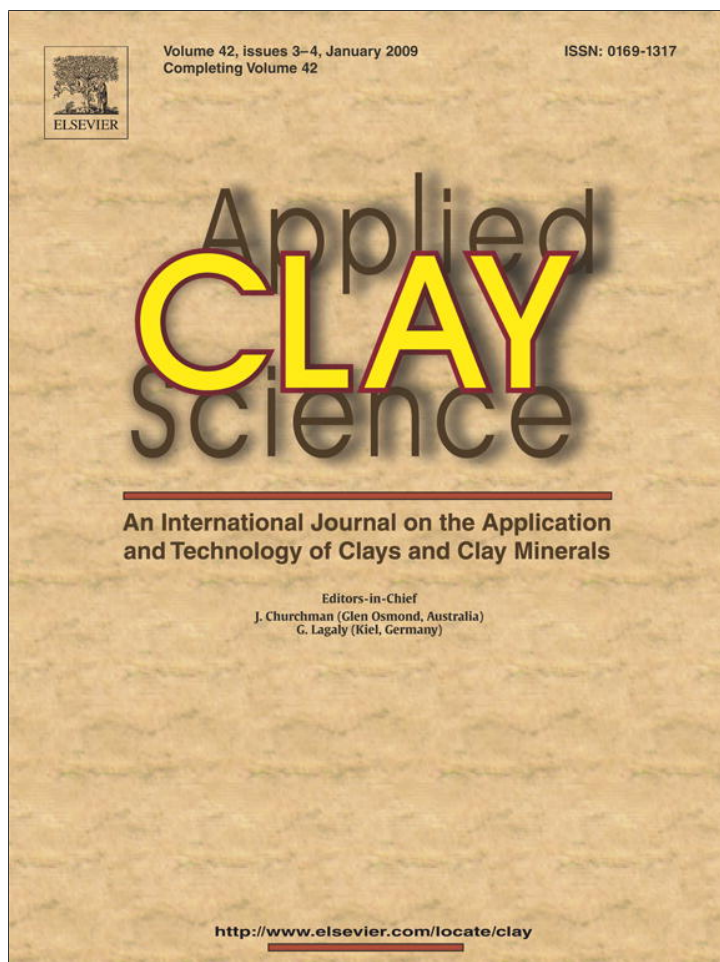


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Mineralogical transformations of calcareous rich clays with firing: A comparative study between calcite and dolomite rich clays from Algarve, Portugal

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ABSTRACT

Mineralogical transformations during firing of two extremely calcareous clays, one calcite and other dolomite rich, and relatively poor in silica were studied. Original clays were mineralogical and chemically characterized with X-ray diffraction (XRD) and X-ray fluorescence (XRF). Firing of both clays was carried out in the temperature range 300–1100 °C under oxidizing conditions and the mineralogical transformations were investigated with XRD, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy associated with energy dispersive X-ray spectroscopy (SEM-EDS). Important compositional differences in the neofomed phases were observed between calcite and dolomite rich clays. In the Ca-rich clay the assemblage gehlenite + wollastonite + larnite was observed. In the Mg(Ca)-rich clay the reaction products included akermanite, diopside, monticellite, forsterite, periclase and spinel. XRD and SEM-EDS showed the presence, in both clays, of a potassium–calcium sulfate in samples fired between 900 and 1100 °C.

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1. Introduction

Ceramic archaeological artefacts are durable pieces produced by firing clays (raw materials), based on the inherent property of clays to harden when heated. Upon firing minerals in clay bodies undergo chemical and structural modifications (dehydration, dehydroxylation, decomposition and formation of new phases, vitrification) transforming deeply the original clayey material. This process occurs by high temperature, low-pressure mineral transformations that are mainly influenced by the chemical and mineralogical composition of the original clay, its grain-size distribution, the maximum heating temperature, heating rate, duration of firing and kiln redox atmosphere (Maggetti, 1982; Moropoulou et al., 1995). The new high temperature minerals can nucleate and grow both by replacing mineral phases present in the clay or along grain boundaries of phases with contrasting chemistry, thus the original and the high temperature phases coexist.

Because the appearance of a particular high temperature mineral assemblage in an archaeological artifact is related, among other factors, to the temperature reached in the kiln (Moropoulou et al., 1995), archaeometric investigations commonly use the firing temperatures to determine some technological attributes of a historical sherd.

In the Meso-Cenozoic Algarve basin there are several archaeological sites of roman age with evidence of ancient ceramic production in local

kilns, which makes very interesting the study of regional clay deposits in order to establish the provenance of raw materials. Particularly, the study of the mineralogical transformations of regional clays with firing and their comparison with mineralogical composition of archaeological ceramics, may help to determine the type of clay deposit used and the firing temperatures range, thus helping in a more precise establishment of geochemical fingerprints characteristic of each production center.

The Algarve basin has a diversity of clay deposits that sometimes are very rich in carbonates, particularly the upper Triassic and Jurassic ones (Trindade, 2007). The upper Triassic to lower Jurassic clays may contain exclusively dolomite or both calcite and dolomite, while the Jurassic clays are generally very rich in calcite. Since these two groups of important clay deposits contain different carbonate minerals, we consider important to determine the modifications clearly induced by the presence of these minerals, when the clays are fired at the same range of temperatures. Hence we studied two naturally occurring clays, with high carbonate contents, one calcite and other dolomite rich, and relatively low silica and aluminum contents.

Several investigators have studied the mineralogical transformations in fired Ca-rich clays in comparison with Ca-poor clays (Peters and Iberg, 1978; Duminuco et al., 1998; Riccardi et al., 1999; Cultrone et al., 2001; Jordán et al., 2001; Traoré et al., 2003). The new phases typically reported are gehlenite, wollastonite and anorthite, formed from initial materials with about 50% SiO₂, 15% Al₂O₃ and 10% CaO. However, studies on extremely carbonate rich clays, like those found in places in Algarve clays, are rare. A precursor composition poor in silica and richer in CaO (and/or MgO) is expected to yield much more complex mineralogy.

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This work aims to contribute to a better understanding of the influence of chemical and mineralogical characteristics of highly carbonate rich clays in the mineralogical transformations during firing.

2. Geological context

Algarve sedimentary basin (Fig. 1), located in South Portugal, is a large E–W trending elongated basin, comprising Triassic to Quaternary sediments, formed as a consequence of rifting initiated in the upper Triassic (Mougenot et al., 1979). From upper Triassic to lower Jurassic (Hettangian) deposition of fluvial or shallow marine sediments, composed by conglomerates and arenites with intercalated clays took place, followed by red pelites with intercalations of thin arenite layers and dolomites with variable spatial distribution. They have a typical red color and evaporitic characteristics as are indicated by the presence of calcium sulfates and, evaporite diapirs with abundant gypsum, often with economic importance (e.g., the Loulé diapir). This unit with pelites, carbonates and evaporites represents a transition facies (pre-rifting phase), whereas the subsequent volcano-sedimentary complex represents a rifting phase, indicating the overture of a new sedimentary basin (Manuppella, 1992).

