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## Evolution with Temperature of Crystalline and Amorphous Phases in Porcelain Stoneware

Jorge Martín-Márquez<sup>a</sup>, Angeles G. De la Torre<sup>b</sup>, Miguel A. G. Aranda<sup>b</sup>, Jesús M. Rincón<sup>a</sup>, Maximina Romero<sup>a\*</sup>

<sup>a</sup> Group of Glass and Ceramic Materials. Department of Building Construction Systems, Eduardo Torroja Institute for Construction Sciences-CSIC, 28033 Madrid, Spain.

<sup>b</sup> Dept. Química Inorgánica, Cristalografía y Mineralogía, Universidad de Málaga, 29071 Málaga, Spain.

\* Corresponding author. E-mail address: [mromero@ietcc.csic.es](mailto:mromero@ietcc.csic.es)

### Abstract

Porcelain stoneware tile is a ceramic building material characterised by high technological properties, especially regarding water absorption, chemical and frost resistance, bending strength and abrasion resistance. Since mineralogy is one of the main factors affecting the mechanical properties of porcelain stoneware, a complete determination and quantification of the mineral and amorphous phases is of special importance in the study of porcelain stoneware tiles. In the present work, a reference industrial composition (50% kaolinitic clay, 40% feldspar and 10% quartz) of porcelain stoneware tiles fired at different temperatures (400°-1400°C) was characterised by X-ray powder diffraction combined with quantitative full-phase analysis using the Rietveld method, including amorphous content. The green composition contained albite, microcline and muscovite as fluxing agents, which start to decompose at low temperatures (400°-800°C range) and are completely dissolved above 1200°C. The mullite phase is formed from 1100° to 1230°C and at the latter temperature, quartz particles start to dissolve.

Studies of mineralogical evolution have revealed that the high heating rate (45-50°C/min) required in ceramic tile manufacture leads to significant differences in comparisons with whiteware ceramics fired at a lower heating rate (10°C/min). Thus, the formation of mullite in porcelain stoneware occurs at higher temperatures (1100°C) whereas the transformation of  $\beta$ -quartz to  $\beta$ -cristobalite does not take place.

The experimental results of this study show that qualitative mineralogical analysis, based on the intensity of a particular diffraction peak for each crystalline phase, is a suitable methodology to obtain preliminary knowledge of mineralogical changes with temperature.

## **Introduction**

Porcelain stoneware tile is a derived porcelain building material fabricated using a fast firing cycle (the tiles are inside the furnace no longer than 60-90 min) and characterised by a very compact microstructure and high technical characteristics<sup>1</sup>. Porcelain stoneware microstructure is of grain and bond type with large particles of filler (usually quartz) held together by a finer matrix, which is almost fully dense, composed of mullite crystals and a glassy phase<sup>2-4</sup>. Porcelain stoneware tile has experienced an increase in production and sales in comparison with all other ceramic building materials, mainly due to its high technological properties, especially regarding water absorption, chemical and frost resistance, bending strength and abrasion resistance.

As a porcelain material, the mechanical properties of porcelain stoneware are affected by both its mineralogical composition and its microstructure. Thus, a complete determination and quantification of the mineral and amorphous phases is of special importance in the study of the performance of porcelain stoneware tiles. For years, conventional X-ray quantitative analysis methods, which are based on the calculation of the relative intensity of a selected diffraction line of a crystalline phase against the reference diffraction line of an internal standard, have been used for phase quantification in both porcelain<sup>5-8</sup> and porcelain stoneware materials<sup>9</sup>.

On the other hand, the Rietveld method<sup>10</sup> is currently the most useful tool to obtain direct quantitative phase analysis (QPA) of complex materials. Inherent advantages of this methodology have increased its application to mineralogical characterisation of porcelains<sup>11-15</sup>, porcelain stoneware materials<sup>16-20</sup> or other industrial materials such as cements<sup>21-22</sup>. This methodology involves no standards, but the crystal structures of every crystalline phase in the sample must be known, as the process consists of the comparison between the measured and calculated powder diffraction patterns. QPA using the Rietveld method gives phase fractions normalised to 100 % of crystalline phases and the amorphous/non-diffracting/non-defined crystalline content is usually not accounted for. However, the amorphous content included in a given crystalline sample may affect its final performance<sup>23</sup>, so its quantification is strongly recommended. The Rietveld methodology is also useful to indirectly determine the amorphous content by adding a suitable crystalline standard<sup>24</sup>.

