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Małgorzata Daszkiewicz

ARCHAEOMETRIC ANALYSES OF BRICK, CLAY, POTTERY AND COMPOSITE MATERIAL FROM A CISTERN, RISAN (MONTENEGRO)

Abstract: Laboratory analysis was performed on various samples from Risan. Local clay samples were analysed, as was a brick sample, pottery sherds (including amphora fragments) and samples of composite material from a cistern discovered during excavations carried out in Risan by a team from the Antiquity of Southeastern Europe Research Centre, University of Warsaw. The following analyses were conducted: MGR-analysis, firing tests, chemical analysis by WD-XRF, thin-section studies using polarising microscopy and scanning electron microscopy, and water permeability analysis.

Keywords: archaeometric analyses, pottery analyses, clay analyses, composite lining, Risan

This preliminary report sets out the results of laboratory analyses carried out on a clay sample (Risan-Saliny), a fragment of brick (from an item produced at a brick factory active during the nineteenth–twentieth centuries), five fragments of pottery vessels, fragments of eight amphorae and three samples of composite lining material taken from the wall of a cistern. All of the analysed pottery and mortar samples came from the excavations carried out in Risan by a team from the Antiquity of Southeastern Europe Research Centre, University of Warsaw.

The first analysis to be carried out was a plasticity test for the Risan-Saliny clay sample, which included gauging the water of plasticity (make-up water) content. Water of plasticity is the amount of water required to bring 100 grams of clay material to a plastic state (in practical terms this means that the material can be shaped into a ball which will not feature any cracks, and which can, depending on the type of clay, have a certain amount of pressure applied to it such that the ball will only become misshapen but no cracks will appear). The Risan-Saliny clay sample is characterised by water of plasticity of 27 g H_2O per 100 g of dry clay, and is a raw material suitable for making a plastic mass that can be readily formed. The next stage was to carry out a firing test. Briquettes for this test were made using a plastic mass (hand-made homogenisation of mass) and non-porous porcelain moulds which yielded dome-shaped samples; these samples were then dried and fired in a laboratory furnace at five temperatures (800, 900, 1100, 1150 and 1200°C).

Firing was carried out in a Carbolite electric laboratory resistance furnace, in static air, at a heating rate of 5°C/min, and a soaking time of 1 hour at the peak temperature; however, in contrast to MGR-analysis, the samples were not removed from the furnace but cooled with it down to room temperature (simulating the original firing of bricks). Two briquettes were fired at each temperature. One of the briquettes was left whole, whilst a thin slice was removed from

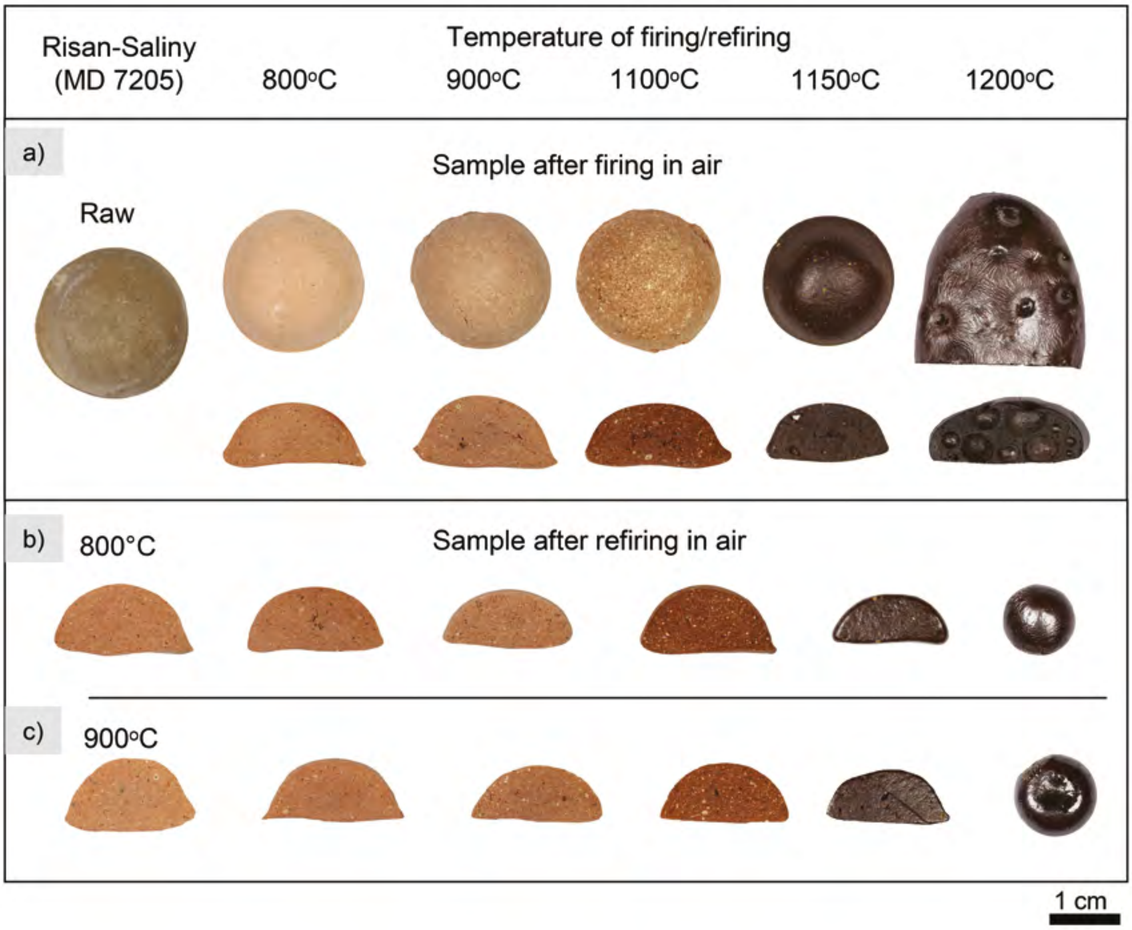

Fig. 1. Clay Risan-Saliny. a) briquettes prepared in laboratory from plastic mass and fired in standardised conditions in laboratory kiln; b) samples removed from briquettes fired at 800°C; c) samples removed from briquettes fired at 900°C; b and c = samples refired in exactly the same way that MGR-analysis is performed on samples of ancient pottery (photos M. Baranowski, drawing H. Baranowska).

the middle of the second briquette. The surface of the briquettes corresponds to the surface of the bricks, and the surface of the thin slice corresponds to the cut-section of a brick (Fig. 1a). Next, 12 more briquettes were made from the clay, and these were fired in the same conditions as described above at 800 and 900°C. Samples fired in this manner simulated brick samples fired at 800 or 900°C, and MGR-analysis was performed on these samples in exactly the same way that MGR-analysis[1] is performed on samples of ancient pottery. This means that thin slices were removed from each briquette and these were subsequently refired at 800, 900, 1100, 1150 and 1200°C (Fig. 1b and 1c). The samples removed from the brick were refired at the standard range of temperatures for abridged MGR-analysis, namely at 1100, 1150 and 1200°C (Fig. 2).

Comparing the thermal behaviour of briquettes made of Risan-Saliny clay, both after the firing test and after MGR-analysis, with the results obtained for the brick showed a slight inhomogeneity of both the raw material and the clay body from which the brick was made. The thermal behaviour is not identical, but it is similar (Fig. 3). The results of chemical analysis

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[1] Firing was done in a Carbolite electric laboratory resistance furnace, in static air, at a heating rate of 5°C/min, a soaking time of 1 hour at the peak temperature, a cooling rate of 5°C/min up to 500°C and then cooling with the kiln for 1 hour.

