Chemical classification of 124 pottery samples from Emecik, Knidian Peninsula, and neighbouring sites by Neutron Activation Analysis

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Aims of the study

Beginning in 1998, the archaic Apollon sanctuary near Emecik village at the Knidian Peninsula was excavated by a German-Turkish team (Berges and Tuna 2000). The sanctuary was constructed at an artificially created terrace bordered by a wall of a height of about 5 m. This wall can be dated to about 550 BC. The material behind the wall was filled in to construct the terrace. The excavations in this area brought to light a large number of archaic Greek pottery sherds dating to the time period about 650 – 550 BC. Because all pieces are found in this intermixed fill, we lack a stratigraphically-based chronology for the Archaic ceramics. It can be considered, that, besides local material, many pieces have been imported and presented as votive gifts to the sanctuary. The sherds have been grouped by archaeological means into several ware types: transport amphorae, fine wares as flat plates decorated with ornamental and figurative motifs (florals, animals, mythological creatures), relief pithoi and amphorae, a large number of local or imported terracotta's used as votive offerings (mainly bull figurines, male and female votive bearers), orientalizing decorated jugs and open vessels, dinoi with their stands and several further, probably imported ware groups including wild goat decorated Ionian jugs and Attic vessels like large dinoi. The main aim of our archaeometric project was to classify these sherds chemically, to confront these chemical groups with the archaeological classification and, thus, to get new results on east Dorian pottery production. Furthermore, a comparison of these results with the ceramic material of other find spots in our databank may reveal imported ware types and their origin.

The Bonn NAA procedure, statistical grouping and samples chosen

Therefore, a representative selection of these wares has been chosen for Neutron Activation Analysis (NAA), a method applied routinely in Bonn since many years. As is well known today, the elemental composition of pottery reflects the composition of the clay paste prepared by the ancient potters according to a certain recipe and, hence, can be used for provenance determination, if reference material is available for comparison (Mommsen 2004 and references therein). Since the Bonn NAA databank contains now more than 6000 samples from Greece and the Eastern Mediterranean, the chances to find known elemental patterns has been considered to be good.

Our NAA procedure (Mommsen et al. 1991) is able to measure about 30 elemental concentrations with precisions of a few percent even for trace elements. As sample about 80 mg of pottery powder is taken with a pure sapphire drill. As standard an in-house pottery standard calibrated with the well-known Berkeley pottery standard (Perlman and Asaro 1969) is used. The statistical data evaluation to form groups of sherds of similar composition is done with our own filtering procedure (Beier and Mommsen 1994). It has, compared to the usually applied methods like Principal Component Analysis (PCA) or cluster analysis (CA), the advantage that measuring errors and also a shift of all concentrations by a constant factor due to a possible dilution of the clay paste can be considered (Mommsen and Sjöberg, to be published). Taking the composition of one sample or of a group of chemically similar samples, a large databank of an unlimited number of samples can be checked stepwise and all samples be sorted out, which are statistically similar.

The 124 sherds selected for analysis come from the sanctuary at Emecik, from the dump heap of the pottery workshop at Resadiye (12 samples) (Empereur et al. 1999) and from the collection of archaic finds of Old-Knidos in the 'Antikensammlung der Staatlichen Museen' in Berlin (11 samples) (Berges 2002). As presented to us before analysis, their archaeological grouping according to ware types is given in Tab. 1, column 1.

Results of the chemical analyses

The search for shreds of similar chemical composition was done just usig the raw data, without considering the archaeological classification. It revealed – besides a number of chemical singles and a few imported pieces - the presence of a number of groups called EME-A, B, ..., G. All these compositional groups were new to us. This result was expected, since we did not have material from the Knidian peninsula or other parts of a Dorian region before. The distribution of the group members into the archaeological groups is shown in Tab. 1. Samples are called associated to a group, if they deviate in one or two concentration values only. They might belong to the group, but they could also be first members of a hitherto unknown group of different origin. Tab. 2 gives the average concentration values of the larger groups and their spreads (root mean square deviations). Associated group members are not included in these patterns. All the different groups are well separated as demonstrated also in Fig 1, where the result of a discriminant analysis is shown taking the 112 samples, which are group members, including 8 samples of a group CYP-I from our databank (see below) assuming a distribution into 11 clusters. All the elemental values given in Tab. 2 have been used for this calculation except As, Ba, and Na (see Mommsen 2004).

