

Low temperature sintering of a pottery clay from Burkina Faso

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Abstract

The sintering at 1000°C of a clay raw material for pottery mixed with calcite was studied to increase the mechanical characteristics of the fired product. The kaolinitic clay used comes from a large pottery production area in Burkina Faso. The experiments of this study were conducted as similar as possible to the traditional practices of potters to ensure a future technological transfer of results. An increase of the flexural strength from 7 to 17 mPa was obtained by adding 15% of calcite. To explain the mechanisms involved, the sintering behaviour was initially observed by dilatometry. Results indicated that at 1000°C, the maximum material densification and properties were obtained after about 15 min of dwell time. Therefore, a quantitative study of crystalline phases nucleated during this period was realised by X-ray diffraction methods. It revealed that anorthite is the most important phase formed during the firing time. Therefore, the nucleation mechanism, mostly involving quartz, but also gehlenite consumption was discussed. At the low firing temperature, it appears that the firing process is characterised by the absence of a liquid phase, drastically limiting the diffusion effect. As a consequence, the sample microstructure, as observed by SEM, shows a network of small dense zones, including quartz grains, interconnected by recrystallized porous phases. The comparison of material containing the natural kaolinitic clay to material obtained from pure reference minerals underlined the important role of iron impurities in anorthite formation. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Clay raw materials for ceramic uses have been extensively studied, by e.g. Jouenne (1979), Alliprandi (1979) and Sigg (1995). With respect to raw materials for traditional ceramic applications in west African countries, only a few of studies have been published (Kabré et al. 1998). This is related to a certain extent to the present situation of the ceramic sector mainly producing pottery and small quantities of bricks and roof tiles. Although these products are really necessary for the construction industry and for everyday life, they are not commonly available. Furthermore, heavy clay products cannot be imported due to transportation and production costs with the exception of cement. In any case, in Burkina Faso, 90% of the population cannot afford to buy manufactured clay products. In this country, a limited production of adobe, which is clay mixed with 5–9% cement and dried in the sun, is used as building material. Moreover, the most important ceramic production comes from local potters who apply very traditional techniques to excavate essentially local clays, to process hollow wares by hand and to fire them in traditional wood heated kilns. In general, the quality of the fired pottery or unfired adobe is often poor, in particular mechanical strength is not sufficient.

In this study, we are interested in an important pottery production area named Poa. It is situated between Ouagadougou and Koudougou (Fig. 1). For many



Fig. 1. Location of the clay quarry in Burkina Faso.

years, about 10 000 potters have been working there during summer (mainly women for whom it is an essential activity). The clay raw materials used in this area are mined by hand in open quarries. The geological details about these raw materials have been reported by Kabré et al. (1998) and Kaloga (1987). The clay raw material deposit belongs to an alluvial plain (with an old stream) over a distance of about 10 km. The clay layers are 3.5- to 5-m deep.

The aim of this work is to contribute to the understanding and improvement of the mechanical properties of fired pottery products, using calcite as an additive, taking into account the traditional practices of potters. Particularly, laboratory methods similar to those used by potters for paste mixing and low firing temperature at 1000°C were used. Calcite is a raw material commonly available in some areas in Burkina Faso.

2. Materials and methods

The P1 clay raw material is a kaolinitic clay. Its qualitative structural characteristics are presented in Fig. 2, and the chemical composition is shown in Table 1. P1 presents the typical X-ray pattern of kaolinite mixed with quartz. Other minor minerals, which could be associated, have not been really detected. From the chemical composition, the semi-quantitative mineralogical composition could be derived and is presented in Table 2, indicating the presence of mainly kaolinite and quartz minerals. From these analyses, the precise nature of iron minerals or the quantity of structural iron in clay minerals could not be determined.

