Małgorzata Daszkiewicz, Gerwulf Schneider, Marcin Baranowski, David Petrut,
Viorica Rusu-Bolindeț & Nicoleta Man

MOESIAN AND DACIAN SIGILLATA – EXPLORING REGIONAL PATTERNS

A methodological approach using chemical analysis by WD-XRF and p-ED-XRF

Chemical analysis by wavelength-dispersive X-ray fluorescence (WD-XRF) was used to establish reference groups for Moesian sigillata produced in Butovo, Pavlikeni and Novae in present day Bulgaria. Sigillata finds from Dacian sites (Buciumi, Brâncoveneşti) were compared. Long-distance traded imports were easily identified as coming from Gaul (Lezoux, Les Martres de Veyre, La Graufesenque). The rest of the finds and ten samples of local sigillata from Dacia (Micăsasa, Cristeşti) could not be distinguished so easily by chemical analysis. Multivariate methods yielded ambiguous results and therefore in publications they should not replace the original analysis results, as it is only the latter which allow the interpretation of data to be verified, e.g. by taking possible alteration effects into account. Finally, the finds could not be attributed securely to any of the regional workshops in Moesia or Dacia. More analyses are necessary to establish secure reference groups. With all samples the use of portable XRF was tested. This method could be very important for future studies of museum objects.

1. Reference groups for pottery from Butovo and Pavlikeni in *Moesia*

To determine the provenance of sherds, e.g. by using chemical analyses, some preconditions are essential:

– the differences between groups must be larger than the differences within one group of samples,
– the data must be precise and accurate,
– the analysis must include as many elements as possible (a minimum of about 15 chemical elements is recommended),
– secure reference groups must be available for comparison and theoretically all hypothesized provenances must be checked,
– chemical alteration effects must be recognized and taken into account,
– it must be borne in mind that the interpretation of chemical data often needs additional methods, e.g. to distinguish calcium in the matrix from calcium in added temper.

Reference groups for sigillata products made at the Moesian sites of Butovo and Pavlikeni have been determined by wavelength-dispersive X-ray fluorescence analysis (WD-XRF), MGR-analysis[1] and thin-section studies, and this pottery can clearly be distinguished from sigillata made in Novae and also from all four groups of Pontic Sigillata produced in SE-Crimea and other as yet unidentified locations[2]. Four reference groups characterize the sigillata products of Butovo and Pavlikeni: products of Butovo (BRG1) are made from calcareous clay with Rb higher than 145 ppm, products from Pavlikeni are made from different clay with higher Ca, Sr and lower Rb (**fig. 1 left**). Three groups of products from Pavlikeni (PRG1, PRG2[3], PRG3) can be distinguished primarily by the Si, Ca and Sr contents (**table 1**). The difference is also seen in thin sections and is confirmed by MGR-analysis. The three different compositions possibly represent different layers of the same clay bed and are mainly connected with different amounts of fine quartz.

All samples from which the reference groups were defined were also analysed using portable energy-dispersive X-ray fluorescence (pXRF). The data used were averages of at least three independent measurements on fresh fractures of each sherd[4]. If the most reliable elements Rb, Sr and

[1] M. Daszkiewicz/G. Schneider, Klassifizierung von Keramik durch Nachbrennen von Scherben. Zeitschr.Schweizerische Arch. u. Kunstgesch. 58, 2001, 25–32; M. Daszkiewicz, Ancient pottery in the laboratory – principles of archaeological investigations of provenance and technology. Novensia 25 (Warszawa 2014) 177–197; M. Daszkiewicz/G. Schneider, Analysis of chemical composition of ancient ceramics. Novensia 25 (Warszawa 2014) 199–206.

[2] M. Daszkiewicz/E. Bobryk/G. Schneider, Some aspects of composition, technology and functional properties of Roman and Early Byzantine pottery from Novae (Bulgaria). Novae 8 (Poznan 2006) 189–214; M. Daszkiewicz/G. Schneider, Naturwissenschaftliche Untersuchungen kaiserzeitlicher und spätantiker Keramik aus Iatrus. In: G. von Bülow et al., Iatrus-Krivina – Spätantike Befestigung und frühmittelalterliche Siedlung an der Unteren Donau 6. Ergebnisse der Ausgrabungen 1992–2000. Limesforschungen 28 (Mainz 2007) 467–482; M. Daszkiewicz/G. Schneider, Chemical Analysis by WD-XRF of Late Hellenistic and Roman Table Wares in the Black Sea Region and of local pottery in NE-Crimea and SW-Crimea (DAI 2015, forthcoming); M. Baranowski, Ceramic production at Butovo – overview and new results (DAI 2015, forthcoming); M. Baranowski/M. Dazskiewicz/G. Schneider, Chemical analysis using WD-XRF, p–ED–XRF and macroscopic analysis of fabrics in studying Moesian sigillata. Workshop 2014 Topoi FU Berlin (Berlin forthcoming); M. Baranowski (unpublished thesis Univ. Warszawa 2017).

[3] PRG2 originally was represented by only two samples found together with the kilns in Pavlikeni Villa. Later on only two more samples could be added to this group which, therefore, has not been regarded further.

[4] Niton XL3t-900s GOLDD, 30 sec for each of the 4 filters, without He. The depth of information depends on the absorption of the matrix and is best for the heavier elements and mainly therefore the data for Rb, Sr, Y, and Zr are more reliable than for the elements lighter than Fe (G. Schneider/M. Daszkiewicz, Testmessungen mit einem tragbaren Gerät für energiedispersive