Basin evolution allowed the development of a marine platform where carbonate sedimentation took place. After Jurassic the deposited sediments are essentially carbonates typical of shallow marine waters (Terrinha, 1998). Subsequently, sedimentation was also essentially marine and characterized by important facies variations, which were triggered by various regression/transgression episodes, yielding both carbonate sediments and detrital deposits (conglomerates, arenites and argillites).

3. Materials and methods

Two carbonate rich clays were collected from the western part of the Algarve basin: a) dolomite rich clay (DC sample) from the *Arenitos de Silves* formation of upper Triassic; and b) calcite rich clay (CC sample) from the *Telheiro* formation of middle Jurassic (Calovian). Both clays were investigated in their natural state and after firing at different temperatures.

3.1. Natural clays

After careful material ground and homogenisation by quartering, a portion was pulverized in an agate mortar for X-ray fluorescence analysis (XRF) of major elements. Powdered samples were mixed with Spectromelt A12 flux in 1:9 ratio, fused in a glassy



Fig. 1. Localization of the studied area, the Algarve Meso-cenozoic basin (South Portugal).

pill and then analysed with a Philips PW 1410/00 spectrometer, using a $\text{CrK}\alpha$ radiation. Because of equipment limitations, Na_2O and K_2O contents were determined by flame photometry, using a Corning 400 spectrometer. Loss of ignition (L.O.I.) was carried out by heating samples at 1000 °C, for 3 h.

Mineralogical composition was determined by X-ray powder diffraction (XRPD), with a PW 3050/6× goniometer, using the $\text{CuK}\alpha$ radiation and 1° divergence slit and operating at 45 kV/40 mA. Bulk mineralogy was determined using random powders and a step size of 0.02° 2 θ in the 4–60° 2 θ range.

For determination of clay mineralogy, 60 g of the clays were treated with a buffer solution at weakly acid pH (pH=5) prepared with acetic acid and sodium acetate in proper amount, in order to eliminate carbonates. After decarbonation samples were washed with distilled water and centrifuged to completely remove free acid. Then samples were dispersed in distilled water to enable sand fraction separation by wet sieving, through a 63 μm sieve. Clay fraction (<2 μm) was obtained from the suspension of the clay/silt fraction by sedimentation according to Stoke's law and then oriented specimens were prepared by pipetting a small amount of the clay–water suspension onto a glass slide and left to dry at room temperature. Diffraction patterns were obtained from oriented mounts (after air-dried, glycerol saturated and heated to 500 °C) in the 2–30° 2 θ range, using a 1/2° divergence slit. Random powder mounts of the clay fraction were also made in order to identify some minor constituents, like hematite in DC.

Identification of crystalline phases by XRPD was carried out using the Joint Committee of Powder Diffraction Standards (JCPDS) data bank.

Semi-quantitative analysis of the bulk and clay mineral assemblage was undertaken measuring the peak areas with intensities correction, using the recommended reflection powers of Schultz (1964), Biscaye (1965), and Martín-Pozas (1968). The proportion of clay minerals was first determined considering the peak area of the most intense reflection of phyllosilicates at $d=4.46$ Å, which gives the total proportion of clay minerals. The percentages of the different clay minerals were then obtained from the peak areas at 10 Å, 7 Å, and 14 Å in the glycerolated X-ray diffraction patterns.

3.2. Fired clays

Powder samples, obtained in an agate mortar, were used to produce cylindrical probes of 4×0.3 cm (diameter×height) by pressing clays (1200 Kg/cm^2) in a Specac hydraulic press. Probes were dried at 110 °C and then fired in an electrical kiln at different temperatures (300, 400, 500, 600, 700, 800, 900, 1000 and 1100 °C), in an oxidizing atmosphere. The heating rate was 5 °C/min with 30 min at maximum temperature. Mineralogical transformations of clays after firing were investigated by XRPD. To enable a more precise comparison of the X-ray patterns between unfired and fired clays, the equipment and analytical conditions were kept identical to the ones employed in the determination of the bulk composition.

After heating at 900 °C several new minerals were formed increasing the complexity of the diffraction pattern. In order to better define the new mineralogical composition it was necessary to amplify both peaks resolution (increasing the integration time up to 15 s) and to enlarge the measuring range (up to 15<2 θ <65). These conditions were used for both clays fired to 1000 °C.

Scanning electron microscopy (SEM) imaging using backscattered electrons and EDS chemical microanalysis was carried out on polished specimens without using any resin. Polishing was first done using a 600 μm grit and then using a rotational lap wheel with (14, 6, 3 and 1) micrometer diamond pulp, for 2 min each. After polishing, the specimen was cleaned by ultrasounds and then air-dried. The polished specimens were coated with carbon. SEM images were obtained by high-resolution scanning electron microscope with X-ray microanalysis, using a JEOL JSM-6301F, Oxford INCA Energy 350 (FESEM/EDS). Secondary electron images were obtained on fresh broken surfaces of the materials.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out simultaneously in powdered samples dried at 110 °C, using a Netzsch Jupiter STA 449 balance. The heating rate was 10 °C/min, up to 1100 °C.

4. Results and discussion

4.1. Mineralogical and chemical characterization of natural clays

Clays consist mainly of clay minerals and carbonates, subordinate quartz, anatase, feldspars and goethite, with the last two being present only in the calcite rich clay (CC) as trace constituents. In the dolomite rich clay (DC) hematite was also detected.

The main difference between the two samples is the composition of the carbonate, calcite in CC and dolomite in DC. Another difference is the clay mineralogy of the two samples, illite is the unique mineral in DC, while CC contain, beside illite as main constituent, kaolinite and smectite.

The chemical composition of the starting clayey material reflects mineralogy and is summarized in Table 1.

Both clays have low SiO_2 and Na_2O , moderate Al_2O_3 and very high CaO and MgO (only in DC) content. The high content of CaO and MgO

Table 1
Chemical analysis of natural clays

Element (% wt)	CC	DC
SiO ₂	25.7	23.8
Al ₂ O ₃	9.39	9.33
TiO ₂	0.49	0.38
Fe ₂ O ₃ total	5.41	3.97
MgO	1.81	11.9
MnO	0.05	0.11
CaO	27.6	17.7
Na ₂ O	0.06	0.23
K ₂ O	2.11	3.93
P ₂ O ₅	0.11	0.11
L.O.I.	26.1	27.8
Total	98.8	99.3

is related to the high abundance of carbonates, justifying the high loss of ignition observed. High K₂O/Na₂O ratios indicate a high illite content and the low SiO₂/Al₂O₃ ratios suggest the predominance of clay minerals over quartz and indicate fine particle size.

4.2. Mineral transformations on fired clays

4.2.1. Thermal behavior of clays

Thermal methods enable to study the different steps of weight loss due to release of OH (dehydroxylation reactions), adsorbed water and CO₂ (decarbonation reactions).

Thermal analysis results are reported in Fig. 2. TG curves of both samples show a total weight loss of about 28% mostly related to the high amount of carbonates. Until 700 °C the loss is gradual and due to release of adsorbed water from clay minerals and goethite dehydroxylation (only in CC), but after 700 °C it diminishes abruptly due to the breakdown of carbonates with high CO₂ releasing as a component of the fluid phase.