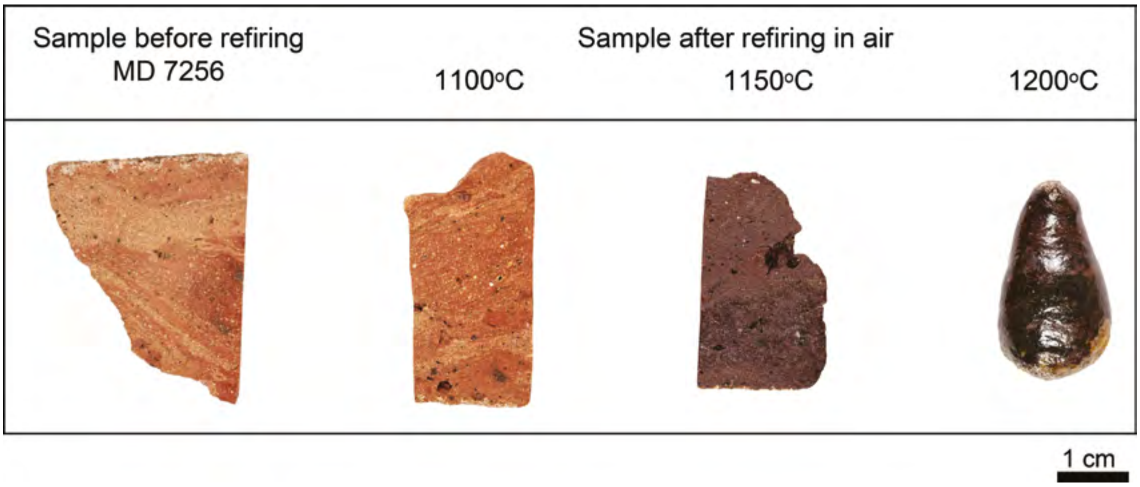

Fig. 2. Samples removed from brick refired at standard range of temperatures for abridged MGR-analysis: i.e. at 1100, 1150 and 1200°C (photos M. Baranowski, drawing H. Baranowska).

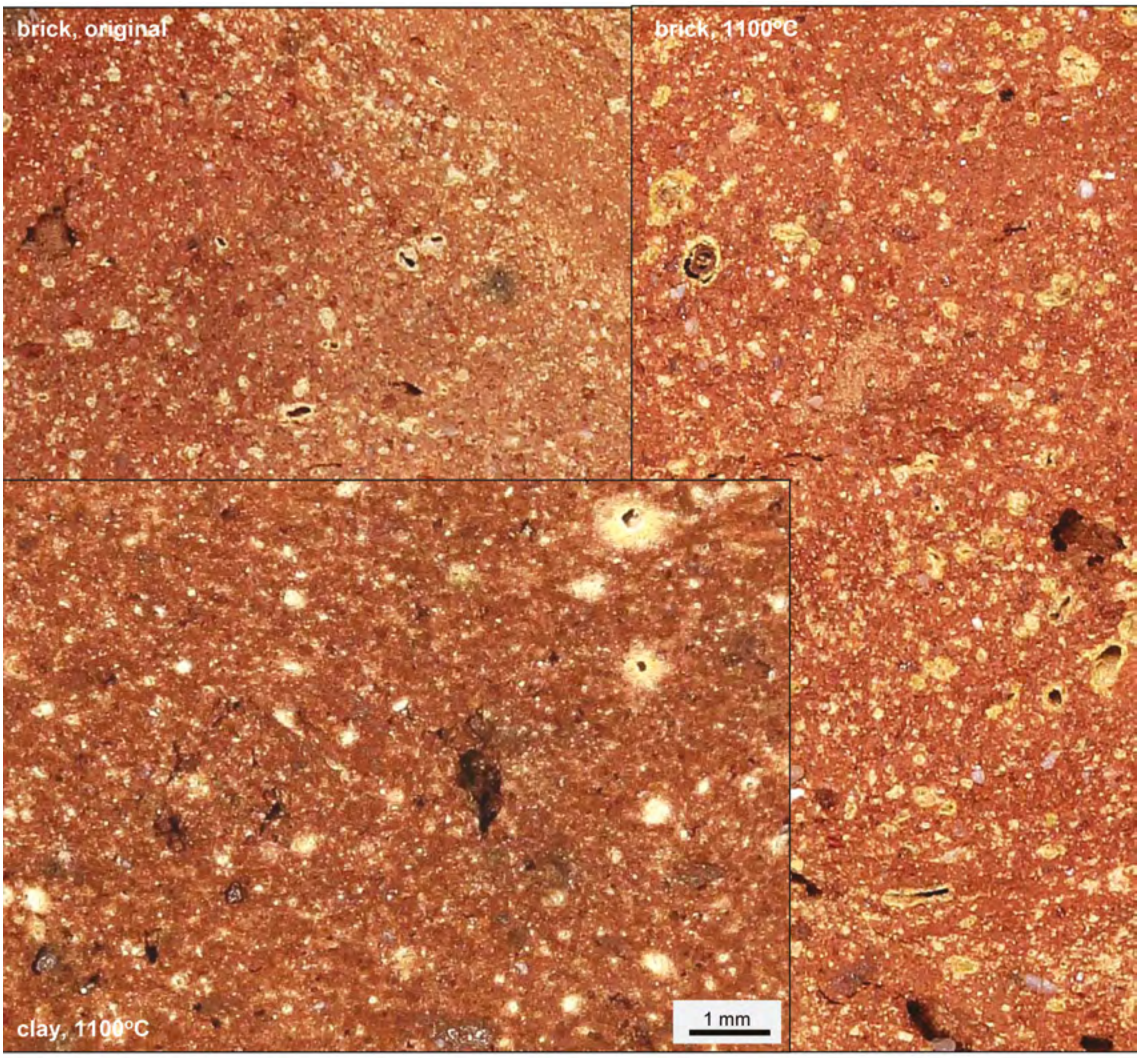

Fig. 3. Comparison of thermal behaviour of brick (original and refired sample) and briquette, refiring at 1100°C (photos M. Baranowski, drawing H. Baranowska).