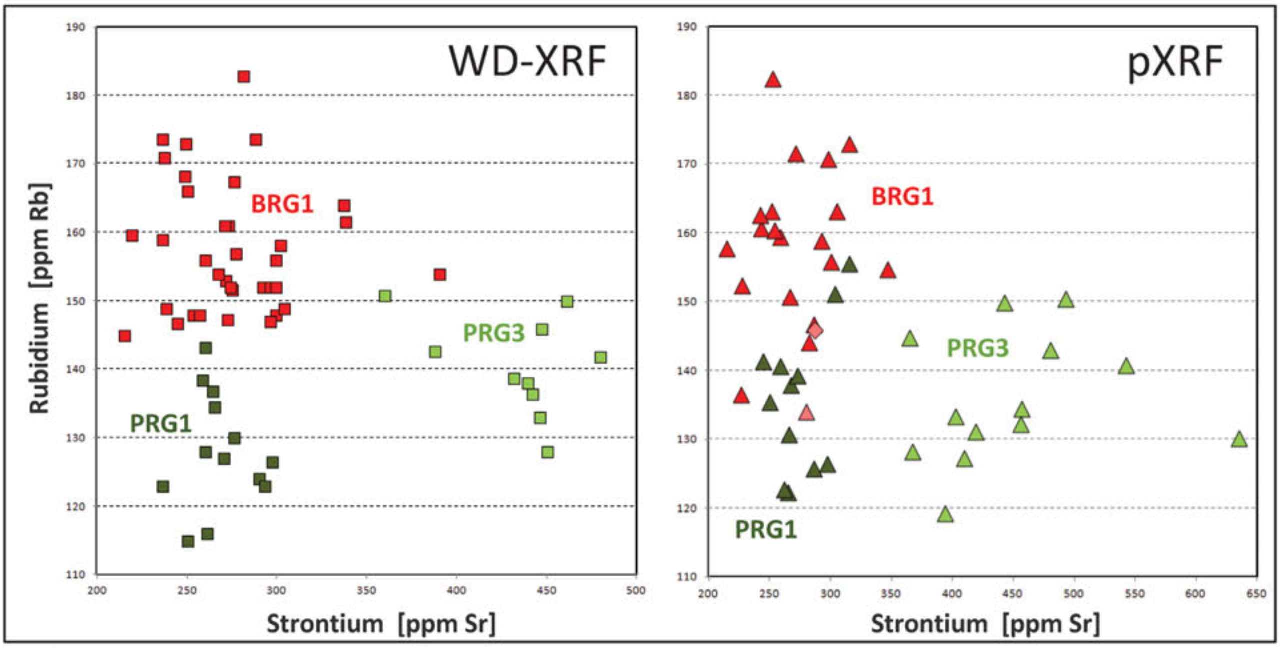

Fig. 1

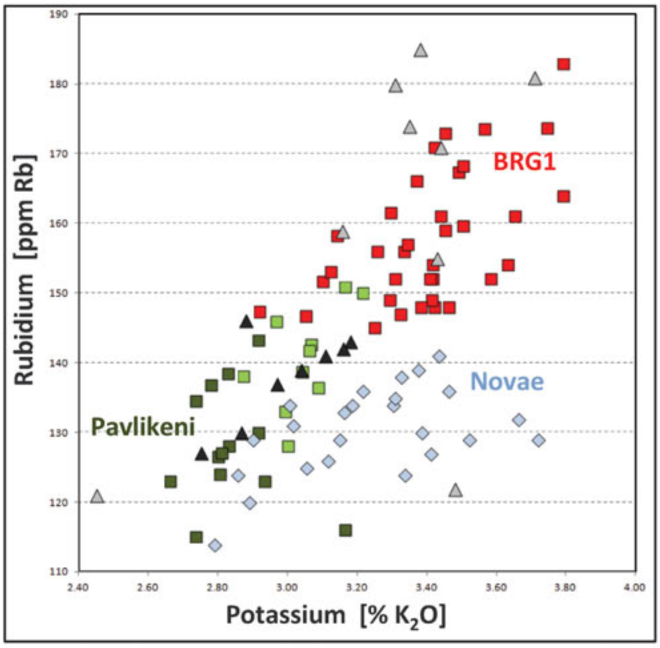

Fig. 2

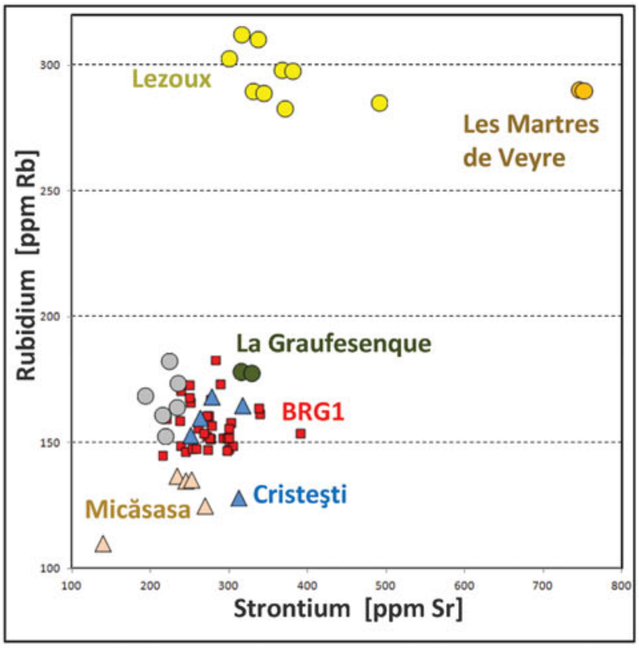

Fig. 3

Fig. 1. Bivariate scatterplot of rubidium vs. strontium for the Butovo (BRG1) and Pavlikeni (PRG1, PRG3) reference groups; left diagram: analyses by WD-XRF; right diagram: analyses by pXRF.

Fig. 2. Bivariate scatterplot of rubidium vs. potassium (WD-XRF) for the Butovo, Pavlikeni, and *Novae* reference groups, including analyses by NAA from Pavlikeni (see text).

Fig. 3. Bivariate scatterplot of rubidium vs. strontium (WD-XRF) for finds from Buciumi and Brâncoveneşti (circles) attributed to Lezoux, Les Martres de Veyre, and La Graufeseqnue, compared to reference groups Butovo (red squares), Micăsasa (orange triangles) and Cristeşti (blue triangles).

