COMPARISON OF MINERALOGICAL TRANSFORMATIONS BY FIRING CALCITE AND DOLOMITE RICH CLAYS, USED AS RAW MATERIALS FOR ANCIENT CERAMIC PRODUCTION IN ALGARVE REGION, PORTUGAL

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In the Algarve basin (south Portugal) there are various roman archaeological sites where is evident the ceramic production in local kilns, which makes very interesting the study of regional clay deposits in order to establish the raw materials provenance.

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. To this propose we choose two naturally occurring clays extremely enriched in carbonates (calcite and dolomite rich clays) and relatively poor in silica. These clays were characterized in the mineralogical and chemically point of view, with X-ray diffraction, X-ray fluorescence, and instrumental neutron activation analysis.

Circular probes (4 cm diameter / 0.3 cm height) formed by pressed powder clay samples, were fired in an electrical kiln at 9 different temperatures (300, 400, 500, 600, 700, 800, 900, 1000 and 1100ºC), in an oxidizing atmosphere. The firing cycle was 5ºC/minute and the residence time at maximum temperature was 30 minutes.

The mineralogical transformations caused by progressive heating were investigated with X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) associated, permitting X-ray microanalysis.

Since the sintering process occurs by relatively short periods of heating, it was created an environment dominated by metastable melting and rapid

mineral reaction rates driven by significant temperature overstepping of equilibrium conditions. This high temperature experiments at atmospheric pressure result in the formation of a large variety of high temperature minerals, many of which are metastable and only found in these conditions. New phases formation was essentially dependent on chemical composition, mainly CaO and MgO abundances. In the calcite rich clay (high $CaCO_3$%) it was formed the next association of calcium silicate minerals: gehlenite + wollastonite + larnite; and in the dolomite rich clay (high MgO%) appeared various calcium-magnesium silicates (akermanite + diopside + monticellite) and other magnesium silicate and oxide minerals, such as forsterite, periclase and spinel.

The XRD patterns and microanalysis able the detection of a potassium-calcium sulfate phase, developed in both samples, at temperatures between 900ºC and 1100ºC.