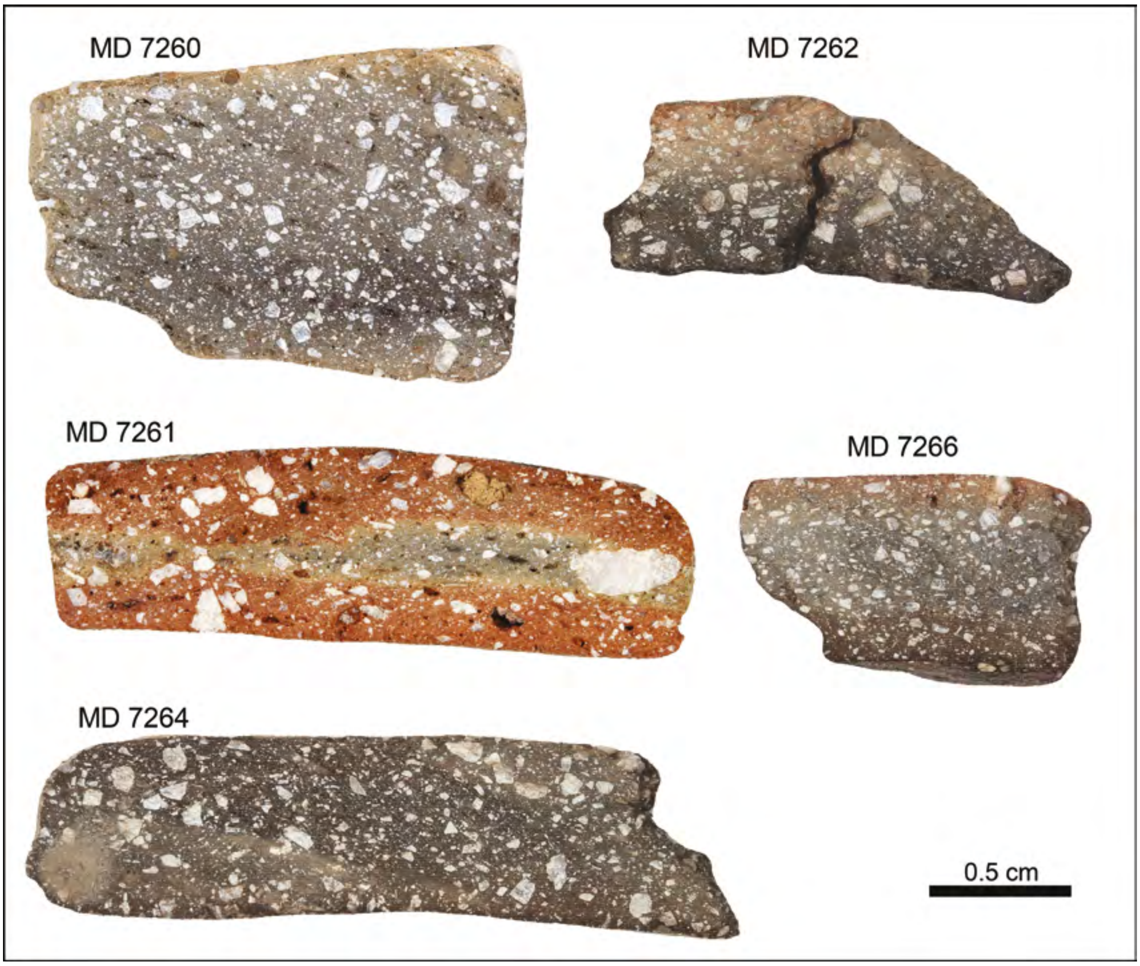

Fig. 4. Cross-section through wall of vessel. In each fragment temper of crushed carbonates is visible (photos M. Baranowski, drawing H. Baranowska).

by WD-XRF reveal the same: the chemical composition is not identical but similar; in the clay there is a higher concentration of Fe_2O_3 and Na_2O, whilst the brick features a higher concentration of SiO_2 (Tab. 1). Taking into account the similarities in phase composition (expressed in thermal behaviour) and chemical composition, we can conclude that the ceramic body used to make the brick was made from a plastic raw material taken from the same deposit (not the same spot) as the analysed clay sample.

The next to be analysed were the pottery samples. Analysis was only performed on seven of the nine ceramic vessel fragments (the other two were not analysed due to the small size of the samples and their temper content). Each fragment has intentional temper comprising crushed carbonates (five sherds are shown in Fig. 4). Chemical analysis by WD-XRF was performed on seven samples, abridged MGR-analysis on two samples, and three samples were refired at only one temperature—1200°C. None of the samples refired at 1100°C and 1150°C were glued on to the MGR-charts or photographed in their entirety, as these samples fell to pieces as soon as they had cooled to room temperature (see MD 7260, Fig. 5). Additionally, one week after refiring at 1200°C, samples MD7260 and MD7262 fell to pieces. This is attributable to the thermal decomposition of carbonates; all of the samples feature temper with a large quantity of carbonate grains. Chemical analysis revealed that CaO content ranges from 22 to 32 wt.% due to the

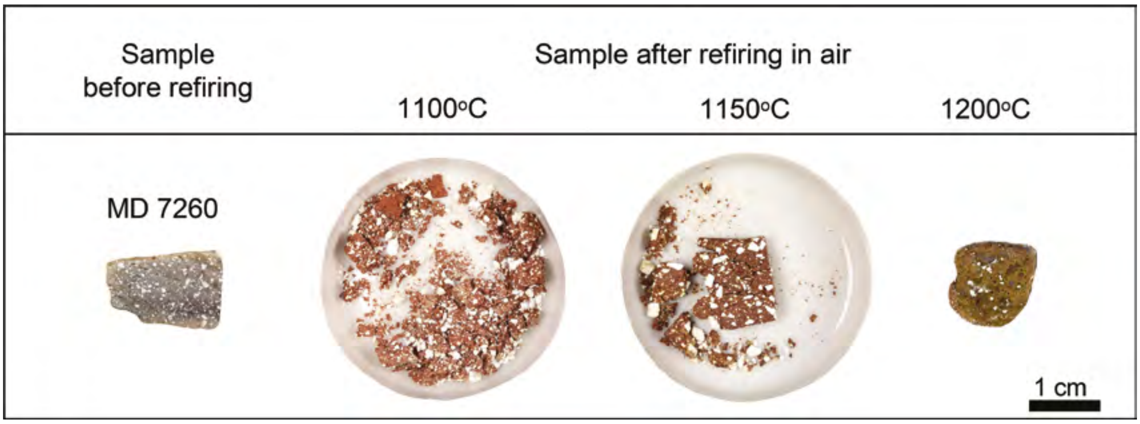

Fig. 5. Samples refired at 1100°C and 1150°C fell to pieces as soon as they had cooled to room temperature (photos M. Baranowski, drawing H. Baranowska).

concentration of strontium (Sr), which indicates that the carbonate grain inclusions were of various origin. Three groups of samples can be identified: the first group has an Sr content of 71–90 ppm (CaO 22–30 wt.%); the second has an Sr content of 117 ppm (CaO 29 wt.%); and the third group has an Sr content of 821 ppm (CaO 32 wt.%). Regardless of differences in Sr content, the samples also differ in their content of elements that are significant in provenance analysis. This means that the analysed fragments were made using various raw materials for the plastic part of the ceramic body. Six groups can be identified based on chemical composition (Tab. 1).

MGR-analysis revealed that the carbonates in sample MD7260[2] not only feature as particles of coarse temper but also as carbonates in the <10 μm fraction, finely distributed in a matrix of non-calcareous iron-rich clay. Sample MD7261[3] was also made from a non-calcareous iron-rich clay, but with few carbonates in the matrix. In contrast, the matrix of MD7262 is slightly coloured by iron compounds after refiring, and carbonates are present not only in coarse fraction as non-plastic temper, but also distributed throughout the matrix. Sample MD7262 differs distinctly from the others because of the colour of its carbonates after refiring at 1200°C (Fig. 6). This sample has a high Sr content (Tab. 1).

In the case of two of the samples which were only refired at 1200°C (MD7264 and MD7266), it is difficult to determine what type the plastic part of the sample represents due to the large number of carbonates.

The results of MGR-analysis and chemical analysis indicate that the samples were made from different ceramic bodies; only two samples (MD7265 and MD7266) belong to one group. These samples could have been made from the same ceramic body in one batch (given that they are not two pieces of the same vessel). No analogy was found for any of the seven analysed samples of pottery among the previously analysed ceramic vessel sherds found at Risan. These samples also exhibit no similarities with basins, bricks (both ancient and modern), Risan-Saliny clay or clay recovered from excavation.

Samples taken from eight amphora sherds underwent both MGR-analysis and chemical composition analysis. Comparison with previously performed analyses[4] revealed that one sample belongs to a group of amphorae tentatively identified as originating from production centre A (MD7332, Tab. 1), two samples belong to a group D-2 (MD7330 and MD7331, Tab. 1) while

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[2] Base sherd, Risan, archaeological season 2006.

[3] Sherd with handle, Risan, archaeological season 2006.

[4] Daszkiewicz, Dyczek, Schneider, Bobryk 2005.

Tab. 1. Results of chemical analysis by WD-XRF, analysis of melted samples after loss on ignition (l.o.i.) at 900°C. Content of major elements calculated to oxides and normalised to 100%.

