Element Concentration Distributions and Most Discriminating Elements for Provenancing by Neutron Activation Analyses of Ceramics from Bronze Age Sites in Greece

A. Hein, J. Maran[&], H. Mommsen

Institut für Strahlen- und Kernphysik, Universität Bonn, Nussallee 14–16, D-53115 Bonn.

Institut für Ur- und Frühgeschichte[&], Universität Heidelberg, Marstallhof 4, D-69117 Heidelberg

Abstract

Based on a data set of about 2000 ceramic samples from Bronze Age Greece, which were measured in Bonn by neutron activation analysis, the general distributions of 30 element concentrations in ceramics are estimated and the total concentration ranges are reported. They are much narrower than expected. Since for many elements these total ranges are only a factor of about 5 larger than the typical range in a group of samples having the same origin, the need of high precision measurements for a successful grouping of pottery according to chemical compositions is obvious. As an additional result the suitability of the different elements to distinguish between different ceramic groups in provenance studies is deduced. With a few exceptions all mesured elements are found to be suitable to about the same extent.

keywords: NAA, ceramics, provenancing, Greece, Bronze Age, elemental concentration

1 Introduction

Measuring chemical compositions of ceramics by neutron activation analysis (NAA) or other comparable techniques is generally accepted to be a well suited method for provenance studies. The chemical patterns measured in pottery sherds found at archaeological sites are supposed to be characteristic for a pottery production workshop and even believed to be unique for the utilized clay and/or a certain processing technique in the workshop. Therefore, the aims of such chemical analyses of pottery are, first, to classify different ceramic products according to their chemical composition, i. e. find all members produced by the same clay or clay mixtures according to the same 'recipe' and, secondly, to assign each of the detected groups to a certain production place or region, if possible (e.g., with the help of analyzed kiln wasters or other material which are taken to be locally produced and not traded).

In a project concerning the chemical characterization of Mycenaean ceramics (Late Helladic period about 1550 - 1050 BC) and the location of the main pottery production workshops of these products, until now about 2000 samples from different regions in Greece have been analyzed by NAA in Bonn (Mommsen et al. 1995). This large body of data offers the possibility of assessing the general trace and minor elemental concentration ranges in ceramics of the Late Bronze Age in Greece and the corresponding median values. For the 30 elements measured here these data will be presented and are taken to represent the general compositions of ceramics in Late Bronze Age Greece.

Furthermore, if for each of these elements the sizes of these general or overall ranges are compared to the typical sizes of the ranges encountered within a chemical ceramic group from a single pottery workshop, the importance of the element for distinguishing different chemical patterns can be assessed. The overall ranges will depend - besides on the analytical errors - mainly on the different compositions of the exploited Greek clay beds, given by geochemical history, and on the kind of material removed or added as temper during the clay refinement. The ranges within a single group produced with a certain 'recipe' in one pottery workshop are expected to be much smaller. For such homogeneous archaeological ceramic groups the spread of the observed analytical values is composed of the natural variability(inhomogeneity) of the raw materials used (the individual clay bed or beds exploited and temper possibly added) and of the analytical errors (sampling, counting and other errors) which have been discussed in many studies(Perlman and Asaro 1969, Harbottle 1976, Mommsen et al 1991, Glascock 1992, Blackman 1993). The individual statistical experimental or counting error of each element can be calculated explicitly from the NAA spectra and describes a lower experimental error limit. The dependence of the group concentration values on any kind of 'dilution' of the clay (e. g., if the ancient potters added less or more pure sand (SiO_2) to the clay) can be mathematically corrected by a 'best relative fit' (E. V. Sayre et al., reference given in Harbottle 1976, p. 47) during the search and formation of the chemical groups from the raw data as described below. If the overall range and the single group range are of the same order of magnitude for one element, it is evident that the concentration value of this element has not any discriminating power between different production sites of Greece, its measurement may be omitted. If, on the other hand, the between group distances of the concentration values of an element are much larger than the within group spread of data, a good separation between different production series or production workshops is possible already for this one element.