A definite assignment to a local production is possible only for group EME-C and subgroup EME-C', a pair of samples, since all (except one single) sherds of the kiln material from Resadiye belong to this groups. The main part of the fine ware samples of different forms, archaeologically considered as locally made products, belongs to group EME-B and its subgroup EME-B'. This subgroup is very similar to group EME-B, but diluted by 5 % (best relative fit factor with respect to B = 1.05) with increased Fe, Co, Ni, and Cr concentrations. Since until now both chemical patterns are not found somewhere else and since they are so abundant at Emecik, a local production can be suggested.

The numbers of the members in the other groups EME-D, -E, -F, and -G are much smaller. These vessels might represent local clay pastes or they might have been imported from somewhere else. Archaeometrically, like for the chemical singles, nothing can be concluded for these small groups without further material given to us for analysis.

For the case of patterns EME-A and EME-A', although also new to us, our databank gives a hint. These patterns, found mainly in the terracotta fragments, have a general Cypriot composition. The concentrations are not very different from several Cypriot patterns in our databank and especially close to group CYP-I, but they are very different from all our Greek and eastern Mediterranean patterns. In Tab. 2, pattern CYP-I, multiplied with a factor 0.83, is confronted with pattern EME-A. CYP-I is known to represent with high probability a Cypriot paste used during Mycenaean times (Mommsen et al. 1996, Mountjoy and Mommsen 2001). The paste used for forming the terracottas was prepared with a clay of quite similar composition, but has been diluted by 17 % compared to the Mycenaean paste used for the production of members of group CYP-I. Or a different clay layer of very similar composition, but with such a natural dilution, has been exploited. Unknown to us, a Cypriot origin of the terracotta pieces had been suspected previously (K. Kleibl working on this material, private communication).

For a few sherds the place of the manufacturing workshop could be determined. Four samples, all Ionian jugs, have been imported from Miletos, three have the well-known composition A of the Kalabaktepe workshops there and one has a second pattern most probably assignable to Miletos and called D (Akurgal et al. 2002). But another Ionian jug has composition EME-B and is, therefore, presumably a local imitation. Two fragments of dinoi come from Attica, they have the composition KROQ known from Mycenaean material from the Acropolis in Athens (Mommsen 2003). The provenance of these pieces, determined by NAA, and the identification of the presumably locally made wares and imitations will help the archaeologists to classify the large number of sherds not subjected to a chemical analysis. A more detailed publication of these results can be found in Mommsen et al. (2006).

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Tab. 1: Archaeological classification of the 124 sherds from Emecik, Old-Knidos, and Resadiye compared to the chemical grouping. Listed are the numbers of group and (+) of associated members.

NAA groups EME- archaeological classification	С	C'	В	Β'	D	Е	F	G	А	A'	other	singles	totals
	local		loca	1?	unkn	own			Cyprus?				
local amphorae	10	2				1						1	14
local decor. fine ware	2		26 +	3 4 + 1	3	2		1	3			1	46
local relief vessels				1			1	4+2				2	10
terracottas			2	1		1	5	2	29 + 1	2		3	46
Ionian jugs			1			1					4 (from Miletos)		6
Attic vessels											2 (from Attica)		2
totals	12	2	29 +	3 6 + 1	3	5	6	7 + 2	32 + 1	2	6	7	124

Table 2: Concentration patterns of the larger groups of this study. Shown are the average values M of the groups in $\mu g/g$ (ppm), if not indicated otherwise, and their spreads (root mean square deviations) σ in % of M. The individual data sets of the samples have been corrected for constant shifts of the concentrations (best relative fit with respect to M). To show the close similarity of subgroup B' to B, pattern B' has been multiplied by a best relative fit factor of 1.05, analogous EME-A to CYP-I, factor = 0.83.

