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TELL RAD SHAQRAH

CHEMICAL AND MINERALOGICAL COMPOSITION AND SOME TECHNOLOGICAL PARAMETERS OF MEDIUM-COARSE WARE FROM TELL RAD SHAQRAH

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This paper is the next in a series of reports on the results of a combined chemical, mineralogical and technological study of North Mesopotamian pottery of the Early Dynastic period. The samples derive from excavations on Tell Rad Shaqrah in northeastern Syria.[1]

The assemblage of pottery samples selected for laboratory analyses represents all kinds of fabrics from the site, as well as examples of the different categories of wares selected by archaeologists, such as: fine ware, medium-coarse ware, kitchen ware, storage vessels and Metallic Ware. This paper is devoted to a presentation of the results of laboratory analyses of ten samples of the medium-coarse ware. The objective of the

[1] In 1991-1995, Tell Rad Shaqrah was excavated by a Polish mission headed by Prof. Piotr Bieliński.

The first article from this series was published in *PAM* 1995 (1996) by M. Daszkiewicz and G. Schneider 1996. Other references:

Daszkiewicz M., Schneider G., Raabe J. (1995), Cypriot Sigillata and Cypriot Red Slip Wares – a comparison of technological and chemical analysis and of thin section studies, in: B. Fabbri, *Fourth Euro Ceramics, The Cultural Ceramic Heritage,* vol. 14, pp. 151-171.

Daszkiewicz M., Schneider G. (1996), Chemical composition of North Mesopotamian Early Dynastic period ceramics from Tell Rad Shaqrah, *PAM* VII, 1995 (1996), Warsaw 1996, pp. 171-175.

Daszkiewicz M., Raabe J., Jelitto J. (1996), Investigations on a marly clay sample from Wadi Qubur in Palmyra [in:] *International Colloquium Palmyra and the Silk Road, Palmyra*, 7-11 April 1992, Damascus 1996, pp. 99-121.

examinations was to compare bodies[2] and the technological aspects of the ware.

METHODS

Refiring

Thin slides cut from each of the sherds were refired in an electrical laboratory chamber furnace in six temperatures (600, 700, 800, 900, 1000 and 1150°C). The refiring was done in air with a heating rate of 200°C/h and 1 h soaking time at peak temperature. This simple analysis permits a rough estimation of the original firing temperatures and a classification of the sherds according to the thermal reaction observed, which is dependent on the composition of the raw materials including the chemical and mineralogical composition of the matrix, the grain-size distribution and the preparation of the body. In this way, different color and sintering distinguishes different raw materials.

Chemical analysis

A wavelength-dispersive X-ray fluorescence analysis was employed to determine the chemical composition of the clay of the body: the phosphorus content and a rough estimation of sulfur and chlorine, as well as fifteen trace elements.[3] Samples were pulverized after removing the outer surfaces and cleaning with distilled water in an ultrasonic device. Further preparation was done by melting the powdered and ignited samples with a lithium-borate mixture and casting to small discs for measurement. Loss of ignition was estimated after refiring in air at 900°C (heating

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[2] The term "body" refers to material for pottery production (pottery = shaped and fired body). The raw material for the body can be taken from a geological source and used without any special treatment or else it requires special treatment, such as e.g.: washing, weakening, mixing with other plastic raw material, adding of special temper.

[3] The analyses were made by Gerwulf Schneider, *Arbeitsgruppe Archaeometrie*, Freie Universität Berlin.

Table 1 . Results of chemical analysis by WD-XRF.
Analysis of ignited samples, major elements normalized to a constant sum of 100%.
LOI - loss of ignition, TOTAL - the original total, elements in brackets are determined with lower precision.
A - major elements (% by weight)