Lab. No.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	V	Cr	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Pb	l.o.i.
	per cent by weight										ppm														%
Risan Saline - clay																									
MD 7205	61.45	0.81	14.43	7.07	0.15	4.79	6.34	2.31	2.51	0.14	138	405	234	62	91	122	140	38	176	13	324	25	59	19	10.19
brick																									
MD 7256	64.17	0.80	13.93	6.73	0.14	3.92	6.36	1.55	2.27	0.13	100	437	226	70	108	111	148	32	187	13	300	18	74	34	0.49
vessels																									
MD 7260	43.20	0.61	16.93	6.13	0.03	1.65	28.60	0.68	1.89	0.27	116	162	87	58	79	102	110	34	208	20	340	34	70	44	19.32
MD 7262	45.41	0.47	15.53	4.03	0.18	0.96	31.54	0.67	1.06	0.16	97	141	69	56	98	63	814	33	174	16	1575	42	59	26	21.66
MD 7265	46.89	0.53	13.81	6.41	0.01	1.07	29.26	0.71	1.12	0.18	114	325	62	31	46	84	71	18	162	12	165	9	30	30	19.35
MD 7266	46.56	0.53	13.62	6.26	0.01	1.01	30.15	0.61	1.05	0.20	106	330	66	36	47	79	76	14	158	13	194	7	49	29	20.23
MD 7264	46.83	0.50	13.07	6.04	0.02	1.27	29.85	0.75	1.27	0.41	102	336	119	45	68	82	77	26	141	10	278	19	66	26	22.26
MD 7261	52.01	0.51	12.89	6.59	0.01	1.21	24.87	0.72	1.02	0.17	109	490	110	52	43	75	69	21	148	8	241	12	32	28	17.52
MD 7263	50.28	0.57	14.50	7.33	0.11	2.64	22.09	0.82	1.45	0.21	134	419	317	59	85	103	82	25	129	9	282	22	64	29	16.81
amphora group A (Daszkiewicz *et alii* 2007)																									
MD7332	59.78	0.808	17.41	6.76	0.106	3.01	6.87	1.43	2.96	0.87	107	137	77	57	117	142	187	38	211	15	551	34	76	35	6.73
amphora group D-2 (Daszkiewicz *et alii* 2007)																									
MD7330	53.19	0.737	17.11	6.64	0.112	3.11	13.76	0.73	2.16	2.45	79	126	78	70	123	81	242	42	211	16	455	49	76	54	10.19
MD7331	53.54	0.787	18.23	7.32	0.172	3.08	11.21	0.81	2.41	2.44	79	134	77	56	119	99	221	42	206	18	480	30	84	54	9.04
various groups of unknown provenance																									
MD7328	54.24	0.749	17.75	7.08	0.144	3.74	11.94	0.71	2.19	1.45	107	172	98	45	110	81	373	33	167	15	438	37	84	43	5.46
MD7329	51.20	0.702	16.98	6.40	0.120	3.62	15.78	0.72	2.18	2.30	103	148	70	58	117	77	363	40	197	13	527	42	75	49	9.61
MD7333	51.02	0.646	16.21	6.05	0.168	2.66	17.22	0.71	1.98	3.32	67	106	60	59	98	66	393	35	201	13	607	47	76	47	11.48
MD7335	54.42	0.680	16.35	6.59	0.140	3.95	13.76	0.90	2.04	1.18	106	159	92	58	109	66	425	32	156	15	399	7	63	44	3.34
MD7334	49.00	0.599	15.65	5.77	0.143	3.07	20.65	0.65	1.42	3.05	100	139	59	52	87	58	412	37	202	14	479	24	59	31	14.13

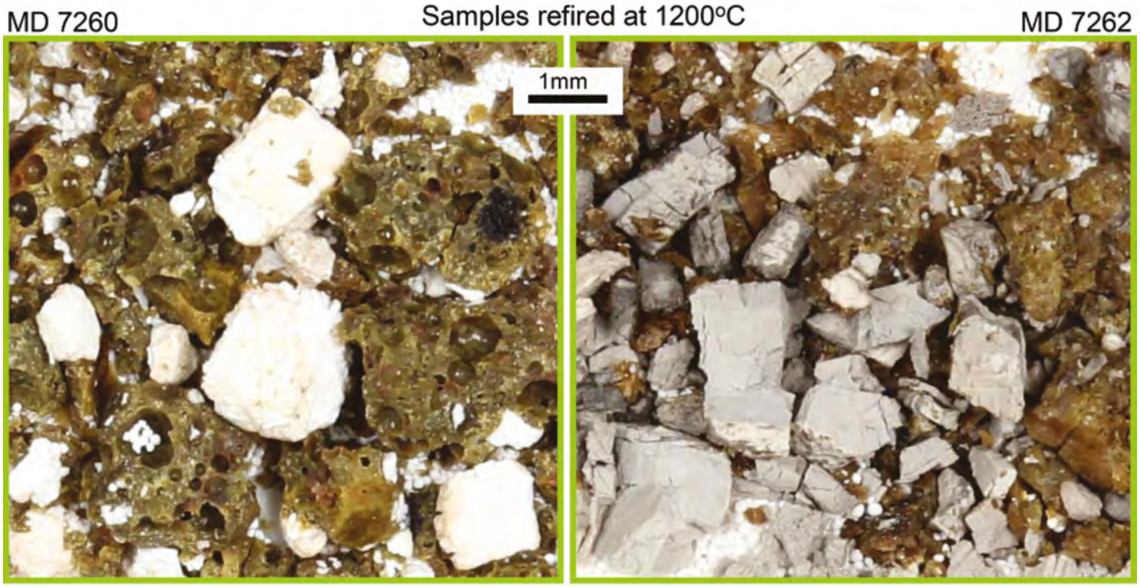

Fig. 6. Samples after refiring at 1200ºC with distinctly different colour of carbonates (photos M. Baranowski, drawing H. Baranowska).

four samples belong to various production groups of Greco-Italic amphorae (Tab. 1). One sample differs markedly from the others (MD7334, Tab. 1), and no analogies could be found for it in either the Schneider/Daszkiewicz database or any published findings. The correlation between the chemical composition of the amphora sherds and the results of residue analysis[5] suggest that this amphora was used to transport garum (as well as six amphorae with high phosphorus content, $P_2O_5 > 1$ wt.%).

The last stage of laboratory studies involved the analysis of three fragments of lining material taken from the wall of a cistern. In two samples, only one thick layer was visible, covered by a very thin white layer (MD7258 and MD7259), while the third fragment (MD7257) featured three readily visible layers (two thick layers covered by a thin white layer, Fig. 7).

Macroscopic analysis revealed that the thick layers in the two-layer samples (MD7258 and MD7259) are composites made by mixing a binding substance with grog.[6] The grog consists mostly of grains measuring up to 5 mm (grains of up to 3 mm predominate), with lime aggregates (mostly up to 3 mm with a few up to 8 mm) and rare inclusions of rounded, gravel-sized quartz (with at least one grain of 8 mm in diameter). The term “lime aggregates” is used even if in reality they consist of lime-derived carbonate aggregates, to be distinguished from original (i.e. geological) carbonates.

In the second and third layer of the three-layer sample (MD7257), grog and lime aggregates are visible, both in the ≤ 3 mm fraction (rare grains of grog up to 5 mm).

A thin white layer visible on the top of all three fragments taken from the cistern is probably plaster (used for coating the walls to make the surface smooth, waterproof or to prepare it for painting).

Theoretically, thick layers in two-layer fragments and a third layer in three-layer fragments with coarse particles of filler should not be called “mortar” or “concrete”. Concrete is a composite made by a binder and a filler in the form of coarse particles (> 5mm fraction), mortar is a composite

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[5] Results of analysis of Ivancea amphorae, project of Prof. M. Meyer FU Berlin, publication in preparation.

[6] Grog = crushed ceramic material: ceramic vessels as well as crushed bricks, tiles.