	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	(Ce)	(Pb)	l.o.i.	total
	% by weight										ppm													%	%
a) reference groups Pavlikeni/Butovo																									
PRG 1 (n=13)	62.66	0.805	16.51	6.22	0.098	1.94	7.75	0.94	2.84	0.213	120	99	53	33	94	**128**	**268**	26	214	14	385	76	23	2.28	
std ±	0.76	0.015	0.37	0.15	0.009	0.09	1.10	0.15	0.12	0.070	10	4	6	10	6	8	17	4	14	2	50	10	6	1.17	
PRG 2 (n=4)	55.64	0.878	20.35	7.04	0.087	2.86	8.68	1.01	3.19	0.173	149	122	61	37	113	144	323	30	171	15	419	92	27	1.34	
std ±	0.37	0.017	0.33	0.10	0.006	0.34	0.34	0.09	0.24	0.004	4	5	4	2	5	14	30	2	7	1	18	4	2	0.31	
PRG 3 (n=12)	59.17	0.769	16.58	5.90	0.088	2.12	11.29	0.73	3.05	0.292	121	97	56	39	95	**138**	**427**	22	202	14	424	68	22	4.26	
std ±	1.17	0.034	0.98	0.31	0.015	0.22	1.23	0.09	0.12	0.078	11	5	7	10	5	9	41	4	13	1	62	10	5	1.44	
BRG 1 (n=37)	59.15	0.875	19.60	6.71	0.090	2.62	6.34	0.96	3.40	0.218	145	117	63	42	108	**157**	**276**	27	189	15	436	81	24	1.54	
std ±	1.57	0.019	0.77	0.40	0.004	0.33	1.12	0.12	0.20	0.074	13	6	6	13	8	10	37	4	17	1	56	9	6	0.74	
b1) finds of sigillata in Buciumi																									
BM378	56.79	0.858	18.47	7.13	0.105	2.84	8.71	0.87	3.69	0.538	142	131	66	56	117	**178**	**316**	23	172	16	821	63	22	3.30	100.47
BM381	58.46	0.865	18.13	6.96	0.121	2.69	7.62	1.04	3.60	0.511	146	128	69	62	129	**178**	**329**	25	185	14	730	58	26	2.56	100.24
b2) finds of sigillata in Brâncoveneşti																									
BM387	58.27	0.931	18.65	7.77	0.138	3.01	6.03	0.98	3.81	0.414	119	126	71	58	134	**183**	**222**	28	214	16	733	78	29	3.23	100.17
BM388	61.29	0.993	18.32	7.64	0.117	2.37	3.02	1.07	3.46	1.721	111	146	78	41	121	**169**	**192**	29	213	16	814	69	24	2.20	99.80
BM389	59.36	0.945	18.59	7.64	0.109	2.64	5.24	1.04	3.69	0.742	123	136	73	45	115	**174**	**233**	29	214	16	759	72	25	1.43	100.23
BM390	62.38	0.849	16.90	6.85	0.134	2.69	4.69	1.09	3.34	1.072	127	113	57	52	112	**153**	**217**	27	212	14	682	77	17	1.37	100.23
BM395	60.21	0.912	17.87	7.13	0.160	2.92	5.92	0.91	3.69	0.282	110	131	66	49	115	**165**	**233**	27	211	17	561	68	19	1.34	100.38
BM396	62.09	0.825	17.56	6.66	0.153	2.52	5.23	0.91	3.67	0.391	139	120	64	51	114	**162**	**214**	27	196	15	602	72	21	1.80	100.04
c) further non-attributed finds of Roman pottery																									
BM369	59.66	0.948	18.56	5.91	0.030	**1.39**	10.09	0.15	3.12	0.152	140	120	61	14	86	161	300	23	254	20	416	74	34	2.75	100.07
BM379	58.62	0.686	15.29	4.92	0.126	**1.80**	13.88	0.70	3.10	0.895	82	106	53	38	131	146	520	26	261	12	1245	57	16	8.13	100.09
BM375	52.94	0.786	15.34	6.51	0.081	**1.67**	19.37	0.48	2.36	0.465	118	153	84	49	87	111	656	15	182	11	560	37	15	7.93	100.09
BM391	59.56	1.024	19.76	6.05	0.025	**1.45**	5.13	0.11	3.21	**3.680**	137	130	70	16	110	165	339	27	278	23	**1247**	99	32	2.65	99.91
BM376	62.13	0.796	23.79	5.64	0.039	**1.40**	1.00	0.68	4.10	0.430	102	85	35	18	98	223	131	35	217	19	824	85	33	1.01	99.84
BM393	75.11	1.114	17.82	2.58	0.009	**0.67**	0.33	0.02	1.84	0.495	92	56	13	5	29	102	66	42	302	21	451	88	15	1.07	98.74
BM377	72.18	0.921	16.62	4.24	0.040	**0.71**	1.09	0.78	2.84	0.587	72	78	30	15	67	135	158	29	296	15	1144	83	27	2.32	97.59
BM380	70.56	0.723	19.45	3.64	0.031	**0.76**	0.57	0.60	3.31	0.365	72	46	24	8	61	186	104	42	238	20	809	94	41	1.19	98.92
d1) imports in Buciumi from Lezoux																									
BM367	56.74	0.781	20.44	4.95	0.050	1.22	12.62	0.15	2.85	0.200	91	86	34	14	111	**285**	**490**	20	177	20	542	79	46	1.09	99.99
BM368	55.35	0.778	22.25	5.33	0.090	1.21	11.10	0.10	3.38	0.419	83	86	37	19	127	**298**	**380**	25	173	22	473	89	49	0.86	100.01
BM371	58.05	0.804	20.79	5.35	0.061	1.16	10.01	0.12	3.44	0.216	89	89	36	32	151	**289**	**343**	23	193	19	478	90	41	0.65	100.37
BM374	58.36	0.767	20.72	6.03	0.092	1.28	8.75	0.18	3.66	0.162	90	82	44	19	159	**303**	**300**	36	199	21	519	88	45	0.79	100.49
BM382	60.38	0.802	20.55	5.34	0.061	1.00	7.66	0.16	3.88	0.168	94	82	39	21	145	**290**	**330**	25	237	24	481	107	41	0.53	100.47
imports in Brâncoveneşti from Lezoux																									
BM385	57.70	0.794	21.65	5.74	0.067	1.16	8.56	0.11	3.60	0.609	91	90	35	27	142	**310**	**335**	20	191	21	609	108	63	1.08	100.49
BM386	56.23	0.778	20.93	5.49	0.074	1.27	11.14	0.14	3.38	0.572	92	86	35	24	151	**298**	**367**	25	189	22	523	81	41	0.93	100.81
BM392	56.06	0.761	20.55	5.21	0.095	1.08	11.34	0.13	3.35	1.423	90	79	40	26	190	**283**	**370**	18	184	19	468	99	56	1.08	99.95
BM394	60.02	0.813	21.87	5.61	0.058	1.17	6.58	0.08	3.55	0.248	101	90	36	17	139	**312**	**315**	25	185	22	517	91	52	1.28	99.32
LEZ_S	56.70	0.780	21.40	5.33	0.074	1.13	10.60	0.34	3.40	0.280		82	35	26	144	284	307		150		506				
std ±	2.04	0.043	0.68	0.33	0.016	0.14	1.80	0.07	0.19	0.218		5	3	4	25	17	40		20		86				
d2) imports in Buciumi from Les Martres de Veyre (V238 sample from MAV found in Cologne]																									
BM372	60.45	0.901	20.18	4.94	0.049	1.59	7.78	0.20	3.70	0.194	96	95	31	22	82	**290**	**746**	23	204	22	494	90	40	1.04	99.70
BM383	60.46	0.903	20.20	4.88	0.045	1.60	7.81	0.18	3.73	0.192	95	91	31	21	83	**290**	**752**	22	206	20	484	93	37	0.87	99.21
V238	58.39	0.896	21.46	5.03	0.038	1.74	7.89	0.56	3.76	0.224	110	93	39	70	88	306	753	43	144	20	402	50	90	0.93	99.93
MAV_P	57.97	0.980	21.10	4.81	0.040	1.81	8.87	0.25	3.82	0.269		107				321									
d3) imports in Buciumi from La Graufesenque																									
BM373	53.44	**1.029**	22.55	5.79	0.078	2.08	10.78	0.21	3.68	0.354	131	134	63	37	103	**175**	**395**	25	190	16	354	91	18	1.66	100.47
BM370	52.85	**1.043**	22.50	5.94	0.064	2.05	10.72	0.22	3.82	**0.788**	133	137	**352**	**435**	**2023**	170	**372**	29	190	18	**624**	108	55	1.29	99.82
BM384	53.16	**0.959**	21.77	6.16	0.077	1.92	11.31	0.13	4.22	0.297	126	130	72	33	139	**219**	**468**	28	181	15	387	75	26	0.67	100.75
LGR_H	52.56	1.035	22.19	6.21	0.059	1.91	11.34	0.14	3.76	0.801	130	164	66	20	145	159	266	31	166	26	**1277**	86	23	6.52	
std ±	1.15	0.034	0.72	0.32	0.010	0.13	1.28	0.06	0.22	0.299	8	16	7	4	30	10	39	2	10	4	307	9	7	3.05	
LGR_S	53.90	1.040	22.40	5.94	0.072	1.84	10.40	0.35	3.75	0.300		134	61	27	119	173	354		163		386				
e) Micăsasa pottery workshop																									
MD5591	60.64	0.844	17.25	7.30	0.150	2.33	6.22	1.04	3.56	0.659	127	116	72	36	114	137	232	37	174	16	867	82	20	5.17	100.00
MD5592	59.16	0.817	16.96	6.77	0.120	2.12	9.23	0.86	3.27	0.683	115	107	69	46	118	125	268	33	174	15	922	76	22	8.84	99.96
MD5593	58.85	0.834	17.77	7.24	0.121	2.24	8.06	0.86	3.55	0.475	132	117	65	41	121	135	244	34	159	16	727	65	19	4.61	97.92
MD5594	70.09	0.737	14.67	5.70	0.186	1.57	3.35	1.14	2.40	0.158	101	99	58	19	86	110	139	33	183	15	537	66	21	0.25	98.48
MD5595	59.44	0.813	16.83	6.67	0.153	2.15	8.91	1.07	3.39	0.566	124	117	71	33	130	136	251	37	171	15	712	63	23	4.86	100.89
f) Cisteşti Vicus militaris																									
MD5924	58.31	0.889	17.74	7.12	0.116	2.87	7.94	1.03	3.76	0.236	131	125	74	52	120	153	250	34	183	17	577	68	25	5.67	100.12
MD5925	57.69	0.967	18.25	7.50	0.118	3.37	7.26	0.98	3.68	0.191	156	145	83	37	117	168	277	35	171	21	467	74	21	0.06	100.55
MD5926	58.47	0.971	18.34	7.18	0.103	2.69	6.01	1.04	3.81	1.381	137	143	74	39	151	165	316	35	178	18	664	84	26	2.43	99.97
MD5927	59.88	0.917	18.44	7.38	0.134	2.78	5.25	1.02	3.85	0.344	144	142	72	35	115	160	262	35	169	15	556	71	23	1.67	100.28
MD5928	58.27	0.853	17.30	7.00	0.128	**2.32**	**9.66**	1.01	**3.08**	0.366	127	123	69	69	135	**128**	311	35	184	17	904	71	22	7.93	99.75

