ARCHAEOCERAMICS FROM ORADEA FORTRESS: A MINERALOGICAL STUDY

Lucreția GHERGARI[1], Corina IONESCU[1], Volker HOECK[2],
Cornelia LAZĂR[1], Carmen PRECUP[1]

[1] Department of Mineralogy, Babes-Bolyai University, 1 Kogalniceanu Str., RO-400084 Cluj- Napoca, Romania; ghergari@bioge.ubbcluj.ro, corinai@bioge.ubbcluj.ro
[2]Department Geography and Geology, Paris Lodron University, 34 Hellbrunner Str., A-5020 Salzburg, Austria; volker.hoeck@sbg.ac.at.

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In the Oradea fortress (*Varadinum*), in NW Romania, a high number of ceramic artefacts were exhumed during the 2001 archaeological campaign. From these, eleven potshard samples dated back to XVIIth century were provided by courtesy of Dr. Adrian Rusu from the National History Museum of Transylvania for mineralogical study. They represent fragments of fine and semifine ware, with thin cream- or brick-coloured walls, coated with cream or light brown slip and rare brown paintings. The study involved plan-polarized light optical microscopy on thin sections (OM), X-Ray powder diffraction (XRD), and electron microprobe (EMP) investigations.

The ceramics consists basically of a matrix, in which variable amounts of inclusions – regarded as nonplastic components occur. The matrix is composed of clay minerals and micas (muscovite, biotite). The Fe-oxides content is relativelly low, as reflected by light cream colour of the matrix (one polarizer). The matrix shows either a microcrystalline, anisotropic fabric (Fig. 1) with rare amorphous/glassy zones or a microcrystalline-amorphous fabric with advanced sintering-amorphization processes.

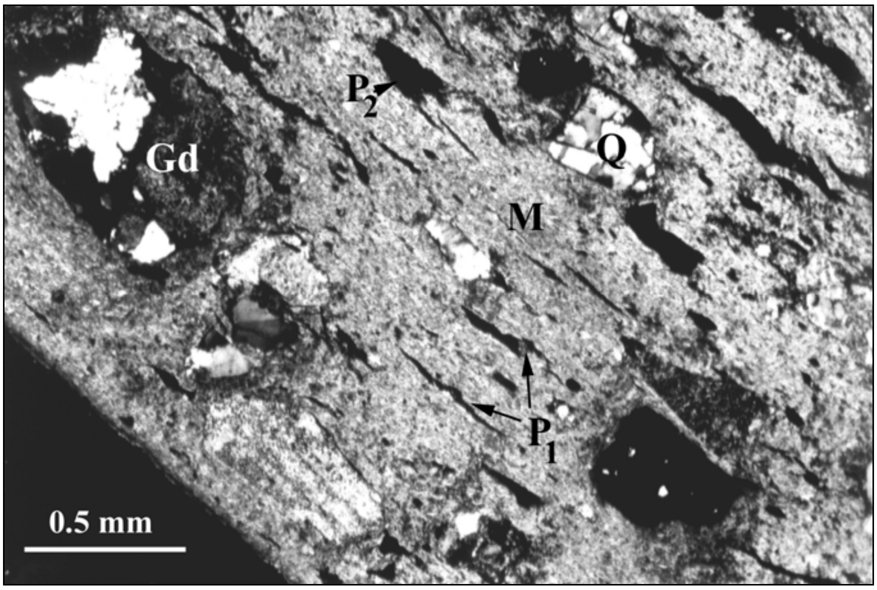

Fig. 1. Optical micrograph of semifine ceramics (sample 60). Abbreviations: M for matrix, Q for quartz clasts, Gd for granodiorite clasts, P_1 for primary pores, P_2 for secondary pores. Crossed polarizers.

The clasts are fragments of magmatic (granodiorites, dacites, rhyolites, andesites, granites), metamorphic (various quartzites, gneises, micaschists ± garnet) and sedimentary (sandstones, siltic clays, cherts) rocks. As crystalloclasts, quartz, plagioclase, K-feldspar, pyroxene, amphibole, garnet, epidote, magnetite, zircon, rutile and tourmaline can be found. The thermal changes noticed by OM regard the sintering process of the matrix, the forming of shrinkage voids around some clasts, the occurrence of reaction zones at the contact of the matrix with some clasts, the partial decomposition of micas, the diffusion of Fe into the softened rims of quartz, the beginning of quartz and feldspar melting.