Knowledge of the mineralogical phase evolution on firing, from the early stages of sintering (lower temperatures) to the complete melting of fluxing agents and formation of new phases (higher temperatures), is of great importance for both understanding the technological properties of porcelain

stoneware tiles and optimising the fast-firing schedule. In the studies focused on porcelain stoneware tiles given above, the mineralogy has only been determined in bodies fired at high temperatures (1180-1280°C). In more recent studies, Tarvornpanich et al.<sup>25-26</sup> revisited the microstructural and mineralogical evolution resulting from the firing of single kaolinite clay, quartz, nepheline syenite, and soda-lime-silica (SLS) glass and their mixtures (binary, ternary and quaternary) to form conventional whiteware compositions (clay:flux:filler 50:25:25). Those investigations included some quenching experiments in which pellets were fired at various temperatures from 600° to 1200°C at a heating rate of 10°C/min. For quenching, after the furnace was heated to the specified firing temperature, specimens were taken from the furnace and immediately dropped in cold water. Although quenched experiments could be correlated to cooling in porcelain stoneware tile production, a heating rate of 10°C is slower than that of 45-50°C/min required by the fast-firing process to ensure “cool-to-cool” in 60-90 minutes.

The aim of the present work is the full quantitative mineralogical characterization of a standard porcelain stoneware body fired between 400° and 1400°C using a fast firing process.

### **Experimental procedure**

The raw materials used in the present investigation were kaolinitic clay and feldspar (provided by Compañía Europea de Arcillas, S.A.) and designated hereafter as AR-2097-G and FC-100, respectively, and quartz sand (facilitated by IETcc, CSIC). Table I displays their mineralogical composition provided by the suppliers (the method used for quantitative phase analysis is unknown). All the above materials were crushed, ground and finally powdered to <160 µm prior to further use.

A standard composition for porcelain stoneware tile production was prepared by mixing 50 wt.% kaolinitic clay, 40 wt.% feldspar and 10 wt.% quartz<sup>27</sup>. Batches (300 g each) were prepared by milling the constituents with distilled water (1:1) for 30 min in a planetary ball mill and using alumina balls as grinding media. The resulting slurry was oven-dried overnight at 110°C, powdered using a porcelain mortar and pestle, and sieved to pass through a 100 mesh (150 µm). Table II shows the chemical analysis obtained by X-ray fluorescence of the starting reference porcelain stoneware powder. SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and alkaline oxides (R<sub>2</sub>O) are the main components (97.99 wt.%) and the remaining 2.01wt.% is considered to be minor impurities

Table I. Mineralogical composition of raw materials

<b>Mineralogical composition (wt.%)</b>		
<b>AR-2097-G</b>	<b>FC-100</b>	<b>Quartz sand</b>
<b>Kaolinitic clay</b>	<b>Feldspar</b>	
70.6% kaolinite	65% microcline	
12.7% muscovite	20% albite	Mainly quartz
10.6% quartz	13% quartz	microcline as minor phase
6.1% others	2% others	

Table II. Chemical analysis (wt.%) of the starting porcelain stoneware powder

<b>SiO<sub>2</sub></b>	<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>Fe<sub>2</sub>O<sub>3</sub></b>	<b>CaO</b>	<b>MgO</b>	<b>Na<sub>2</sub>O</b>	<b>K<sub>2</sub>O</b>	<b>TiO<sub>2</sub></b>	<b>MnO</b>	<b>P<sub>2</sub>O<sub>5</sub></b>
70.34	21.55	0.89	0.37	0.24	0.96	5.14	0.42	0.01	0.08

The powder was moistened by spraying with distilled water (6.0 wt.%), hand granulated, and uniaxially pressed at 40 MPa in a steel die. Discs 20 mm in diameter and 5 mm in height were formed from 3 g of powder. After drying in an oven at 110°C, the compacts were placed on alumina rollers in an electric furnace and fired between 400 and 1400°C following a fast firing process. After drying in an oven at 110°C, the compacts were placed on alumina rollers in an electric furnace and fired between 400° and 1400°C following two different heating schedules. Thus, samples fired at temperatures lower than 1000°C were heated from room temperature to the required firing temperature at 50°C/min. On the other hand, samples fired at temperatures higher than 1000°C were heated from room temperature to 1000°C at 50°C/min, and from 1000°C to the specified firing temperature at ~20°C/min. In all cases, after being held for 15 min at the maximum temperature, the samples were cooled in the furnace at 50°C/min to room temperature.

Phase identification was carried out by X-ray diffraction (XRD, Philips X'PERT MPD) using CuK<sub>α</sub> radiation and operating at 50 kV and 30 mA. For XRD, powder samples (sieved <60 μm) were scanned in the 5°-75° (2θ) interval at a scanning speed of 0.5 °min<sup>-1</sup>. Table III lists the powder diffraction files,

selected from the *International Centre for Standard Data (ICSD)*<sup>28</sup>, and used to identify the present crystalline phases.

