

Comparison of calcite and dolomite rich clays, used as raw materials for ancient ceramic production in Algarve region, Portugal

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Introduction

Roman archaeological sites in the Algarve region have evidences of ceramic production in local kilns, making the study of regional clay deposits an interesting subject in provenance studies, in order to better establish the mineralogical fingerprinting of raw materials used in those archaeological ceramics manufacture.

Because many clay deposits from Algarve are rich in carbonates of various compositions, we think its important a better comprehension about the mineralogical transformations clearly induced by the presence of carbonate phases, when the clays are fired at the same temperature.

The objective of this study is to compare mineralogical transformations of two clayey materials highly enriched in carbonates and relatively poor in silica:

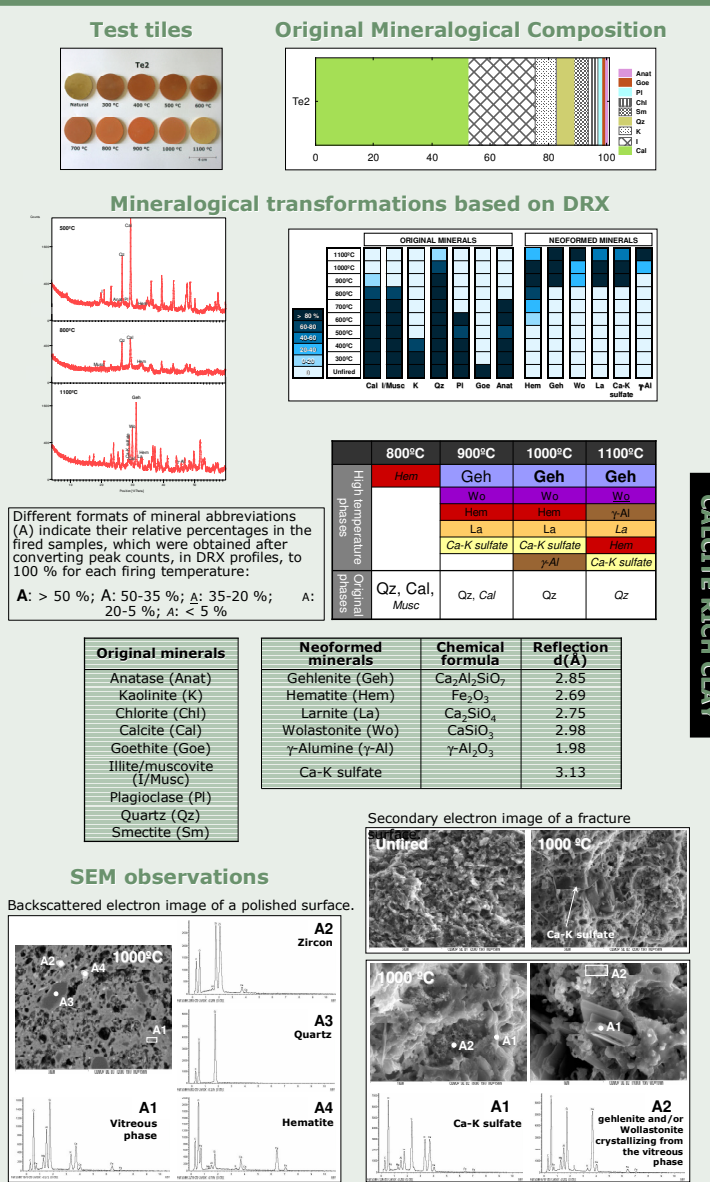
CALCITE RICH CLAY / DOLOMITE RICH CLAY

Methods

Circular test tiles (4 cm diameter / 0.3 cm height) formed by pressed powder clayey materials were dried in an electric stove at 110°C and then fired in an electrical kiln at 9 different temperatures, from 300 °C to 1100 °C at steps of 100 °C, in an oxidizing atmosphere. The firing cycle was 5 °C/minute and the residence time at maximum temperature was 30 minutes.

Mineralogical transformations caused by firing were mainly investigated with X-ray diffraction (XRD) and also by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) associated to enable X-ray microanalysis.

XRD measurements were performed using a X'Pert Pro diffractometer, working with CuK α radiation and with 45 kV and 40 mA operation conditions. Scans were run between 4 $^\circ$ and 60 $^\circ$ 2 θ in random preparations.



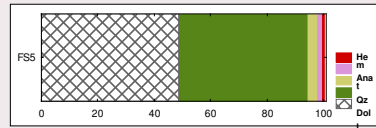
CALCITE RICH CLAY

- Chemical composition of fired samples is expressed in the Al_2O_3 -CaO-SiO₂ system, originating just a few new crystallized minerals.
- Hematite is the first mineral formed due to goethite decomposition at firing temperatures below 300 °C, but only after 800 °C it becomes well-crystallized.
- **New phases**, besides hematite, **appeared at 900 °C**.
- **Gehlenite** (Mellilite) is the **main component** in fired samples from 900 °C to 1100 °C.
- **Wollastonite and larnite** are two minerals **formed due to the presence of calcite** in the original clayey material, appearing from 900 °C to 1100 °C. **Larnite is indicative of high calcite percentages**. Wollastonite resulted from the reaction between quartz and CaO (generated from calcite decomposition), and gehlenite was formed by the reaction of CaO and an aluminous-rich amorphous substance, coming from clay minerals decomposition.
- **A transitional aluminum phase (probably γ -alumine)** was formed between 900-1100 °C as the result of Al liberation from clay minerals. At the same temperature range occurred the formation of a **Ca-K sulfate**, which was identified on SEM images and justifies the 3.13 Å peak observed in DRX curves.
- **The abundance in calcite conditioned the formation of the vitreous phase**. This started before 800 °C, as showed by the decrease of peaks intensity in DRX curve at 800 °C, but at 1100 °C the sample is well crystallized with new minerals (quartz is the only original phase) and the vitreous phase almost disappeared.

