Analysis of elemental composition, fabrication texture and inclusions in pottery samples from Vashtemia, site of the Early Neolithic period in Albania.

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Abstract

- A necessary expansion of the study on human behaviour and social organization in prehistoric periods leads us to study in more detail the elemental composition of the materials the products of human activity, such as ceramics, were made of.
- It takes the main place in the production of this period and its analysis helps us to know more about the advancement of production technologies and shed light on the origin of clay sources.
- From the Vashtemia site, a number of samples have been selected for analysis, by means of different techniques, in order to identify the raw materials used for the production of ceramic vessels, the technique of surface processing, the style of decoration and also to understand the construction of the furnaces used for clay firing, starting from the characterization of the mineral phases of the ceramics that we studied.

Historical background

- The Neolithic settlement of Vashtemia is located on a flat alluvial plain, at the western edge of the village of the same name, on the right side of the Korçë-Maliq road in Albania.
- The first information on this settlement dates back to 1972, which was followed by a control excavation in 1973 and systematic excavations in 1974.



View of the Neolithic site of Vashtemisa (photo A. Bunguri 2011)

Historical background

- Ceramics appear abundant throughout the layer depth and are represented by several categories such as:
 - bright red monochrome pottery,
 - painted pottery,
 - monochrome gray black pottery,
 - impresso pottery and barbotine,
 - the latter quite limited.

Texture analysis

• The group of samples taken in the study from the Vashtemia site includes 31 samples of which 14 belong to thin-walled ceramics and the rest are from thick-walled ceramics.

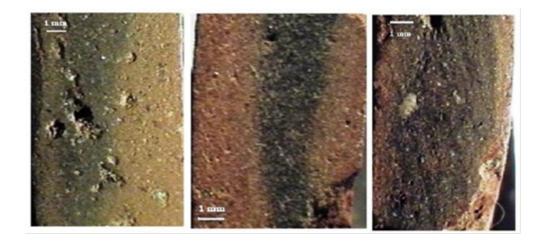
 Samples are not cataloged. Among them, the main place is occupied by light red fragments, usually with a weak glaze and a small number have remnants of decorations on the surface



View of the pottery group from the Vashtemia site.

Texture analysis

• The baking is not complete, which is also evidenced by the non-uniform color, especially in the cross-section, where in almost all samples the existence of a dark band between the two side bands of red color can be observed. Many authors explain this with baking conditions.



Cross-sectional view of some ceramics from Vashtemia taken by μ -FRX.

The study of elemental composition

- The table shows the results of the elemental composition of the samples analyzed by the X-Ray Fluorescence method, as well as of some clay samples collected around the Vashtemia site.
- They are collected by archaeologists and represent soils collected in different layers of the excavation.
- The identification of clay sources in the Korça area is quite difficult due to the great changes that the terrain has undergone with the drying of the Maliqi marsh, around which all the early settlements in this area were located.

The study of elemental composition

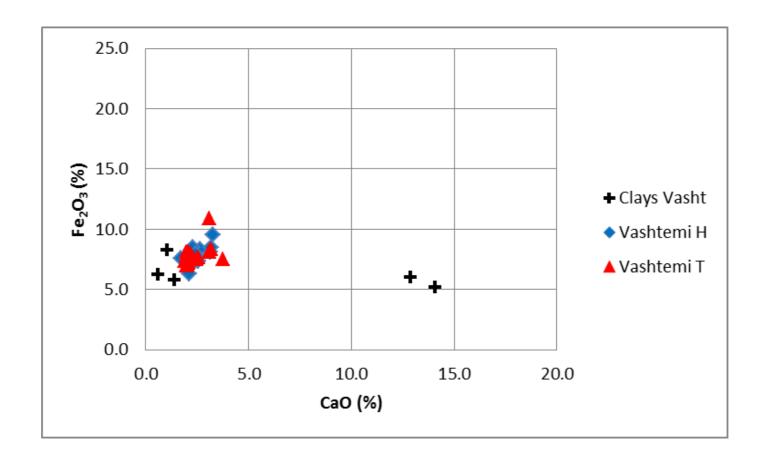
Data on the content of major elements testify to a group of samples with similar composition.