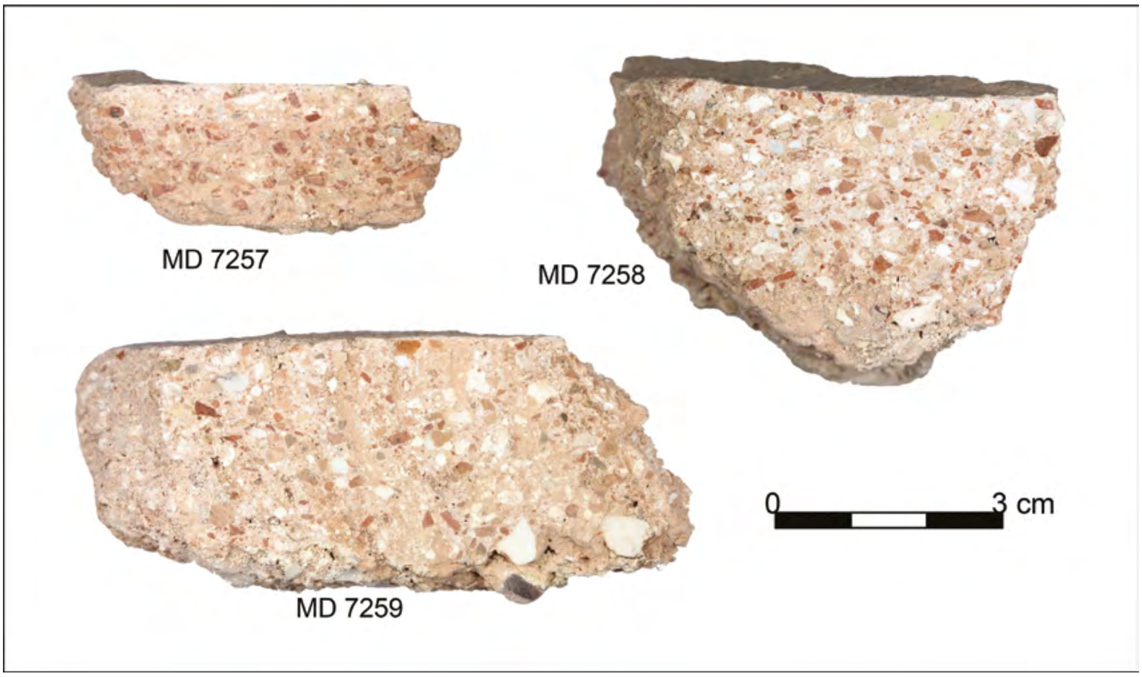

Fig. 7. Samples of lining material taken from a cistern wall (photos M. Baranowski, drawing H. Baranowska).

made by a binder and a filler in the form of small particles (all grains in the < 5mm fraction).[7] The two-layer samples (MD7258 and MD7259) are composites ranging between mortar and concrete—due to negligence or limited technological know-how?

The second and the third layer in the three-layer fragment (MD7257) should be called “mortar” as both layers have particles of filler in the < 5mm fraction.[8]

In spite of differences in the filler, in all cases all layers represent composites with a lime-based binder containing a filler in the form of grog derived from very different ceramic materials and lime aggregates. The texture of these layers is not dense; a lot of small round pores are macroscopically visible. For the thick layers of the two-layer samples, values of apparent density and open porosity were estimated by hydrostatic weighing. In both cases they represent a light mortar with apparent densities of 1.40 g/cm^3 (MD7258) and 1.27 g/cm^3 (MD7259). Open porosity values amount to: 43.7 vol.% (sample MD7258) and 52.76 vol.% (sample MD7259). These estimated values are comparable with the values of the thick layers in samples from Roman cisterns discovered at Uthina, Northern Tunisia.[9]

The analysed composite material was used as a coating to line the cistern, therefore it had to be waterproof. In cisterns and other water installations, filler in the form of grog can be used instead of volcanic ash to produce a waterproof hydraulic mortar (or mixture of grog and volcanic ash). Unfortunately, the samples submitted for analysis were small, and it was not possible to carry out a standard test to determine the degree of water resistance, and nor was a calculation of permeability using the Carman–Kozeny equation performed. However, a water permeability test was conducted on two samples in accordance with the method devised for the

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[7] Hobbs, Siddall 2011.

[8] < 1 mm according some scholars.

[9] Farci, Floris, Meloni 2005.

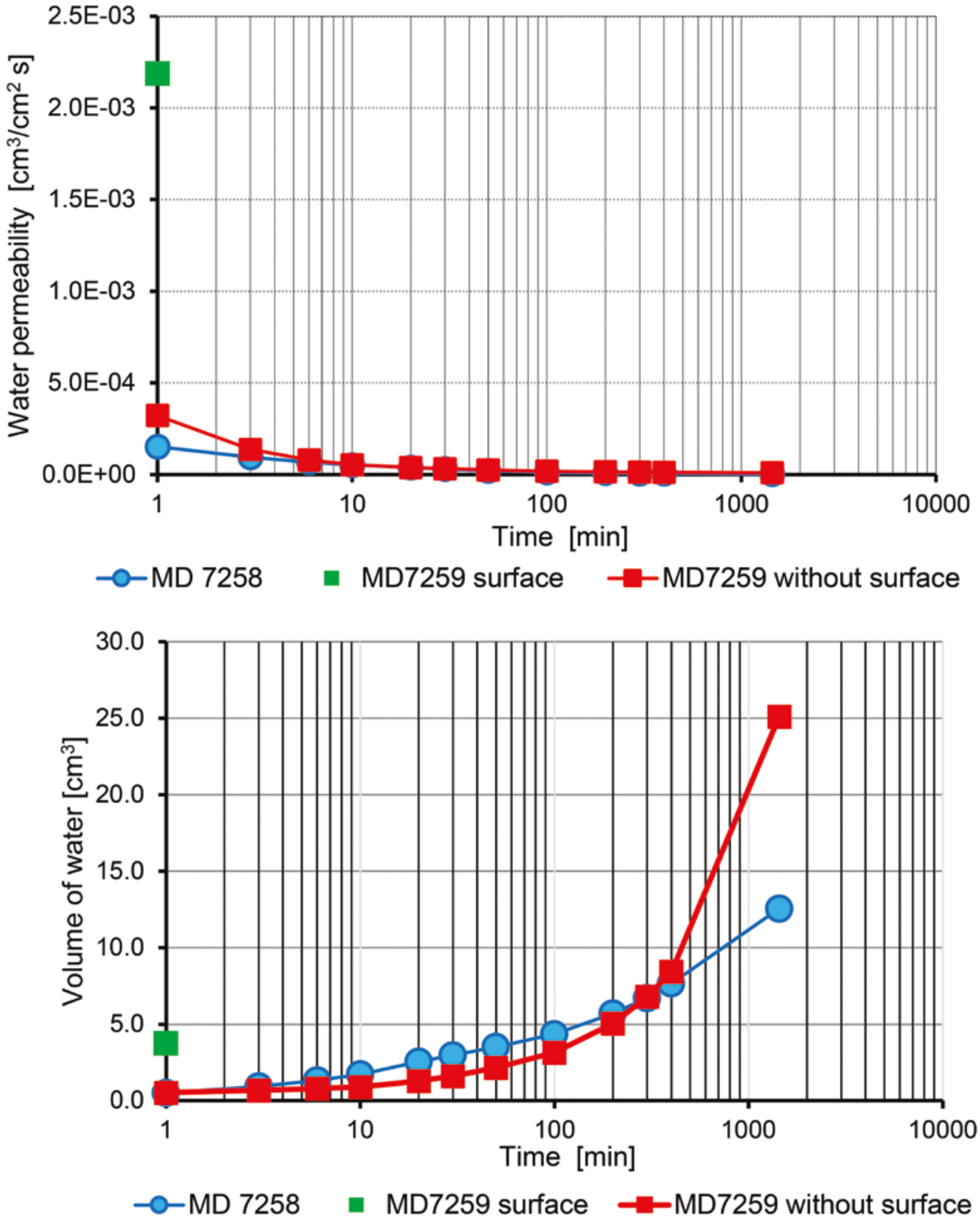


Fig. 8. Permeability test: readings taken for sample MD7258 and sample MD7259.
a) water permeability; b) water volume; sample MD7259: green – water passing through outer part of composite layer (water penetrates into sample through thin white layer); red – water passing through composite without thin white layer (M. Daszkiewicz).

analysis of ancient pottery. Figure 8 shows the readings taken for these samples, water passing through the outer part of the composite layers. Figure 8a shows the water permeability values and Fig. 8b shows the water volume passing through the composite material.

