 2362

For XRPD analyses to identify mineral phases, the dried raw and fired clay samples were gently crushed in an agate mortar to a fine texture. The powder samples were mounted on the sample holder with very little pressure, using a blade to minimize preferred orientation of the kaolinite particles (Hughes and Brown, 1979) and later scanned in the XRPD. Montmorillonite was distinguished from chlorite and vermiculite groups by rendering the clay homoionic with preferably Mg^{2+} , solvating with glycerol (under-estimates smectite content) and ethylene glycol (over-estimates smectite content) and observing shifts in the (001) spacing (Bühmann *et al.*, 1985).

A Philips PW 3710 XRPD system operated at 40 kV and 45 mA, having a $Cu-K\alpha$ radiation and a graphite monochromator. A PW 1877 Automated Powder Diffraction, XPERT Data Collector software package was employed to capture raw data and a Philips XPERT Graphics and Identify software package was used for qualitative identification of the minerals from both the data and patterns obtained by scanning at a speed of $1^\circ 2\theta \text{ min}^{-1}$. 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 Diffraction Data (2001) for confirmation.

RESULTS AND DISCUSSION

A summary of minerals contained in the various raw clay samples as identified by XRPD are as follows: smectite (montmorillonite), beidellite, lepidolite, kaolinite, dickite, illite, cristobalite, calcite and quartz. The mineral phases identified by XRPD analyses of the fired clay samples at 950°C were as follows: cristobalite, spinel, quartz, kalsilite ($KAlSiO_5$). Strong amorphous phases were present in some of the samples as could be depicted from the very noisy background. At 1250°C, the following mineral phases were identified in the fired clay samples: cristobalite, amorphous phase, spinel, quartz, cordierite, hematite, tridymite and mullite.

Reactions discussed were those that occurred at 950 and 1250°C, respectively for all the samples. In the equations of reactions, the first part listed the reactants; the second part was the products at 950°C and the third part was the products at 1250°C. In some reactions, the equations were split into a and b due to the nature of the products at 950°C. It should be pointed out that these equations are only true for ideal montmorillonite, ideal

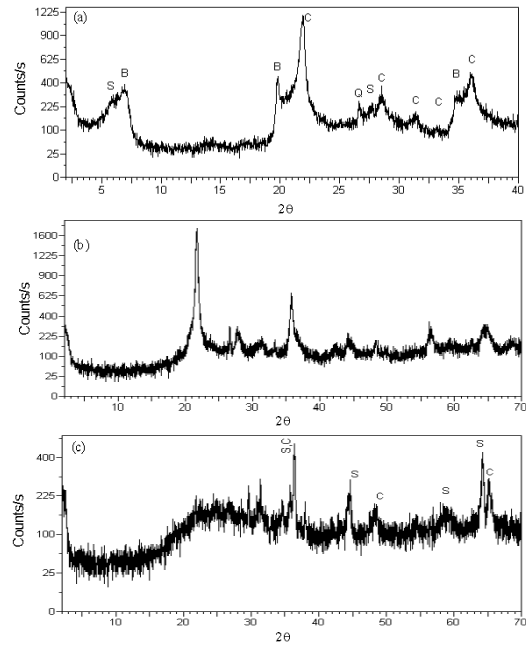
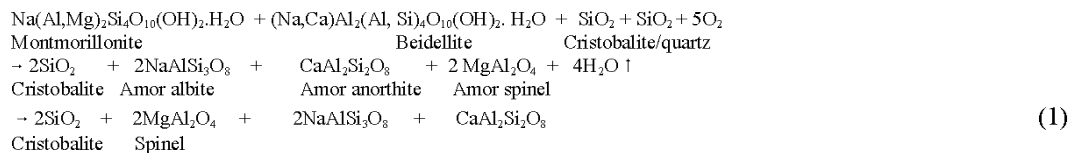


Fig. 1: X-ray diffractograms of the raw and fired sample 1 (a) S: Smectite, B: Beidellite, Q: Quartz and C: Cristobalite, (b) Main peaks identified arecristobalite. Strong amorphous phase illustrated by the noisy background and (c) S: Spinel and C: Cristobalite

beidellite and ideal cristobalite/quartz, an assumption of ideal state for the studied samples is maintained. Samples used in this study were from clay occurrences and deposits; hence contained some Fe and other metals such as Mn as impurities and/or isomorphous substitutions. These impurities/substitutions have been reflected in the mineralogical and chemical results.