DSC curves show that dehydroxylation and decarbonation occurring at lower temperatures are endothermic processes and after about 900 °C appears various exothermic effects, corresponding to crystallization of high temperature phases.

4.2.2. X-ray diffraction

The overall chemical composition of CC and DC is plotted in the systems Al₂O₃–CaO–SiO₂ (ACS) and MgO–CaO–SiO₂ (MCS) (Fig. 3). New minerals that may form in CC should be explained in the system ACS,

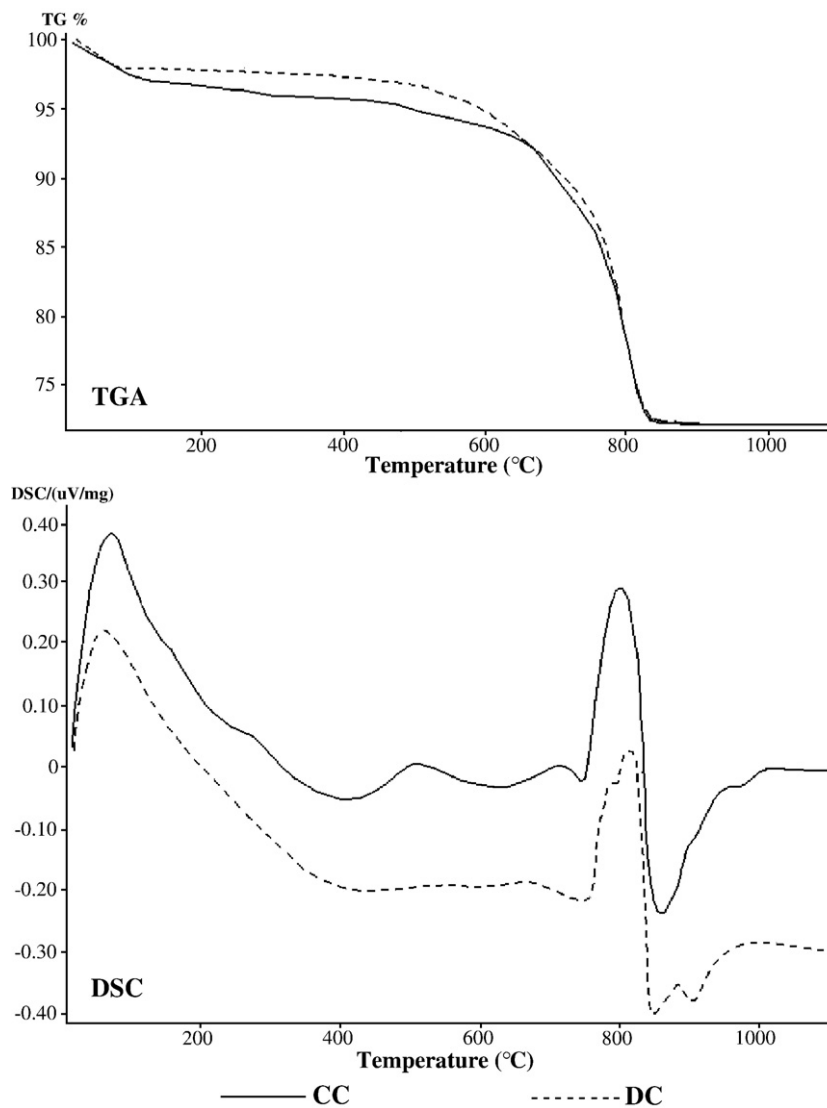


Fig. 2. TGA/DSC curves of CC and DC clays.

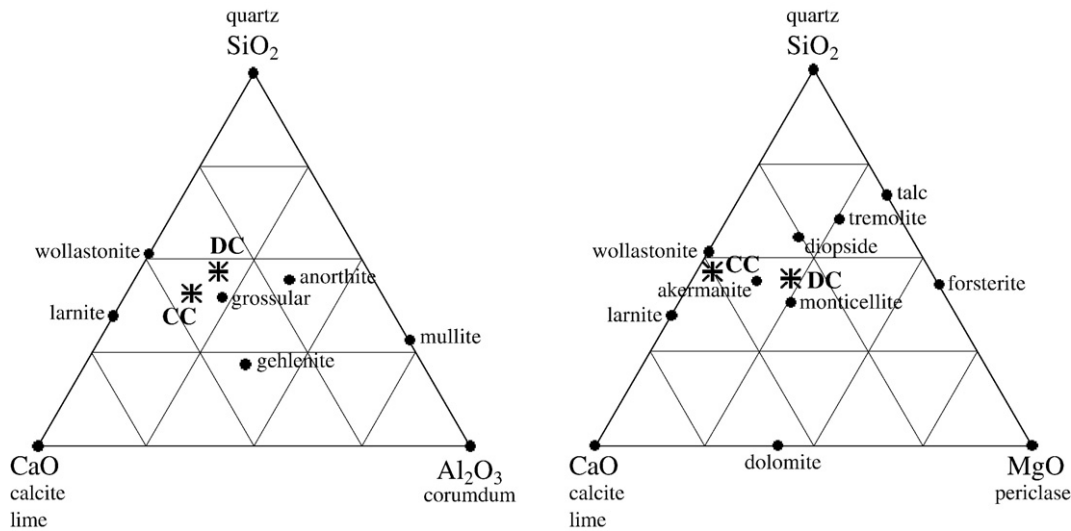


Fig. 3. Comparison of CC and DC clays reported on Al_2O_3 -CaO-SiO₂ (ACS) and MgO-CaO-SiO₂ (MCS) systems. Possible mineral compositions are shown by full dots.

while in DC, due to high MgO content, it is necessary to consider both systems to explain possible formation of high temperature minerals.

4.2.2.1. Calcite rich clay (CC). Fig. 4 shows a schematic representation of the mineralogical transformations (appearing/disappearing of minerals) in CC during heating in the temperature interval studied. The first transformation during firing is the disappearance of goethite at 300 °C (lower heating temperature). Goethite becomes unstable at low temperatures (230–280 °C, according to Brindley and Brown, 1980) and decomposes to form hematite according to the reaction $2FeOOH \rightarrow Fe_2O_3 + H_2O$. Although hematite could be identified in the XRPD pattern at 500 °C, well-crystallized hematite is a significant component only after heating at 900 °C.

Kaolinite decomposes to amorphous metakaolinite at 500 °C by removal of the hydroxyl groups of the silicate lattice (Chen et al., 2000; Toledo et al., 2004), according to the reaction $Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 2H_2O$. The diffraction maximum at 10 Å corresponds to dehydroxylated mica like phase (illite/muscovite). The peak intensity of this phase was reduced drastically with increase firing temperature from 700 to 800 °C, disappearing at 900 °C. Anatase disappeared after 700 °C and feldspars were only identified in the natural clay as residual compounds.

At 700 °C CaCO₃ begins to decompose yielding CaO (lime) with release of CO₂ from the fired body. This process is very effective mostly at about 800 °C and the calcite remaining up to the maximum firing temperature almost disappeared.

Quartz decomposes gradually from 800 to 1100 °C, diminishing drastically at 1100 °C.