Table 1. Results of analyses by WD-XRF: ignited samples, loss on ignition at 900°C (l.o.i.), major elements normalized to a constant sum of 100% (melted samples were measured at GeoForschungsZentrum GFZ Potsdam using spectrometer AXIOS by courtesy of A. Schleicher). The original totals are indicated; for reference groups means and standard deviations (std ±) are given. Some significant data mentioned in the text are highlighted in bold.

a) Pavlikeni and Butovo reference groups (means from BARANOWSKI ET AL. 2017, see text)
b) finds of purported regional sigillata found at Buciumi and Brâncoveneşti,
c) further non-attributed finds from Buciumi and Brâncoveneşti,
d) imports from Gaul: mean LEZ_S, SCHNEIDER 1978, 90 (n=15); mean MAV_P, PICON 1977 (n=10, Na, Cr, Rb by NAA); mean LGR_H, unpublished data by B. Hoffmann/G. Schneider (n=61); mean LGR_S (n= 15), (SCHNEIDER 1978, see Text),
e) preliminary reference group Micăsasa,
f) preliminary reference group Cristeşti.

Zr are regarded, the Moesian reference groups, in spite of greater variation, can be distinguished from each other if a few misclassifications due to Rb are accepted (**fig. 1 right**).

Sigillata found in Butovo and Pavlikeni has also been analysed by Kuleff and Djingova using NAA[5]. Thanks to the published table of the original NAA results, Fe, Na, K, Cr, Rb and Ba could be used for comparison of the same series of elements also determined by WD-XRF. Rb and K have been included in the diagram shown in **figure 2,** even though these two elements were not used in the cluster analysis by Kuleff and Djingova. In spite of some erroneous determinations (e.g. Rb varies from 18 to 332 ppm), the eight samples of their cluster 1 (all representing finds from Pavlikeni Villa, including three kiln wasters) are a good match for our reference groups PRG1 and PRG3, thus confirming our attribution of these groups to Pavlikeni. Some samples of other clusters match our reference group BGR1. Later data published by Kuleff et al.[6] showing results obtained by ICP-AES for compositional groups attributed to Pavlikeni/Butovo, *Novae* and North Italy deviate too much from our results to be taken into consideration.

2. Attributions of finds, the easy case: Imports from Lezoux, Les Martres de Veyre and La Graufesenque

After having established the reference groups for Moesian sigillata we asked if we could determine Moesian imports in Dacia. As a pilot project, a series of finds from Buciumi (Sălaj County) and Brâncoveneşti (Mureş County) was analysed (**table 2; fig. 4**). Initial examination of the chemical data (**table 1**) showed several more or less easily distinguishable groups. Looking just at the contents of Rb, Sr and Ti these groups are as follows: b1 and b2, more or less similar to BRG1, two groups (d1 and d2) with very high Rb levels, distinguished from each other by Sr content, and one group with a high Ti content (d3). Comparison with analyses in our data bank clearly showed that group d1 could be attributed to Lezoux (LEZ), group d2 to Les Martres de Veyre (MAV), and group d3 to La Graufesenque (LGR). For comparison to LEZ we could not only use our own results from forty years of analysis of Roman sigillata but also those obtained from analyses carried out in Lyon by Maurice Picon and in Louvain-La-Neuve by Benoit Misonne[7] (**table 3**). The accordance of the mean of 15 own analyses made in 1976[8] with the mean of 18 analyses made in our lab after 1996 as well as the accordance with data from other labs may demonstrate the precision and accuracy of the data[9]. The two samples attributed to MAV (**table 1**, d2) show a nearly identical composition, which makes it very probable that the two fragments belonged to a single vessel. Here, for comparison, the data kindly provided by Maurice Picon in 1977 could be used as well as a sample (V238) from Cologne attributed some years ago to MAV. For LGR, own data and data from Maurice Picon was used. Sample BM370 is heavily contaminated, probably due to alteration caused by specific burial conditions (P, Ni, Cu, Zn, Ba)[10]. Sample B384, despite having slightly too high levels of K, Rb, and Sr, may still be attributed to LGR[11].