Sample No.	SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5	(S)	(Cl)	LOI	TOTAL
MD 2109	54.39	0.90	13.59	6.67	0.120	4.36	15.79	1.18	2.48	0.53	0.51	0.01	6.66	99.60
MD 2110	57.15	0.74	12.23	5.55	0.106	4.43	15.92	1.19	2.12	0.56	0.18	0.00	3.99	99.52
MD 2111	50.04	0.80	13.43	6.56	0.105	5.24	20.20	1.11	2.32	0.21	1.54	0.01	5.32	98.39
MD 2112	54.81	0.79	13.41	6.31	0.120	5.56	15.31	1.42	1.92	0.35	0.08	0.01	1.82	100.52
MD 2113	50.78	0.75	13.21	6.43	0.098	5.37	20.34	1.34	1.43	0.26	0.56	0.01	5.40	99.53
MD 2114	54.79	0.77	13.46	6.20	0.093	4.06	16.46	1.49	2.18	0.50	0.50	0.01	4.05	98.16
MD 2115	58.79	0.77	13.52	6.18	0.101	4.70	11.64	2.08	2.09	0.13	0.33	0.05	8.12	99.93
MD 2116	51.38	0.84	13.75	6.84	0.117	4.74	18.59	1.01	2.40	0.34	0.30	0.01	4.63	99.94
MD 2117	58.28	0.72	12.02	5.42	0.096	4.27	15.56	1.32	2.07	0.25	0.25	0.00	5.67	99.72
MD 2118	50.86	0.77	13.00	7.26	0.115	7.12	16.75	1.15	2.73	0.24	1.00	0.00	6.70	99.10

B - trace elements (ppm)

Sample No.	V	Cr	Ni	(Cu)	Zn	Rb	Sr	Y	Zr	(Nb)	Ba	(La	Ce	Pb	Th)
MD 2109	130	404	159	37	73	58	485	23	159	16	314	20	55	17	12
MD 2110	108	368	138	34	49	54	838	19	161	15	362	16	48	<10	10
MD 2111	116	261	152	37	51	47	637	20	156	17	505	<10	55	12	<10
MD 2112	118	273	162	39	68	43	560	21	171	19	301	28	55	20	11
MD 2113	132	198	138	43	70	27	918	20	144	14	430	17	27	12	11
MD 2114	136	226	118	36	42	38	493	19	133	13	443	15	39	10	<10
MD 2115	131	269	114	42	59	35	1236	16	142	11	439	<10	37	14	<10
MD 2116	126	292	153	36	61	49	517	22	156	17	576	22	37	13	<10
MD 2117	119	348	133	33	45	50	1150	20	153	14	258	14	45	14	11
MD 2118	119	472	253	35	66	57	406	19	132	16	272	10	38	12	10

rate 200°C/h, 1 h soaking time at peak temperature). Results for the major elements, with the exception of sulfur, are normalized to a constant sum of 100%.

Thin-section studies

Thin-sections were examined on a Carl Zeiss Jena polarizing Amplival type microscope. Non-plastic inclusions and the image of the matrix can be used for a classification of potsherds. Quantitative mineralogical composition was determined using the point-counting method (c. 1000 counts per sample). Grain-size distribution (granulometric analysis) was determined by area-counting.

Measurement of ceramic properties

Open porosity, water absorption and apparent density were determined before and after refiring. Small parts of potsherds were refired in a laboratory chamber furnace in 12 temperatures in a range from 400 to 1200°C. Refiring was carried out as described above. Ceramic properties were measured using a hydrostatic weighing method. This is another means of characterizing groups based on different ways of body preparation (Daszkiewicz *et al*. 1995) and estimating original firing temperatures.

RESULTS

The results of this study can be summarized as follows: All of the investigated samples were made from a calcium-rich clay, the CaO contents varying from 11% to 20% (table 1). Refiring experiments at 1150°C indicate clearly that all the investigated samples were made from marly clays more or less colored by iron compounds. Calcium (Ca) is present in the samples as very fine calcite dispersed in the matrix and/or as non-plastic inclusions of calcite of larger size or aggregates of marl. In a low-fired sherd (MD 2115), the calcium content derives from primary carbonates, dispersed in the marly clay matrix, and

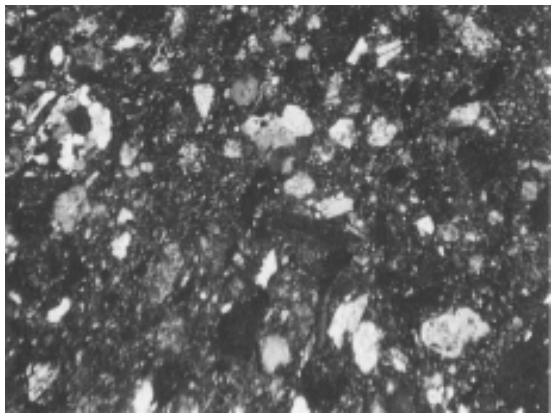

Fig. 1. Sample MD 2115. Marly clay matrix slightly thermally changed; clastic material: quartz, coarse and cryptocrystalline carbonates, opaque mineral and rock fragments. The sample was originally fired at 800-850°C.
Microphotos, XPL. Bar represents 200μm.