The diffraction patterns of the ceramic samples[1] show the presence of quartz and feldspar (representing lithoclasts and crystalloclasts) as well as micas and clay minerals (representing the matrix). It is not possible to specify the primary clay minerals species due to the partial or total destroying of their structure upon firing. Only two diffraction lines are marked (~4.5 and ~2.6 Å), common to kaolinite and illite, and reflect the partial preservation of undisturbed crystalline structures in the ceramics fired at lower temperatures (800^{o}C). The 10 Å reflection, assigned to the dehydrated phase of illite, decreases with increasing temperature and according to Cultrone *et al.* (2001, 2005) disappears over 900^{o}C. As firing minerals, only mullite and gehlenite were so far identified by XRD, in sample 51 and 49, respectively. They indicate middle temperatures, e.g. 800-850^{o}C for gehlenite (Maggetti and Küpfer, 1978; Matsuoka and Ikeya, 1995) or higher ones, e.g. at least 900^{o}C for mullite (Cultrone *et al.*, 2004).

The EMP and EDS[2] reveal basic characteristic of the ceramics regarding both the chemistry and the relation between matrix, clasts, pores and the newly-formed mineral phases (Figs. 2-4).

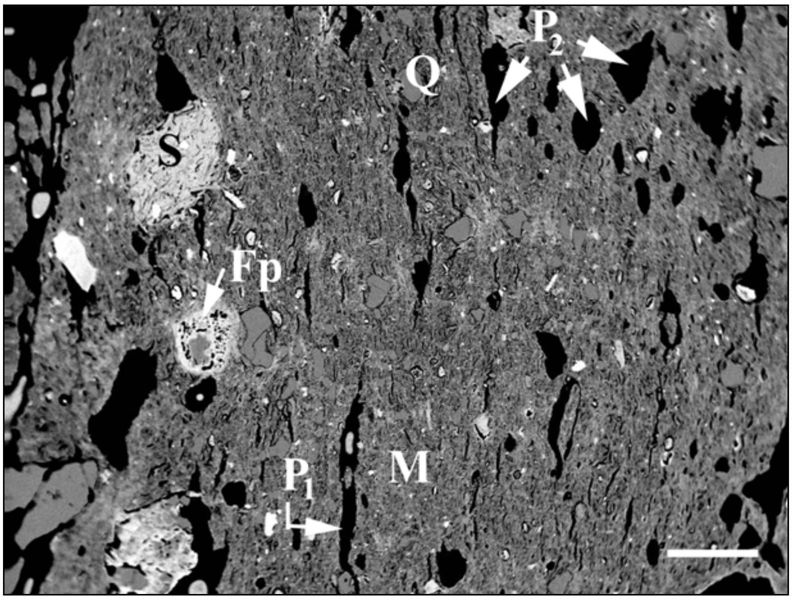

Fig. 2. BSE image of sample 58, with inhomogeneous matrix (M), quartz (Q) and plagioclase (Fp) clasts, soil aggregate (S) and primary (P_1) and secondary (P_2) pores. Note the K-feldspar reaction rim (brighter colours) around plagioclase albite. Length of the scale-bar: 0.2 mm.

The BSE images show a relatively porous ceramic body, with mainly primary pores and only subordinately secondary ones. The matrix is inhomogeneous and has a spotted appearance. The clasts e.g. quartz, micas, feldspars are lightly thermally altered. Fe migrates from matrix into the softened rims of quartz grains or from the areas of Fe-rich clays towards Fe-poor clays. Micas show thermal exfoliation processes along basal planes, probably due to dehydroxylation (Fig. 4) pointing to temperatures below 950^{o}C (De Benedetto *et al.*, 2002) or at least between 700-800^{o}C (Cultrone *et al.*, 2004). Some of feldspars, which are parts of lithoclasts, show melting.

[1] Dron-3 diffractometer operating at 20 kV and 20 mA, from 2 to 64^o 2θ, using CuK_α radiation with λ = 1.54051 Å (Babes-Bolyai University of Cluj-Napoca).
[2] Microprobe analyses on polished thin sections coated with carbon, performed with a JXA Superprobe 8600, equipped with three wavelength dispersive spectrometers (WDS) and Si (Li) energy-dispersive spectrometer (EDS), at the University of Salzburg (Austria).

The number of new firing mineral phases as evidenced by EMP is relatively low and is restricted to melt (glass), albite and potassic feldspar. The glass represents an amorphous mixture, composed mainly of Si, with variable amounts of Al, K, Fe resulted from illite and/or illitized micas melting.