The decomposed and disappearing phases all contribute to the formation of a vitreous phase, up to 800 °C, and besides hematite formation no new crystalline phases were formed. The main difference between the samples fired to 500 and 800 °C is the complete disappearance of some phases and the diminishing of the remaining, as suggested by the decrease in the intensity of the diffraction maximum or rising of the background noise, suggesting the presence of an amorphous phase. At this step the clay body would essentially be an amorphous material with some residual grains of calcite and quartz, and neofomed hematite. This is in accordance with Tite and Maniatis (1975) who suggested that in carbonate rich clays melting begins at lower temperatures (approximately at 800 °C) than in carbonate poor clays, because Ca and Mg may act as fluxes (Segnit and Anderson, 1972). That is why ancient potters might have explored this kind of clays to make their pots using less energy.

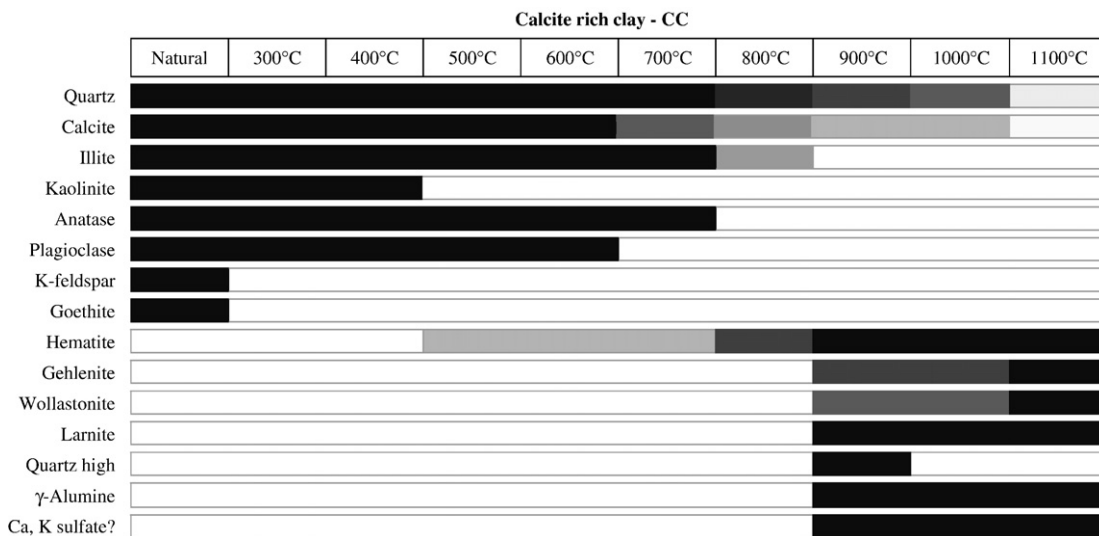


Fig. 4. Diagram representing the mineralogical transformations in calcite rich clay (CC) induced by heating in the 300–1100 °C temperatures range. Dark/light bars indicate approximately the abundance of minerals.

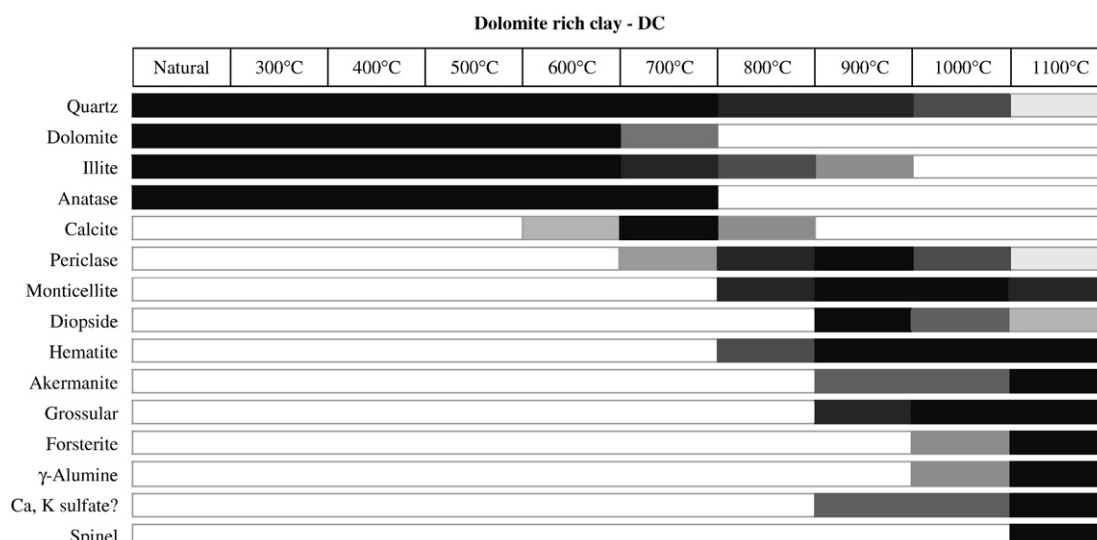
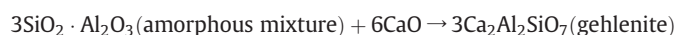


Fig. 5. Diagram representing the mineralogical transformations in dolomite rich clay (DC) induced by heating in the 300–1100 °C temperatures range. Dark/light bars indicate approximately the abundance of minerals.

At 900 °C new crystalline phases nucleate and grow from the vitrified material yielding the association gehlenite+wollastonite+larnite+γ-alumina, which is maintained between 900 and 1100 °C.

After 700 °C the free CaO reacts with free silica and alumina derived from decomposition of illite, the most abundant clay mineral, forming gehlenite according to the following reaction (Peters and Iberg, 1978):



Wollastonite (CaSiO₃) is another abundant phase, formed by the following reaction:



In CC both gehlenite and wollastonite nucleate between 800 and 900 °C, becoming more important at higher temperatures (1100 °C).

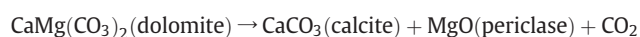
Usually, wollastonite and gehlenite are considered intermediate compounds (Traoré et al., 2000; Riccardi et al., 1999), which became unstable in presence of SiO₂ and react to give anorthite (CaAl₂Si₂O₈). However in this study, anorthite was not detected; instead the association gehlenite+wollastonite remained stable at least to 1100 °C. This is due to the low SiO₂ content of CC (Table 1) (Riccardi et al., 1999).

Larnite (Ca₂SiO₄) was also formed as a minor phase from reaction between lime and quartz: 2CaO+amorphous SiO₂→Ca₂SiO₄.

A transitional aluminum phase (probably γ-alumina) was formed at 900–1100 °C, due to release of Al from clay minerals (Brindley and Brown, 1980).

The formation of mullite as expected from the system ACS (Fig. 3) as a consequence of decomposition of clay minerals (Aras, 2004), was not observed in the present study, probably because the products of clay minerals decomposition were all combined with the excess of CaO, yielding gehlenite instead of mullite. Finally an additional phase with diffraction maximum at *d*=3.13 Å was observed, but the identification by XRPD was difficult, and this phase will be discussed later.