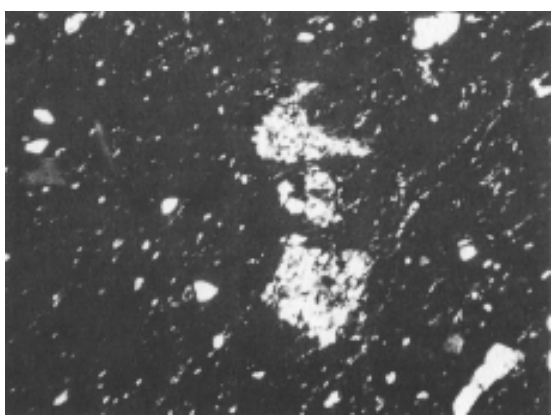

Fig. 2. Sample MD 2112. The matrix is isotropic, strongly changed thermally; clastic material: quartz, some pores with rims from cryptocrystalline carbonates, rock fragments. The sample was originally fired at 1000-1050°C. Microphotos, XPL. Bar represents 200μm.

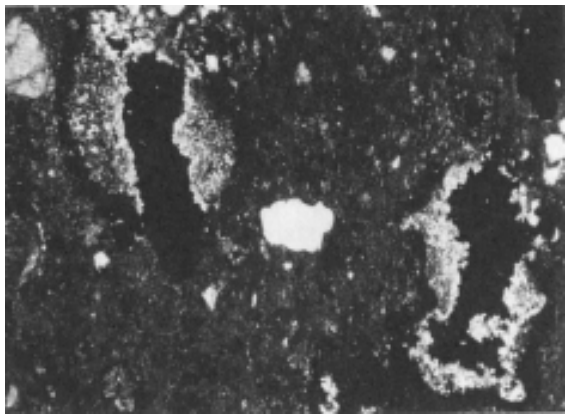

Fig. 3. Sample MD 2111. Marly clay matrix thermally changed; clastic material: quartz, pores with wide rims from cryptocrystalline carbonates. The sample was originally fired at 950-1000°C. Microphotos, XPL. Bar represents 200μm.

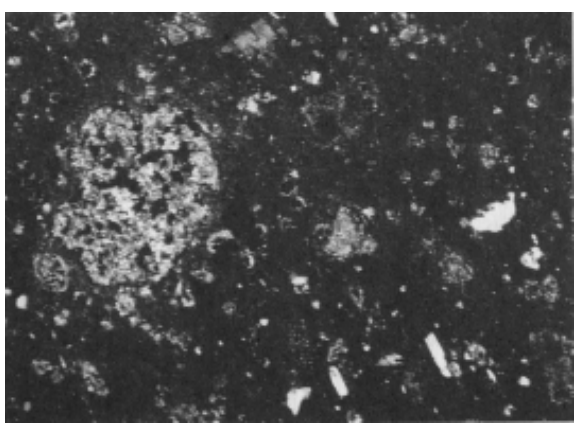

Fig. 4 Sample MD 2118. Marly clay matrix thermally changed; clastic material: quartz, pores nearly all filled by cryptocrystalline carbonates. The sample was originally fired at 900-950°C. Microphotos, XPL. Bar represents 200μm.

from coarse crystalline carbonate compounds of the non-plastic part of the body (beside some cryptocrystalline carbonates after recarbonisation and secondary calcite deposited during burial; fig. 1). In a high-fired sherd (MD 2112), the matrix is isotropic, strongly changed thermally, and the calcium is built-in the structure of calcium silicates or calcium aluminum silicates (fig. 2). Beside this, some pores with rims from cryptocrystalline secondary carbonates can be observed. In the remaining samples, coarse crystalline carbonates were not observed. Cryptocrystalline carbonates are only detected as small non-plastic particles, as rims inside pores or locally dispersed in the matrix. The matrix of particular samples represent different stages of the thermal transformation (figs 3 and 4).