- •The content of K2O varies between 1.3 2.5%,
- •CaO between 1.7 3.7%,
- •TiO2 0.6 1%
- •Fe2O3 6.3 10.9%.

Three of the clay samples have content of major elements close to those of ceramics, while the other two have different compositions, especially high content of CaO, which is not found in any of the samples.

The content of major elements (%) in the ceramics and clays of Vashtemia

| Sampl e | | | | | Sampl | | | | |
|------------|----------------------------|------|---------|---------------------------------|--------|------------------|-------|---------|---------------------------------|
| Code | $\mathbf{K}_{2}\mathbf{O}$ | CaO | TiO_2 | $\mathbf{Fe}_{2}\mathbf{O}_{3}$ | e Code | K ₂ O | CaO | TiO_2 | $\mathbf{Fe}_{2}\mathbf{O}_{3}$ |
| MVT-1 | 2.24 | 3.07 | 0.72 | 10.86 | MVH-1 | 2.55 | 1.72 | 0.90 | 7.57 |
| MVT-2 | 1.89 | 2.57 | 0.65 | 7.67 | MVH-2 | 2.13 | 2.10 | 0.85 | 6.86 |
| MVT-3 | 1.80 | 2.06 | 0.69 | 8.14 | MVH-3 | 2.30 | 2.53 | 0.80 | 7.76 |
| MVT-4 | 2.14 | 2.26 | 0.91 | 7.72 | MVH-4 | 2.41 | 3.11 | 0.94 | 8.14 |
| MVT-5 | 2.30 | 3.16 | 0.90 | 8.36 | MVH-5 | 2.11 | 1.98 | 0.93 | 7.59 |
| MVT-6 | 2.39 | 1.89 | 0.79 | 7.37 | MVH-6 | 1.97 | 2.56 | 0.69 | 7.33 |
| MVT-7 | 1.96 | 2.48 | 0.74 | 7.54 | MHV-7 | 2.32 | 2.64 | 0.85 | 8.34 |
| MVT-8 | 1.83 | 1.98 | 0.74 | 8.13 | MVH-8 | 2.13 | 3.16 | 0.72 | 8.52 |
| MVT-9 | 1.84 | 2.00 | 0.65 | 7.90 | MVH-9 | 2.07 | 3.25 | 0.74 | 9.57 |
| MVT- | | | | | MVH- | | | | |
| 10 | 2.26 | 2.23 | 0.99 | 7.54 | 10 | 2.08 | 2.13 | 0.83 | 6.29 |
| MVT- | | | | | MVH- | | | | |
| 11 | 2.14 | 2.07 | 0.92 | 7.24 | 11 | 2.09 | 2.29 | 0.94 | 7.42 |
| MVT- | | | | | MVH- | | | | |
| 12 | 2.21 | 2.01 | 0.93 | 7.03 | 12 | 2.53 | 2.22 | 0.94 | 8.23 |
| MVT- | | | | | MVH- | | | | |
| 13 | 1.28 | 1.98 | 0.89 | 6.94 | 13 | 2.42 | 2.28 | 0.97 | 8.52 |
| MVT- | | | | | MVH- | | | | |
| 14 | 2.21 | 3.08 | 0.90 | 8.10 | 14 | 2.14 | 2.41 | 0.84 | 7.99 |
| MVT- | | | | | | | | | |
| 15 | 2.14 | 3.73 | 0.74 | 7.52 | | | | | |
| MVT- | | | | | Vasht | | | | |
| 16 | 2.04 | 2.20 | 0.85 | 7.94 | Ag1 | 2.66 | 1.41 | 0.84 | 5.77 |
| MVT- | | | | | Vasht | | | | |
| 17 | 2.36 | 2.07 | 0.99 | 7.42 | 500 | 3.12 | 14.07 | 0.64 | 5.17 |
| | | | | | Vasht | | | | |
| | | | | | 501 | 2.31 | 1.04 | 0.79 | 8.26 |
| | | | | | Vasht | | | | |
| | | | | | 502 | 2.42 | 12.87 | 0.61 | 6.03 |