4.2.2.2. Dolomite rich clay (DC). Sample DC remained unchanged with heating until about 600 °C, when dolomite becomes unstable (Fig. 5):

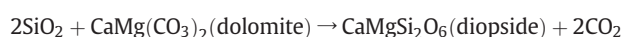
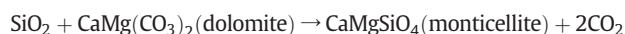


The calcite formed is a transitional phase that begins to crystallize at 600 °C, acquires maximum abundance at 700 °C and after 800 °C it disappears.

Periclase, the other product of dolomite decarbonation, occurs between 700 °C and 1000 °C, its abundance being maximum at 900 °C.

Reaction of calcite (or lime), periclase, quartz and in some cases aluminum silicates (clay minerals) yields several calcium and/or magnesium metastable phases: diopside (CaMgSi₂O₆), monticellite (CaMgSiO₄), a member of the solid solution series gehlenite–akermanite (Ca₂Al₂SiO₇–Ca₂MgSi₂O₇), grossular (Ca₃Al₂Si₃O₁₂), forsterite (Mg₂SiO₄), spinel (MgAl₂O₄), γ-alumina (γ-Al₂O₃) and hematite, probably due to the presence of moderate iron level in the starting clay.

Unlike in CC, in the DC sample the thermal decomposition of the original phases is progressively accompanied by the concomitant blastesis of new phases. In fact, at 800 °C the XRPD pattern evidences the occurrence only of residual minerals like quartz and phyllosilicates, and also newly crystallized minerals such as calcite, periclase, monticellite and hematite. The formation of calcium–magnesium silicates like monticellite and diopside, started at 800 and 900 °C respectively, probably at the dolomite–quartz interfaces according to the reactions:



Because calcite is consumed more quickly than periclase, the excess MgO leads to the transformation of calcium–magnesium silicates into magnesium silicates, like forsterite, which began to form at 1000 °C and

Table 2
List of the neoformed minerals in CC and DC samples, due to firing up to 1100 °C

Neoformed minerals	Chemical formula	Main reflection <i>d</i> (Å)	CC	DC
Wollastonite	CaSiO ₃	2.98	X	
Larnite	Ca ₂ SiO ₄	2.75	X	
Gehlenite	Ca ₂ Al ₂ SiO ₇	2.85	X	
Grossular	Ca ₃ Al ₂ Si ₃ O ₁₂	2.62		X
Akermanite	Ca ₂ MgSi ₂ O ₇	2.87		X
Diopside	CaMgSi ₂ O ₆	2.99		X
Monticellite	CaMgSiO ₄	2.66		X
Forsterite	Mg ₂ SiO ₄	2.46		X
Spinel	MgAl ₂ O ₄	2.48 (1.58)		X
Periclase	MgO	2.11		X
Hematite	Fe ₂ O ₃	2.70	X	X
γ-Alumine	γ-Al ₂ O ₃	1.98	X	X
Calcite	CaCO ₃	3.04		X
Quartz (high)	SiO ₂	3.40	X	
Ca–K sulfate	?	3.13	X	X

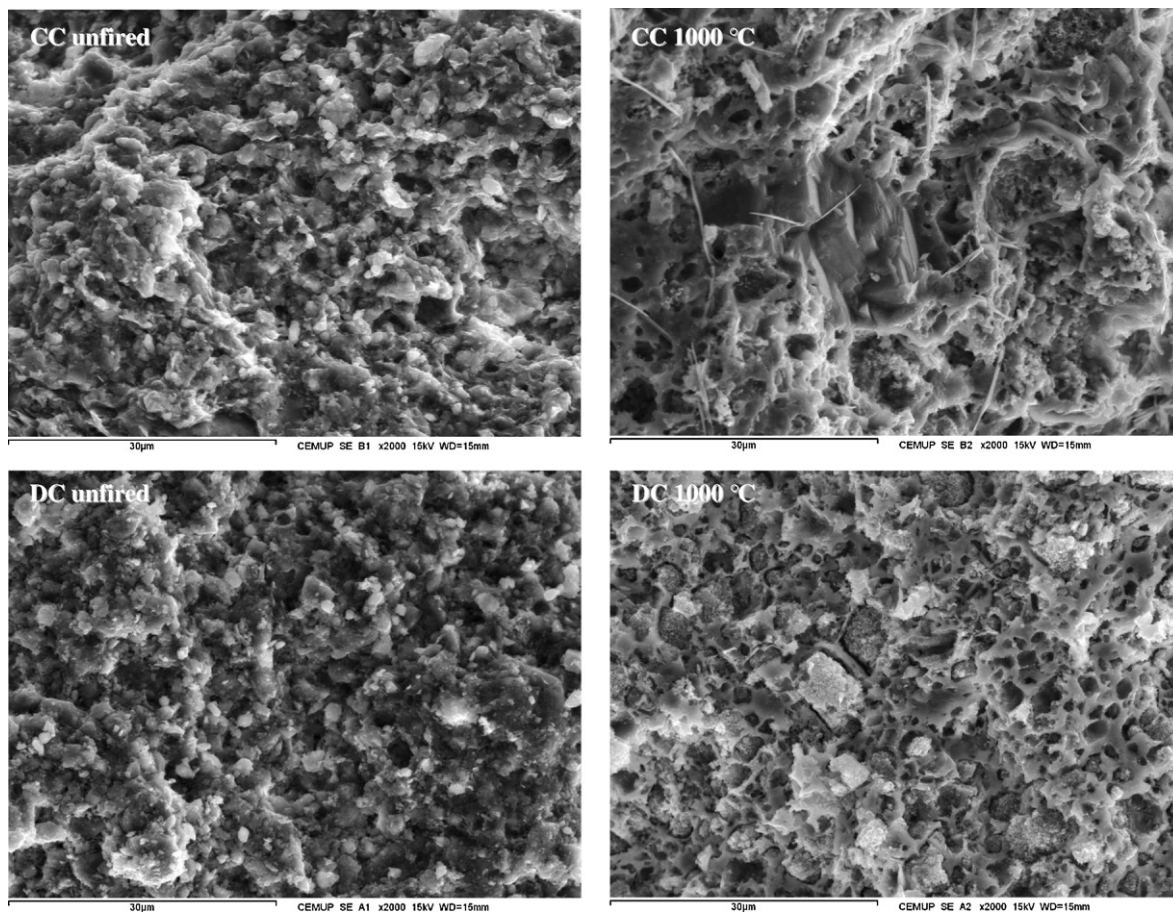
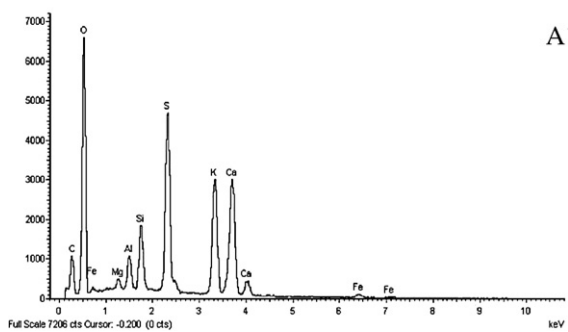
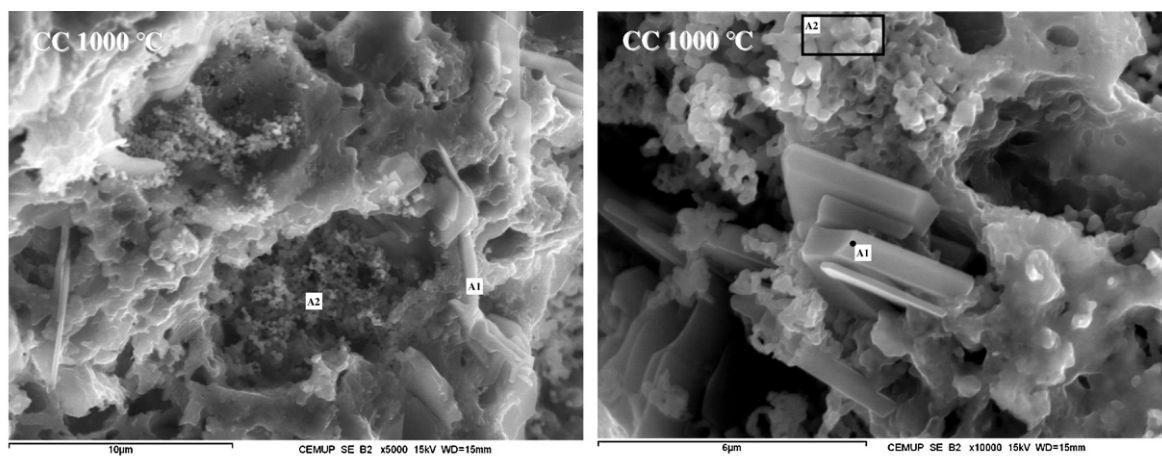
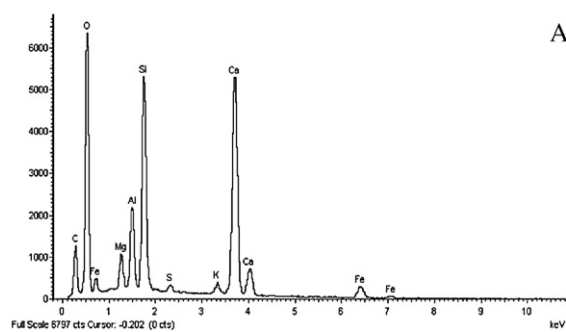