A bivariate plot of rubidium vs. strontium (**fig. 3**) shows the groups of LEZ and MAV clearly distinguished by WD-XRF results, whilst the rest of the analysed samples, including two preliminary Dacian reference groups, are very similar. This was also the result of multivariate comparison. Other than the identification of LGR by typical contents of Ti, Al and K, the distinction of the rest of the analysed samples is not easy. Their distinction will be discussed in chapter 3.

In the easy cases, as represented by LEZ and MAV because of their very typical levels of elements such as Rb, Sr, and Zr, pXRF analysis can also be used to distinguish the reference groups. Averages of threefold measurement on fresh fractures as well as the averages of threefold measurement on the cleaned gloss surfaces of the LEZ samples are shown in **table 3** in comparison to the WD-XRF data. The measurements on fresh fractures gave quite similar results to WD-XRF. Some elements, however, cannot be detected by pXRF (Na, Ce) or can only be detected with very low precision (Si, Al, Mn, Mg, P, V, Cr, Ni, Cu). As expected, however, the composition of the gloss differs clearly from that of the body in having lower Si and Ca levels and higher Al, Fe, and K. A cluster analysis using Ti, Fe, Ca, K, Cr, Zn, Rb, Sr, Y, Zr, Nb, and Ba, non-destructively measured by pXRF on gloss surfaces, more or less clearly distinguished the three groups LEZ, MAV and LGR from the combined group of the rest of the samples. The attribution of pXRF data on gloss surfaces by using reference groups determined by WD-XRF is, however, very limited because the reference groups established by WD-XRF are based on analyses of the body, and due to the preparation of the sigillata gloss the surfaces have a different composition.

3. Attribution of finds, the difficult case: Dacian or Moesian sigillata in Buciumi and Brâncoveneşti?

The distinction of the other part of the analysed finds from reference group BRG1 is not easy because of their chemical similarity (**table 2**)[12]. Multivariate methods yielded unequivo-

Röntgenfluoreszenz [P-XRF] zur Bestimmung der chemischen Zusammensetzung archäologischer Keramik. In: O. Hahn/A. Hauptmann/D. Modarressi-Tehrani/M. Prange (eds.) Archäometrie und Denkmalpflege 2010. Jahrestagung im Deutschen Bergbaumuseum Bochum. Metalla Sonderh. 3 [Bochum 2010] 110–112).

5 I. Kuleff/R. Djingova, Chemical profile of the pottery production in the ceramic centre near Nicopolis ad Istrum. Analytical Laboratory 5, 1996, 238–244.

6 I. Kuleff/R. Djingova/G. Kabakchieva, On the origin of the Roman pottery from Moesia inferior (North Bulgaria). Arch. Bulgarica 3, 1999, 29–38.

7 B. Misonne, Terres sigillées de l'antiquité tardive et dérivées en Gaule et en Grande-Bretagne: characterisation archéométrique des productions et étude technologique (Louvain-la-Neuve 2002).

8 G. Schneider, Anwendung quantitativer Materialanalysen auf Herkunftsbestimmungen antiker Keramik. Berliner Beitr. Archäometrie 3, 1978, 63–122.

9 Some of the trace elements are not always determined.

10 The high Ba and P of nearly all sigillata samples found in LGR analysed by us are not found in clay from LGR and not in finds from some sites such as Heidelberg, Velsen, and Nijmegen (probably due to different environmental conditions).

11 This, however, in spite of some chemical similarity, seems not to be possible for sample BM391.

12 The analysed finds in table 1c could not be attributed either to Butovo/Pavlikeni or to the two Dacian reference groups (comparison with analyses of common pottery from *Apulum* makes this provenance unlikely, too). The analyses results are given here for possible later attributions.

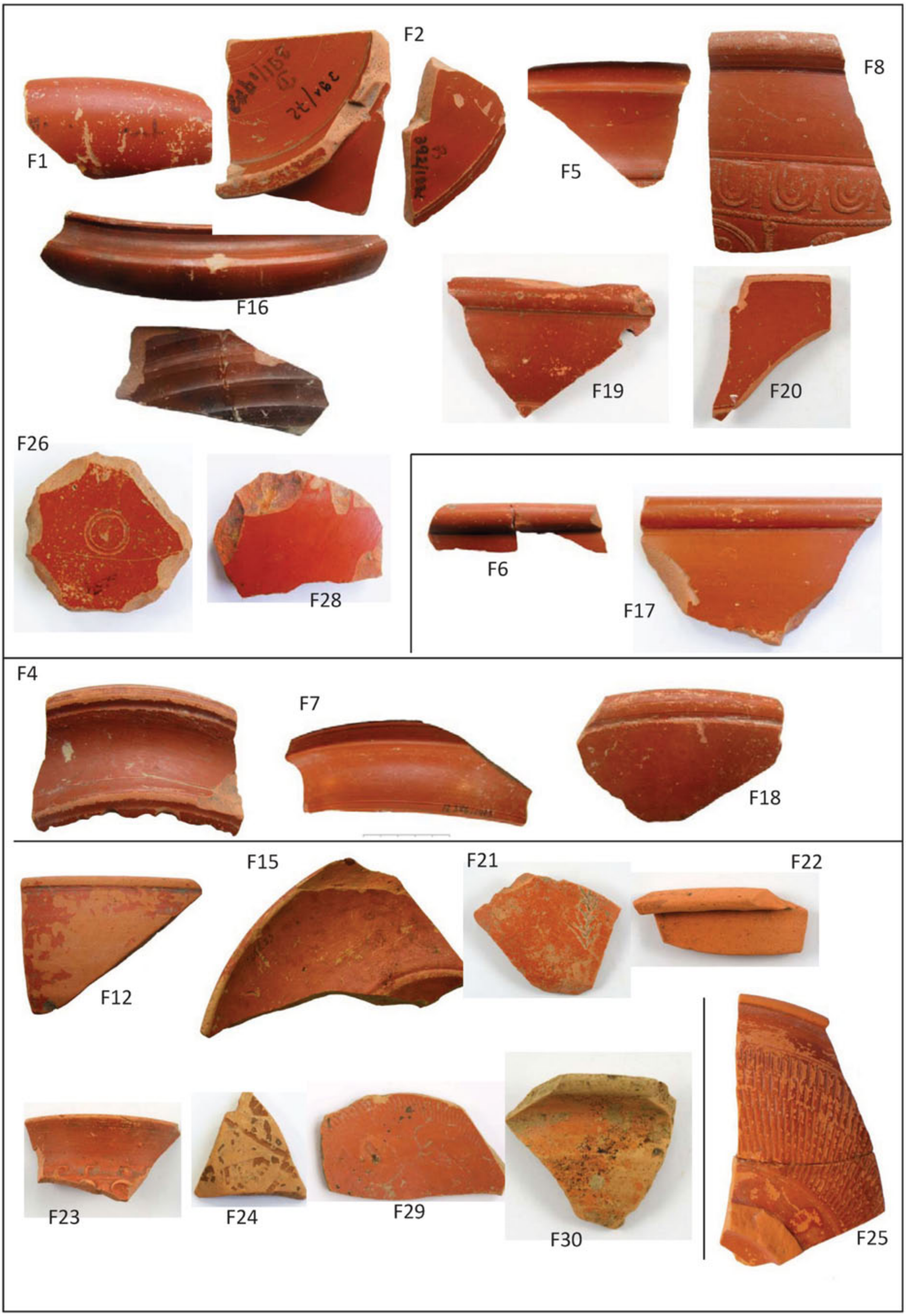

Fig. 4. Photos of some of the analysed finds (not to scale), sorted according to their attribution to Lezoux, Les Martes de Veyre, La Graufesenque, group b1 and b2, and one sample of unknown group.