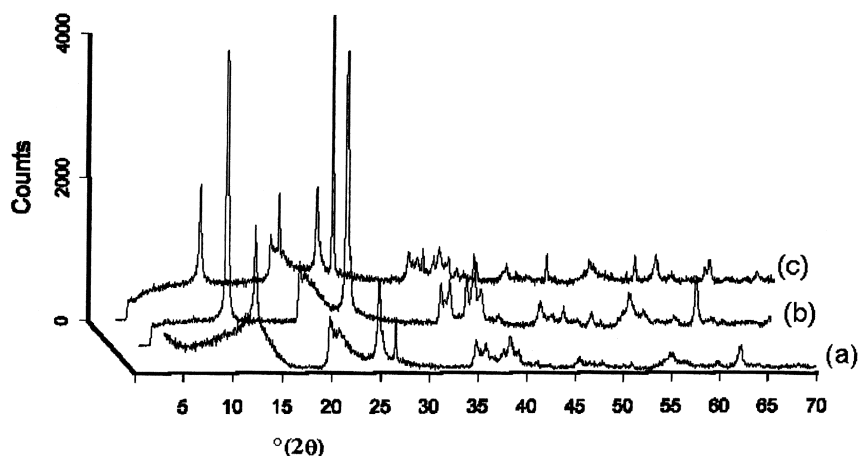


Fig. 2. X-ray patterns of (a) = P1; (b) = Kg2; (c) = P1 finer fraction (< 2 μm).

Table 1
Chemical composition of raw materials and reference materials

Sample (wt.% dry mass)	Al ₂ O ₃	Fe ₂ O ₃ + FeO	Na ₂ O	K ₂ O	SiO ₂	CaO	MgO	TiO ₂	LOI 1000°C	Total
P1	28.2	4.48	0.06	0.72	54.3	0.01	0.33	1.37	11.1	100.57
P2	23.97	3.81	0.05	0.61	46.16	24.57	0.28	1.16	–	100.61
M2	38.5	0.98 + 0.15	< 0.005	0.065	43.9	–	0.03	2.08	13.77	99.48

To study the thermal behavior of a raw material, a common practice is to consider the behaviour of a raw material in terms of an ideal formula of a pure mineral mix presenting well-known chemical compositions and structural characteristics (although small physico-chemical differences in raw material characteristics can affect the thermal behaviour). To this end, a poorly crystallised kaolinite, Kg2, was used as a reference mineral. It is provided by the Clay Mineral Society (Missouri University). Its chemical composition is given in Table 1, indicating a pure kaolinite mineral, containing at least 93% of kaolinite (Table 2). Information about kaolinite crystallinities can firstly be obtained from the broadening of [001] diffraction peaks (Amigo et al., 1994) and secondly from the [110] and [111] peak heights against the [02,11] band, which is also a usual criterion of structural organisation. In Fig. 2, besides the X-ray patterns of P1, the P1 finer fraction (< 2 µm) and the Kg2 materials are also presented. The aspect of the two latter patterns indicate the importance of the above-mentioned criteria. As a result, the P1 finer fraction clay mineral appears to be similar to Kg2 kaolinite, which contains a reduced quantity of impurities. Apart from kaolinite, the P1 mineralogical composition was assessed using a pure quartz powder, in a size range similar to the quartz phase in P1 (C600, Sifracco). The calcite powder used as additive was provided by Lambert Riviere (> 98% CaCO₃) with a similar grain size range.

Ceramic paste compositions are indicated in Table 3. P1 is the original paste containing only P1 raw material. P2 is the improved composition with 15% of calcite added. M2 is a mix of reference minerals, similar to P2 mineralogical

Table 2
Mineralogical composition of raw materials and reference materials

Sample (wt.% dry mass)	kaolinite	quartz	calcite	Organic matter and other minerals
P1	71.4 ± 1	21.1 ± 1	0	7.5 ± 1
P2	60.7 ± 1	17.9 ± 1	15 ± 1	6.4 ± 1
Kg2	> 93	–	–	< 7

Table 3
Ceramic paste compositions

Ceramic paste (wt.% dry mass)	P1	Kg2	Quartz	Calcite
P1	100	0	0	0
P2	85	0	0	15
M2	0	64.2	20.8	15

composition. In this latter case, it should be possible to test the iron influence on the thermal behaviour of the ceramic material, as this element is the major impurity in the P1 natural clay.

