GLAZED POTTERY OF THESSALONIKI: AN ARCHAEOMETRICAL APPROACH

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ΠΕΡΙΛΗΨΗ: Μελετάται το κεραμικό υλικό είκοσι οστράκων εφυαλωμένης κεραμικής του 13ου-14ου αιώνα, που βρέθηκαν σε ανασκαφές στη Θεσσαλονίκη και πιστεύεται ότι κατασκευάστηκαν σε τοπικά εργαστήρια. Η μεθοδολογία περιλαμβάνει εξέταση με οπτικό και ηλεκτρονικό μικροσκόπιο σαρώσεως, ανάλυση με φασματοσκοπία διασποράς ενέργειας και περίθλαση ακτίνων X των ίδιων των δειγμάτων, καθώς και ξαναψημένων σε δεδομένες θερμοκρασίες δειγμάτων. Διαπιστώνεται η προσεκτική επιλογή των πρώτων υλών της κεραμικής τεχνολογίας και των αναλογιών τους, δηλαδή ασβεστούχων (CaO>5%) και εύτηκτων πηλών με καλό και λεπτό διαμερισμό του ασβεστολιθικού υλικού. Οι συνθήκες ψησίματος είναι οξειδωτική ατμόσφαιρα και θερμοκρασία στην ευρεία περιοχή θερμοκρασιών 850-1050°C.

The ceramic body of twenty glazed pottery sherds (named TT1 to TT20) of the 13th-14th centuries era found in excavations in Thessaloniki, Greece are studied by means of optical (OM) and scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and X-ray diffraction (XRD) analyses. The corresponding articles are believed to be manufactured in workshops of Thessaloniki (Papanikola-Bakirtzis 1999). The aim of the present work is to assess the technology used by the potters of these workshops and especially the kind of the clay and the conditions of firing (temperature and atmosphere).

The colour of the fabric of the sherds is reddish brown (mostly 2.5 YR 5/6 according to Munsell Soil Colour Charts) indicating an oxidising kiln atmosphere. Two sherds (nos. 13, 16) very hard and too dark grey were considered as overfired.

The microscopic vitrification morphology and the pore structure of the ceramic body combined with the type of clay used and the assumption of the atmosphere of the firing can yield the firing temperature range employed (Maniatis 1981). To test the development of the vitrification with temperature, pieces of all sherds were refired at known temperatures and re-examined in the SEM.

Fresh cut out of the sherds surfaces were coated with a thin layer of carbon in an evaporator to make the surfaces conducting. The samples were then examined in a JEOL 840 SEM with a typical X2000 magnification, adequate to examine the morphology of ceramic body, slip and glaze. The extent of vitrification and consequently the properties of the pottery depend critically on both the particle size and the distribution of calcite in the calcareous clays used (Maniatis 1981).

Quantitative analyses of the specimens for the elements Na, Mg, Al, Si, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn and Pb were taken using the electron dispersive OXFORD ISIS 300 spectrometer of the SEM. The electron beam covered a $220\times170\ \mu m^2$ broad regular area without any large aplastic inclusions. The elements were expressed as oxides, the analyses totals were high ranging from 99.33% to 102.50% and they were normalized to 100% for comparison purposes (Freestone 1982). On the basis of the quantitative analyses it is concluded that in all pottery products the kind of the clay used was calcareous (CaO content more than 5.1%, CaO+MgO content more than 7.1%) and low refractory (fluxes CaO + MgO + FeO + Na_2O + K_2O + TiO_2 more than 23.5%). The results of the quantitative analyses are plotted in ternary diagrams, one for silica (SiO_2), alumina (Al_2O_3) and CaO + MgO and a second for silica (Si_2O), alumina (Al_2O_3) and CaO + MgO + FeO + Na_2O + K_2O + TiO_2 (Fig. 1). The composition of the samples is found to be uniform.

Fine-grained and well distributed particles yield a stable vitrification structure by the formation of the necessary framework of calcium and aluminum silicates. The X-ray mapping based on CaKa in SEM of the fresh-fractured surfaces of all the as-received sherds shows that in the original clays used in all twenty sherds the calcite was carefully ground and dispersed (Fig. 2).

All the examined surfaces (except nos. 13 and 16) exhibit extensive vitrification (V) morphology and open porous structure (in Fig. 3 the microstructure of the samples TT2

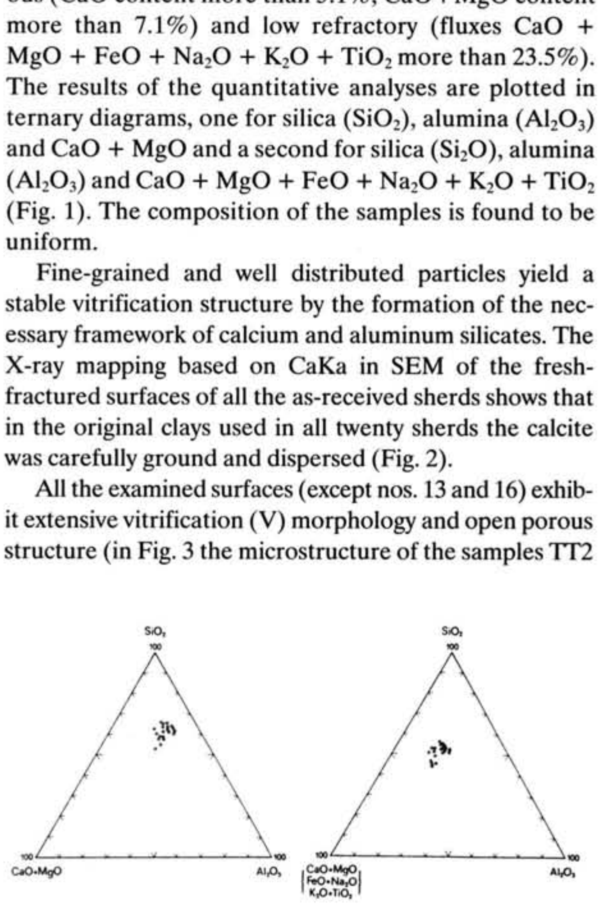

Fig. 1. Ternary diagrams of the as-received.