Thin-section studies generally revealed very similar recipes of the clay preparation for all the samples. The matrix covers 55 to 65 percent of the volume (table 2a).

Grain fraction [0.01-0.1mm] constituting 92-96% of the whole predominates. In sample MD 2115 alone is the percentage of this fraction below 90% (88%) due to the fact that larger grains of carbonates are still observed because of the low original firing temperature. More than 10% (12%) of the whole was represented here by the grain fraction [0.1-0.5mm]. Grains with diameters larger than 0.5 mm, consisting of marly clay aggregates, are found only in a few samples. These represent not temper, but a not very well homogenized body.

Non-plastic components in all the samples are dominated by quartz (tables 2a and 2b). It can be observed in fractions below and above 0.1 mm. Muscovite, biotite, pyroxenes and amphiboles are only found in the fine fraction [0.01-0.1mm] with the exception of the low fired sample MD2115 in which micas are larger than O.lmm. In quantitative estimation (tables 2a and 2b), marly clay inclusions, which can be observed in all the samples, are counted as rock fragments. Beside them, sedimentary rock fragments, such as cryptocrystalline silica and fragments of magmatic rocks (quartz + micas)

A

Sample No.	Matrix	Clastic material									
		Q	Pl	Af	Cc	Bio	Mus	Px	Amf	Om	Rf
	% by volume										
MD 2109	59.3	21.3	2.0	1.8	5.3	2.1	2.4	0.7	0.3	1.1	3.8
MD 2110	65.3	23.3	1.4	0.6	3.5	0.5	0.4	-	-	0.9	4.1
MD 2111	62.4	27.0	0.5	0.4	1.5	0.9	0.7	-	-	2.7	3.9
MD 2112	60.8	29.5	0.8	2.1	0.8	1.2	1.5	-	-	0.8	2.3
MD 2113	62.0	25.0	0.9	0.7	2.8	1.0	0.5	-	-	2.6	4.6
MD 2114	59.1	26.8	1.1	0.4	2.4	0.4	0.9	-	-	3.0	5.9
MD 2115	56.2	24.3	1.2	1.0	5.2*	1.7	1.9	0.1	0.2	3.6	4.6
MD 2116	61.5	23.4	0.4	0.3	4.9	1.3	1.1	0.3	0.2	1.1	5.5
MD 2117	54.7	26.2	0.4	0.9	4.1	1.0	1.0	0.2	-	1.9	9.6
MD 2118	58.8	20.2	2.1	1.1	5.3	0.9	1.1	0.5	0.3	2.0	7.6

B

Sample No.	Clastic material (clastic material equal 100%)									
	Q	Pl	Af	Cc	Bio	Mus	Px	Amf	Om	Rf
	% volume									
MD 2109	52.3	4.9	4.3	12.9	5.1	5.9	1.6	0.8	2.7	9.4
MD 2110	67.2	4.1	1.8	10.0	1.5	1.1	-	-	2.6	11.8
MD 2111	71.8	1.3	0.9	4.1	2.5	1.9	-	-	7.2	10.3
MD 2112	75.4	2.1	5.5	2.1	3.0	4.0	-	-	2.1	5.8
MD 2113	65.7	2.2	1.9	7.4	2.6	1.3	-	-	6.7	12.2
MD 2114	65.4	2.7	1.1	5.9	1.1	2.1	-	-	7.2	14.5
MD 2115	55.5	2.8	2.4	11.8*	3.8	4.3	0.2	0.5	8.3	10.4
MD 2116	60.7	1.1	0.8	12.8	3.3	2.8	0.8	0.6	2.8	14.2
MD 2117	57.8	0.9	2.0	9.0	2.2	2.2	0.4	-	4.3	21.1
MD 2118	49.0	5.2	2.7	12.9	2.2	2.7	1.1	0.8	4.9	18.4

Q - quartz
Pl - plagioclase
Af - alkali feldspars
Cc- cryptocrystalline carbonates
* - coarse and cryptocrystalline carbonates
Bio - biotite
Mus - muscovite
Px - pyroxenes
Amf - amphiboles
Om - opaque minerals
Rf - rock fragments

Table 2. Results of planimetric analysis. Point-counting, c. 1000 counts per sample.

