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Vassilis Kilikoglou, A.P. Grimanis, A. Tsolakidou, A. Hein, Dimitra Malamidou, Zoï Tsirtsoni

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**NEUTRON ACTIVATION PATTERNING OF  
ARCHAEOLOGICAL MATERIALS AT THE NATIONAL  
CENTER FOR SCIENTIFIC RESEARCH 'DEMOKRITOS':  
THE CASE OF BLACK-ON-RED NEOLITHIC POTTERY  
FROM MACEDONIA, GREECE**

V. KILIKOGLU, A. P. GRIMANIS, A. TSOLAKIDOU and A. HEIN

*Institute of Materials Science, NCSR 'Demokritos', Aghia Paraskevi, 15310 Athens, Greece*

D. MALAMIDOU

*18th Ephorate of Prehistoric and Classical Antiquities, Erythrou Stavrou 17, 65110, Kavala, Greece*

and Z. TSIRTSONI

*UMR 5138 Archéométrie et Archéologie, Universités Lyon 2, Lyon 1, CNRS, 7 rue Raulin,  
69365 Lyon, France*

*A short history of the application of NAA in the characterization of archaeological materials at the National Center for Scientific Research 'Demokritos', Athens, is presented. NAA was first applied in archaeology in 1974 at the Radioanalytical Laboratory, and since 1989 has been one of the primary analytical techniques of the 'Demokritos' archaeometry programme. A case study is also presented, concerning chemical patterning of the black-on-red Neolithic pottery class from Macedonia. Four chemical groups were identified, each corresponding to a different area of production. It is shown that this standardized concept of pottery technology and style was spread out within at least eastern Macedonia.*

**KEYWORDS:** NEUTRON ACTIVATION ANALYSIS, BLACK-ON-RED POTTERY, LATE NEOLITHIC, MACEDONIA, DEMOKRITOS

**NAA AT 'DEMOKRITOS'**

Neutron activation analysis activity at the National Center for Scientific Research 'Demokritos', Athens, is directly related to the operation of the Demokritos nuclear reactor, which is located on the premises. It is a pool-type, light water moderated and cooled, reactor, which first went critical, at low power, in 1961. In 1964, the power was increased to 1 MW and the reactor became the main facility of the Center, acting as a reference point for the research groups that were about to be formed at Demokritos.

In this context, Dr Apostolos P. Grimanis established the Radioanalytical Laboratory in 1963, its mission being the development and application of nuclear techniques, with special emphasis on NAA, in medical, environmental and archaeological research. A lot of the work during the first years was devoted to radiochemical separations combined with NAA, for the determination of several trace elements in various materials, since high-resolution Ge detectors appeared later. Thus, the first papers were more about the development of radiochemical

NAA rather than instrumental. Some typical examples include the development of a technique for the determination of Re, Zn and Au in lake waters (Grimanis *et al.* 1964), Cl in beer (Souliotis *et al.* 1965), As in copper and brass (Grimanis and Souliotis 1967), Cu in plants (Grimanis 1968) and As, Sb and Hg in biological materials (Hadzistelios and Grimanis 1969).

The reactor was upgraded in 1970, reaching 5 MW and with improvements made to its cooling system. This event coincided with the first serious attempts for collaborative projects between archaeologists and scientists in Greece, and Demokritos was the first institution to play an active role in this. The experience of the research staff in the field of materials characterization, in combination with the formation of more sophisticated archaeological questions, led to the development of the multidisciplinary field of archaeological science in Greece. In 1983, all of the different archaeometric activities at various Laboratories of Demokritos were coordinated under the umbrella of the 'Archaeometry Programme'. In this scheme, the Radio-analytical Laboratory played an important role in the area of provenance investigations of archaeological materials, contributing with research and supervision of Ph.D. research. In 1985, a new Laboratory of Archaeometry was established at the Institute of Materials Science, which, by the end of that decade, had developed activities in dating and materials characterization, including NAA. Gradually all the archaeometric work was concentrated in this laboratory, and this is where all neutron activation analysis of archaeological materials has occurred since the early 1990s.

#### NAA AND ARCHAEOLOGY

The first archaeometric application of NAA focused on the trace element characterization of Venetian paper, and was published in 1974 (Karayannis *et al.* 1974). Since then, most research has concentrated on ceramics and stones, starting with small-scale studies that typically evolve into Ph.D. theses or European Union funded long-term projects.