Table III. Powder diffraction files (PDF) used to identify the crystalline phases present in porcelain stoneware bodies fired at different temperatures and ICSD codes of the crystal structures used to perform Rietveld quantitative phase analyses.

<b>Crystalline Phase</b>	<b>PDF</b>	<b>ICSD</b>
Kaolinite	06-0221	
Quartz	46-1045	63532
Microcline	19-0926	201601
Muscovite	06-0263	74608
Mullite	15-776	66263

For Rietveld analysis, finely powdered porcelain stoneware samples were mixed with ~30% high purity calcined  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (PDF 43-1484; ICSD 73725) as is the internal standard. The mixture was homogenized by hand milling for 5 minutes in an agate mortar with acetone.

Powder diffraction patterns suitable to perform Rietveld QPA were collected at room temperature using a Siemens D5000 (CuK <sub>$\alpha$</sub>  radiation) diffractometer working at 40 kV and 30mA. Intensities were collected by step-scanning in the 10°-70°(2 $\theta$ ) range, with steps of 0.03° and a counting time of 8 s for each step. In order to minimise the preferred orientation effects and to enhance the average particle distribution, the samples were spun at 15 rpm during data collection. QPA was performed by means of the GSAS (Generalized Structure Analysis System) suite of programs<sup>29</sup>. The Inorganic Crystal Structure Database (ICSD) codes for the crystal structure descriptions used for Rietveld QPA are given in Table III. When anisotropic vibration temperature factors were reported, these were converted to the corresponding isotropic values and introduced in the Rietveld analysis. The atomic parameters were not refined. The optimised parameters in the final refinements were background coefficients, cell parameters, zero shift error, peak shape parameters, preferred orientation (when appropriate), and phase fractions.

The microstructure of fired specimens was examined by Scanning Electron Microscopy (SEM, Philips XPERT microscope) using an accelerate voltage of 20 kV. For analysis of phase assemblages and morphology, the fresh fracture surfaces were etched for 4 min in 15% HF solution, washed ultrasonically

with distilled water and ethylic alcohol, dried and subsequently Au-Pd coated (Balzers SCD 050 sputter). Secondary electron images (SEI) were used for microstructural examination.

## Results and Discussion

Figure 1 shows the X-ray powder patterns of the standard porcelain stoneware body after firing between 400 and 1400°C. All the peaks due to a given phase have been labeled. At 400°C, the main mineralogical phases of the raw materials are identifiable. The intensity of peaks resulting from kaolinite decrease after firing at 500°C because of its transformation to metakaolinite by loss of –OH groups from its structure, which is complete at 800°C. Albite and microcline phases, constituents of FC-100 feldspar, remain in the fired body up to 1100°C (partial melting) and are completely melted at 1200°C, which is in agreement with the results of former studies on melting in the albite-quartz system<sup>30</sup> and on heating nepheline syenite<sup>25</sup>. Quartz is present at all firing temperatures, although the intensity of peaks decreases above 1100°C, indicating a partial dissolution concomitant with the formation of the liquid phase. In the earlier investigation of the mineralogical evolution of clay-based ceramics, Tarvornpanich et al. clearly detected  $\alpha$ -cristobalite after holding quartz for 3 h at 1300°C, and cooling slowly to room temperature<sup>25</sup>. However, in the present study,  $\alpha$ -cristobalite is not distinguishable in the diffractogram of the porcelain stoneware body after firing at 1300°C, probably due to the fast firing feature of the process. Finally, mullite is detected in the pattern of the porcelain stoneware body fired above 1100°C, whereas Tarvornpanich et al. found mullite formation at 1000°C in binary mixtures of kalonite clay and nepheline syenite. This discrepancy may also be explained by the higher heating rate used in the fast firing process.

The qualitative mineralogical evolution occurring during firing in the 400°-1400°C interval was estimated by following the intensity of a particularly strong and non-overlapped diffraction peak for each crystalline phase. The diffraction lines of quartz at 3.359 Å (101), mullite at 1.526 Å (210) and albite at 3.199 Å (220) were selected. The development of an amorphous phase was estimated from the baseline. This study was not applicable to microcline due to preferred orientation.

Figures 2-4 show the evolution of the measured intensities of these selected peaks as a function of temperature. In Figure 3, the derived amorphous content is also included. Albite decreases from 400°C and leads to an amorphous phase, which substantially increases above 1000°C, corresponding to a clear decrease of quartz by dissolution in the liquid phase. Crystalline mullite is first detected at 1110°C and increases up to 1400°C.