X-ray diffraction qualitative and semi-quantitative characterisations of powders were achieved using a Brüker D5000 diffractometer equipped with a backward graphite monochromator, using Cu K α radiation. Measurements were performed using a step scan of 0.03° (2 θ), and 5 s/step. The semi-quantitative measurements were deduced from intensity ratios, using an added standard to the powder, according to Brindley and Brown (1980), Alessandro et al. (1999) and Wang et al. (1996). In our case, the internal standard was a fine calcite powder because the corresponding mass attenuation coefficient (73.40) is close to the coefficient of the fired P2. Moreover, a particular measurement range between 25° and 33° (2 θ) presents the largest reflections of the crystalline phases of fired products, with only reduced overlappings. An example of such a pattern is presented in Fig. 3: the characteristic reflections are of quartz ([101] at $d = 3.342$ Å), calcite ([104] at $d = 3.034$ Å), anorthite ($[\bar{2}04]$ $d = 3.195$ Å) and gehlenite ([211] at $d = 3.844$ Å).

The semi-quantitative determinations took into account the peak appearances. The diffractograms were processed using the DIFRACPLUS DQUANT software. For quartz, peaks are well resolved and a method based on the fixed area was used. In the case of anorthite, the selected line is not well resolved and an optimised peak height method was used. For gehlenite, the corresponding peak is not strong enough, thus we used a method based on the optimised peak area. In all cases, a preliminary calibration was performed using a chosen proportion of calcite mixed with quartz as synthetic anorthite and gehlenite phases. The latter crystalline phases were obtained from solid state sintering and controlled using X-ray files N°73-1435 and N°79-2421, respectively.

Dilatometric measurements were achieved with a DI10 Adamel apparatus, at 10°C min⁻¹ in air atmosphere. In similar conditions, differential thermal analysis (DTA) was obtained with a Linseis equipment. Paste mixes were prepared from dry powders and water to obtain a plastic paste in a relatively intensive mixer, a procedure which is analogous to the traditional technique. Rectangular bars were shaped by low pressure casting, carefully dried and fired

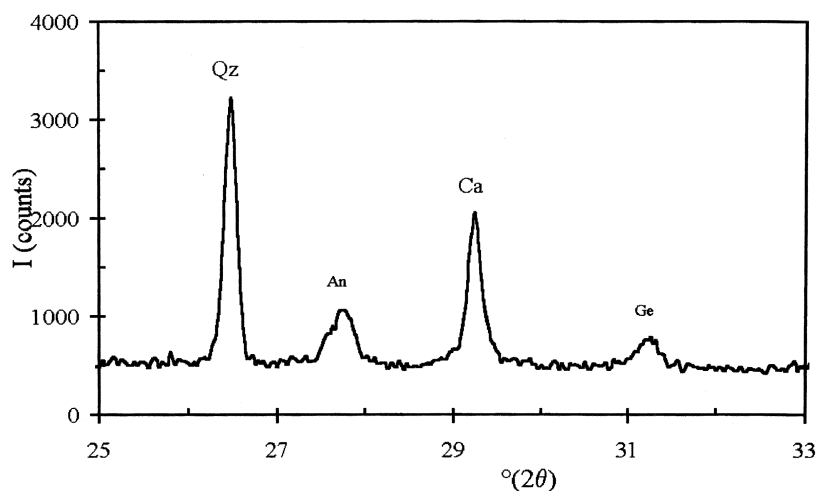


Fig. 3. X-ray pattern of the fired sample P2 containing calcite as internal standard, in the $2\theta^\circ$ region of 25–33°. An = anorthite; Qz = quartz; Ge = gehlenite.

at 1000°C according to the temperature profile as given in Fig. 4, which is similar to the wood heated kilns.