By means of the whole data set of Mycenaean ceramics the general distributions of the 30 elements in ceramics measured in Bonn will be estimated. Such overall concentration ranges for Late Bronze Age ceramics of Greece to our knowledge have not yet been reported, although many datasets for single individual groups exist (see e. g., Jones 1986). They will be compared with the variability in several archaeological sample groups of the same chemical pattern and with the individual statistical experimental or counting error of each element. This will demonstrate the importance of high precision measurements in provenancing of ceramics. Finally the suitability of particular elements mesured by NAA in discriminating different chemical patterns is estimated and discussed.

2 Analytical procedure and statistical grouping

The NAA used in Bonn is a method which ensures a high measurement precision for many elements. With an amount of about $80\,mg$ more than 30 elements in each sample are measured routinely (Mommsen et al. 1995 and references therein). The procedure is a modified version of that described by Perlman and Asaro (1969). With the help of an automated sample changer and an elaborate spectrum evaluation program we are able to measure about 600–800 samples per annum. The element concentrations are obtained by means of the Bonn pottery standard, which is calibrated against the Berkeley pottery standard (Perlman and Asaro 1969). Measurement precisions of a few percent are achieved for many elements. This is found to be necessary to distinguish different production patterns as will be shown.

The chemical patterns of the samples can be classified by multivariate statistical methods independently of the archaeological classification. The additional consideration of a possible 'dilution' factor ('best relative fit' factor) helps to obtain sharper chemical patterns. Thus, different pottery producing practices like adding variable amounts of temper to the clay are taken into account. Moreover, all constant shifts in the measured values due to experimental errors (e. g., in sample weighing or inhomogeneities of the neutron flux during the irradiation) are corrected as well by such a fit. The application of a best relative fit to the data of repeated measurements of a standard material was found to lower the spread values on average about 4 % (Mommsen et al. 1991). Since this standard material is supposed not to be diluted, this is taken to be the correction only due to the experimental uncertainties. Additional real clay dilutions of up to 10–15 % are encountered quite often. Our multivariate filter method which is used to allocate samples of similar composition in the data set considers besides such 'dilutions' elemental correlations and takes the individual experimental errors of the concentration values into account as well. It is based on a measure of pattern dissimilarity which is a modified Mahalanobis distance (Beier et al., 1994).

3 Results of chemical analyses

In the course of our project, about 2000 samples of pottery sherds from Bronze Age sites in Greece have been measured. They cover the regions from Macedonia and Thessaly in the north to the Peloponnes, Melos and Crete in the south. Chemical grouping of these data reveals a large number of different patterns (Mommsen et al., 1995), altogether about 80 different data sets of 3 or more samples each. The groups with the largest number of members and/or assignable with high probability to workshops at definite places or regions are (the groupnames are tentatively chosen): Mycenae/Berbati (MB, 247 samples), Tiryns/Asine (TA, 96 samples), Aigina (Aig, 88 samples), two groups from Eastern Locris (Locris-l, 42 samples; Locris-m, 18 samples), two groups from Knossos/Phaistos (KP-1, 19 samples; KP-2, 10 samples) and one group from Melos (8 samples). Besides these 8 main groups 6 more groups are detected in the material mainly from the Argolid, each with sample numbers > 10, and, correspondingly 3 more groups in material from Aigina, each with sample numbers > 6. The locations of the workshops for these 9 additional groups are as yet unknown. The analyzed material may represent imported ware types. All the 17 groups mentioned comprise about 40 % of the total Greek databank. About mbox25

% are chemical loners (ungrouped samples) and the remaining part contains many more groups of only a few members with, for that reason, statistically not well defined concentration patterns. As an example for measured group patterns, the average elemental concentration values M for 30 elements and their spreads σ (root mean square deviations) in % of M are listed in Table 1 for four groups.

Based on the values of the 17 groups mentioned, different kinds of elemental distributions (i. e. spreads σ of data) can be compared. The calculated spreads within the individual groups (σ_i) as listed in Table 1 result from the single values of the group members. Based on the spreads measured in all the 17 groups, an average spread (σ_{ave}) for each element can be calculated representing the average variability of an individual ceramic group. With the help of σ_{ave} the inhomogeneity of elements within ceramics of the same chemical pattern can be assessed. As mentioned, besides on the natural inhomogeneity of the clays, the spreads of the patterns depend on the analytical error as well. Since the values will spread at least in the range of the experimental counting error, the average experimental counting error (σ_{exp}) for each element is given in the last column of Table 1 as lower limit.