Sample 1: From XRPD analysis for sample 1 as depicted in Fig. 1a, the raw clay consisted of montmorillonite, beidellite, cristobalite and quartz. Upon heating to 950°C, amorphous (hence forth abbreviated in equations as amor) albite, amorphous anorthite and amorphous spinel were formed as well as the conversion of quartz to cristobalite (Fig. 1b). Further heating to 1250°C, led to the crystallization of spinel whereas anorthite and albite remained in amorphous non-crystalline states (Fig. 1c).

The thermochemical reactions of the sample have been summarized in Eq. 1.



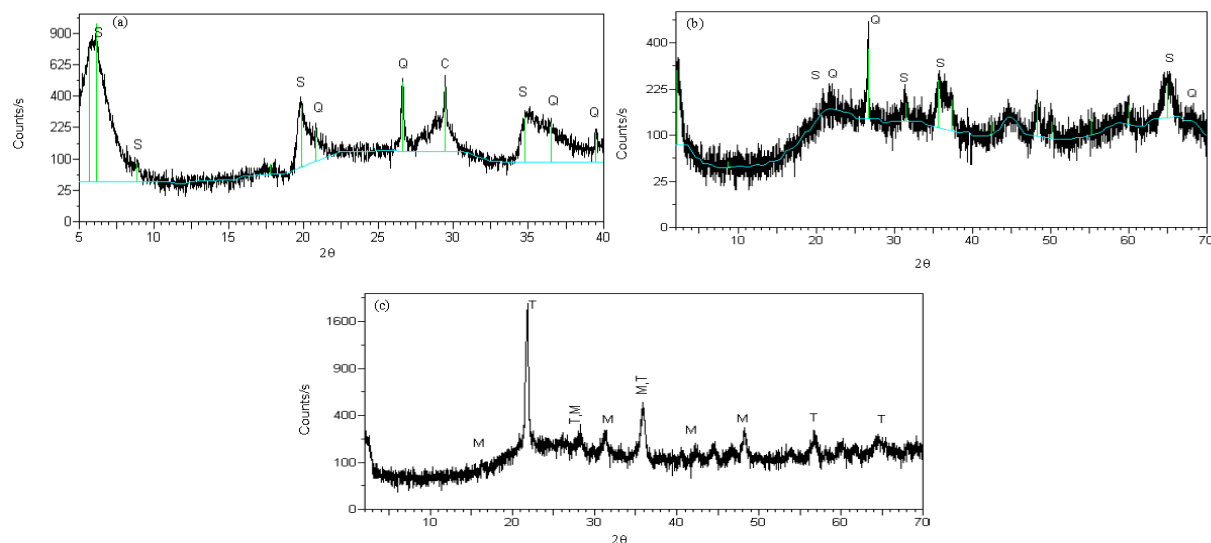
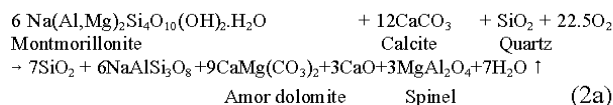


Fig. 2: X-ray diffractograms of the raw and fired sample 2 (a): S: Smectite, Q: Quartz and C: Calcite, (b) S: Spinel, Q: Quartz and (c) M: Mullite, T: Tridymite

Spinel as a member of the group has been reported; and where indicated, it could be spinel ($MgAl_2O_4$), ferrian spinel $\{(MgAl,Fe)_2O_4\}$, hercynite $FeAl_2O_4$, or magnesioferrite ($MgFe_2O_4$). Spinel is found naturally in contact metamorphic environments (Mottana *et al.*, 1978). Anorthite and albite are widely used in industrial ceramics and could also be found associated with metamorphic terrains. These thermochemical reactions favour the use of the clay represented as sample 1 in ceramics.