The flexural strength was measured on rectangular-shaped samples preliminary polished. A three-point bend test measured strength at 1 mm min^{-1} speed. Results were averaged on 12 samples.

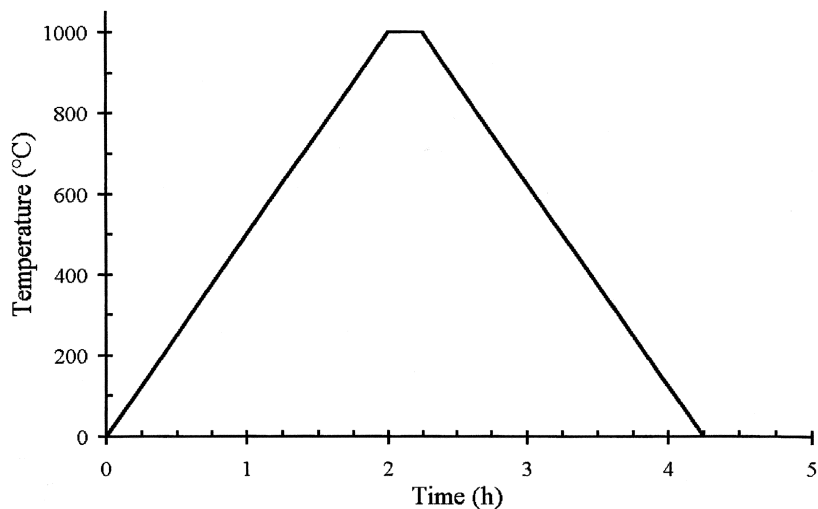


Fig. 4. Firing temperature vs. time.

Table 4
Flexural strength of fired samples

Sample	σ (mPa) 0.1-h dwell time	σ (mPa) 0.3-h dwell time
P1	7	7
P2	17	17

SEM pictures were used to observe the microstructure of sintered samples and EDS microanalysis (using a Hitachi S 2500 scanning electron microscope) to qualitatively describe the spatial distribution of major elements.

3. Results

In Table 4, the flexural strengths are presented as a function of calcite addition in the raw clay. As can be seen, values were highly increased (which was the primary objective of this study).

In Fig. 5, the dilatometric curves of the three compositions as a function of time are given. When the sintering temperature is reached and maintained at 1000°C, a progressive densification for 15 min and a subsequent volume stabilisation (even after long dwell times) was observed. Finally, P2 is more densified than P1 and M2 is the most highly densified composition.

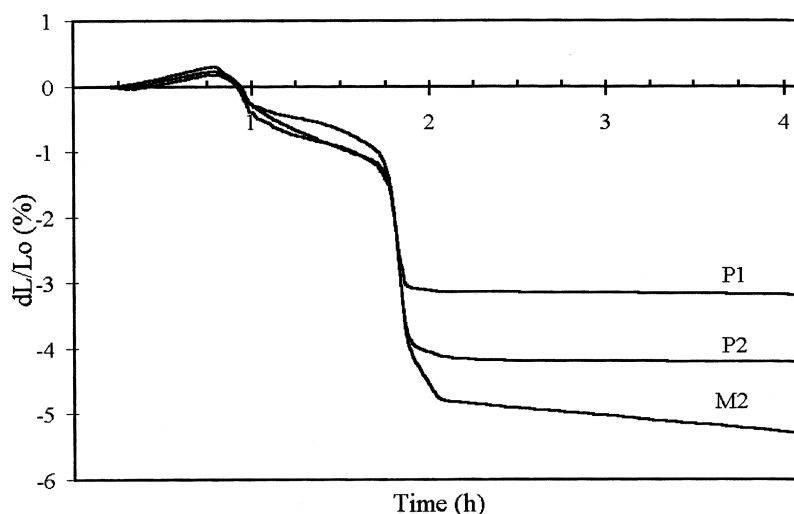


Fig. 5. Dilatometry characteristics of the three samples studied. After attaining 1000°C, the temperature is maintained.