The general distribution of element concentrations in Greek Bronze Age ceramics can be estimated by the spread of the mean values of the 17 group patterns (σ_M) assuming a normal distribution. Another way to estimate the general concentration range of one element would be to calculate the spread of the single data in the whole heterogeneous data set of 2000 samples. But due to archaeological sample choice and varying sampling quotas, the selection of the samples in this set is not balanced. Therefore, the distribution of concentration values obtained in this way will depend strongly on the number of samples analyzed from each group. Nevertheless, the maximum range of concentration values and lower and upper deciles can be estimated with the help of the single data.

As an example, the distributions of the La concentration in the whole data set and in the four groups given in Table 1 are shown in Figure 1. Most of the samples have La concentration values between 22.5 and 38.6 ppm (lower and upper decile) with a median value of 30.4 ppm. The median value depends here clearly on the high quota of samples from the Argolid. Just the two groups MB (La=31.4 $\pm$ 2.7 ppm) and TA (30.8 $\pm$ 2.0 ppm) shown in the Figure contain about 350 samples. The mean value calculated from the average La concentration values of the 17 groups is 29.5 ppm with a spread of $\sigma_M = 5.2\,ppm$, which is drawn in the Figure.

The absolute concentration ranges in the Greek ceramics of the Bronze Age for the 30 elements measured by NAA are given in Table 2, columns 1–3. The values represent the lower and upper deciles (excluding therefore measurement outliers and single, unusual concentration values) and the median. The spreads σ_M of the mean values of the 17 considered groups representing the spreads of the overall distributions are given in the last column.

In Figure 2 a comparison between the different kinds of spread is shown. For each of the 30 elements, the estimated general spreads σ_M, the spreads of the 17 individual group patterns σ_i, the average group spreads σ_{ave} and the average experimental counting errors σ_{exp} are shown each in percent. As expected, the average experimental counting error is a lower limit for the individual group spreads. For some elements like Tb or Zr it seems to be the main reason for the spread of the concentration data, since the value of σ_{ave} is about equal to σ_{exp}. A higher measurement precision for these elements would be desirable. Other elements like As or Na can be measured very precisely ($\sigma_{exp} < 1.5$ %) but have large spreads in the single patterns ($\sigma_{ave} = 46$ % and 22%, respectively). The really interesting comparison is that between σ_{ave} and σ_M. To distinguish two patterns with the help of only one element the concentration values must clearly differ. In case of Ca it seems generally to be difficult to find patterns with clearly different concentration values, since the spreads of the individual group values σ_i and with them σ_{ave} are in the range of the general distribution σ_M of Ca concentrations in ceramics. The same seems to apply also for Ba showing also a high value of σ_{ave} compared to σ_M. The large variability of Ca and Ba concentrations in otherwise well defined chemical patterns can be seen in Table 1 and was reported also by Picon (1985). More suitable elements for group discrimination are La or Sc. The spreads of the individual group patterns σ_i and again with them σ_{ave} are clearly less than the estimated spreads in the general distribution σ_M.

To simplify the comparison between σ_M and σ_{ave} the ratio between the two kinds of spread is shown in Figure 3 for each element. This quotient can help to value the suitability of a single element to distinguish between chemical groups of ceramics generally, although the values shown are obtained with our NAA procedure in Bonn for the case of Greek Bronze Age ceramics. About half of the elements have quotients in the range of 3 to 5, only. None of these elements has a quotient which is clearly higher. This means that the range of possible concentration values of samples with any pattern is only about a factor 3 to 5 higher than the range of possible values of samples with the same chemical pattern. For the remainig elements this quotient is even lower, they are less suitable for provenancing. It follows, since the analytical errors including the experimental counting errors σ_{exp} contribute to the spreads σ_i of each of the group values, that measurements should be performed with the highest possible precision. This corroborates the efforts taken by Perlman, Asaro and co-workers at Berkeley to achieve high analytical precision and refutes somewhat the less stringent position of Harbottle (1976, p. 37). As mentioned, some elements like Ba or Ca scatter in the single group patterns as widely as in the whole data set so that they do not give any information normally. The same applies to elements measurable only with large experimental counting error like Ti in Bonn. Nevertheless, even those elements can help to distinguish between group patterns in special cases. The described quotient is only an attempt to estimate the suitability of single elements in a general way.

