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Electron Microprobe Analysis for Archaeoceramics

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The use of the Electron Microprobe (EMP) for studying the archaeological ceramics is not widely applied, even it enables the identification of (a) the mineral compounds of the matrix, (b) the temper grains, (c) the firing minerals and (d) the post-depositional alteration products.
In turn, the detailed knowledge of the mineral phase composition allows inferences of the classification of shards, the identification of raw materials and the technological conditions of firing.

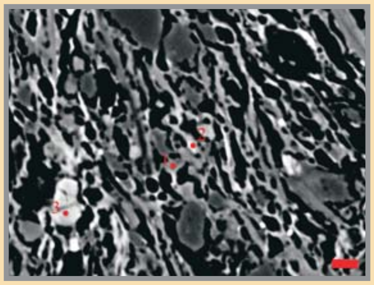
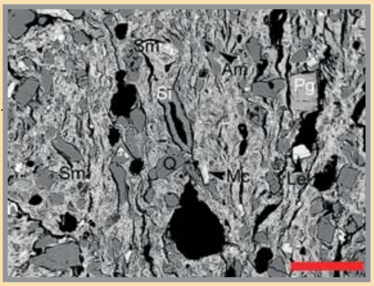


Fig. 1. BSE image of Neolithic ceramics (Cucuteni) showing the high porosity (blacks parts) and the inhomogeneous matrix. The ED spectra of points 1, 2 and 3 are shown in Fig. 3 and 4 respectively. Scale bar = 5 microns.

Apart from the obvious advantage, several problems are inherited to the method, such as:

A) **The low total sum of EMP analyses:** can be due to various factors, such as:
- the fine porosity of samples (Fig. 1);
- the incomplete dehydroxylation during the firing;
- re-hydration and/or re-hydroxylation during the burial (Fig. 2).

Fig. 2. BSE image of Bronze Age ceramics (Ilisua). Sm - smectitic matrix, Pg - plagioclase clast, Si - post-depositional silica, Le - leucite clast, Mc - mica lamella, Am - analcime. Scale bar = 200 microns.



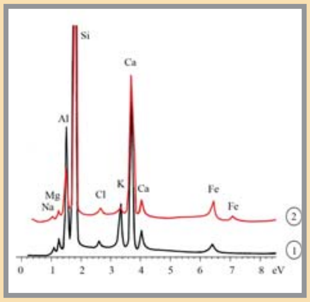


Fig. 3. ED spectra of different parts (points 1 and 2) of the matrix (Fig. 1). Note the enrichment of Fe and the depletion of Mg and K in the point 2.

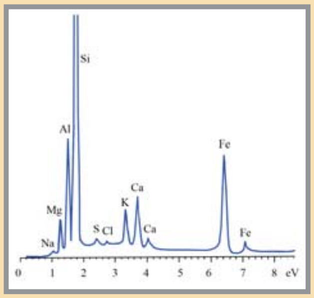


Fig. 4. ED spectrum of point 3 (Fig.1) showing a mixed phase consisting of Si, Al and Fe with significant amounts of Mg, K, Ca. Note the presence of Na, S and Cl in small quantities.

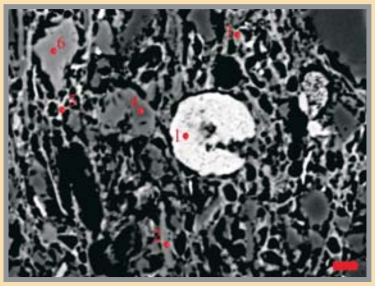


Fig. 5. BSE image of Neolithic ceramics (Cucuteni). The measured points are:
- *1 - apatite grain;*
- *2 & 3 - mixed phase (similar composition with point 3/Fig. 1 and almost identical spectrum as shown in Fig. 4);*
- *4 - mixed phase (with Al, Si, K and Na and low amount of P);*
- *5 - mixed phase, with high Si, Ca and Al and significant amounts of Fe, K and Mg;*
- *6 - K-feldspar with some Mg, Ca and Fe.*

Scale bar = 5 microns.

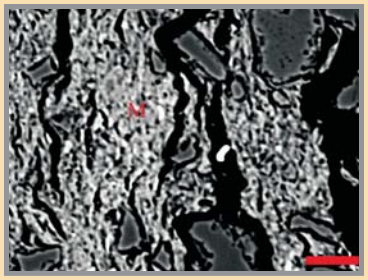


Fig. 6. BSE image of Bronze Age ceramics (Ilisua). A relatively compact matrix (M). Large pores due to shrinkage. Scale bar = 5 microns.

B) **The identification of small mineral components** of the clayish matrix as it represents a more or less homogeneous mixture of extremely-fine grained minerals (Figs. 1, 2, 5, 6). Usually they are smaller than the beam diameter (2-5 microns). The presence of an amorphous or vitreous phase complicates the situation.

C) **The distinction between the primary and the secondary (firing) phases** can be also relatively difficult, as the same mineral may occur as both (K-feldspars, plagioclase, leucite a.o.) (Figs. 4, 5, 7).

D) The firing products represent basically **metastable phases,** with non-stoichiometric composition, difficult to be characterized from mineralogical point of view (e.g. Ca-K phases). Additionally, they are “contaminated” with elements such as e.g. Fe, K or P trapped inside the new lattice (Figs. 4, 5, 7).

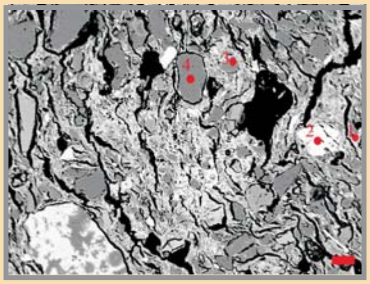


Fig. 7. BSE image of Bronze Age ceramics (Ilisua) showing a highly inhomogeneous matrix and various clasts.1 - illitic matrix with P content; 2 - illitic soil concretion with Fe and P content; 3 - plagioclase; 4 - quartz clast. Scale bar = 50 microns.

Several measuring runs under different conditions resulted in different analytical data. We compared a) low beam current (10 nA) & focused conditions with b) high beam current (40 nA) & focused conditions and with c) low current & de-focussed conditions. In general, the measurements with low beam current & focused conditions gave the best results. As can be seen from Figs. 1, 2 and 5, a defocused beam would integrate over this network of fine phases or compounds and the pores in-between The accuracy of the repeatability of the microprobe stage is in the same range as the thickness of the network compounds.

Despite the difficulties inherent in the samples and the constraints of the microprobe equipment, with careful selection of the measured points and microprobe conditions, reasonable good result can be achieved.