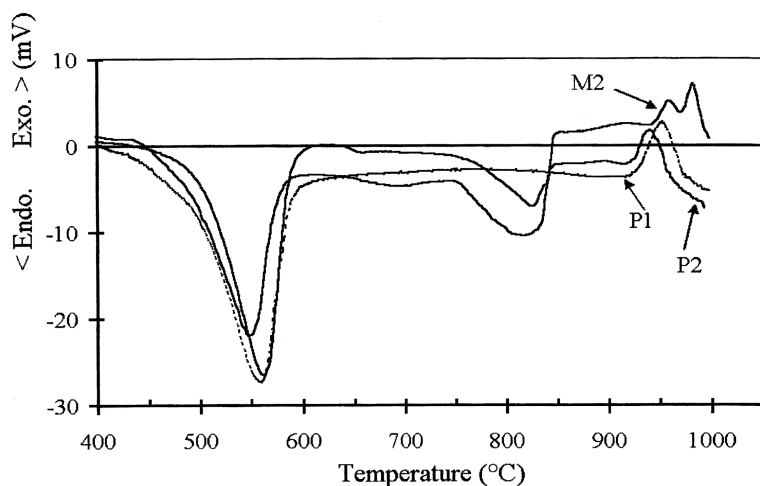


Fig. 6. DTA curves for the three samples studied.

DTA curves reveal below 600°C, the typical endothermic phenomenon relative to kaolinite dehydroxylation (Fig. 6). In the 700–850°C temperature range, the other endothermic phenomenon for P2 and M2 corresponds to calcite decomposition. Above 920°C, the exothermic phenomenon corresponding to the kaolinite structural reorganisation is clearly present in the P1 curve. In the case of P2, the peak appears at a slightly lower temperature and for M2, two separated exothermic phenomena are present in a narrow temperature range.

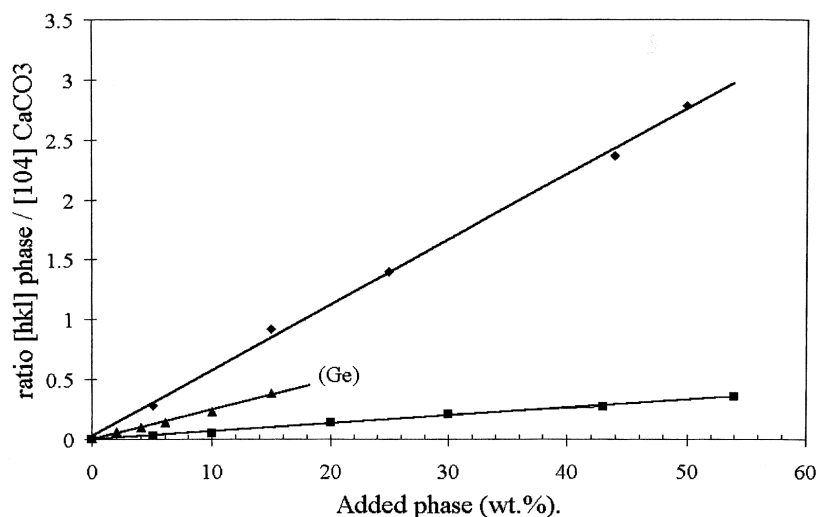


Fig. 7. Calibration curves for the determination of crystalline phases, based on the internal standard method using the (104) calcite peak: (An) = anorthite; (Ge) = gehlenite; (Qz) = quartz.