The naturally limited concentration ranges of the elements in ceramics show that chemical grouping is only possible when a large set of elements is considered. We use the concentration data of 26 elements (see Table 1) routinely. Therefore, despite the small ranges a very large number of distinguishable chemical patterns are possible and a single pattern which is found by grouping can still be considered as unique with high probability. As an example, the results of a discriminant analysis of some of the groups mentioned above are depicted in Figure 4. In Figure 4a, 450 samples are shown assuming eight groups. The three groups which differ most clearly (Locris-m, Aig and Melos) are omitted in a second discriminant analysis calculation with the result shown in Figure 4b. As can be seen, the cluster of the remaining five groups can be separated, too, in this plot of discriminant functions W1 and W3. The overlapping patterns from Crete can be distinguished in diagrams of higher order discriminant functions.

4 Conclusions

The result of this study was quite unexpected in its extent: For all of the measurable elements by NAA in Bonn a relatively narrow range of possible concentrations was determined in Late Bronze Age ceramics in Greece. It reflects the close compositional similarity of the clay beds exploited in Greece during that time period. In our databank of about 2000 samples from Bronze Age pottery, mainly of the Mycenaean period, the estimated overall spreads of the concentration distributions are at most only a factor of about 5 higher than the average spreads of a pattern of a single pottery group which is assumed to be produced according to a certain recipe in one pottery workshop. Therefore, our data accentuate the need of high precision measurements of each of the elements. Furthermore, given the small ranges of element concentrations, as many elements as possible should be measured to be able to distinguish between patterns of different production workshops or of different production series in one workshop, especially if the number of expected ceramic groups increases in the course of a study. These basic facts of ceramic provenance determination work have been cited often in a general way, but are emphasized here by the range values presented. How far these results, especially the concentration ranges of the different elements deduced from the limited number of Greek samples can be taken to reflect the general composition of ceramics in other regions outside Greece is still an open question. A similar estimation of concentration ranges with ceramic samples from the Rhineland stored in our second large databank in Bonn is in preparation.

References:

Beier, Th. and Mommsen, H. (1994). *Modified Mahalanobis Filters for grouping pottery by chemical composition*, Archaeometry 36, 287–306.

Blackman, M. J., Stein, G. J. and Vandiver, P. B. (1993). *The standardization hypothesis and ceramic mass production: technological, compositional and metric indexes of craft specialization at Tell Leilan, Syria*, American Antiquity 58, 60–80.

Glascock, M. D. (1992). *Characterization of archaeological ceramics at MURR by neutron activation analysis and multivariate statistics*, in Chemical characterization of ceramics pastes in archaeology, ed. H. Neff, 11–26.

Harbottle, G. (1976). *Activation Analysis in Archaeology*, Radiochemstry Vol. 3, Special Periodical Reports, The Chemical Society, London.

Jones, R. E. (1986). *Greek and Cypriot Pottery*, The British School at Athens, Fitch Occasiaonal Paper 1.

Mommsen, H., Beier, Th. and Weber, J. (1991). *Precision of Neutron Activation Analysis in archaeometric studies of ceramics*, Applications of Nuclear Techniques, eds. G. Vourvopoulos and Th. Paradellis, World Scientific, Singapur, 197–201.

Mommsen, H., Beier, Th., Hein, A., Ittameier, D. and Podzuweit, Ch. (1995). *Ceramic production and distribution in Bronze Age settlements in Greece -*

status report on NAA results, in: The Ceramics Cultural Heritage, P. Vincenzini (ed.), Techna, Faenza, 513–520.

Perlman, I. and Asaro, F. (1969). *Pottery Analysis by Neutron Activation*, Archaeometry 11, 21–52.

Picon, M. (1985). *Un example de pollution aux dimensions kilometriques: La fixation du Barium par les céramiques*, Revue d'Archéométrie 9, 27–29.