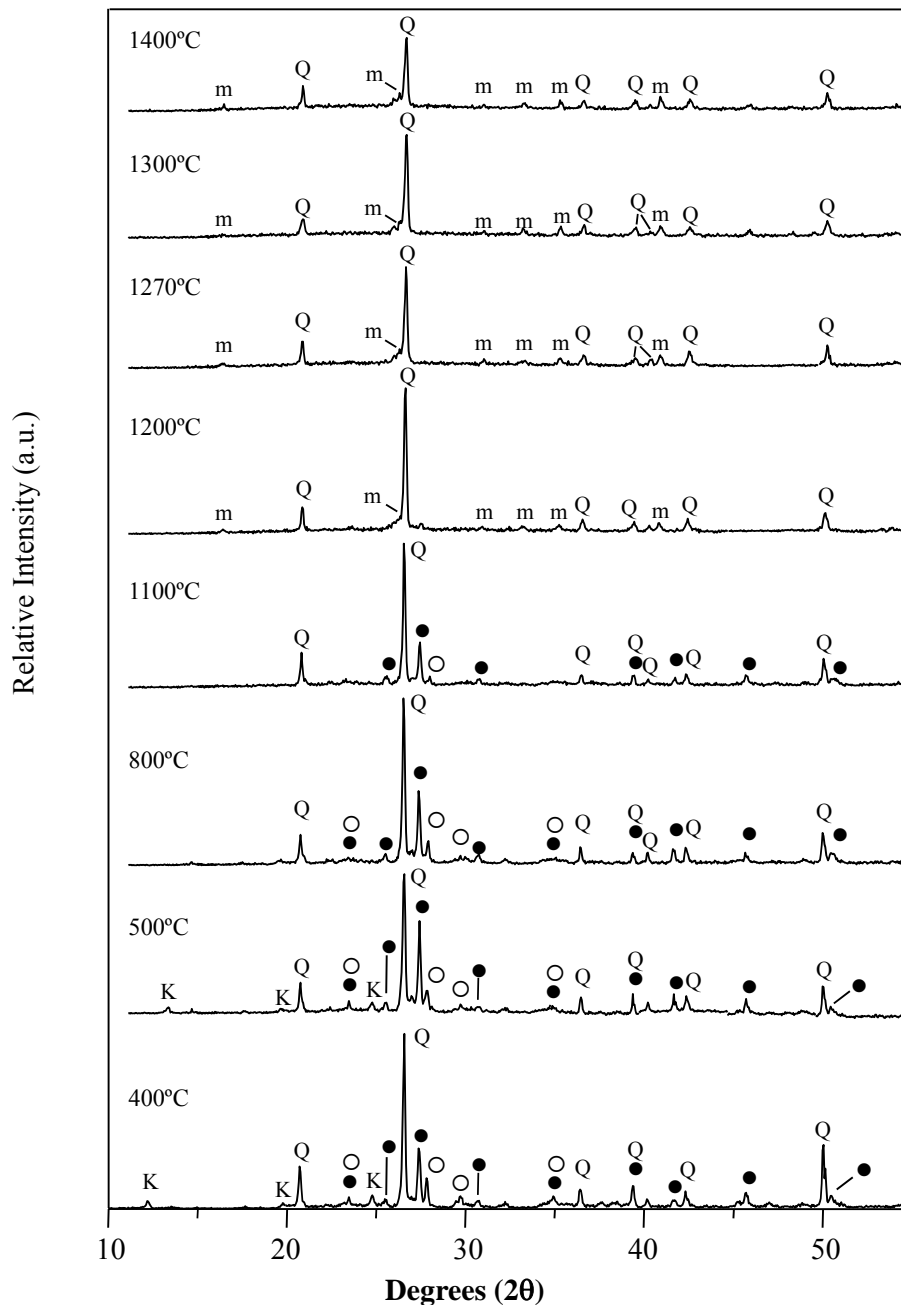


Figure 1. X-ray diffractograms of a standard stoneware body fired in the 400°-1400°C interval (Q = quartz, K = kaolinite, ● = microcline, ○ = albite, m = mullite).