	EME 12 sa facto	EME - C 12 samples factor 1.0		EME - B 29 samples factor 1.0		E - B' mples r 1.05	EMI 32 sa facto	E – A Imples or 1.0	CYP – I 8 samples factor 0.83		
	М	σ (%)	Μ	σ (%)	Μ	σ (%)	М	σ (%)	М	σ (%)	
As	10.6	44.	6.54	28.	6.74	23.	8.47	19.	-		
Ва	487.	9.7	498.	14.	504.	14.	441.	24.	500.	56.	
Ca %	3.84	35.	5.54	20.	5.68	16.	9.95	19.	6.89	35.	
Ce	97.0	3.8	69.8	2.8	66.8	3.0	34.5	3.5	35.8	1.9	
Со	30.2	6.1	39.1	7.3	50.4	7.6	26.8	3.3	25.7	5.3	
Cr	322.	8.2	393.	14.	574.	2.9	311.	22.	252.	13.	
Cs	12.7	9.2	7.77	15.	6.98	10.	3.26	9.8	3.60	6.5	
Eu	1.34	5.4	1.13	3.5	1.13	2.4	0.86	4.3	0.86	3.4	
Fe %	5.26	3.5	5.10	3.3	5.58	2.4	5.07	3.4	4.77	4.5	
Ga	26.5	10.	19.6	11.	19.7	13.	16.1	11.	13.2	25.	
Hf	6.79	5.3	4.59	4.3	4.36	5.0	2.82	8.3	2.80	6.0	
Κ %	3.31	9.7	2.17	8.2	1.96	3.5	1.45	9.9	1.67	12.	
La	46.5	5.9	34.1	2.7	33.1	2.8	16.1	3.6	17.2	2.7	
Lu	0.55	4.2	0.46	7.7	0.44	6.9	0.35	5.4	0.34	8.1	
Na %	0.78	21.	0.62	13.	0.63	16.	0.87	11.	1.03	13.	
Nd	36.9	10.	27.4	8.3	26.0	7.4	14.7	10.	16.3	9.6	
Ni	280.	20.	407.	16.	648.	11.	214.	18.	229.	6.8	
Rb	170.	5.2	113.	13.	102.	6.3	52.6	10.	58.9	12.	
Sb	0.79	17.	0.75	22.	0.81	18.	0.60	23.	0.76	16.	
Sc	20.6	2.2	18.0	3.1	18.5	1.8	21.3	5.1	19.6	5.7	
Sm	6.36	7.7	5.01	5.2	4.67	11.	3.05	4.1	3.14	6.1	
Та	1.30	3.6	0.98	4.1	0.93	4.2	0.53	6.0	0.54	6.9	
Tb	0.81	9.2	0.69	7.3	0.70	11.	0.50	10.	0.51	7.6	
Th	16.7	2.7	12.8	2.0	12.2	3.4	5.50	4.6	5.61	2.6	
Ti %	0.57	12.	0.47	18.	0.53	16.	0.52	19.	0.40	24.	
U	3.16	6.4	2.23	5.2	2.09	4.9	1.60	14.	1.75	19.	
W	3.03	8.9	2.24	13.	2.28	7.0	1.48	15.	1.32	17.	
Yb	3.71	4.6	2.88	3.2	2.82	2.1	2.04	5.0	1.97	2.4	
Zn	109.	16.	98.3	15.	101.	26.	96.5	12.	83.4	6.9	
Zr	217.	18.	141.	20.	135.	23.	86.6	36.	126.	19.	



Fig. 1: Result of a discriminant analysis of the 112 grouped samples including 8 samples of group CYP-I and assuming 11 clusters. Plotted are the discriminant functions W1 and W2, which cover 90% and 5%, respectively, of the between group variance. The ellipses drawn are the 2σ boundaries of the groups. The different groups are well separable.