The main body of NAA work conducted at Demokritos for the past 30 years can be classified into three categories: (a) methodology, either analytical or in the approach followed for materials characterization and provenance; (b) background analytical work on geological raw materials such as clays, obsidian, marble and metal ores; and (c) archaeological applications on the provenance of materials.

One of the main research interests has been the investigation of the natural, technological, post-depositional, and cultural parameters that affect clay and ceramic composition, and the assessment of these effects on provenance investigations. Such parameters include the mixing, purification and firing of clays (Kilikoglou *et al.* 1988a), the geochemical variability of clays in relation to their mineralogical and petrological composition (Hein *et al.* 2004a,b), and/or the burial environment in relation to mineralogical composition and firing temperature of ceramics (Buxeda *et al.* 2001; Hein *et al.* 2002a). Furthermore, the study of the cooking pot production for a traditional potting village in Spain revealed that a variable local geology, along with the preferences in clay collection, can induce a high chemical variability in the output of a single production centre to an extent where chemical compositions from one 'workshop' could be classified as having different provenances (Buxeda *et al.* 2003a). In terms of methodology, it was realised early on that the best approach in the physicochemical characterization of pottery was one that included data derived from mineralogical, chemical, microstructural and stylistic analyses. This was exercised either in the form of comparative studies among different approaches (Day *et al.* 1999; Tsolakidou *et al.* 2002) or interdisciplinary archaeological applications (e.g., Grimanis *et al.* 1989; Buxeda *et al.* 2003b; Kilikoglou *et al.* 2003).

Several methodological aspects concerning the increase of numbers of elements determined by NAA or comparative analyses with alternative techniques, in order to get the optimum analytical performance, have also been studied. More specifically, the use of a rapid system for short irradiations and subsequent counting has been explored and established, which has been used for archaeological applications as well as environmental ones (Kilikoglou *et al.* 1991; Grimanis *et al.* 1997). Within the framework of a European Union funded project, GEOPRO, a standardization of the main analytical techniques used for pottery characterization took place among the partners, in an attempt to make analytical databanks compatible to one another (Hein *et al.* 2002b; Tsolakidou and Kilikoglou 2002). Finally, multidisciplinary approaches were developed for the provenance determination of stone materials such as flint and marble (Mitropoulos *et al.* 1990; Kokkorou Alevras *et al.* 1995).

Sourcing of archaeological materials and objects requires background analytical work on the geological deposits of raw materials, in an attempt to achieve a match among them and the samples under question. This is common practice, especially when stone objects are analysed, because contrary to clays and metal ores, a straightforward match with the source material is possible. Accurate geochemical characterization has been achieved for the obsidian sources in the Aegean and Central Europe (Kilikoglou *et al.* 1997), which has enabled us to prove long-distance obsidian trade from the Carpathian source to Macedonia during the end of the Neolithic period (Kilikoglou *et al.* 1996). Successful source characterization has also been carried out for flint (Mitropoulos *et al.* 1990) and marble (Grimanis and Vassilaki-Grimani 1988; Mandi *et al.* 1995). Steatite source characterization in Crete and the Shetland Islands, by NAA, inductively coupled plasma mass spectrometry (ICP-MS), and X-ray diffraction (XRD), is in progress, and has shown that mineralogical composition controls the discriminative power of the elements. In the Shetland sources, which consist of almost pure talc, rare earth elements offer the possibility for discrimination among sources. Cretan sources are geologically younger and are mainly characterized as serpentinized pyridotite, containing considerable concentrations of metallic elements, which provide grounds for chemical separation (Jones *et al.* 2007).