sample/inv. no.	lab.-no.	description	chemical attribution
Buciumi – Sălaj county, Romania (samples selected by D. Petrut)			
F 1	BM367	Dragendorff type 36 plate	Lezoux
F 2	BM368	Curle type 23 plate	Lezoux
F 3	BM369	Dragendorff type 33 cup	?
F 4	BM370	Curle type 15 plate	La Graufesenque
F 5	BM371	Dragendorff type 37 bowl	Lezoux
F 6	BM372	Unknown type bowl/plate	Les Martes de Veyre
F 7	BM373	Curle type 15 plate	La Graufesenque
F 8	BM374	Dragendorff type 37 bowl relief-decorated	Lezoux
F 9	BM375	Goethert-Polaschek type XIX lamp (?)	?
F10	BM376	Imitation of Dragendorff type 37 bowl	?
F11	BM377	Unknown type bowl/plate	?
F12	BM378	Imitation of Dragendorff type 37 bowl	group b1
F13	BM379	Dragendorff type 32 plate	?
F14	BM380	Dragendorff type 36 plate	?
F15	BM381	Imitation of Dragendorff type 32 plate (?)	group b1
F16	BM382	Curle 21 type mortarium	Lezoux
F17	BM383	Dragendorff type 37 bowl	Les Martes de Veyre
F18	BM384	Dragendorff 18/31 plate	La Graufesenque
Brâncovenești – Mureș county, Romania (samples selected by D. Petrut)			
F19	BM385	Dragendorff type 37 bowl	Lezoux
F20	BM386	Dragendorff 18 (?) type plate	Lezoux
F21	BM387	Unknown type of jug/flagon with graffito	group b2
F22	BM388	Unknown type bowl (without slip)	group b2
F23	BM389	Unknown type of cup with barbotine decoration	group b2
F24	BM390	Unknown type bowl fragment with stamped decoration	group b2
F25	BM391	Dragendorff type 37 bowl with roulette decoration	?
F26	BM392	Unknown type bowl/cup base	Lezoux
F27	BM393	Loeschcke type IX-X lamp (red slip)	?
F28	BM394	Unknown type of vessel fragment	Lezoux
F29	BM395	Unknown type of plate/bowl fragment with roulette decoration	
F30	BM396	Dragendorff type 36 plate with roulette decoration	group b2
Micăsasa, Romania, pottery workshop (samples selected by V. Rusu-Bolindeț)			
V.43260	MD5991	TS mould with relief decoration, trench I	Micăsasa
V.43168	MD5992	TS bowl with relief decoration, trench I	Micăsasa
V.43270	MD5993	TS mould, surface I	Micăsasa
V.47269	MD5994	overfired waster of common pottery, trench II (kiln 4)	(Micăsasa)
V.42925	MD5995	TS bowl (probably a waster?), surface II	Micăsasa
Cristești, Romania, vicus militaris (samples selected by N. Man)			
inv.no.3050	MD5924	local TS	Cristeşti
inv.no. F.N.	MD5925	local TS	Cristești
inv.no. 957	MD5926	waster of local TS	Cristeşti
inv.no.3599	MD5927	TS mould	Cristeşti
inv.no.3052	MD5928	local TS	Micăsasa?

Table 2. List of analysed samples from Romania with results of chemical attributions.

WD-XRF	SiO_2 % by weight	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
a) Schneider 2016	56.76	0.769	21.27	5.46	0.076	1.23	10.42	0.19	3.44	0.385
std ±	1.75	0.026	0.58	0.24	0.013	0.14	1.81	0.08	0.23	0.290
b) Schneider 1978	56.70	0.780	21.40	5.33	0.074	1.13	10.60	0.34	3.40	0.280
std ±	2.04	0.043	0.68	0.33	0.016	0.14	1.80	0.07	0.19	0.218
c) Picon 1977	57.08	0.812	21.65	5.38	0.064	1.44	9.41	0.23	3.52	
d) Misonne 2002	56.87	0.715	22.27	5.17	0.063	1.15	9.17	0.20	3.62	0.773
e) pXRF break	51.9	0.77	21.2	6.2	0.06	(1.4)	7.7		3.7	
std ±	5.4	0.06	3.8	1.1	0.02	(0.4)	2.7		1.0	
f) pXRF slip	45.1	0.77	25.6	8.0	0.08	(1.7)	3.0		5.4	
std ±	4.2	0.11	3.8	0.5	0.07		1.0		0.8	

WD-XRF	V ppm	Cr	Ni	(Cu)	Zn	Rb	Sr	Y	Zr	(Nb)	Ba	(Ce)	(Pb)
a) Schneider 2016	92	86	39	23	138	282	335	27	168	23	483	89	51
std ±	7	5	4	5	19	18	51	5	29	4	64	15	15
b) Schneider 1978		82	35	26	144	284	307		150		506		
std ±		5	3	4	25	17	40		20		86		
c) Picon 1977		92			154	321							
d) Misonne 2002	82	76	54	49	126	287	330	41	147	18	542		64
e) pXRF break	143	121	(37)	(17)	155	281	347	29	162	22	457		50
std ±	30	37			21	16	52	4	18	1	104		9
f) pXRF slip	210	196	65	(23)	173	274	329	32	165	22	496		48
std ±	34	16	20		15	16	55	4	16	1	103		6

Table 3. Lezoux reference group, 2nd century calcareous sigillata (WD-XRF of ignited samples).