Table 1: Mean concentrations M_i of 30 elements of four patterns assigned to pottery workshops at Aigina (Aig), Mycenae/Berbati (MB), Tiryns/Asine (TA) and Knossos/Phaistos (KP-1). The values are in ppm if not indicated otherwise and the spreads σ_i are in % of M_i. All of the elements except As, Ba, Ca and Na are used for chemical grouping and the dilution factor fit. The average experimental counting error σ_{exp} is listed for each element in the last column.

	Aig 88 samples		MB 247 samples		TA 96 samples		KP-1 19 samples		average statistical
Element	M	σ(%)	M	σ(%)	M	σ(%)	M	σ(%)	error(%)
As	8.08	39.	5.31	36.	6.43	48.	8.39	42.	1.4
Ba	399.	35.	386.	27.	475.	20.	461.	58.	5.2
Ca%	11.1	26.	9.80	24.	9.16	19.	9.93	36.	5.2
Ce	47.0	4.7	62.5	2.6	66.7	2.0	55.9	1.8	1.4
Co	20.0	9.1	28.1	6.2	23.2	5.5	36.1	7.5	0.58
Cr	439.	11.	249.	11.	203.	9.8	462.	12.	0.63
Cs	5.52	12.	8.69	11.	4.63	9.0	7.03	13.	1.5
Eu	0.96	3.5	1.14	4.5	1.31	3.5	1.06	7.9	2.2
Fe%	4.18	3.9	5.15	3.8	4.99	2.8	5.74	3.6	0.42
Ga	11.9	28.	21.6	28.	18.7	25.	18.1	15.	15.
Hf	4.15	5.1	3.56	9.6	4.40	7.9	3.52	6.4	1.8
K %	1.72	15.	2.59	11.	2.13	15.	2.20	7.6	2.1
La	22.7	3.5	31.4	2.7	30.8	2.0	25.9	2.6	2.2
Lu	0.35	4.5	0.42	4.6	0.43	4.2	0.41	6.8	4.3
Na%	0.97	14.	0.56	33.	1.33	17.	0.70	28.	1.1
Nd	20.3	5.7	26.0	5.5	28.4	4.9	22.2	4.1	5.7
Ni	319.	12.	215.	13.	175.	9.8	445.	11.	6.3
Rb	70.9	12.	149.	8.6	106.	9.6	117.	7.7	2.3
Sb	0.76	19.	0.57	13.	0.63	20.	0.69	15.	9.4
Sc	16.3	4.1	21.2	4.3	19.7	3.1	22.0	4.9	0.17
Sm	3.99	3.0	4.88	3.8	5.53	2.5	4.22	2.5	0.76
Ta	0.68	6.5	0.81	6.6	0.87	6.9	0.85	4.7	3.1
Tb	0.56	6.0	0.66	6.7	0.76	6.4	0.58	6.1	6.3
Th	7.78	5.8	10.9	3.1	11.0	3.3	9.60	3.4	0.66
Ti%	0.43	21.	0.44	19.	0.47	21.	0.49	18.	8.6
U	2.07	14.	2.28	5.3	2.06	6.8	2.18	8.1	4.0
W	1.39	15.	2.18	19.	2.10	22.	1.74	14.	9.3
Yb	2.24	4.7	2.59	3.4	2.73	4.1	2.37	4.2	2.1
Zn	95.4	18.	113.	11.	91.5	18.	105.	5.9	2.5
Zr	177.	14.	153.	21.	180.	17.	174.	21.	16.

Table 2: Concentration ranges of 30 elements measured by NAA. The upper and lower deciles represent the boundaries which exlude the 10% lowest and highest concentration values. The median is the value which splits the dataset in two parts of 50% of the samples each. The spread σ_M of the mean concentration values of the 17 groups mentioned is shown in the last column.