Fig. 6. SEM secondary electron photomicrographs comparing CC and DC clays unfired and fired to 1100 °C.



A1



A2

Fig. 7. SE photomicrographs of CC fired to 1000 °C and two chemical microanalyses by EDS: A1—a crystal of potassium–calcium sulfate; A2—small granular crystals of probably a mixture of calcium silicate (wollastonite) and calcium–aluminum silicate (gehlenite).

became more abundant at 1100 °C. Forsterite probably formed at the expense of diopside, which diminished at 1000 °C and almost disappeared at 1100 °C:



Aluminum minerals, such as spinel and a transitional aluminum phase (probably $\gamma\text{-Al}_2\text{O}_3$), tend to form also at high temperatures, mainly at 1100 °C. The neoformed phases in both CC and DC are shown in Table 2.

Mineralogical changes are interpreted considering local disequilibrium in a system that resembles a small-scale high-*T* metamorphic process at atmospheric pressure, like contact aureoles in pyrometamorphism (Grapes, 2006). Short periods of heating like those made in a laboratory kiln, induces significant temperature overstepping of equilibrium conditions and consequent rapid mineral reaction rates, favoring metastable phases formation instead of stable ones (Grapes, 2006). High-temperature, low-pressure conditions characterize the sanidine facies of contact metamorphism (Miyashiro, 1994; Grapes, 2006) and, in fact, almost all the new minerals crystallized are typical of these metamorphic facies, such as akermanite, gehlenite, forsterite, monticellite and larnite. The presence of such rare minerals indicates advanced decarbonation reactions, whose equilibrium temperatures are considerably higher than those for the reactions to form wollastonite, periclase, diopside and grossular (Miyashiro, 1994).

4.2.3. Scanning electron microscopy observations

SEM photomicrographs exhibit the microstructure differences between unfired and fired to 1000 °C calcite and dolomite rich clays

(Fig. 6). These differences result from transformations in the clay matrix, in mineral phases and at boundaries between clay matrix and mineral phases (Riccardi et al., 1999). Crystalline phases are embedded in a vitreous phase and secondary porosity is evident. In DC exists abundant glass and high secondary porosity, with pores free or filled with minerals. In CC glass is less abundant, its organized structure not so evident and some elongated crystals occur besides the small granular phases. Fluids containing Mg may have greater viscosity and cannot penetrate easily in the pores of the fired body, thereby decreasing the reaction rates between fluid and residual minerals and increasing vitrification range. In the present case the possible role of Mg can be attributed to the presence of dolomite in DC.

Dehydration and decarbonation reactions are important factors controlling reaction kinetics and occurrence of new phases, because they release H₂O and CO₂ at different temperatures (Duminuco et al., 1998). Decomposition of carbonates at about 800 °C, releases 18–20 wt.% of CO₂ in the fluid phase (Fig. 2) and generates secondary porosity during firing.

Formation of pores totally or partially filled with aggregates of neoformed phases observed mainly in DC, has already been described in literature (Dondi et al., 1995) and can be related to transient fluid pore pressure, produced by the fluid phase in a system not completely opened to fluids.

The nucleation mechanism of new phases involves the consumption of carbonates, quartz and clay minerals. CC displays recrystallization of the aluminum-silicate vitreous phase into small granular crystals (Fig. 7), probably a mixture of calcium silicate (wollastonite) and calcium–aluminum silicate (gehlenite). The presence of MgO