a) mean of 18 analyses carried out since 1996 on sherds attributed to Lezoux (including the finds from Dacia),
b) mean of 15 samples of sherds found in Heidelberg archaeologically attributed to Lezoux (Schneider 1978, see text),
c) mean of 61 sigillata samples from Lezoux (M. Picon, personal communication 1977),
d) mean of 48 sigillata finds in Lezoux (B. Misonne 2002, see text);
e) mean of measurements by pXRF on fresh fractures of nine Lezoux samples,
f) mean of measurements by pXRF on slip surfaces of nine Lezoux samples

cal results. After a first interpretation the two samples found at Buciumi were attributed to BRG1[13]. After the publication of these results ten samples from Micăsasa and Cristeşti were analysed as a pilot project to get an idea of the reference groups in Dacia. A cluster analysis using the same elements as in the publication of 2015, but including the two Dacian reference groups, distinguished clear groups (**fig. 5)** and did not attribute any of the finds to BRG1 or to the reference groups from Dacia, with the possible exception of the two finds from Buciumi, which may be attributed to Cristeşti (not to BRG1) if seven instead of eight clusters are made. The multivariate distances can also be seen using principal component analysis (PCA) with the same set of elements (**fig. 6**). None of the samples from Dacia is attributed to BRG1, thus confirming the dendrogram[14]. The other groups are less clearly separated. The waster of common ware is an outlier in the reference group Micăsasa in both approaches. Sample BM388 is obviously altered from burial, as demonstrated by the high P content; however, this element is not used in the calculation. It is identified as an outlier in the dendrogram but is less aberrant in the PCA. Regarding the preliminary reference groups Micăsasa and Cristeşti, one sample from Cristeşti could be attributed to Micăsasa like in the dendrogram. The questionable eight finds, however, cannot be attributed securely.

The ambiguous results of multivariate methods gave reason to look again at the original data. All eight questionable finds showed lower alumina contents in a biplot of rubidium vs. aluminium than the reference groups (**fig. 7**). At least BRG1, PRG and Micăsasa can clearly be distinguished. Such a diagram provides sufficient evidence for differentiating between groups if errors or alteration effects for thes indivi-

13 M. Baranowski/M. Daszkiewicz/D. Petrut/G. Schneider, Moesian or Dacian Sigillata – A provenance study by WD-XRF and p-XRF). In: T. Gluhak/S. Greiff/K, Kraus/M. Prange (eds.), Archäometrie und Denkmalpflege 2015. Metalla Sonderh. 7 (Bochum 2015) 95–97.

14 The PCA used the same set of elements as in 2015 but includes the finds together with BRG1, Micăsasa and Cristeşti, instead of PRG, NOV, LEZ and MAV. This causes a different diagram in which now the finds are clearly distinguished from BRG1 contradicting the diagram published in 2015. Such diagrams therefore do not show an objective interpretation.

dual elements are excluded[15]. This is certainly the case for Al and Rb determined in a powder sample by WD-XRF, but certainly not when using pXRF, where the precision for Al is very bad because of the low information depth of the long-waved X-rays in a sherd's fresh fracture. So, the distinction as seen in **figure 7** did not work when using pXRF results. In this figure we can also see that one sample from Cristeşti is more similar to Micăsasa because of its low Rb content (the too low Rb is also confirmed by pXRF).

Whilst the groups in **fig. 7** are independent of alteration effects this is not true for the multivariate calculations which used Ba as one of the 18 elements. Because there is a slight correlation of the Ba contents with the P contents, this shift to higher Ba is certainly caused by alteration during burial[16]. Both element concentrations are generally higher in the samples from Dacia than in the samples from Moesia (**table 1**) which means that the multivariate separation of the questionable finds from BRG1 is more obvious. This does not happen if we use the same set of elements but exclude Ba (**fig. 8**). Four of the finds from Buciumi and Brâncoveneşti may now be attributed to BRG1. The reference groups Micăsasa and Cristeşti, however, are separated like in **figure 7,** with sample MD5928 from Cristeşti again attributable to Micăsasa. The multivariate attribution of this sample is confirmed by univariate checking of the original analysis results (**table 1**). Whether this small fragment of local relief-decorated sigillata found in Cristeşti was really made in Micăsasa or whether the chemical compositions of the groups overlap can only be decided once more samples from both production sites have been analysed. These analyses should include WD-XRF, MGR-analyses and thin-section studies.

4. Conclusions

- Exploring regional patterns needs secure attribution of finds to their places of manufacture. This is easy when the groups in question are homogeneous and when their chemical differences are large, which is mainly dependent on the geological variability of the raw materials. In many cases the chemical compositions of provenance groups are very similar and cannot be securely distinguished without applying additional methods, such as MGR-analysis or thin-section studies.
- The basis for determining provenance are secure reference groups of precise and accurate chemical data of at least 18 elements. Therefore non-destructive analyses by pXRF with about ten reliably determined elements are insufficient for defining secure reference groups. Reference groups for the more or less high quality sigillata products of Butovo, Pavlikeni and Novae have been successfully established. For Dacia ten analyses of probable local products offer a first step in the definition of the Micăsasa and Cristeşti reference groups. For Apulum only limited data on common wares and clay are available.
- Chemical analyses of thirty samples of pottery found in Buciumi and Brâncoveneşti easily distinguished fourteen long-distance traded imports of sigillata from Lezoux, Les Matres de Veyre and La Graufesenque from the rest of probably local or regional sigillata and lamps. Imports from *Moesia* could be excluded.
- From the rest of the analysed samples two finds from Buciumi and six finds from Brâncoveneşti are regarded as regional sigillata of unknown origin. Initial multivariate examination of the finds from Buciumi show that they are chemically similar to the products from Butovo, but their alumina content is significantly lower so that this provenance is excluded. This is also true of the finds from Brâncoveneşti, for some of which a provenance from Cristeşti cannot be excluded securely but more samples have to be studied especially from Cristeşti. This would be the nearest sigillata workshop. Micăsasa is excluded in view of the rubidium contents.
- Eight further finds could not be classified. All of them differ from the eight previous samples of very probably Dacian origin in having lower magnesium levels. Three are made from highly calcareous clay (including one Goethert type XIX lamp), four are made from non-calcareous clay (including one Loeschcke type IX-X lamp). For these samples provenances may later be found when more reference groups of Dacian pottery are known.
- Difficult cases of provenance determination occur when within a limited region, which may be small or large, the chemical differences between reference groups are small and not all possible necessary reference groups are known. This is the case with the finds from Buciumi and Brâncoveneşti, where the reference groups for workshops in Dacia are not all known.
- There is also a methodological problem. Multivariate methods yield results depending very much on the set of elements (attributions) and on the samples (objects) used in the classification, and thus conclusions only based on multivariate calculations are not objective. The examples cited herein show that contradicting interpretations are possible. When publication of dendrograms or diagrams obtained by principal component analysis or by discriminant analysis replaces publication of the original data, the conclusions presented can either be believed or disbelieved. A critical review is impossible in this situation. When analytically insufficient data, such as e.g. those obtained by pXRF, are used this becomes an even more important issue.

m.dasz@wp.pl
schnarch3@gmail.com
bmjj@o2.pl
petrutdavid@gmail.com
viorusu1@yahoo.com

[15] To prove the attribution to a group, however, all elements must be compared!