Element	lower decile in ppm	upper decile in ppm	median in ppm	σ_M in %
As	3.4	23.6	7.5	78.
Ba	300.	760.	445.	24.0
Ca%	1.6	11.7	6.8	21.8
Ce	47.	79.	63.	16.0
Co	16.8	35.5	26.7	31.
Cr	153.	485.	263.	49.
Cs	3.7	10.3	6.6	50.
Eu	0.93	1.43	1.16	15.1
Fe%	3.8	5.9	5.0	14.1
Ga	11.4	29.9	19.7	24.1
Hf	3.2	6.1	4.2	21.0
K %	1.60	2.94	2.31	19.0
La	22.5	38.6	30.4	17.6
Lu	0.34	0.56	0.43	12.1
Na%	0.44	1.45	0.89	33.
Nd	19.5	33.9	26.2	18.3
Ni	85.	365.	213.	57.
Rb	72.	163.	119.	24.1
Sb	0.45	1.18	0.64	61.
Sc	15.0	24.0	20.3	14.6
Sm	3.8	6.4	5.0	18.3
Ta	0.65	1.09	0.84	15.7
Tb	0.54	0.91	0.69	18.5
Th	7.8	14.1	10.9	15.6
Ti%	0.32	0.57	0.44	17.2
U	1.72	3.03	2.25	19.9
W	1.39	2.96	2.04	19.2
Yb	2.16	3.24	2.63	14.6
Zn	76.	140.	104.	14.5
Zr	131.	246.	183.	18.1

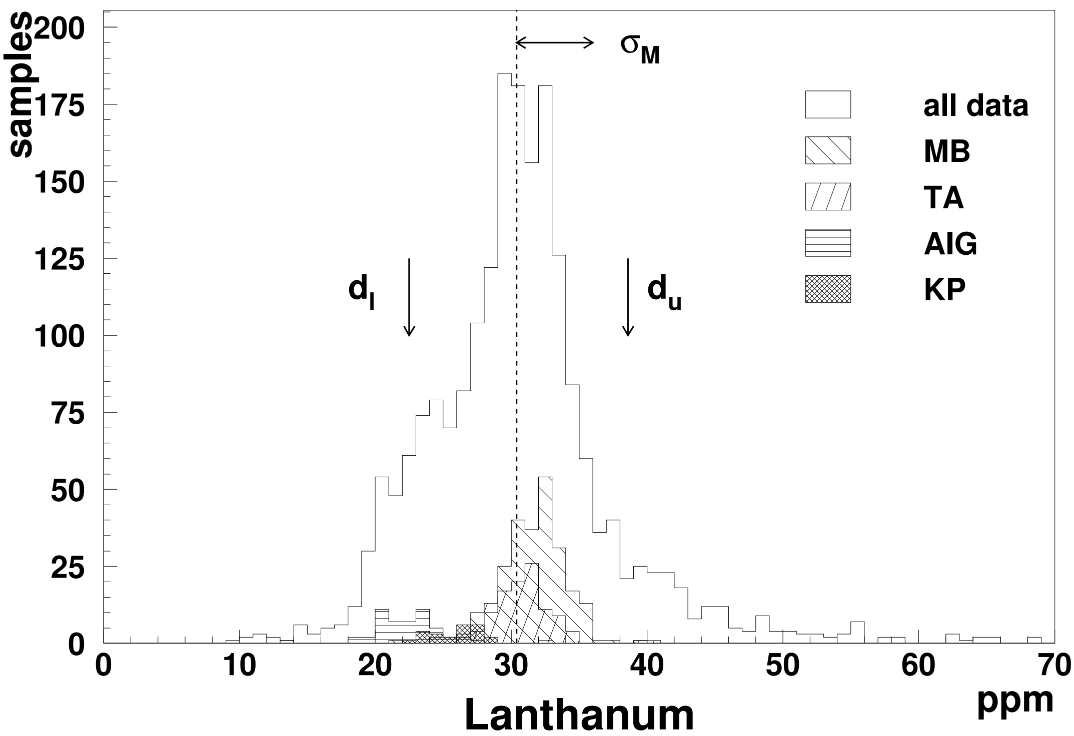

Figure 1: The distribution of La concentrations in ceramics and its lower and upper deciles d_l and d_u with regard to the data set of 2000 samples. In comparison the distributions for four identified groups are shown. Furthermore the spread σ_M of the mean values M of the 17 groups used (see text) are indicated. The distributions of the group patterns will be narrower regarding 'dilution'.