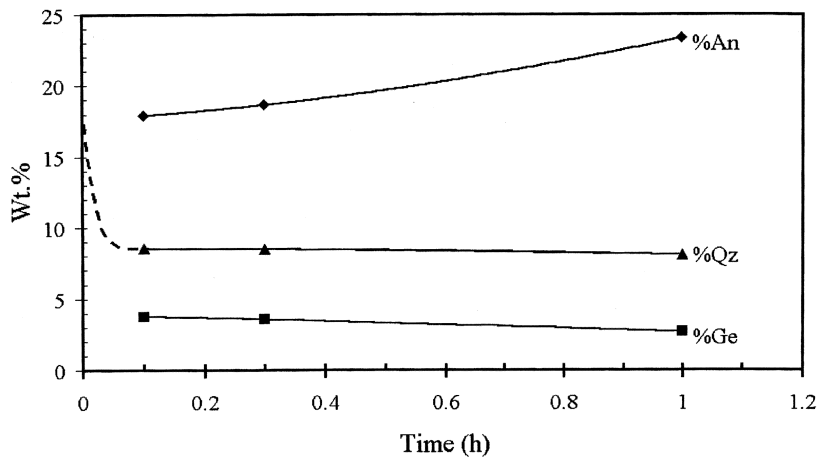


Fig. 8. Crystalline phases evolution with time at 1000°C for sample P2 (solid line) and for sample P1 (dashed line): An = anorthite; Qz = quartz; Ge = gehlenite.

Semi-quantitative powder characterisation was obtained from an internal calibration method using calcite. The obtained relationship between peak characteristics and phase contents was always linear enough, as can be seen in Fig. 7. The resulting quartz, anorthite and gehlenite quantities are plotted versus the dwell time at 1000°C in Figs. 8 and 9 for P2 and M2, respectively. Mainly for P2, but also for M2, the quartz content is reduced from its initial concentration. For both compositions, the anorthite quantity increases continuously (mainly for M2) while the gehlenite amount is slightly reduced.

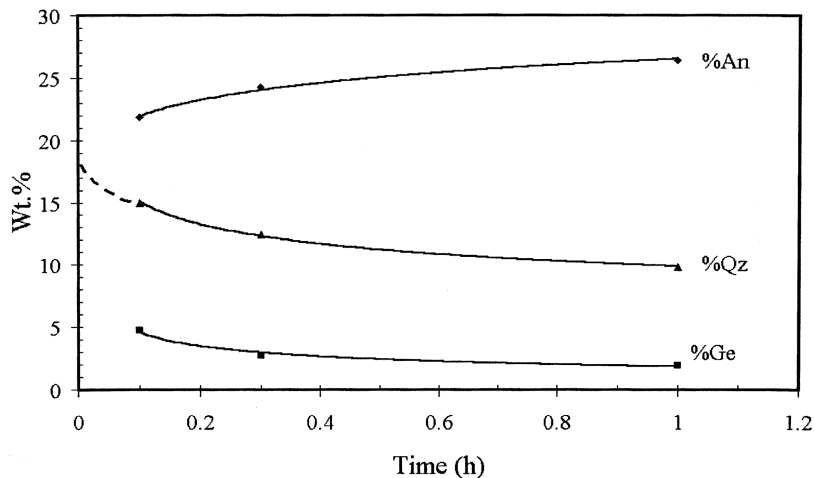


Fig. 9. Crystalline phases evolution with dwell time at 1000°C for sample M2: An = anorthite; Qz = quartz; Ge = gehlenite.

An SEM photo showing the fired P2 microstructure is given in Fig. 11, indicating the localisation of Ca and Fe elements.

4. Discussion

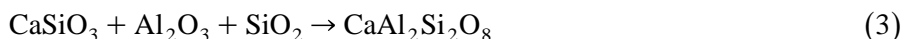
As it is indicated in Table 4, the strength of the fired material has increased substantially. Particularly, the material strength values are the same for dwell times of 0.1 and 0.3 h. The effect of longer times have not been investigated since they are not applied in traditional firing. The calcite addition in P1 clay leads to a slight additional densification (Fig. 5), while the sample open porosity is reduced from 35 to 34 vol.%. It must be emphasised that the apparent densities of P1 and P2 pastes remain almost constant, even after 2 h at 1000°C, while the M2 paste containing reference minerals densifies slowly.