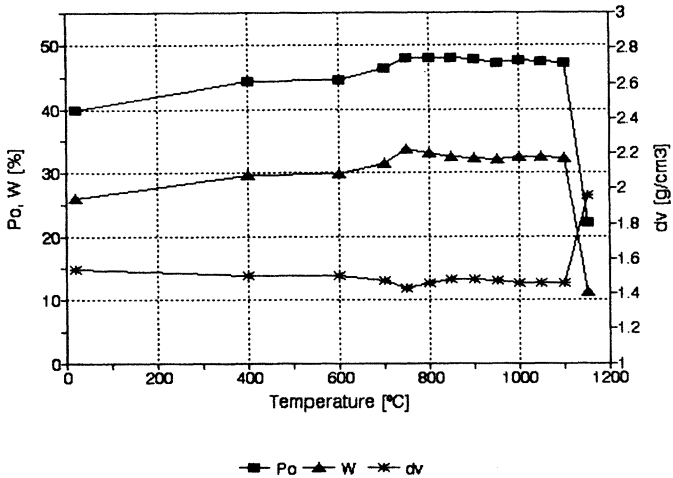

Fig. 5. Sample MD 2115. Open porosity (Po), water absorption (W) and apparent density (dv) versus temperature. The sample was originally fired at 800-850°C.

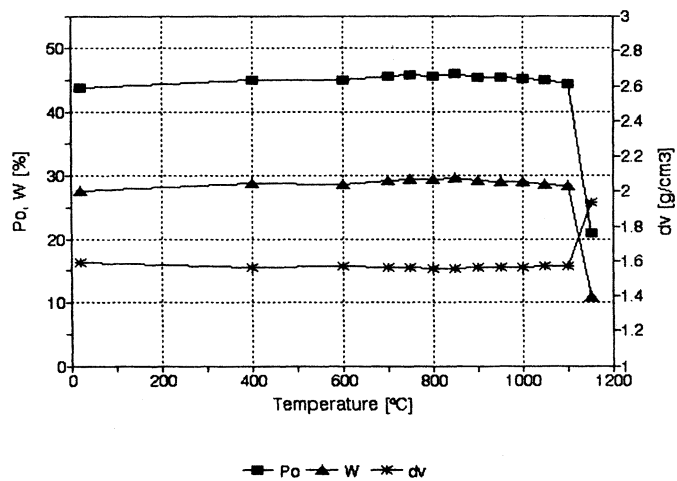

Fig. 6. Sample MD 2112. Open porosity (Po), water absorption (W) and apparent density (dv) versus temperature. The sample was originally fired at 1000-1050°C.

(quartz + micas + feldspar) (quartz + feldspar) (quartz + biotite + plagioclase + opaque minerals) (feldspar + quartz + opaque minerals) were observed.

The results of three independent analyses (retiring, thin-section study and ceramic properties measurement) permit the following ranges of the original firing temperature to be inferred:

800-850°C for sample MD 2115 (fig. 5)

900-950°C for samples MD 2109, MD 2117 and MD 2118

950-1000°C for samples MD 2110, MD 2111, MD 2113, MD 2114 and MD 2116

1000-1050°C for sample MD 2112 (fig. 6)

All the samples are characterized by very high open porosity covering the range between 34% and 49%. After refiring at 1150°C, the samples show different degrees of density, which is not only connected with the properties of the raw material, but also with the way in which the clay was prepared. Open porosity is within the range from 4% to 35% (table 3). Such big differences in open porosity are hard to explain by the small differences in the composition of the clay alone. It may be supposed, therefore, that samples MD 2110, MD 2112, MD 2113, MD 2115 and MD 2118 were prepared intentionally to make the vessels porous. Measuring the water permeability could provide support for this suggestion.

The chemical composition of the investigated samples is generally similar, but bearing in mind the results of the refiring experiments, it may be concluded that samples MD 2109, MD 2115 and MD 2118 are different from the rest (and from each other, too). Two samples (MD 2115 and MD 2117) are characterized by a higher strontium content, which need not be an indication of a different primary carbonate, but could be a secondary effect of deposit conditions. All the samples could have been made from the same raw material, taking into account the natural variation of the composition.