[16] Such alteration effects are discussed by G. Schneider, Mineralogical and chemical alteration. In: A. Hunt (ed.), The Oxford Handbook of Archaeological Ceramic Analysis (Oxford 2016, forthcoming).

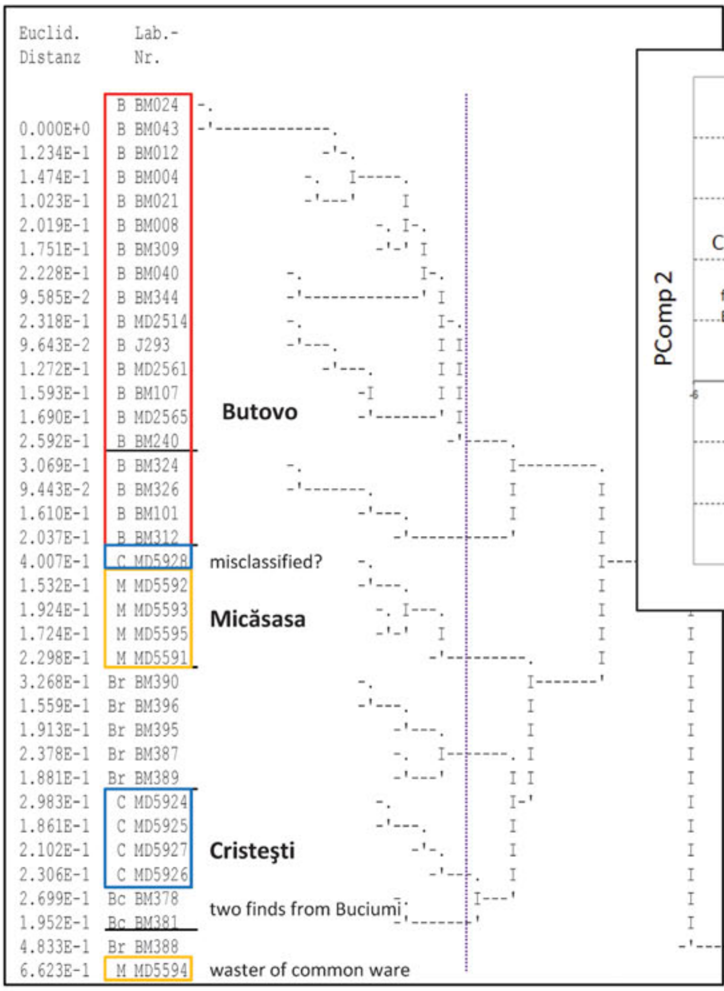

Fig. 5

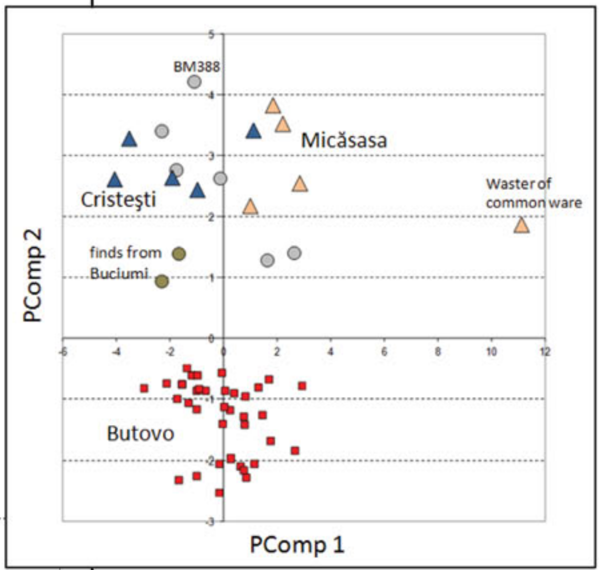

Fig. 6

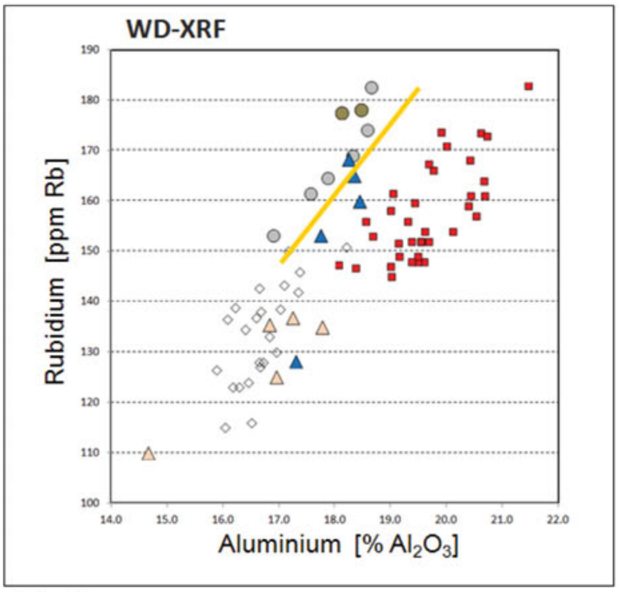

Fig. 7

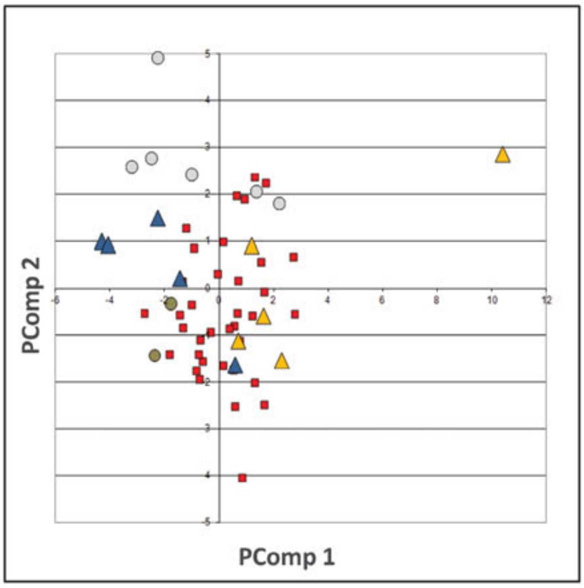

Fig. 8

Fig. 5. Dendrogram of cluster analysis of finds from Buciumi and Brâncoveneşti compared to reference groups (logged WD-XRF data of Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, V, Cr, Ni, Zn, Rb, Sr, Y, Zr, Ba, average linkage).

Fig. 6. Principal component analysis of the chemical composition of the analysed finds using the same elements as in **fig. 5**.

Fig. 7. Bivariate scatterplot of rubidium vs. aluminium for finds from Buciumi and Brâncoveneşti compared to reference groups Butovo (squares), Pavlikeni (rhombs), Micăsasa (orange triangles) and Cristeşti (blue triangles).

Fig. 8. Principal component analysis of the chemical composition of the analysed finds using the same data as in Fig. 6 but without Ba.