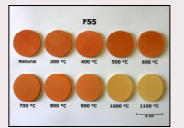
Conclusion

Since the firing process was conducted in a laboratory kiln by high heating rates, it was created an environment dominated by metastable melting and rapid mineral reaction rates driven by significant temperature overstepping of equilibrium conditions. This work revealed that the large variety of high temperature minerals formed, generally metastable, was essentially dependent on mineralogical/chemical composition, mainly on CaO and MgO abundances. In the calcite rich clay (high CaCO₃ %) it were crystallized various calcium silicate minerals, forming the association: gehlenite + wollastonite + larnite; and in the dolomite rich clay (high MgO %) appeared various calcium and/or magnesium silicates (akermanite, diopside, monticellite) and oxide minerals, such as, periclase and spinel. The presence of these minerals indicates advanced decarbonation reactions. This work enhances the importance of consider mineralogical phases transformations with temperature in ancient ceramic raw materials rich in calcareous clays, in order to better establish provenances.

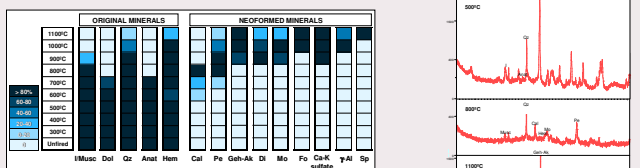
Original Mineralogical Composition



Test tiles



Mineralogical transformations based on DRX



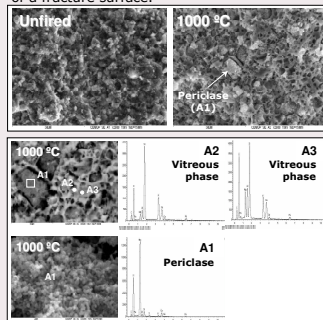
Temperature (°C)	High temperature phases	Original phases
600	Cal	Dol, Oz, Musc, Anat, Hem
700	Cal	Dol, Oz, Musc, Anat, Hem
800	Pe, Cal	Oz, Hem, Musc
900	Geh-Ak, Pe, Di, Ca-K sulfate, Mo	Oz, Hem, Musc
1000	Geh-Ak, Fo, Mo, Ca-K sulfate, Di, γ -Al	Oz, Hem
1100	Geh-Ak, Fo, Ca-K sulfate, Sp, Mo, γ -Al, Pe	Oz, Hem

Original minerals
Anatase (Anat)
Dolomite (Dol)
Illite/Muscovite (I/Musc)
Hematite (Hem)
Quartz (Qz)

Neoformed minerals
Calcite (Cal)
Diopside (Di)
Gehlenite-Akermanite (Geh-Ak)
Forsterite (Fo)
Monticellite (Mo)
Periclase (Pe)
Spinel (Sp)
γ -Alumine (γ -Al)
Ca-K sulfate

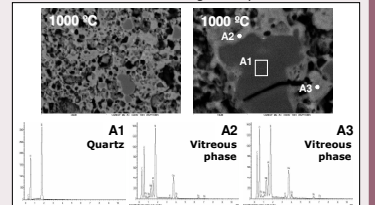
Chemical formula	Reflection d(Å)
CaCO ₃	3.04
CaMgSi ₂ O ₆	2.99
Ca ₂ Al ₂ SiO ₇	2.85-2.87
Ca ₂ MgSi ₂ O ₇	2.85-2.87
Mg ₂ SiO ₄	2.46
CaMgSiO ₄	2.66
MgO	2.11
MgAl ₂ O ₄	2.42
γ -Al ₂ O ₃	1.98
Ca-K sulfate	3.13

Secondary electron image of a fracture surface.



SEM observations

Backscattered electron image of a polished surface.



DOLOMITE RICH CLAY

- Chemical composition of fired samples is expressed in the Al_2O_3 -CaO-SiO₂-MgO system, justifying the formation of more diverse new minerals.
- Hematite was an initial product that persists until 1100 °C.
- **The majority of the neoformed phases crystallized at 900 °C**. Although, **calcite and periclase**, formed due to dolomite decomposition, **are intermediate phases** which appeared earlier (calcite: 600-800 °C; periclase: 700-1100 °C).
- **Mellilite** is the **main component** in fired samples from 900 °C to 1100 °C. Is not a pure gehlenite but an intermediate member of the **solid solution between gehlenite (Ca+Al) and akermanite (Ca+Mg)**.
- **The high dolomite content** of the original clayey material was responsible for the formation of several magnesium silicates, namely **monticellite, diopside and forsterite**. The first two may crystallize in the dolomite/quartz interface or from the vitreous phase. Both tended to diminish in percentage at the highest temperatures analysed, while forsterite only appeared at 1000 °C and increased with temperature. Forsterite probably crystallized directly from the reaction between quartz and periclase, but at some extend may result from reaction of monticellite or diopside with periclase.
- It was also formed **Ca-K sulfate** and a **γ -alumine phase**. At high temperatures (1100 °C) it was crystallized a **magnesium rich spinel**.
- **The abundance in dolomite conditioned the formation of the vitreous phase** in the some way as did calcite.