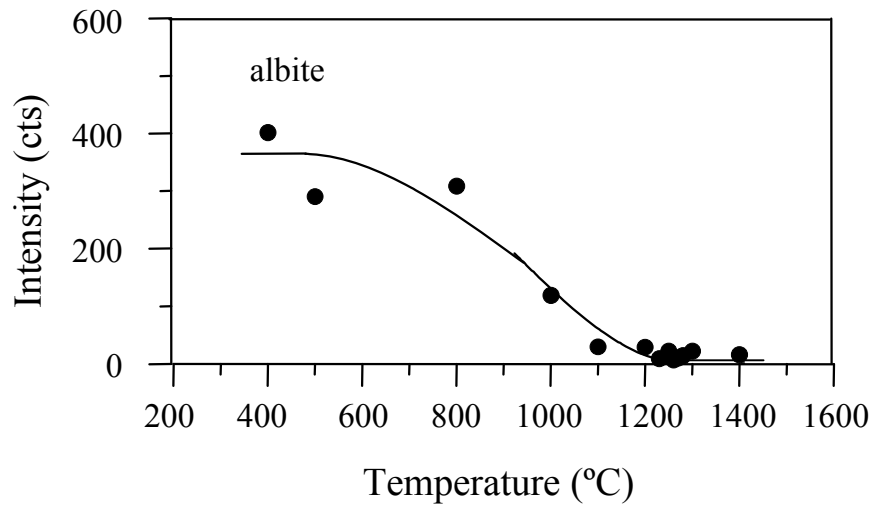


Figure 2. Intensity of albite diffraction peak (220) as a function of temperature.

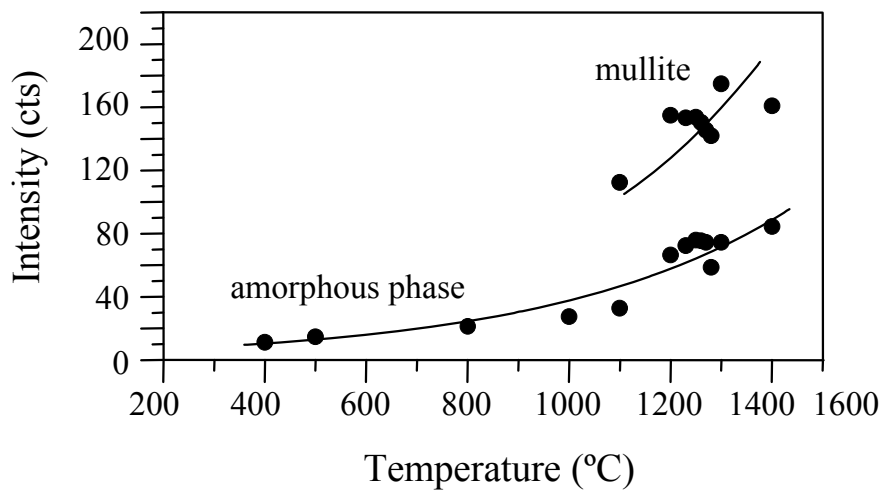


Figure 3. Intensity of mullite diffraction peak (210) and derived amorphous phase as a function of temperature.



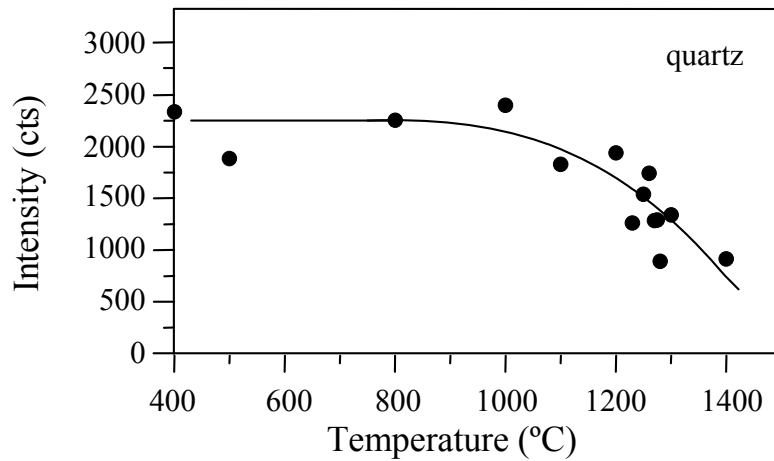


Figure 4. Intensity of quartz diffraction peak (101) as a function of temperature

Rietveld QPA, including amorphous content, was performed on porcelain stoneware samples fast fired at 1000, 1100, 1200, 1230, 1260, 1270, 1300 and 1400°C. In order to determine indirectly the amorphous content, the procedure described in reference 24 was followed. Figure 5 gives the Rietveld plot of the porcelain stoneware sample fired at 1260°C and mixed with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, as an example of the series, where the main peaks chiefly due to a given phase have been labeled.