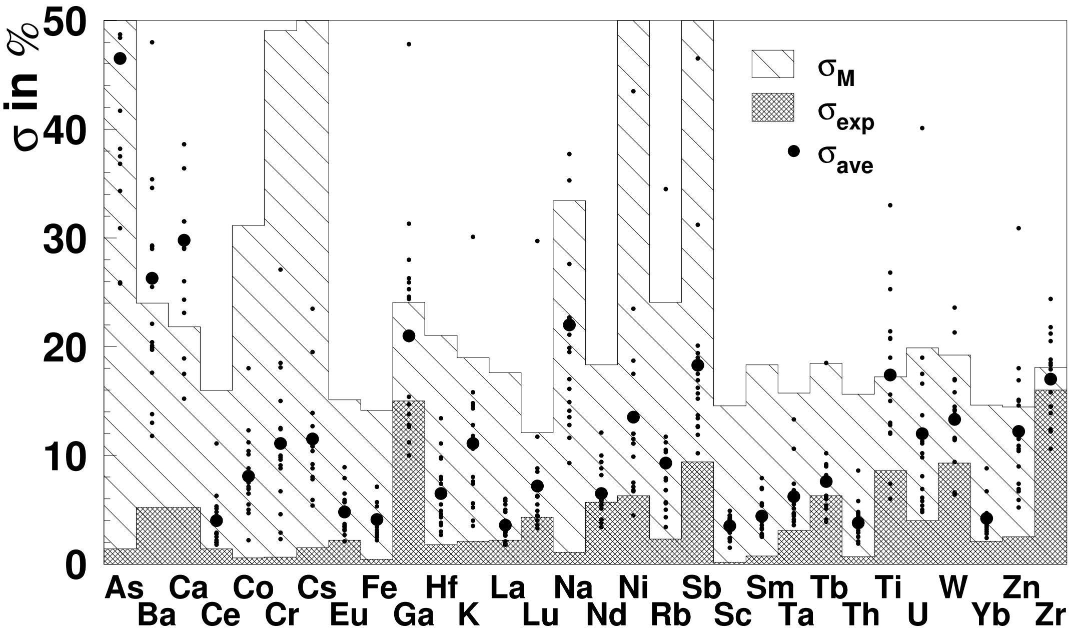

Figure 2: Different kinds of spread are compared. The general distribution of element concentrations is estimated by the spread of the mean values of 17 group patterns σ_M. The small points are the individual spreads σ_i of the 17 different groups and the thick points are the averaged group spreads σ_{ave}. Finally the averaged experimental counting errors σ_{exp} are shown for each element.

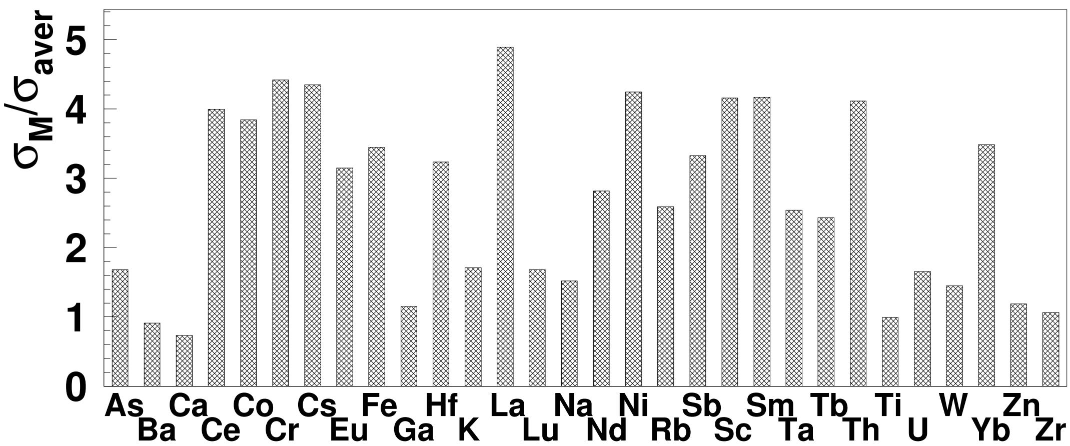

Figure 3: Ratios of the general spread σ_M and the average group spread σ_{ave} for 30 elements. Large bars indicate the most discriminating elements.