The application of NAA to archaeological questions has primarily concerned the analysis of ceramics. The main geographical areas of interest have been the Cycladic islands, Crete, the south/central Greek mainland and Macedonia, covering the principal chronological periods of prehistory. A large number of analyses were conducted on pottery from the site of Akrotiri, Thera. It was found that a large-scale local production existed, that supported the idea of the Cycladic character of the island (Papagiannopoulos *et al.* 1985; Kilikoglou *et al.* 1990a,b), and at the same time that there were strong contacts with the neighbouring islands and Crete (Kilikoglou and Grimanis 1993). Contacts among the Cycladic islands and with the North Aegean, during the Geometric period, were investigated through the analysis of pottery (Grimanis *et al.* 1977, 1980). The analytical work over the years on pottery from Crete has shown that chemical discrimination amongst north and south Mesara (central Crete) and the south coast of the Isthmus of Ierapetra (eastern Crete) is very difficult due to widespread compositional similarities in Neogene clays used in these areas (Jones 1986). One way to tackle this problem is the formation of reference groups using kiln pottery, which is by definition local. For this reason a systematic study of kiln material is a long-term project, and so far the important sites of Knossos, Phaistos and Kommos have been studied successfully (Shaw *et al.* 1997, 2001; Tomlinson and Kilikoglou 1998; Belfiore *et al.* 2003). Two systematic studies of Middle Bronze Age assemblages from Eleusis and Aspis at Argos provide contradictory views regarding the pottery production character: Eleusis proved to be a consumption site, whereas Aspis was a production site (Cosmopoulos *et al.* 1999; Kilikoglou *et al.* 2003). The study of technology transfer in pottery production to the periphery of the

Mycenaean world has been addressed by considering two different areas, southern Italy and central Macedonia. Our results have revealed the existence of two different models. On the one hand, southern Italy seems to exhibit a centralized pottery production, which follows a Mycenaean-like technology, whereas central Macedonian production was probably more varied, in part based on the technology of the local tradition (Buxeda *et al.* 2003b). Finally, it has been shown that pottery products have travelled far from their places of production, at least since the Neolithic. Three chronologically diverse examples are the Neolithic case study presented in detail in this paper, Hellenistic imports to Thebes from Asia Minor (Schwedt *et al.* 2006) and trade of Corinthian roof tiles during the Hellenistic period (Kilikoglou *et al.* 1988b).

Archaeological applications concerning the question of provenance have also been carried out for materials other than pottery. Among the most characteristic examples is the case of limestone either for the reconstruction of temples (Theoulakis *et al.* 1988) or the authentication of museum statues (Grimanis 1986; Herz *et al.* 1989). Compositional analysis of metals has also proven to be successful for source attribution of objects. Although in the case of copper this has been achieved in combination with lead isotopes (Pernicka *et al.* 1990), in the case of lead from Aktotiri trace elements alone were sufficient to prove local production (Bassiakos *et al.* 1990). Finally, obsidian is the most successful case in analytical projects. The importance of the Melian obsidian sources has been confirmed, although long-distance imports from Central Europe to the Aegean were also evident (Filippakis *et al.* 1981; Kilikoglou *et al.* 1996).

#### ROUTINE ANALYTICAL PROCEDURE

For routine analyses of ceramics, carbonates, silicates and steatite, a long irradiation is performed, followed by two measurements. This analytical scheme follows that employed at most NAA-based archaeometry laboratories. Approximately 130 mg of powdered and dried sample is carefully weighed into polyethylene vials, which are then heat-sealed. The vials are irradiated for 45 min in the Demokritos swimming pool reactor, at a thermal neutron flux of about  $6 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ , in batches of 10. Usually two batches are simultaneously irradiated, each of which includes eight samples with unknown composition and two standards. Seven days after the irradiation, the vials are placed in a sample changer and counted for one hour on a Ge  $\gamma$ -detector with a calibrated energy range of 80–1600 keV. The concentrations of As, Ca, K, La, Lu, Na, Sb, Sm, U and Yb are determined from the first count. Three weeks after irradiation, samples and standards are counted a second time for two hours each, and the concentrations of Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, Nd, Ni, Rb, Sc, Ta, Tb, Th, Zn and Zr are determined. All of the above-mentioned elements are typically determined in ceramic materials, whereas fewer elements are measured in other matrices.

The primary standard is SOIL-7—a standard reference material issued by the International Atomic Energy Agency. For silicate materials, SOIL-7 is used in combination with SRM-278 Obsidian Rock, issued by the US National Institute of Standards and Technology (NIST). Calibration tests have been carried out against SL-1 (IAEA), SRM 679 (brick clay, NIST), SRM 2711 (Montana soil, NIST) and two in-house standards that have been used in ceramic analyses for decades—the ‘Bonn standard’ and the ‘Perlman and Asaro standard’.