Two measurements were taken before and after removing the very thin white outer layer on sample MD7259. This layer absorbed water so quickly that the measurement had to be stopped before 3 minutes had elapsed (Fig. 8a and 8b; solitary green square). This phenomenon

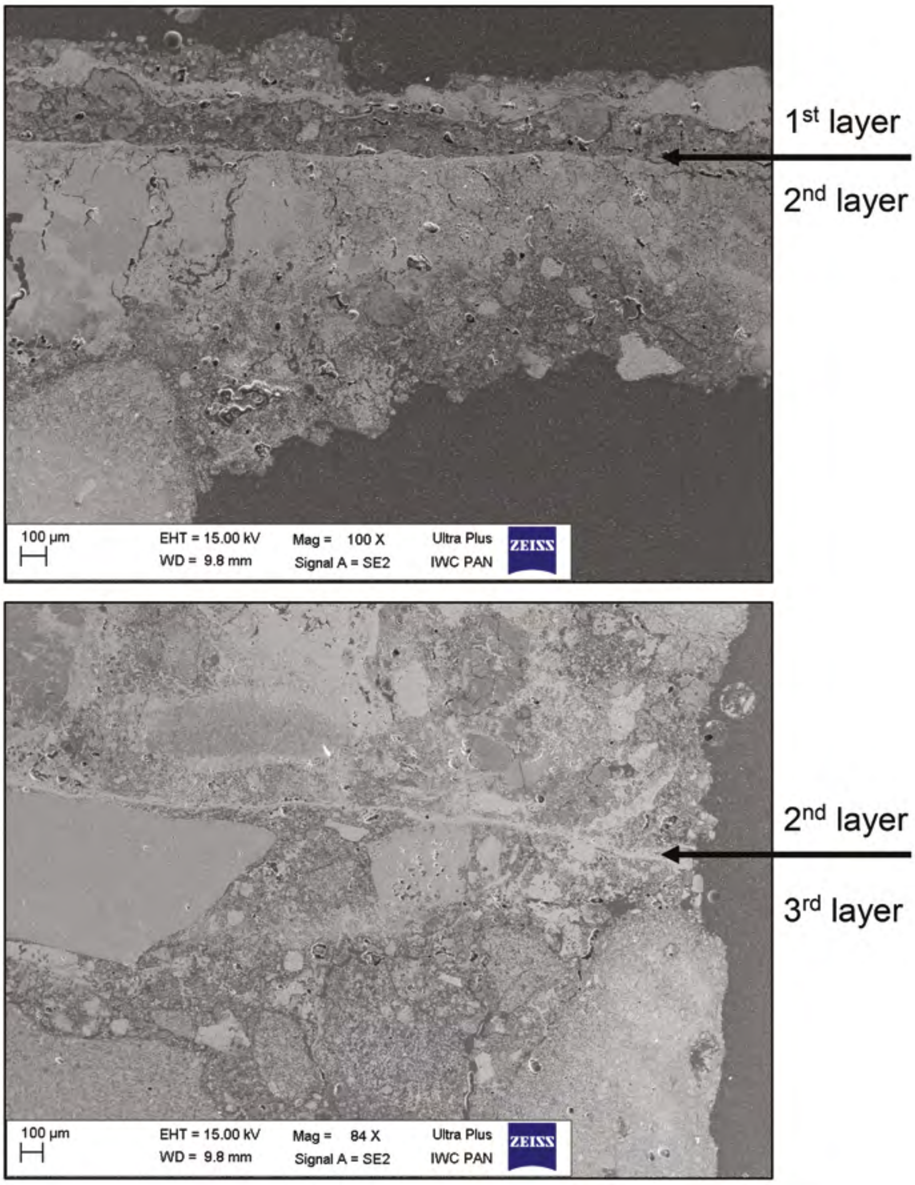
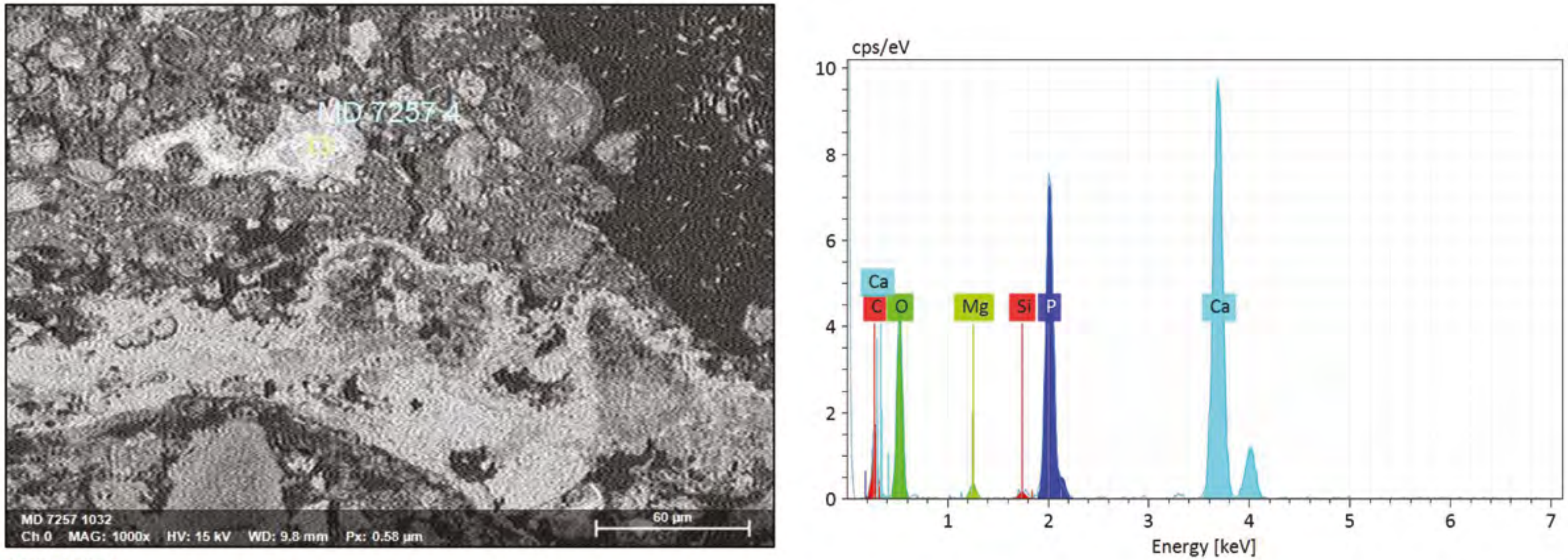


Fig. 9. SEM images of interface between layers (M. Daszkiewicz).

was not observed in sample MD7258. After removing the white layer, water passes through MD7259 at a significantly slower rate than with the layer, and also at a slower rate than noted in sample MD7258. Droplets appear on the outer surface of sample MD7258 after 3 minutes, and after 20 minutes on sample MD7259 while absorbing more than twice the volume of water (Fig. 8b). These results are surprising and were not taken into account in the case of samples taken from the cistern.

The three-layer piece of composite was selected for SEM/EDS analysis and thin-section studies using a polarising microscope. Fig. 9 shows SEM images of the borders between layers. In the first thin layer the binder is whitish in colour. Small fragments of bone were found in this layer (Fig. 10). The second layer (pale beige), in contrast to the third (dark beige) layer, contains more binder than filler and the grog particles are smaller. In the second layer, white lime inclusions dominate over reddish-brown grog inclusions in the filler.