The strength increase could be related to the material microstructure, particularly when decreasing the pore fraction, as illustrated in Kingery (1976) and discussed by Boccaccini (1994). In all cases, the empirical relationships generally used to connect strength σ , and porosity p , is in the form:

$$\sigma = \sigma_0 \exp(-np) \quad (1).$$

Although it is an exponential law, the curve slope is moderate at high porosity values, as in the case for fired P1 (35%) and P2 (34%). Given the small difference between these values, it can be assumed that the strength increase should be more correlated to the crystalline phases quantities and spatial repartition.

The changes of phase quantities with firing time in Figs. 8 and 9 suggest the following reactions. First, anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) appears below 1000°C. Sigg (1995) and Sandoval and Ibanez (1999) suggested a two-step reaction:



Wollastonite is an intermediate compound detected only in the case of heterogeneous structures at contact points between large CaO and quartz grains (Piponnier et al. 1997). In this study, wollastonite (CaSiO_3) was not observed on X-ray patterns. Reaction (2) seems thus to be intermediate. This two-step reaction is quartz consuming as soon as the firing temperature is attained, as mainly observed for P2, but also for M2. Later, the metakaolinite product will also provide reaction compounds, containing alumina and free silica.

The second reaction sequence describes the change of the anorthite/gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) ratio during the firing time:



The occurrence of simultaneous reactions (2) and (3) and also of reaction (4) can be associated with P2 transformation up to 1000°C (Fig. 8). A quartz quantity disappears at the beginning of the firing time. After 0.1 h., anorthite and gehlenite quantities are high. For longer dwell times, their quantities respectively increase and slightly decrease, whereas the quartz content almost remains constant.

In the case of M2, the occurrence of reactions (2)–(4) is more clearly indicated, although wollastonite was still supposed to be a transitional compound. The phase quantities are continuously changing (Fig. 9). Although the early anorthite quantity is high, it still increases during dwell time, accompanied with a subsequent quartz and gehlenite reduction.

A correlation of these observations is found in DTA results. The curves relative to the M2 reference material reveal two exothermic phenomena at 960°C

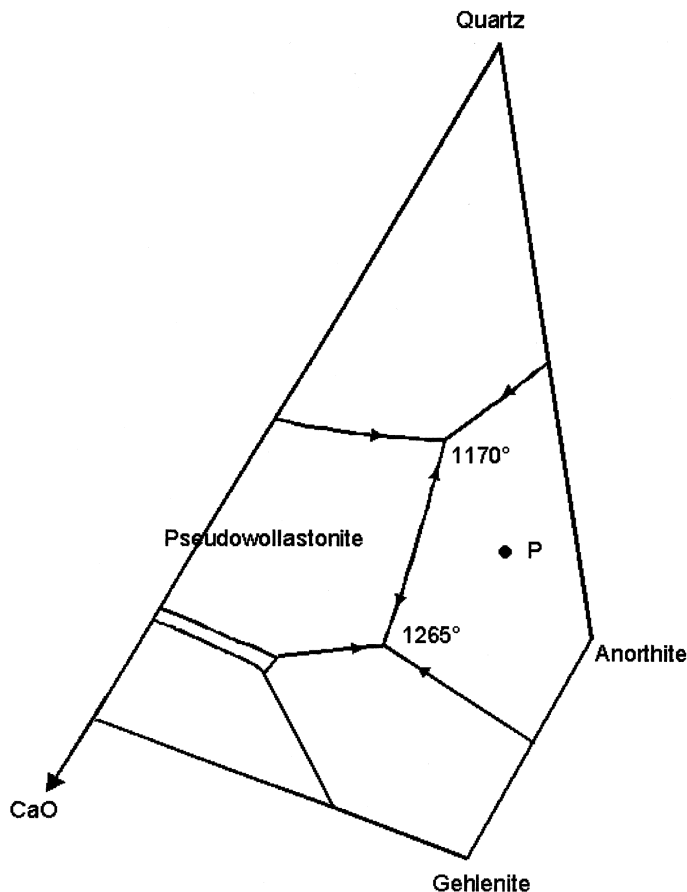


Fig. 10. Ternary subsystem Quartz–Anorthite–Gehlenite of the ternary system $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO}$; the P point denotes the P2 fired global composition.