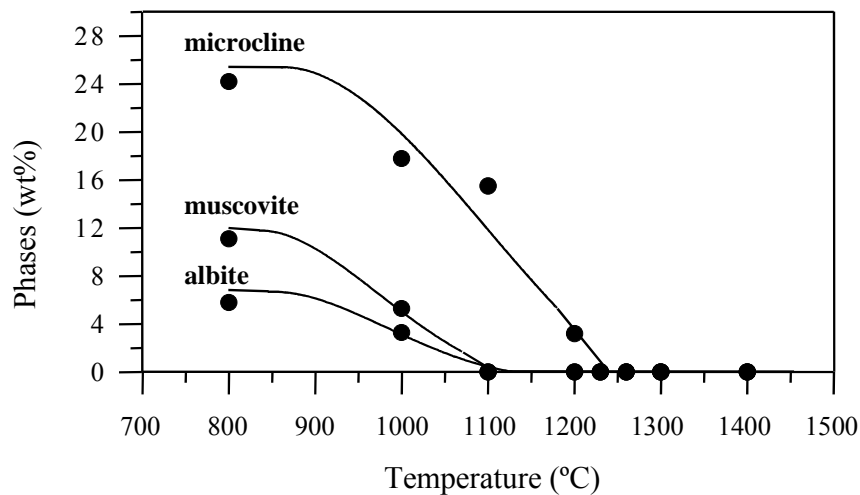


Figure 5. Rietveld plot for porcelain stoneware sample fired at 1260°C with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> added as an internal standard to perform amorphous quantitative phase analysis. Bragg peaks from bottom to top: SiO<sub>2</sub>, mullite (m) and Al<sub>2</sub>O<sub>3</sub>.

Table IV shows the evolution of phases on firing for a standard porcelain stoneware composition. It should be noted that the amorphous content, given in Table IV, includes the glassy phase together with non-diffraction phases such as intrinsic defects or grain-boundary regions.

Table IV. Rietveld quantitative phase analysis results, including amorphous content, for porcelain stoneware body fired at different temperatures.

	Temperature (°C)						
	1000	1100	1200	1230	1260	1300	1400
Amorphous phase	44.2(7)	52.8(6)	56.9(3)	61.5(3)	61.2(3)	61.4(3)	67.0(5)
Quartz	29.3(2)	28.2(2)	27.7(2)	24.1(1)	24.2(1)	24.6(1)	19.3(3)
Microcline	17.8(3)	15.5(4)	3.2(3)	-	-	-	-
Albite	3.3(3)	-	-	-	-	-	-
Muscovite	5.3(4)	-	-	-	-	-	-
Mullite	-	3.6(3)	12.2(3)	14.4(2)	14.5(2)	14.0(2)	13.7(2)

Albite ( $\cong 8$  wt.% in the green body) and muscovite ( $\cong 6.35$ wt.% in the green body) show a similar behaviour. They partially breakdown at 1000°C and are totally dissolved at 1100°C. Microcline ( $\cong 26$ wt.% in the green body) starts to decrease around 800°C and totally dissolves in the melt above 1200°C. As a result, the percentage of the amorphous phase continuously increases from 800°C up to 1230°C because of the partial dissolution of albite, muscovite and microcline. In the 1230°-1300°C range, the formation of the amorphous phase reaches a constant value due to the complete melting of fluxing agents. Above 1300°C, the amorphous phase starts to increase again owing to the partial dissolution of quartz particles in the formed glassy phase. The mullite phase is first detected in the porcelain stoneware sample fast fired above 1000°C and increases up to 1230°C. In the 1230°-1400°C interval the percentage of mullite remains constant.

It is necessary to point out that qualitative curves, shown in figures 2-4, present a similar trend to the results obtained from Rietveld analysis. This indicates that qualitative analysis is a suitable methodology for preliminary knowledge of mineralogical changes with temperature.

According to its main components, the composition of the starting porcelain stoneware powder (Table II) can be represented within the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O ternary system<sup>31</sup> in Figure 6 with the point labeled with a P. Moreover, by considering that the contribution of non-diffraction phases to the amorphous phase is

negligible and hence, the overall amorphous phase determined by the Rietveld method is owing to a glassy phase, the chemical composition of such a phase can be calculated from Tables II and IV. The composition of the glassy phases developed after firing at 1230°C (approx. 71wt.% SiO<sub>2</sub>, 19wt.% Al<sub>2</sub>O<sub>3</sub> and 10wt.% R<sub>2</sub>O) and 1400°C (approx. 73wt.% SiO<sub>2</sub>, 18wt.% Al<sub>2</sub>O<sub>3</sub> and 9wt.% R<sub>2</sub>O) are represented in Fig. 6 by the points labeled as L<sub>1</sub> and L<sub>2</sub>, respectively.