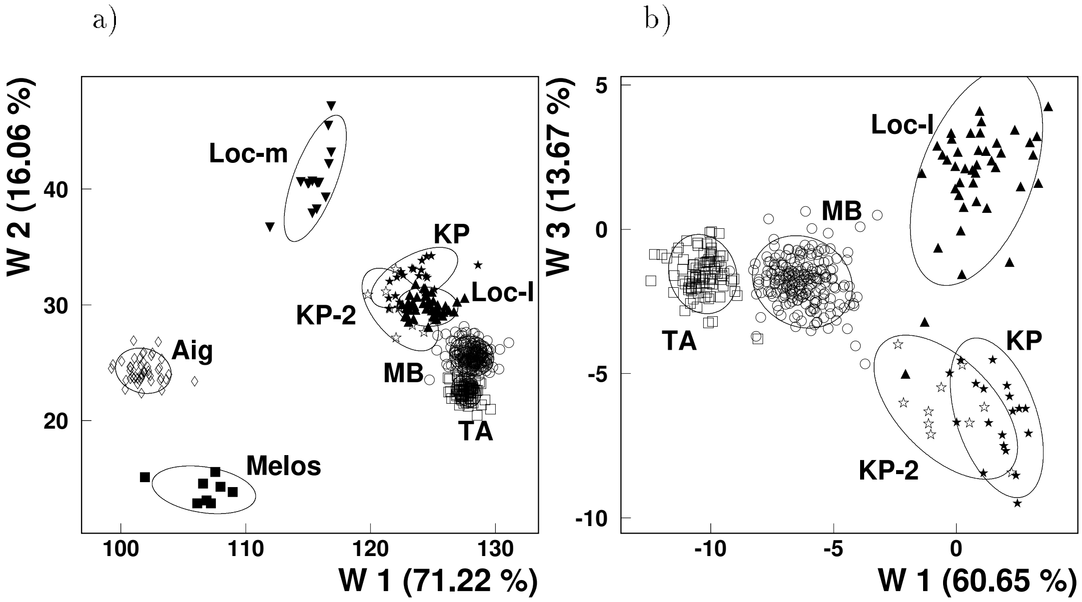

Figure 4: Discriminant analysis of a) 450 and b) 378 samples of ceramics from Bronze Age Greece assuming 8 and 5 groups, respectively. Plotted are the discriminant functions W1 vs W2 and W1 vs W3, respectively which cover 71% and 16% (61% and 14%) of the between group variance. The ellipses drawn are the 2σ boundaries of the groups.

List of figures

Figure 1: The distribution of La concentrations in ceramics and its lower and upper deciles d_l and d_u with regard to the data set of 2000 samples. In comparison the distributions for four identified groups are shown. Furthermore the spread σ_M of the mean values M of the 17 groups used (see text) are indicated. The distributions of the group patterns will be narrower regarding 'dilution'.

Figure 2: Different kinds of spread are compared. The general distribution of element concentrations is estimated by the spread of the mean values of 17 group patterns σ_M. The small points are the individual spreads σ_i of the 17 different groups and the thick points are the averaged group spreads σ_{ave}. Finally the averaged experimental counting errors σ_{exp} are shown for each element.

Figure 3: Ratios of the general spread σ_M and the average group spread σ_{ave} for 30 elements. Large bars indicate the most discriminating elements.

Figure 4: Discriminant analysis of a) 450 and b) 378 samples of ceramics from Bronze Age Greece assuming 8 and 5 groups, respectively. Plotted are the discriminant functions W1 vs W2 and W1 vs W3, respectively which cover 71% and 16% (61% and 14%) of the between group variance. The ellipses drawn are the 2σ boundaries of the groups.

List of tables

Table 1:Mean concentrations M_i of 30 elements of four patterns assigned to pottery workshops at Aigina (Aig), Mycenae/Berbati (MB), Tiryns/Asine (TA) and Knossos/Phaistos (KP-1). The values are in ppm if not indicated otherwise and the spreads σ_i are in % of M_i. All of the elements except As, Ba, Ca and Na are used for chemical grouping and the dilution factor fit. The average experimental counting error σ_{exp} is listed for each element in the last column.

Table 2: Concentration ranges of 30 elements measured by NAA. The upper and lower deciles represent the boundaries which exlude the 10% lowest and highest concentration values. The median is the value which splits the dataset in two parts of 50% of the samples each. The spread σ_M of the mean concentration values of the 17 groups mentioned is shown in the last column.