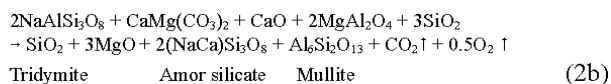
Sample 2: Although sample 2 is smectitic (Fig. 2) as sample 1, its mineralogy is different from that of the previous sample. The XRPD results for sample 2 showed that the raw clay consisted of montmorillonitic smectite, calcite and quartz (Fig. 2a). Upon heating to 950°C, spinel was formed and quartz persisted (Fig. 2b). Further heating of the sample to 1250°C led to the crystallization of mullite and tridymite (Fig. 2c). Amorphous material in the heated sample for both high temperature reactions is depicted by noisy background on the diffractogram.

The thermochemical reactions of the sample have been summarized in Eq. 2.



The reaction represented in Eq. 2a is an oxidation reaction whereby montmorillonite and calcite were reduced to spinel and an amorphous non-crystalline phase, which might have been composed of amorphous

albite, amorphous calcium oxide and amorphous dolomite. The further heating of the sample to 1250°C, led to the formation of an amorphous phase, which might possibly have constituted non crystalline sodium calcium silicate and non crystalline magnesium oxide. This second phase of reaction is a reduction process represented as Eq. 2b.



The gas, CO_2 was given off in this reaction. Mullite, which could be written either as $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ or $\text{Al}_6\text{Si}_2\text{O}_{13}$, must have crystallized from the breaking down of the oxides of montmorillonite and the reaction of Al_2O_3 with SiO_2 under high temperature. Mullite is found in igneous rocks and in thermally metamorphosed lateritic lithomarges (Deer *et al.*, 1983). It is a well recognized ceramic and refractory product. In this regard, the clay presented herein as sample 2 could be gainfully utilized in the ceramic industry.

Sample 3: For sample 3, kaolinite, dickite, illite and quartz (identified by XRPD in the raw sample as shown in Fig. 3a) reacted together at 950°C to produce kalsilite and amorphous mullite and quartz (Fig. 3b), as shown in Eq. 3. The sample was further fired to 1250°C and it yielded mullite as the crystalline neomineralized phase and orthoclase as a non crystalline phase, which were detected as amorphous material by XRPD (Fig. 3c). The equations of reaction are presented in below:

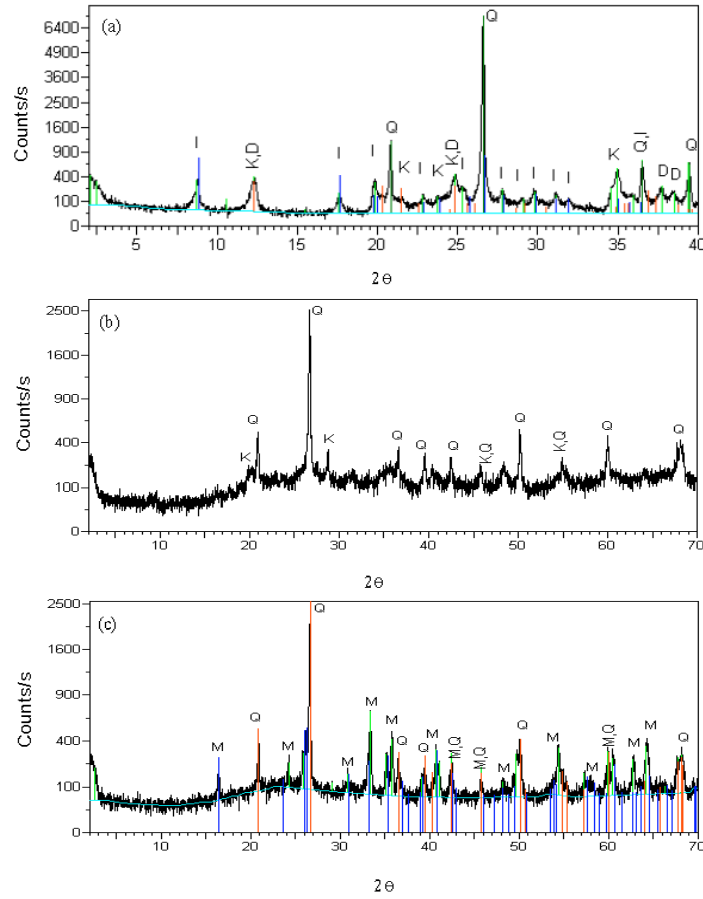
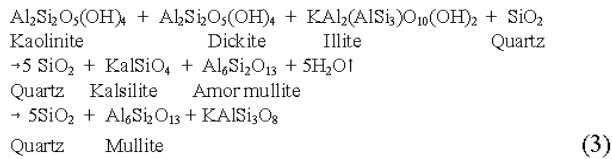
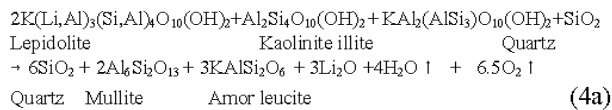