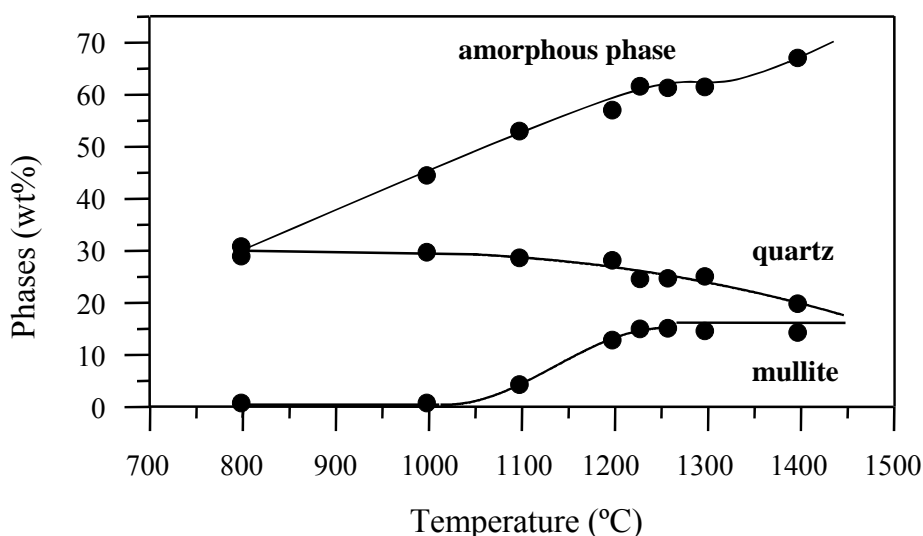


Figure 6. Detail of the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O ternary system.

On the other hand, the ratio of Si to Al in the crystalline phase can be calculated from Table IV (73.38/26.62 at 1230°C and 70.19/29.81 at 1400°C) and the points are represented in Figure 6 as Si/Al<sub>1</sub> and Si/Al<sub>2</sub>, respectively. Furthermore, the proportions of amorphous to crystalline phases have been determined using Rietveld QPA results (61.5/38.5 at 1230°C and 67/33 at 1400°C). Therefore, the composition of the porcelain stoneware body can be located within the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O system (points labeled as RM<sub>1</sub> and RM<sub>2</sub> respectively) by applying the lever rule<sup>32</sup>. It can be seen that the data obtained from the chemical analysis agree with those achieved using the Rietveld method.

The mineralogical composition of porcelain stoneware bodies fast fired in the 1230-1300°C interval was found to be approximately 61% glassy phase, 24% quartz, and 14% mullite (Table IV). This composition concurs with the typical mineralogical composition of commercial porcelain stoneware tiles, which commonly is 55-65% glassy phase, 20-25% quartz and 12-16% mullite<sup>8</sup>. The percentage of mullite

formed is slightly below 19.4%, which is the maximum amount of mullite that could be formed on firing using the assumption that all the kaolinite contained in the green composition is transformed to mullite. This difference in mullite formation is due to the fast firing process used for porcelain stoneware production. Most of the reactions occurring during firing are kinetically governed processes<sup>33</sup> that do not reach thermodynamic equilibrium during fast firing. Nevertheless, upon comparing the theoretical value with the experimental data, it is shown that the proportion of crystallized mullite is ~ 72% of the amount that could be stoichiometrically formed from the kaolinitic clay and this value is above the data reported by other studies on porcelain stoneware<sup>34</sup>.

Another way to evaluate mullite crystallization is to use the mullite formation index (MFI) given by the ratio between the experimentally determined quantity ( $M_{\text{exp}}$ ) and the potential mullite ( $M_{\text{pot}}$ ). The latter is calculated by assuming that all the alumina in the body can be converted into mullite during firing:

$$\text{MFI} = M_{\text{exp}}/M_{\text{pot}} = 0.718 M_{\text{exp}} / \text{Al}_2\text{O}_3$$

The MFI values obtained after fast firing above 1230°C are around 0.48, indicating that only half of the mullite phase that could potentially be generated from raw materials upon firing is actually formed. This value is in good agreement with data reported by other studies on porcelain stoneware<sup>9, 35-37</sup>.

Figure 7 shows SEM images of the standard porcelain stoneware body after firing in the 500°-1400°C interval. Bodies fired from 500° to 1000°C (Fig.7a-b) show a typical underfiring ceramic microstructure with high-interconnected porosity. The general microstructure consists of angular quartz particles, clay-derived agglomerates and a fine matrix of decomposed clay, feldspar and quartz. Tarvornpanich et al.<sup>26</sup> have sketched the microstructure of a standard whiteware fired at 600°C as quartz and feldspar grains surrounded by clay relicts, without observing the fine matrix of decomposed clay, feldspar and quartz detected in the present study, and this might be due to the greater particle size distribution in their formulation (the powder was passed through a 212 µm sieve instead of the 160µm sieve used in the present study). They have also detected primary mullite in clay relict agglomerates and secondary mullite from feldspar/clay relict particles after firing at 1000°C. The lack of mullite crystals the standard porcelain stoneware body fired at 100°C may possibly be due to the higher heating rate and lower holding time used in the fast firing process. At 1100°C (Fig.7c) the general microstructure is comprised of pure clay and clay-feldspar relicts together with rounded quartz particles. Although Rietveld analysis allowed the quantification of 3.6(3) wt.% of mullite at this firing temperature, its formation is not visible by SEM, likely due to the small size of the first developed mullite crystals. The microstructure of the sample fired at