CaO - Fe2O3 graph for the ceramics and clays of the Vashtemia site

The content of minor elements (mg/kg) in the ceramics and clays of the Vashtemia site.

| Sample | | | | | | | | | | | | | | | | | |
|-----------|------------------|------|------|-----|----|-----|----|-----|-----|--------------|-----|----|----|------|----|----|----|
| Code | $ _{\mathbf{V}}$ | Cr | Mn | Ni | Cu | Zn | Ga | Rb | Sr | \mathbf{Y} | Zr | Pb | Th | Ba | La | Ce | Nd |
| MVH-1 | 186 | 239 | 929 | 137 | 27 | 136 | 18 | 130 | 170 | 40 | 300 | 28 | 15 | 872 | 30 | 74 | 27 |
| MVH-2 | 167 | 185 | 592 | 110 | 20 | 103 | 19 | 118 | 192 | 30 | 247 | 27 | 13 | 978 | 20 | 49 | 22 |
| MVH-3 | 189 | 303 | 867 | 156 | 26 | 130 | 18 | 104 | 199 | 38 | 242 | 27 | 18 | 1153 | 21 | 63 | 24 |
| MVH-4 | 134 | 238 | 1233 | 120 | 32 | 132 | 26 | 111 | 222 | 38 | 267 | 28 | 13 | 1021 | 26 | 73 | 26 |
| MVH-5 | 201 | 156 | 794 | 121 | 27 | 110 | 21 | 113 | 178 | 28 | 260 | 28 | 16 | 970 | 17 | 64 | 22 |
| MVH-6 | 237 | 151 | 862 | 129 | 22 | 98 | 16 | 87 | 206 | 54 | 142 | 16 | 16 | 1060 | 28 | 64 | 34 |
| MHV-7 | 96 | 218 | 1044 | 135 | 35 | 134 | 23 | 112 | 248 | 43 | 269 | 49 | 12 | 1038 | 28 | 76 | 28 |
| MVH-8 | 163 | 235 | 666 | 153 | 24 | 121 | 17 | 106 | 203 | 39 | 186 | 41 | 12 | 896 | 28 | 70 | 24 |
| MVH-9 | 300 | 149 | 760 | 123 | 20 | 125 | 18 | 86 | 278 | 42 | 123 | 13 | 15 | 1107 | 26 | 61 | 31 |
| MVH-10 | 209 | 409 | 899 | 151 | 26 | 123 | 15 | 116 | 211 | 30 | 202 | 14 | 18 | 1078 | 17 | 57 | 15 |
| MVH-11 | 285 | 268 | 1032 | 96 | 17 | 100 | 19 | 101 | 224 | 38 | 261 | 16 | 18 | 1086 | 28 | 68 | 23 |
| MVH-12 | 222 | 302 | 1219 | 156 | 29 | 139 | 21 | 122 | 200 | 46 | 277 | 34 | 18 | 927 | 29 | 78 | 23 |
| MVH-13 | 274 | 280 | 1196 | 139 | 15 | 132 | 19 | 121 | 201 | 43 | 250 | 18 | 22 | 924 | 32 | 80 | 25 |
| MVH-14 | 228 | 255 | 844 | 114 | 22 | 124 | 20 | 116 | 202 | 36 | 243 | 23 | 19 | 976 | 30 | 66 | 25 |
| MVT-1 | 184 | 204 | 801 | 130 | 32 | 146 | 15 | 101 | 180 | 34 | 167 | 13 | 14 | 884 | 22 | 60 | 29 |
| MVT-2 | 166 | 169 | 918 | 134 | 29 | 95 | 20 | 85 | 199 | 51 | 120 | 12 | 17 | 819 | 25 | 65 | 34 |