Fig. 3: X-ray diffractograms of the raw and fired sample 3 (a) I: Illite, K: Kaolinite, D: Dickite, Q: Quartz, (b) K: Kalsilite, Q: Quartz and (c) M: Mullite and Q: Quartz

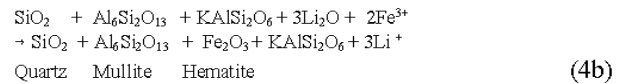


The reactions for sample 3 depict those of standard processes for claybodies to be transformed to ceramicwares.

Sample 4: Regarding sample 4, lepidolite, kaolinite, illite and quartz (identified by XRPD in the raw sample as shown in Fig. 4a) reacted together at 950°C to produce mullite and possibly amorphous leucite, whereas quartz did not change its phase (Fig. 4b), as shown in Eq. 4.



The second phase of the reaction at 1250°C involves free Fe being oxidized to hematite as indicated in Eq. 4b. The main end products were quartz, mullite and hematite (Fig. 4c). In a reverse manner, LiO is reduced to Li and amorphous leucite remains in a non-crystalline state.



Leucite is an α -tectosilicate of the feldspathoid group, being the primary mineral constituent found in volcanic rocks rich in K (Whitten and Brooks, 1972), but undersaturated in SiO₂. Quartz, mullite and hematite are minerals present in finished ceramic products. Consequently, the clay presented as sample 4 is suitable for use in the ceramic industry.

The XRPD results indicated that the mineral assemblages contained in the raw clay samples were similar to those contained in clays, which are normally