and 980°C. The first one is attributed to the structural reorganisation of the metakaolinite material, which results from a low crystallised mineral (as in the X-ray study in Fig. 2). The higher temperature peak can be attributed to the two-step reactions (2) and (3). For the P2 mix, there is only one exothermic phenomenon at 960°C characterised by a smoother peak. It seems that a series of reactions as indicated above, probably associated with the metakaolinite structural reorganisation, could exist simultaneously and progressively. As a result, the impurities in the raw material, such as structural iron or associated iron minerals, might play an important role.

For P2, the phase transformations are not associated with a more significant densification than that for P1. The product density is almost constant and a large open porosity remains. Consequently, it can be assumed that a liquid-phase sintering process is not the most effective process. This is illustrated by the central area of the ternary diagram $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO}$ in Fig. 10 (Osborn and Arnulf, 1960). The overall chemical composition of P2 is situated on the P point, inside the area delimited by silica, wollastonite, anorthite and gehlenite. Furthermore, additional information is found on the three pseudo binary diagrams, which are also published by Osborn and Arnulf (1960), illustrating the effect of temperature. Therefore, the P composition at 1000°C contains anorthite, gehlenite and quartz, which coexist without any solid solution. Here, the first eutectic liquid appears at about 1170°C. As a result, it is assumed that the

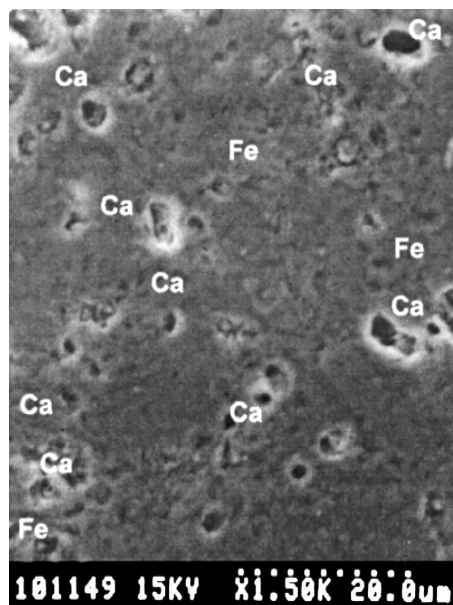


Fig. 11. SEM observation of the fired P2 sample, indicating the presence of large concentrations of Ca and Fe elements, by EDS characterisations.

sintering process should not be associated with large transport processes, a situation which is very different from the sintering of whitewares like porcelain. In this study, however, only diffusion mechanisms, limiting the microstructure homogeneity at a large scale have to be taken into account. This is illustrated in Fig. 11, where Ca and Fe elements are located mainly in restricted but not corresponding areas. Here, it can be seen that Ca-rich regions contain larger pores resulting from the carbonate loss. As these regions seem to connect more densified zones and larger quartz grains, they seem to increase the material strength. Therefore, a study of the phase distribution and role in the product properties is required.

5. Conclusion

In this study, the strength of the material appears to be related to the type and quantity of crystalline phases rather than to a decrease of porosity. The microstructure of samples shows Ca-rich regions in which an anorthite phase predominates. These regions form a connecting network between more highly densified zones where larger quartz grains remain. In this case, a particular correlation between Fe concentrations and Ca-rich regions could not be found. Furthermore, the use of reference minerals revealed the particular role of raw material impurities, which reduce crystalline phase formation.

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