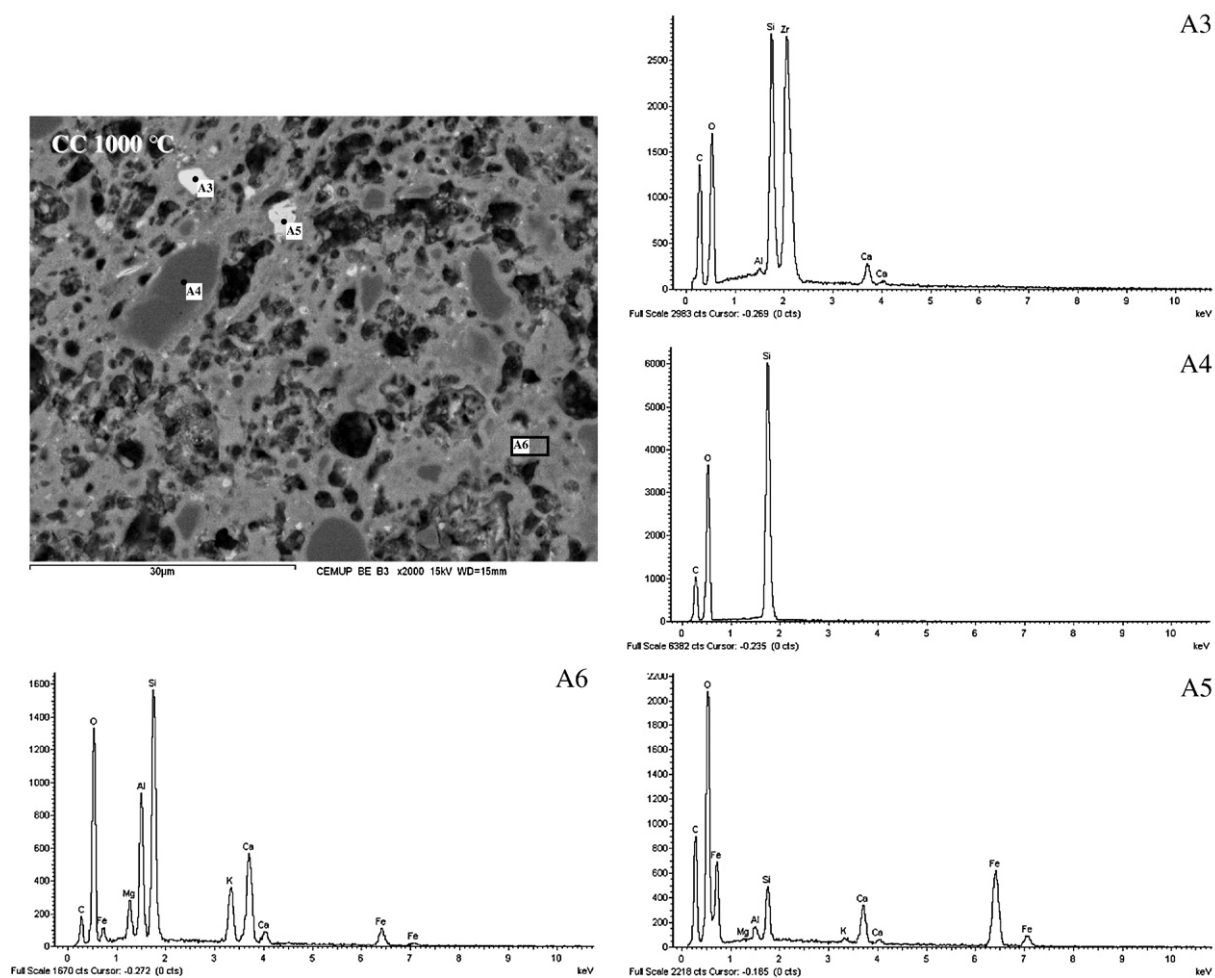


Fig. 8. BE image of polished CC fired to 1000 °C and four chemical microanalyses by EDS: A3—zircon; A4—quartz; A5—hematite and A6—vitreous phase.

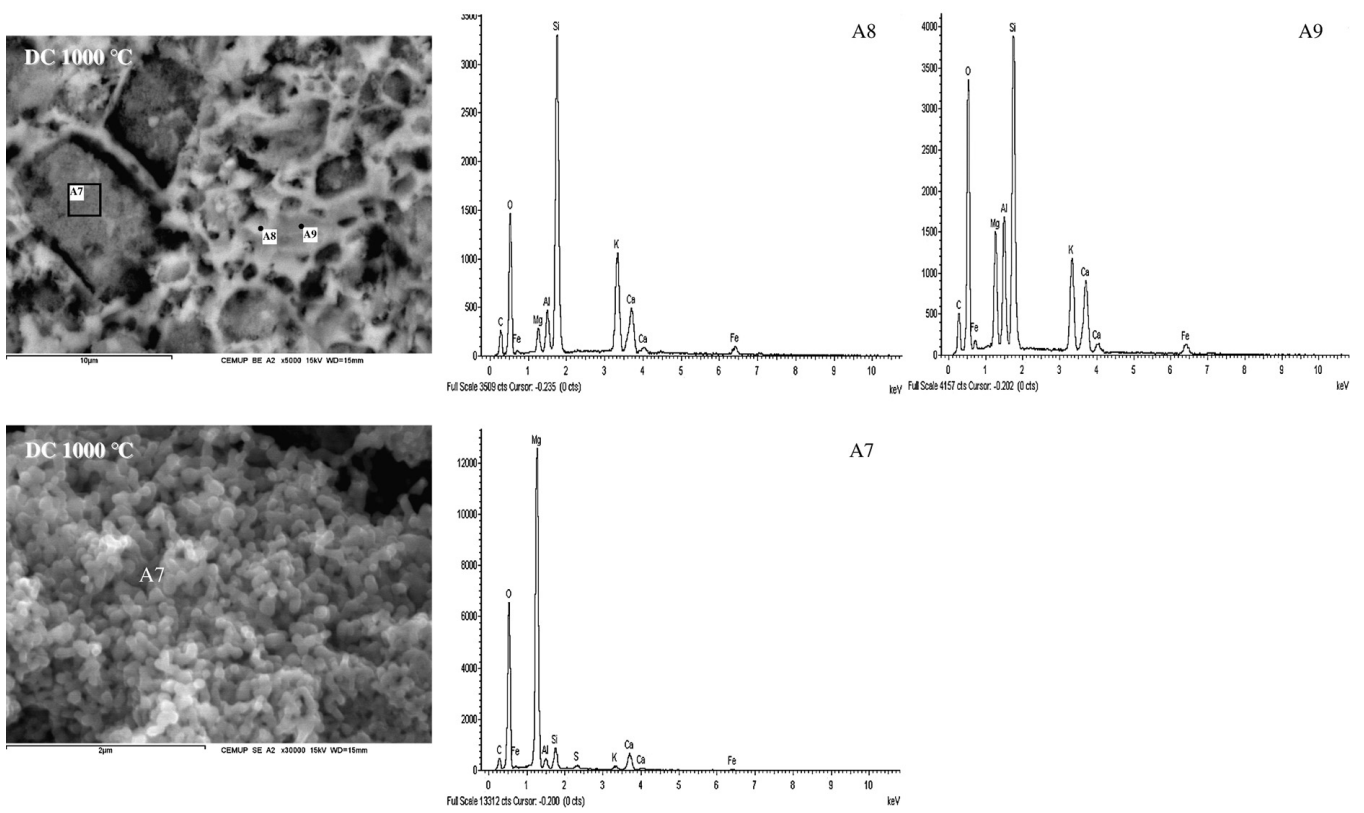


Fig. 9. BE image of DC fired to 1000 °C and a high amplification SE image of the mineral phase identified as A7 in the upper image. Three chemical microanalyses are also shown representing the composition of: A7—periclase; A8/A9—glassy phase.