| MVT-3 | 160 | 1226 | 1023 | 476 | 36 | 109 | 16 | 75 | 178 | 23 | 176 | 43 | 6 | 840 | 11 | 46 | 14 |
| MVT-4 | 224 | 158 | 704 | 113 | 21 | 110 | 23 | 119 | 185 | 34 | 229 | 31 | 17 | 928 | 22 | 60 | 19 |
| MVT-5 | 223 | 160 | 962 | 117 | 32 | 105 | 20 | 108 | 205 | 44 | 302 | 42 | 12 | 880 | 26 | 67 | 18 |
| MVT-6 | 261 | 134 | 916 | 123 | 36 | 124 | 26 | 109 | 190 | 31 | 234 | 23 | 9 | 954 | 17 | 57 | 22 |
| MVT-7 | 217 | 482 | 858 | 214 | 25 | 110 | 14 | 81 | 213 | 34 | 160 | 19 | 15 | 1001 | 19 | 53 | 25 |
| MVT-8 | 166 | 452 | 959 | 225 | 29 | 97 | 20 | 81 | 170 | 38 | 175 | 23 | 15 | 702 | 19 | 54 | 27 |
| MVT-9 | 246 | 1351 | 1037 | 457 | 36 | 112 | 7 | 75 | 180 | 24 | 168 | 10 | 14 | 853 | 11 | 45 | 19 |
| MVT-10 | 213 | 648 | 1062 | 122 | 22 | 126 | 23 | 121 | 212 | 32 | 300 | 31 | 15 | 945 | 24 | 73 | 21 |
| MVT-11 | 269 | 139 | 731 | 116 | 30 | 101 | 25 | 106 | 196 | 33 | 262 | 36 | 15 | 1032 | 17 | 61 | 24 |
| MVT-12 | 161 | 308 | 704 | 112 | 21 | 107 | 18 | 102 | 182 | 30 | 256 | 47 | 15 | 1029 | 20 | 58 | 23 |
| MVT-13 | 193 | 196 | 694 | 105 | 13 | 102 | 17 | 105 | 182 | 29 | 276 | 18 | 20 | 1034 | 23 | 62 | 25 |
| MVT-14 | 138 | 189 | 998 | 110 | 22 | 103 | 20 | 108 | 205 | 40 | 258 | 40 | 19 | 876 | 28 | 72 | 33 |
| MVT-15 | 236 | 210 | 952 | 113 | 21 | 99 | 20 | 96 | 223 | 36 | 174 | 16 | 16 | 890 | 25 | 64 | 25 |
| MVT-16 | 151 | 335 | 748 | 128 | 24 | 113 | 25 | 118 | 187 | 36 | 237 | 29 | 15 | 905 | 28 | 66 | 27 |
| MVT-17 | 230 | 316 | 1038 | 123 | 20 | 122 | 23 | 116 | 213 | 34 | 309 | 34 | 15 | 945 | 22 | 75 | 28 |
| | | | | | | | | | | | | | | | | | |
| Vasht Ag1 | 328 | 597 | 958 | 118 | 13 | 90 | 4 | 123 | 91 | 31 | 279 | 39 | 8 | 531 | 38 | 78 | 37 |
| Vasht 500 | 318 | 255 | 546 | 106 | 16 | 106 | 5 | 129 | 277 | 27 | 232 | 41 | 11 | 621 | 34 | 55 | 28 |
| Vasht 501 | 455 | 926 | 995 | 586 | 17 | 79 | 8 | 119 | 56 | 31 | 198 | 43 | 10 | 343 | 30 | 60 | 30 |
| Vasht 502 | 209 | 575 | 711 | 391 | 11 | 71 | 3 | 92 | 173 | 24 | 184 | 30 | 8 | 263 | 30 | 49 | 22 |

