# ANCIENT POTTERY AS "THERMOMETAMORPHIC" PRODUCTS: MINERALOGICAL AND MICROSTRUCTURAL INDICATORS FOR CONSTRINING THE FIRING TEMPERATURE

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Ancient pottery represents the oldest synthetic material produced in the human history. Under a petrological point of view, it can be considered as a low pressure "thermometamorphic product", obtained for heating of clayey raw materials, which therefore represent the protolites. During the firing process, the clayey materials underwent a series of sub-solidus transformations, in some cases reaching the partial melting. This thermal process transforms raw incoherent clayey material into ceramics and determines its mineralogical and physical properties. On the basis of ethnographic studies, ancient firing technologies can be referred to open firing (bonfire) and kiln firing, respectively characterized by different pyrotechnological installation and type of fuel, the temporal and geographic distribution of which are related to the social organization.

Firing is a very complex process with myriad variables each contributing to the mineralogical and performance characteristics of the vessel; duration of the firing cycle, heating and cooling rate, maximum temperature, soaking time (time of maintenance of the maximum temperature), draft, and atmosphere (oxidizing or reducing) control the thermodynamic reactions in mineral phases contained in the ceramic fabric and degree of vitrification, as well as physical properties of the vessel such as porosity, strength, toughness and thermal conductivity. Since for most the ancient productions information on the technological choices of the potters are not reported in written texts, the ceramic remains represent the fossil record of the ancient productions. Therefore, the study of their mineralogical association and the microstructure can constrain their production technology in terms of the firing process, as well as the type of raw materials used.

Transformation reactions (like the breakdown of mineral phases occurring in the green body, crystallization of new minerals, formation of an amorphous phase) generally occur at the sub-solidus state and are thermodynamically and kinetically dependent. This means they can occur at different temperatures in relation both to the heating gradient and the firing atmosphere. Therefore, the mineral associations that are produced during firing, and which can be detected for instance by X-ray powder diffraction, can change in dependence on the length of the firing process and the type of firing atmosphere. Therefore, in order to constrain the firing temperature of ancient pottery, the mineralogical composition and/or the microstructural features of the ceramic bodies of archaeological ceramics need to be compared with those of ceramic replicas obtained through firing experiments carried out on a base clay materials analogous, in terms of chemical, mineralogical and textural composition, with those used in the archaeological ceramics of interest.

The mineralogical associations detected on ancient pottery (generally numerous phases) represent the most abundant phases formed during firing. Detailed microstructural analysis can point out that local equilibria are micro-domain dependent, as evidence for instance by reaction rims, presence of a higher number of newly-formed mineral phases respect to those which should have formed on the basis of the bulk composition. This means that a multiplicity of reactions can occur in the pottery, in relation to the pristine mineral phases of the clayey materials which are in contact each other. The diffusion of chemical elements is, in fact, very limited in these system, due to the short duration (compared with the geological processes) of the firing process. Therefore, considering the bulk composition of the raw materials, a pottery never represents condition of equilibria in its entirety, but a series of local equilibria strongly dependent from the micro-domain. Changes in porosity, such as shape, besides depending on the material, preparation of the body and forming technique, are also related to firing temperature; transforming from small and irregular voids, characteristic of low firing temperature, to larger regular vesicles at higher temperatures. Other important changes related to firing temperature and conditions take place in the microstructure of the groundmass as it undergoes gradual vitrification, like the loss of birefringence, which determine an optically active micromass to become inactive with firing increasing temperature, and the formation of bridging structures, caused by the partial melting of the mineral phases for local reactions, that can be observed between grains.