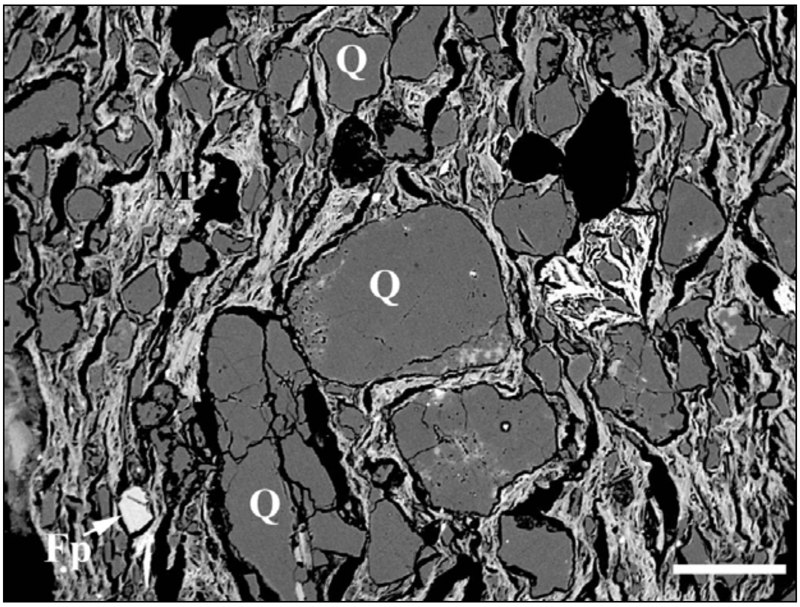

Fig. 3. Detailed BSE image of ceramic, sample 62. Abbreviations: Q and Fp for quartz and feldspar clasts, respectively. M for matrix. Length of the scale-bar: 0.1 mm.

According to Broeckmans *et al.* (2004), its presence indicates at least 800^{o}C firing temperature. The mottled aspect of matrix may reflect the partial transformation of kaolinite clay into mullite (Steele Jr., 2003). Some of albite crystals show K-feldspar reaction rims which might have been formed on muscovite expenses. The same process has been previously noticed by Gliozzo and Memmi Turbanti (2004).

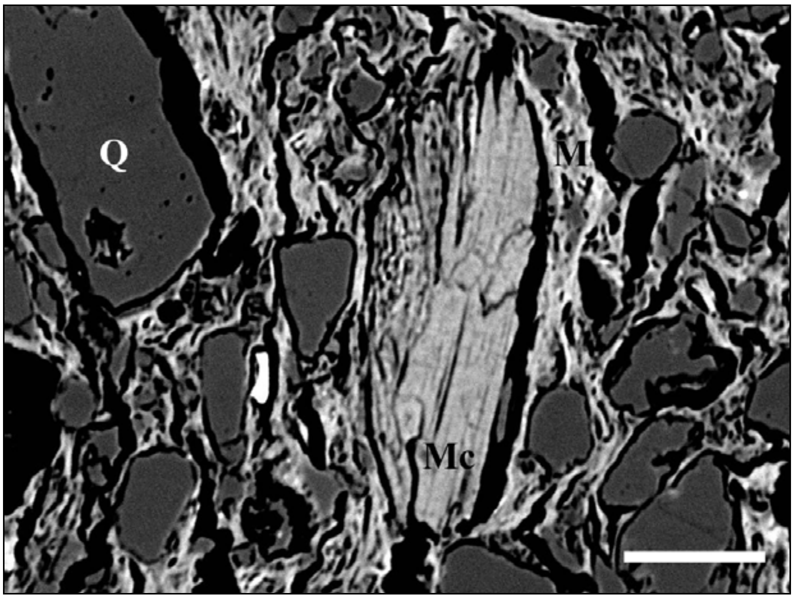

Fig. 4. BSE image of sample 62 showing thermal exfoliation process of a mica lamella (Mc) along basal planes. M for matrix, Q for quartz clasts. Length of the scale-bar: 0.05 mm.

The modal composition of the matrix calculated from EMP measurements indicates a kaolinitic (maximum 70%) - illitic (30%) clay. It is possible that at least partly, some illite/montmorillonite phase to be also present. Most likely, illites have been formed on the expense of biotite, as proved by the low amounts of Fe, Ti, Ca, Na, Mg and Mn, “trapped” inside the sintered matrix upon firing.

Compared with references data (Ghergari and Lazo, 1996), the composition of ceramic sample suggests that kaolinitic-illitic clays with low Fe similar with those cropping out nearby Şuncuiuș, westward Oradea, have been used as raw materials. Only accidentally the raw materials contained carbonates.

According to the thermal alterations noticed by OM, XRD and EMP investigations, three firing temperatures ranges, a) 800-850, b) 850-900 and c) 900-950, possible even a little higher, can be assumed for these samples. The presence of fine-grained magnetite indicates a reducing atmosphere of firing.

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