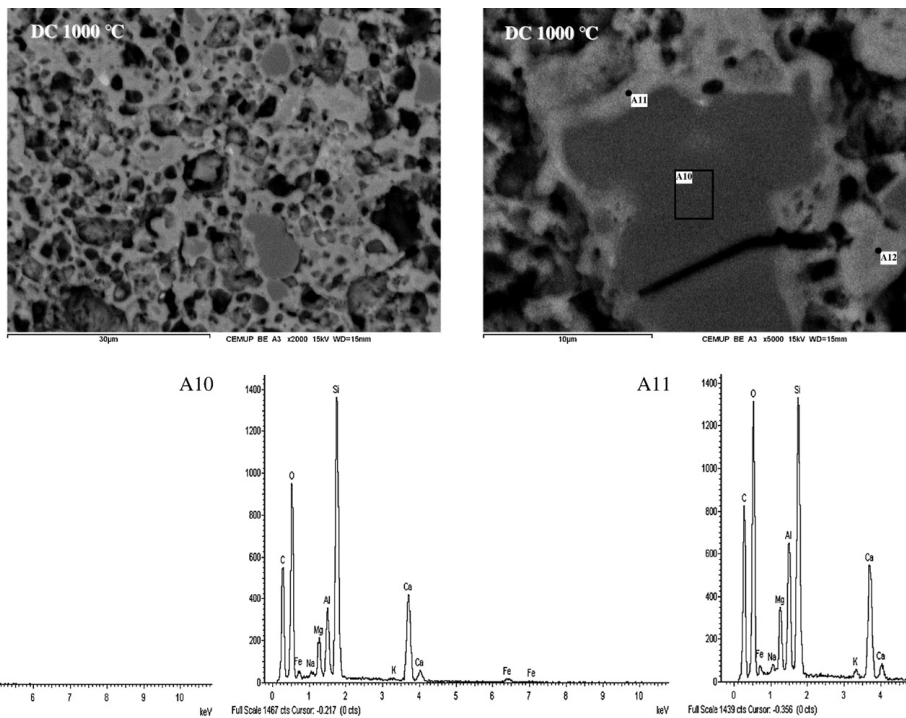


Fig. 10. BE images of polished DC fired to 1000 °C. Also shown are three chemical microanalyses, representing the composition of: A10—quartz; A11/A12—compositional variability of the vitreous phase around a quartz crystal.

indicates that not pure end-member gehlenite, but an intermediate member of the solid solution between Al-rich (gehlenite) and Mg-rich (akermanite) with higher proportion of the gehlenite component.

Sintering yielded a silicate amorphous phase rich in Al, Ca, K, Mg and Fe (analysis A6 in Fig. 8). Secondary hematite (analysis A5) was identified in backscattered electron image. Although glassy phase formed some residual minerals remained with a thin coronitic layer, showing local phase transformations at grain boundaries. Residual minerals observed include zircon and quartz (analyses A3 and A4 respectively, in Fig. 8).

SEM observations on calcite-rich clay fired to 1000 °C revealed the existence of a euhedral mineral phase essentially made of O, S, K and Ca, i.e. probably a potassium and calcium sulfate (Fig. 7). This phase corresponds to the mineral compound with a diffraction maximum at $d=3.13$ Å, which was not possible to identify solely by XRPD.

Formation of sulfate phases by heating has been observed in Portland cement clinkers that generally result from high temperature firing of a mixture of limestone, shale, iron ore and gypsum (Arceo and Glasser, 1990; Taylor, 1999; Stutzman, 2004). As reported in these works, alkalis combine preferentially with sulfate and the remaining sulfate is balanced by calcium. At ambient temperatures, where equilibrium conditions are attained, the most probable sulfate assemblages are the stable phases formed in the system K_2SO_4 (arcanite)– $CaSO_4$ (anhydrite)– Na_2SO_4 (thenardite). At high temperatures disequilibrium occurs and substantial regions of solid solutions are possible. For example, K_2SO_4 can accommodate Ca^{2+} and CO_3^{2-} , yielding a potassium and calcium-rich sulfate (Arceo and Glasser, 1990).

In both samples decomposition of illite may provide enough potassium to the new mineral phase. From comparison of the neoformed assemblage in samples heated above 900 °C with that formed in high- T metamorphism, it would be expected the formation of a potassium feldspar such as sanidine. However, since the raw materials were very poor in SiO_2 and relatively poor in Al_2O_3 , Al-silicate phases like anorthite, mullite or potassium feldspar were not formed and the remaining potassium reacted with sulfur to form sulfates. The presence of sulfates is not usually reported in works about fired clays.

XRPD did not reveal the presence of sulfates such as gypsum or anhydrite in the raw materials, but as was explained previously, the conditions of clays formation were evaporitic, mostly in the case of DC. Although not determined by chemical analysis, sulfur was a probable constituent of natural clay samples in a soluble form, which at high temperatures (above 900 °C) reacted with the potassium and calcium from the melt and crystallized as a sulfate mineral.

The general micro structure of DC is shown in Fig. 6 and as it has already been observed the pores are sometimes filled with extremely fine crystals with size about 0.2 μm and composition corresponding to periclase (MgO) (analysis A7 in Fig. 9). Other new phases formed are difficult to identify because of their small crystal size. The brightness differences in the BSE image suggest variability in the composition of the amorphous phase (Fig. 9) and this is confirmed by the chemical composition of different regions (A8 and A9 points).

The BSE image (Fig. 10) of DC polished specimen is similar to that of CC. It consists essentially of gray glassy and new crystalline silicate phases, darker grains of quartz and high porosity. Part of this porosity resulted from the polishing process, which removed periclase aggregates. Fig. 10 shows progressive transformations occurring in quartz borders due to reaction with the evolving fluid phase, becoming progressively enriched in Al, Ca, Mg and C (analyses A11 and A12).

5. Conclusions

The presence of abundant carbonate in clays promotes high porosity and lowers the starting temperature of vitrification (between 700 and 800 °C) when compared to that reported in literature relatively to Ca-poor clays. On the other hand, the extend of

vitrification is limited at higher temperature due to intense crystallization of high temperature Ca and/or Mg silicates and other minerals, after decomposition of phyllosilicates.

The main resemblances/differences in mineralogical transformations with firing between studied samples are: a) dolomite in DC decomposed at lower temperatures than calcite in CC; in DC calcite is an intermediate phase occurring between 600 and 800 °C; b) in both samples quartz starts to react slowly after 700 °C, being a residual phase at 1100 °C; c) in CC, with the exception of hematite, neoformed minerals appeared at 900 °C and most of them were maintained until 1100 °C; whereas in DC some of the new phases appeared at 700–900 °C but tended to disappear at higher temperature, accompanied by crystallization of other phases; d) a transitional aluminum phase (γ -alumina), hematite and a calcium–potassium sulfate phase appeared in both fired clays; e) a mineral of melilite group formed, being richer in gehlenite component (with Al) in CC and enriched in akermanite component (with Mg) in DC; f) other neoformed minerals have distinct composition in the two samples: in CC calcium silicates like gehlenite, wollastonite and larnite formed mainly by reaction of calcite with clay minerals; in DC periclase formed due to decomposition of dolomite and other Mg-rich minerals like diopside, monticellite, akermanite, forsterite, grossular, and spinel resulted from reaction of CaO and/or MgO with clay minerals and silica. These characteristics show rapid heating of clays with a firing rate faster than nucleation and growth rate, which induced the formation of metastable phases. Comparison between phases developed in both clays highlights a wider mineralogical variability in the Mg-rich clay (DC), which is caused by the richer precursor composition where different proportions of CaO, MgO, SiO_2 and Al_2O_3 play a role, whereas in CC neoformed phases are explained in the simpler system CaO – SiO_2 – Al_2O_3 .

This study of the mineralogical transformations induced by firing of potential ceramic raw materials available in the Algarve region may contribute to a more precise correlation between composition of ancient ceramic pastes and potential raw materials in further ancient pottery studies, namely its provenance.

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