MD 7257 4

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	Comp.	Sto. Norm. [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Oxygen	8	3556	35.13	38.56	59.23		0.00	6.00	17.07
Phosphorus	15	8502	13.95	15.31	12.15	P2O5	35.08	0.60	4.31
Calcium	20	14883	41.16	45.18	27.70	CaO	63.21	1.33	3.23
Magnesium	12	349	0.61	0.67	0.68	MgO	1.11	0.10	15.89
Silicon	14	166	0.25	0.28	0.24	SiO2	0.59	0.07	28.17
		Sum	**91.10**	**100.00**	**100.00**		**100.00**		

Fig. 10. SEM image and EDS results. Small fragments of bone visible (M. Daszkiewicz).

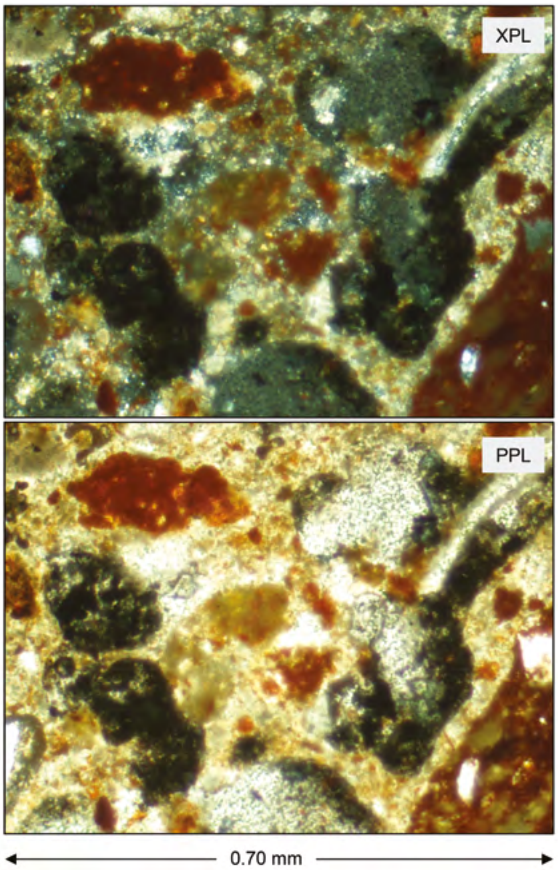


Fig. 11. Thin section: XPL micrograph (top) and PPL micrograph (bottom). Fine to very coarse reddish-brown grog and white lime inclusions as well as fine carbonized particles visible (M. Daszkiewicz and G. Schneider).

Fine to very coarse reddish-brown grog and white lime inclusions (grains of grog are more common) as well as fine carbonized particles (Fig. 11; remains of the fuel used for burning the lime?) were observed in the third layer.

The results of SEM/EDS analysis of lime-saturated binders in the second and third layers reveal a high concentration of Ca (95–80 wt.% and 83–67 wt.% of CaO respectively) with Si, Al and Mg making up the rest of the chemical composition. In the second layer some grains of quartz (0.08 mm) with reactions rims are observed in the binder. The high concentration of Mg points to the use of Mg-rich calcium carbonates (but not dolomite) for preparing slaked lime. The reactive pozzolanic material[10] in the case of the analysed samples from the cistern in Risan was ceramic (grog).

It is evident from both thin-section studies and SEM/EDS analysis that at least three types of grog were used. Under the polarizing microscope, apart from grog fragments, a filler in the form of carbonate rocks was also observed. Fig. 12 shows grog particles: with biogenic carbonates

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[10] Artioli, Secco, Addis 2019, p. 170: "*The reactive pozzolanic material may be natural or synthetic silica glass, volcanic ash, radiolarite or diatomaceous earth, phytoliths, ceramics, clay, metallurgical slags, or any other reactive aluminosilicate compound*".

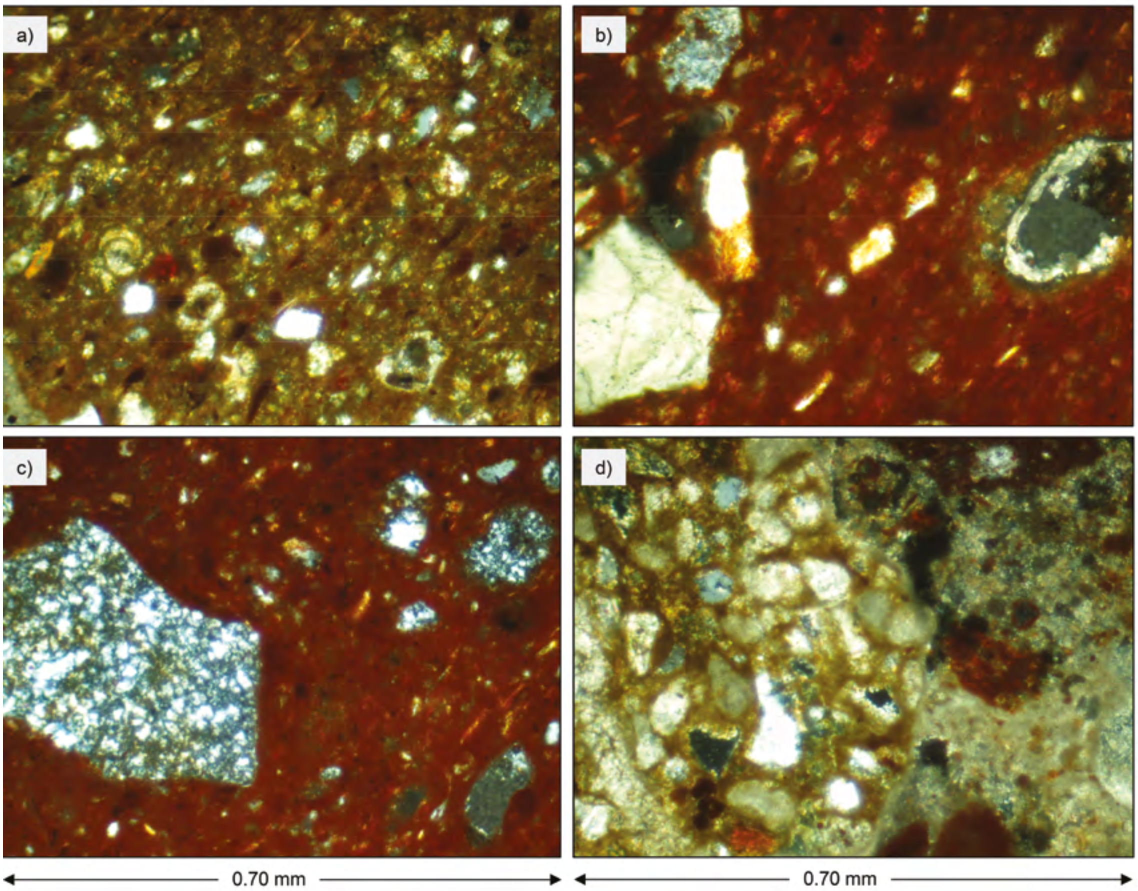

Fig. 12. Thin sections, XPL. Grog particles: a) with biogenic carbonates; b) with a large quartz crystal and hole left by a carbonate; c) with inclusions of flint; d) inclusion of rock fragments consisting of carbonate sand (Daszkiewicz and G. Schneider).

(Fig. 12a); with a large quartz crystal and hole left by a carbonate (Fig. 12b); and with inclusions of flint (Fig. 12c) and added as a filler, not for lime burning, a singular inclusion of rock consisting of carbonate sand (Fig. 12d). The SEM image of the three different grog particles and the element mapping for this area (elements used: Si, Ti, Al, Fe. Mn, Mg, Ca, Na, K, P, Cr, Ni, V, Zr) are shown in Fig. 13. The mapping of individual elements is shown in Fig. 14. EDS analysis, which established the chemical composition of the mortar samples, revealed that one type of grog came from a region where clay with a high magnesium content occurs. This composition is similar to that of black-coated ceramic vessels found at Risan and identified as pottery from workshops in present-day Albania. It is possible that sherds of this pottery may have been used as grog; however, it seems more likely that other products were used which have not previously been analysed, for example common wares or ceramic building materials made at a workshop within the same production area.