Mineralogical composition

• Information on the mineralogical composition of the ceramics is mainly based on the petrographic and X-ray diffraction study of a limited number of samples from this site.

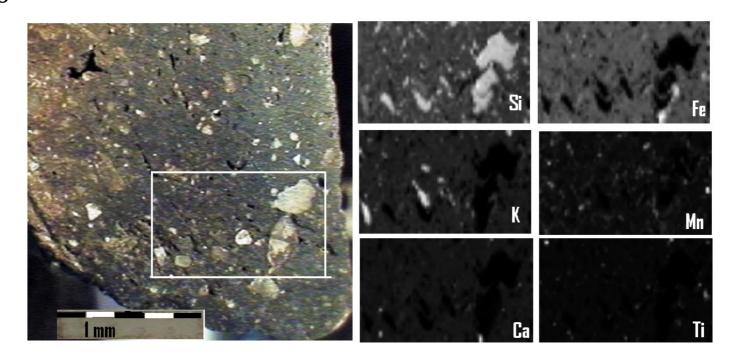
• It is noted that among the observed inclusions, those rich in Si predominate, which should be quartz particles. In smaller quantities, particles rich in K, Ca and Fe were also observed.

• As expected from the overall low CaO content of the ceramics, the amount of Ca-rich particles is relatively low.

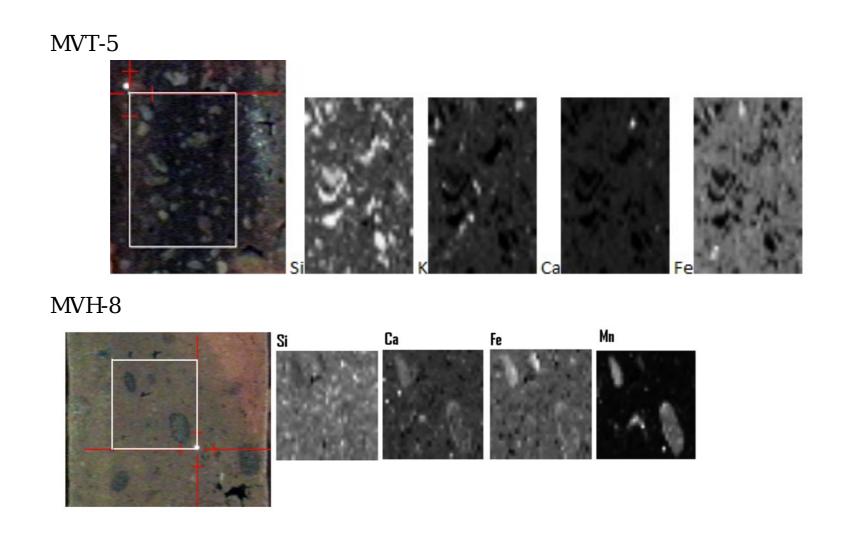
• Through these measurements it is not possible to distinguish whether the observed inclusions were part of the clay or related to the materials added as temper during the pottery production, although the particles with larger dimensions must have been added as temper.

Distribution maps of major elements in the inclusions of ceramic samples from the Vashtemia site

MVT -16



Distribution maps of major elements in the inclusions of ceramic samples from the Vashtemia site

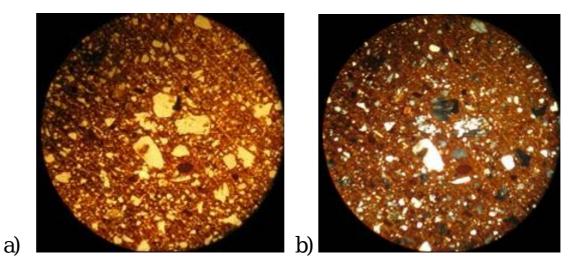


Petrographic Study

Sample V/11. The matrix (without analyzer) is presented with a reddish color, which is more intense in the center and paler in the periphery, a fact that speaks of a "sandwich" type structure, with good sorting, anisotropic.

Aplastic material is represented by a) minerals: granular quartz, plagioclase and mica (biotite muscovite) as well as b) rock fragments (lithoclasts): metamorphosed quartzites, serpentinites, amphibolic schists, biomicrites and hematitic pellets. Aplastic material ranges from highly angular (abrasive) to poorly rounded.

Gaps: lens-shaped gaps.

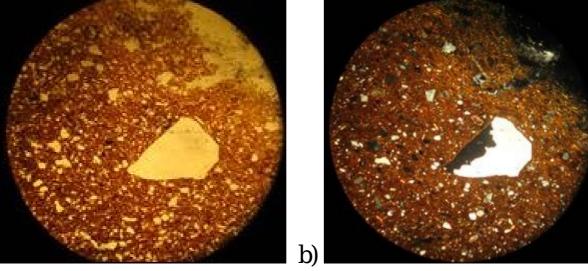


Analysis of sample V/11 with a polarized light microscope (x10) a) (parallel polars=PPL, and b) crossed polars (=+PL).