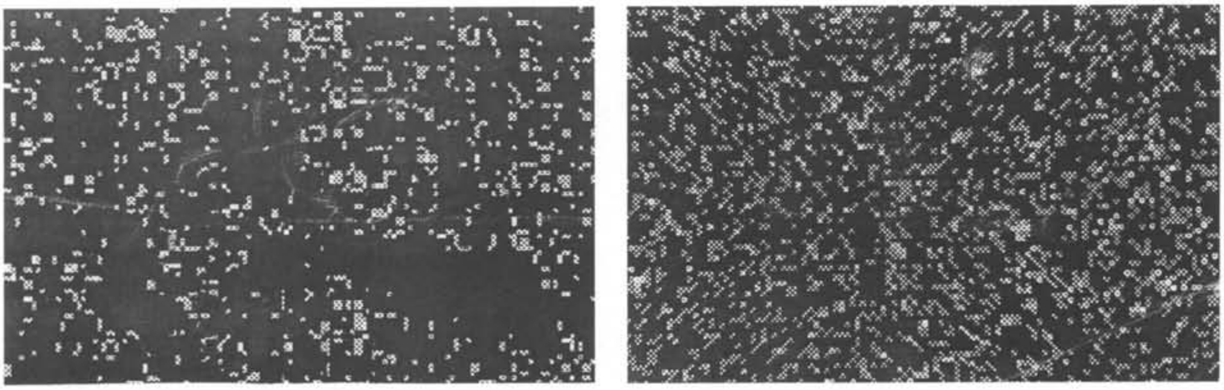

Fig. 2. Distribution and size of the calcite particles in the fabric.

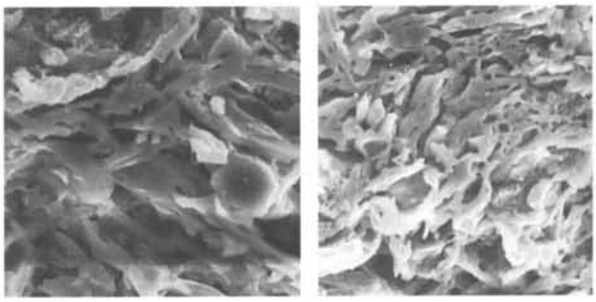

Fig. 3. Microstructure of the as-received fabric.

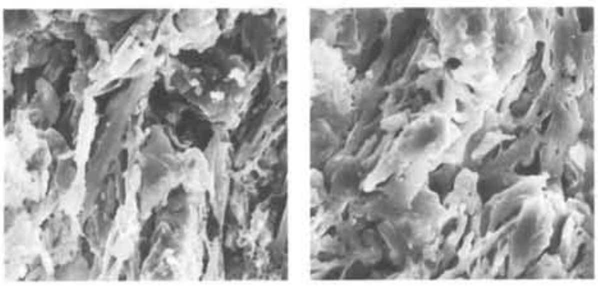

Fig. 4. Microstructure of the fabric refired at 1050 °C.

and TT10 in the as-received state). Since the pottery samples are made of calcareous, low refractory clays and fired in an oxidising atmosphere the firing temperature range of 850°-1050°C can be assessed to the corresponding pottery manufacture (Maniatis 1976).

Pieces of all sherds were refired at 900°, 950°, 1000°, 1050° and 1100°C in a LINDBERG tubular furnace in air (oxidising atmosphere) at a heating rate of 200°/h with a soaking time of one hour at the peak temperature. The cooling rate was also approximately 200°/h. In all samples the microstructure (vitrification stage V) remained unchanged or in some cases exhibited a slight advance in the amount of the amorphous phase in the temperature range of 900°-1050°C (in Fig. 4 the microstructure of the same samples TT2 and TT10 refired at 1050°C). It is shown that the control of firing temperature is not a critical factor to achieve the good quality pottery associated with the extensive vitrification microstructure.

X-ray diffraction analyses of powdered pieces of the ceramic bodies of all sherds were carried out by the Bragg-Brentano method on a Philips diffractometer aimed to determine the presence of minerals indicating with their formation temperatures more precise firing temperature ranges. Although in a few cases of both the as-received and the refired samples weak peaks of diopside and spinels were found it was not considered a strong evidence of a minimum firing temperature.

The ceramic bodies of the pottery articles studied were produced by a consistent technology. First a careful and deliberate selection of both the kind and the proportion of the clay raw materials, i.e. the use of calcareous low refractory mixtures with fine dispersed calcite. Second, in the context of the materials used, the application, in an oxidising atmosphere, of a comparatively low firing temperature (>850°C) extended in a wide range (200°C) needed no critical control over the vitrification state and consequently the mechanical properties of the pottery produced.

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