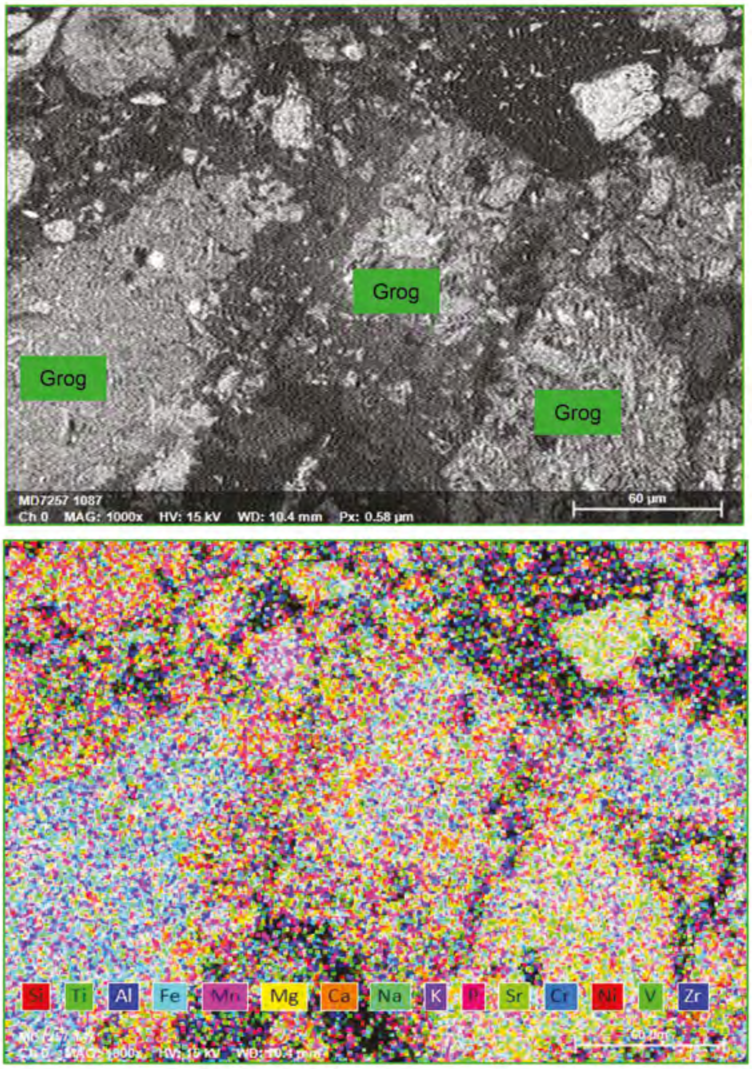

Fig. 13. SEM image of three grog particles and element mapping for this area; elements used: Si, Ti, Al, Fe. Mn, Mg, Ca, Na, K, P, Cr, Ni, V, Zr (M. Daszkiewicz).

Conclusions

Both the second and third layers of sample MD7257 are composites with a lime-based binder containing a filler in the form of grog derived from very different ceramic materials and in the form of some carbonate rocks as well as lime aggregates. Both layers can be called mortar. As for the three-layer sample, a water permeability test could not be done and it remains unclear whether the second layer was applied during the repair/remodelling of the cistern or whether it was a feature of the cistern's original structural design and had an impact on its water resistance. The differences in mortar technology (MD7257 vs. MD7258 and MD7259) could express the different know-how of engineers.

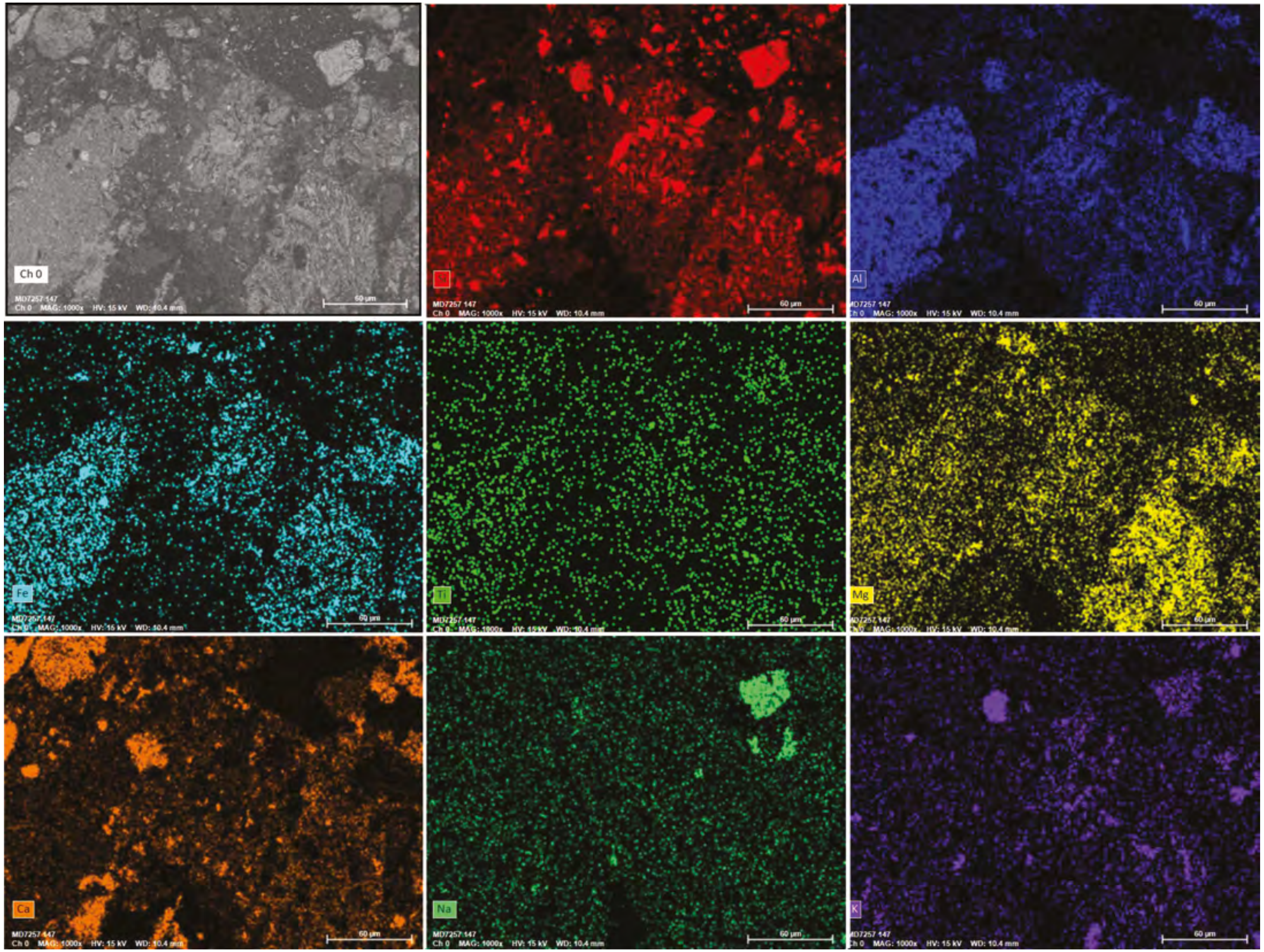

Fig. 14. Mapping of individual elements (M. Daszkiewicz).

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Małgorzata Daszkiewicz
Freie Universität Berlin
Institut für Prähistorische Archäologie
and
ARCHEA Warszawa
m.dasz@wp.pl
orcid.org/0000-0002-8735-0649