Petrographic Study

- **Sample V/2.** The matrix (without analyzer) is presented with a reddish color, which is more intense in the center and paler in the periphery, a fact that speaks of a "sandwich" type structure, with very good sorting, anisotropic.
- Aplastic material is represented by a) minerals: granular quartz, plagioclase and mica (biotite muscovite) as well as b) rock fragments (lithoclasts): polygranular quartz, amphibolic schists, biomicrites and hematitic pellets.
- Aplastic material ranges from highly angular (abrasive) to poorly rounded, grainy. Carbonate recrystallization material is evidenced.

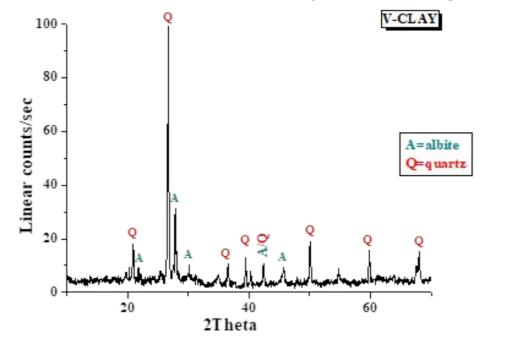
Voids: lenticular voids, but also cavid



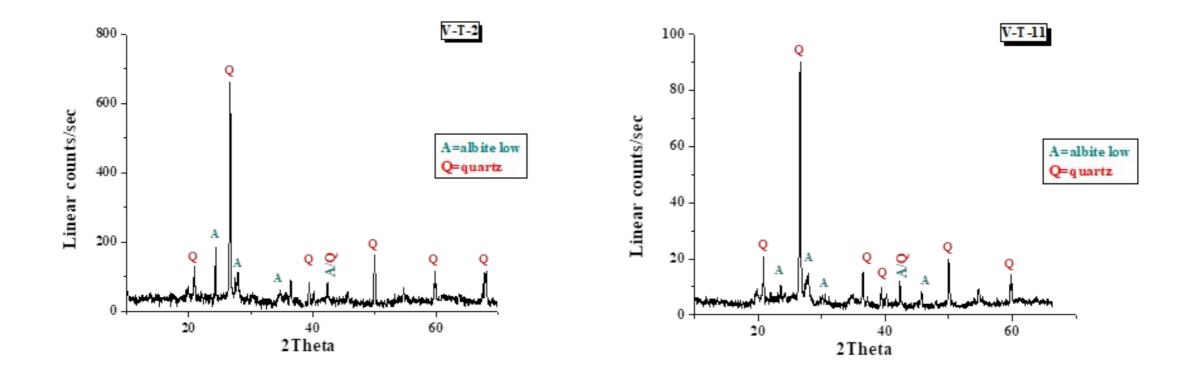
Analysis of sample V/2 with a polarized light microscope (x10) a) (parallel polars=PPL, and b) crossed polars (=+PL).

X-ray diffractometry analyses

- The main phases identified by the X-ray diffraction method in the analyzed ceramic and clay samples are quartz (SiO₂) and albite (NaAlSi₃O₈). These results agree with the results obtained from the petrographic study as well as those with μ-XRF, which have identified minerals containing these phases.
- We think that the low sensitivity of the XRD method does not allow the identification of some minor minerals that have been observed by the petrographic study.



XRD spectrum of clay from the Vashtemia site.



XRD spectrum of two ceramic samples from the Vashtemia site.

Conclusions

- Since the CaO content in the ceramic samples from the Vashtemia site is lower than 5%, it follows that the clays used are of the low-calcium (non-calcareous) type.
- Comparing the composition of thin-walled ceramics with those with thick walls, testifies to similar raw materials used for each group.
- Thus, both the average values of the groups and the variation of the values do not show any significant difference.

Conclusions

- Petrographic analysis shows low degree of vitrification and presence of recrystallized carbonates. These data suggest baking in an oxidizing environment (open oven or closed oven with final oxidizing stage) and moderate temperature for a short time.
- The presence of the same main phases, quartz and albite, with similar intensities both in the samples and in the clay suggest low reactivity of the mineral phases due to low temperatures of the order of 700 750°C.

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