Sample No.	Temperature [°C]												
	20	400	600	700	750	800	850	900	950	1000	1050	1100	1150
	Open porosity [%]												
MD 2109	36.5	43.1	42.9	44.4	45.7	45.5	47.4	46.5	46.4	46.7	46.6	45.8	6.2
MD 2110	48.0	50.4	50.3	51.9	52.4	52.5	52.8	52.2	52.2	51.8	51.8	51.7	28.2
MD 2111	36.9	41.6	42.8	46.0	47.6	49.1	49.5	49.1	49.9	50.1	50.6	50.6	9.0
MD 2112	43.7	44.9	44.8	45.6	45.8	45.5	45.9	45.4	45.3	45.2	44.8	44.4	20.9
MD 2113	48.4	51.2	51.7	53.3	54.8	54.9	58.0	55.2	55.1	55.0	55.2	55.1	35.3
MD 2114	48.7	52.7	52.9	54.3	54.4	54.4	54.9	54.4	54.4	54.2	54.0	53.7	10.0
MD 2115	40.0	44.4	44.6	46.3	48.1	47.9	48.1	47.8	47.2	47.5	47.4	47.2	22.1
MD 2116	49.1	52.3	52.8	54.1	54.4	54.6	55.1	55.0	55.6	55.8	55.6	55.5	4.1
MD 2117	37.9	40.3	40.6	43.0	44.8	45.2	46.8	45.5	45.2	45.8	45.9	45.3	12.6
MD 2118	33.9	37.7	38.9	41.9	44.3	45.3	46.7	46.0	46.8	46.8	47.1	47.2	30.5
	Apparent density [g/cm3]												
MD 2109	1.66	1.57	1.58	1.53	1.53	1.52	1.51	1.52	1.52	1.49	1.50	1.52	1.89
MD 2110	1.42	1.38	1.37	1.36	1.35	1.34	1.34	1.35	1.35	1.35	1.35	1.35	1.83
MD 2111	1.59	1.54	1.52	1.47	1.46	1.46	1.45	1.45	1.45	1.45	1.45	1.46	2.16
MD 2112	1.59	1.56	1.57	1.56	1.56	1.55	1.55	1.56	1.56	1.56	1.57	1.57	1.94
MD 2113	1.43	1.41	1.42	1.36	1.35	1.34	1.36	1.34	1.33	1.33	1.33	1.33	1.77
MD 2114	1.38	1.33	1.31	1.30	1.30	1.29	1.29	1.30	1.30	1.30	1.30	1.32	1.82
MD 2115	1.54	1.50	1.50	1.47	1.43	1.46	1.48	1.48	1.47	1.46	1.46	1.46	1.96
MD 2116	1.36	1.31	1.30	1.28	1.27	1.27	1.27	1.27	1.27	1.27	1.28	1.30	1.92
MD 2117	1.71	1.65	1.64	1.63	1.60	1.58	1.56	1.57	1.57	1.56	1.55	1.56	2.09
MD 2118	1.59	1.55	1.54	1.48	1.47	1.47	1.46	1.46	1.46	1.46	1.46	1.47	1.86

Table 3. Ceramic properties (open porosity and apparent density) before and after refiring in air.

In one case only, the sample originally fired in the lowest temperature, 0.05% of Cl is detected in the chemical analysis, in contrast to the rest of the samples where the chlorine contents is below 100 ppm. Even if it is kept in mind that the chemical analysis was made on ignited samples, the result provides grounds for the assumption that the ancient potters used NaCl (salty make-up water) to make such marly clays workable (Daszkiewicz *et al*. 1996).

CORRELATION OF SAMPLE NUMBERS

Sample number	Inventory number
MD 2109	RS'94D-94
MD 2110	RS'94B1-122
MD 2111	RS'94C85
MD 2112	RS'93A4-6-3
MD 2113	RS'94D-87
MD 2114	RS'93Bl-75
MD 2115	RS'94B1-144
MD 2116	RS'93B2-61
MD 2117	RS'94B3-73
MD 2118	RS'94B3-75