1200°C (Fig.7d) is more compact than that observed at lower temperatures because of the liquid phase formed from the fluxing agents and secondary mullite crystals with needle shape are clearly identified by SEM (Fig.7e-f). A deeper study on the microstructural evolution on firing in porcelain stoneware will be presented in a forthcoming publication.

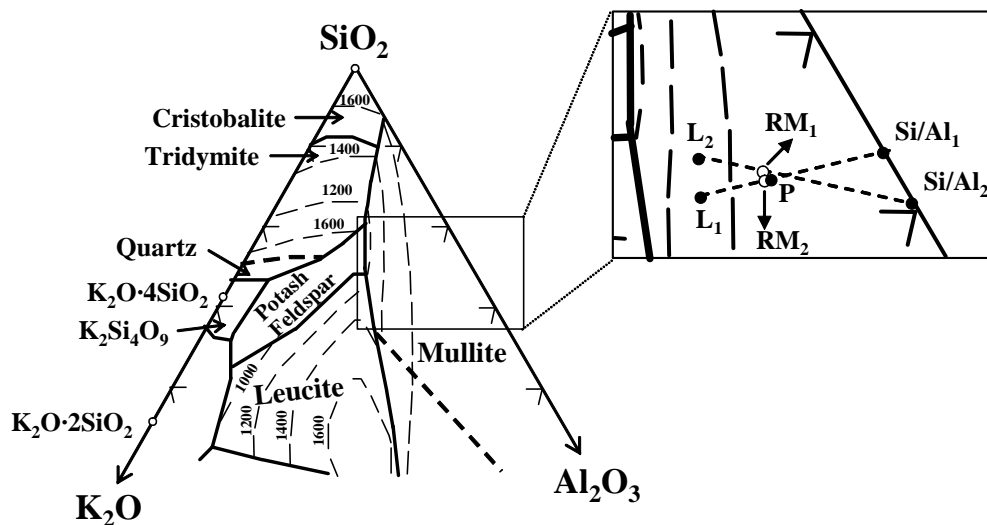


Figure 7. SEM images of a standard porcelain stoneware body fast fired at: a) 500°C, b) 1000°C, c) 1100°C, d) 1200°C, e) 1300°C and f) 1400°C.

## Conclusions

A mixture of 50% kaolinitic clay, 40% feldspar and 10% quartz was selected as a representative composition of commercial porcelain stoneware tiles produced via a fast-firing process. Mineralogical evolution revealed that the high heating rate (45-50°C/min) required in ceramic tile manufacture leads to significant differences from that in whiteware ceramics fired at a lower heating rate (10°C/min). Thus, the formation of mullite occurs at higher temperatures (1100°C) whereas the transformation of  $\beta$ -quartz to  $\beta$ -cristobalite does not take place.

After the qualitative and quantitative characterization of mineral and amorphous phases present in the body after firing in the 400°-1400°C interval, the following conclusions can be made:

- The fluxing constituents (albite, microcline and muscovite) start to decompose at low temperatures (400°-800°C interval) and are totally dissolved above 1200°C.

- Quartz particles start to dissolve in the formed glassy phase around 1230°C.
- As result of the former remarks, the amorphous phase continuously increases in the complete temperature interval studied.
- Mullite is first detected in the porcelain stoneware sample fast fired above 1000°C and increases up to 1230°C. At higher temperatures, the percentage of mullite remains constant.
- The mineralogical composition of porcelain stoneware bodies fast fired in the 1230°-1240°C range was found to be approximately 61% glassy phase, 24% quartz, and 14% mullite.
- Because of the fast firing process, the percentage of mullite formed is ~ 72% of the maximum amount of mullite that could be formed during firing based on the assumption that all the kaolinitic clay contained in the green composition is transformed into mullite.
- For the same reason, the MFI values obtained after fast firing above 1230°C are around 0.48, indicating that only half of the mullite that could potentially be generated from raw materials during firing, is actually formed.

The experimental results of this study show that qualitative mineralogical analysis, based on the intensity of a particular diffraction peak for each crystalline phase, is a suitable methodology to obtain preliminary knowledge of mineralogical changes with temperature.

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