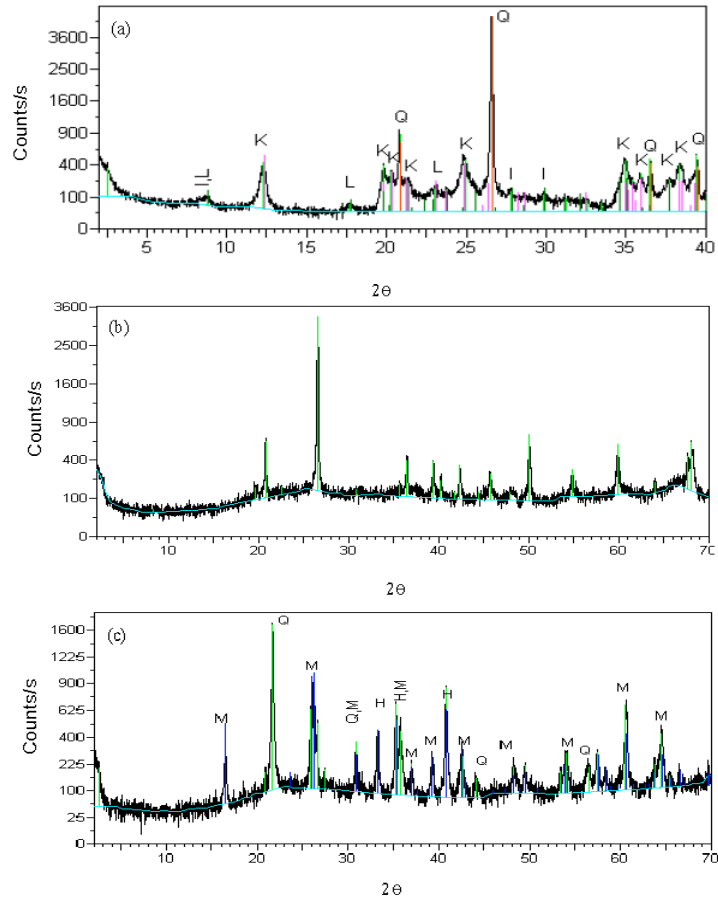


Fig. 4: X-ray diffractograms of the raw and fired sample 4 (a) I: Illite, L: Lepidolite, k: Kaolinite, Q: Quartz, (b) All the peaks identified as quartz. Strong amorphous phase illustrated by noisy background and (c) M: Mullite, Q: Quartz and H: Hematite

utilized in the ceramics industry (Aydın, 2004; Konta and Kühnel, 1997; Murad *et al.*, 2002; Murray, 2000). At 950°C, most the samples sintered and vitrification was observed at 1250°C. At both temperatures, the fired clay samples had amorphous phases, which constituted non crystalline minerals. Cristobalite, spinel, hematite and an indistinguishable amorphous phase were identified in the samples at both fired temperatures. At 950°C, kalsilite and at 1250°C, tridymite, were the new mineral phases. In the thermochemical reactions, the amorphous phases constituted the chemical compositions of high temperature minerals, which are associated with metamorphic and igneous terrains.

In the low temperature reactions, it was mainly sintering of the components of the clayey material (Hajjaji *et al.*, 2002; Pilipchatin, 2001) and in the high temperature reactions, vitrification was the main reaction (Souza *et al.*, 2002; Wagner *et al.*, 1999). Knowledge of metamorphic mineralogy and petrology aids in

understanding reactions related to traditional and industrial ceramics mineralogy and chemistry (McConville and Lee, 2005). However, these equations of reactions have confirmed that because clays have varying chemical compositions, when used in ceramics, the claybodies yield products having a wide range of varying mineralogical and chemical compositions. Unfortunately, not much is known of artificial metamorphism of clayey materials and phyllosilicates related to ceramics (Castelein *et al.*, 2001; Prodanović *et al.*, 1997). It is anticipated that the results of this study have brought some understanding on the subject of mineral thermochemistry of bentonite and kaolin.

CONCLUSION

This study addressed the chemical reactions which take place during clay mineral phase transformations as a result of their firing. Two smectitic and two kaolinitic

clays of different mineralogical compositions were investigated. Each of the clay samples had a unique response to thermochemistry. Clay minerals in the raw clay sample 1 and 2 were mainly montmorillonite; and sample 1 also contained beidellite. Samples 3 and 4 contained kaolinite as major and illite as minor clay minerals; and sample 3 also had dickite. Quartz was the dominant non clay minerals present in the four studied samples. Calcite occurred in sample 2 and lepidolite in sample 3.

Firing of the clay samples at 950 and 1250°C, respectively yielded different minerals products in the samples. The formation of neomineralised phases were governed by the type and amount of minerals in the raw clays and the firing temperatures. Upon firing of the raw clay samples, spinel was the dominant mineral phase in the bentonitic clays and mullite was the main constituent in the kaolinitic clays. Spinel and mullite are high temperature minerals usually present in fired ceramic bodies. Other mineral phases present in the samples when fired to 1250°C included tridymite, orthoclase and leucite; which are usually associated with metamorphic terrains. These findings are contributory to understanding ceramics and artificial metamorphism.

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