#### THE BLACK-ON-RED POTTERY PROJECT

Black-on-red painted pottery is one of the most characteristic typological groups that appeared during the final phases of the Late Neolithic (*c.* 4800/4700–3900/3800 BC) in northern Greece



Figure 1 A typical two-handle pot of Variety 1.

(Fig. 1). The largest quantities of this kind of pottery have been found in eastern Macedonia and Thrace. However, significant amounts also have been excavated in central and western Macedonia. This pottery also occurs in minor quantities, further up to the valley of Struma, in south-west Bulgaria, and in Thessaly (Fig. 2). The importance of this ware has long been appreciated by the researchers of the Neolithic period in the Aegean, who use this ceramic ware as a diagnostic element for the relative dating and cultural attribution of ceramic assemblages originating from this region (Koukouli-Chryssanthaki 1996).

This ware's diagnostic attributes lie not only in the remarkable aesthetic value of the vivid dark-on-light contrast, but also in its high technical quality, as witnessed by the fineness of the fabric, the uniformity of the surface colours, and the metallic ring of the vessels' walls. Recognizable among hundreds, this pottery has aroused the interest of archaeologists since the early decades of the 20th century (Heurtley 1939; French 1961). Material from systematic excavations comes from several Neolithic settlements, such as Paradimi, Dikili Tash, Sitagroi and Dimitra, and more recently from Kryoneri in eastern Macedonia and Thrace, Slatino, Strumsko and Promachon-Topolnitsa in the middle Struma Valley, Vassilika, Stavroupoli and Messimeriani Toumba in central Macedonia, and Giannitsa, Polyplatanos, Makriyalos and Megalo Nisi Galanis in western Macedonia. Despite the importance of these ceramics as chronological and cultural markers, no systematic study of their modes of production and patterns of distribution has been undertaken until recently (Kilikoglou *et al.* 2002).

The purpose of our study was to search for production patterns for this ceramic group. More specifically, we sought to examine questions such as the degree of standardization in the



Figure 2 A map of northern Greece, showing the areas mentioned in the text.

production, localization of the production centres and scales of production, and to differentiate ceramic recipes within this specific ceramic group that could reflect variation (geographical or other) in pottery traditions.

To date, stylistic (macroscopic) analysis based on shape, decoration, surface treatment and fabric has been conducted on whole vessels and fragments obtained from 36 excavated settlements and from surface surveys of about 100 sites in northern Greece. Four main varieties have been identified, each having its own specific features that apparently correspond to different geographical regions (Malamidou 2005).

The first stylistic group, Variety 1, features an extremely fine fabric, practically free from inclusions, and a bright red/orange surface colour. Decoration is executed with a black or brownish-black paint, which sometimes turns to grey or whitish. A great variety of vessel shapes is recorded, including both small and large open and closed vessels with simple or complex profiles (Fig. 1). The main distribution area of this stylistic group is eastern Macedonia, especially the Drama and Serres plains and the Pieria Valley (Fig. 2). Similar pottery is also found, but in substantially lower quantities, in Thrace and in some parts of central and western Macedonia. Pottery of this variety has also been found in the site of Pefkakia of Thessaly, which is clearly outside the area of its immediate distribution, indicating long-distance trading in this pottery type.

Variety 2 is only known from fragments. It is much coarser than Variety 1, and the paint, which is always black or dark brown, is thick and matte. It is found exclusively in Bulgaria's middle and upper Struma Valley (Fig. 2).

The next two varieties feature different decorative motifs and much thinner paints used for decoration. In Variety 3, the paint can be almost transparent; this is characteristic of settlements

in central Macedonia. In Variety 4, the matte paint comes into contrast with the shiny ground: this is typical of western Macedonia (Fig. 2).

The four varieties that have been distinguished from macroscopic analysis reflect apparent differences within a broader pottery tradition of two-coloured black-on-red decoration in northern Greece. The common technical standards shared in all varieties are the use of iron-rich clays, manganese-rich black paints, and the introduction of high firing temperatures (Yiouni 2001). The macroscopic variability, therefore, must result from differences in locally available raw materials, as well as differences in each area's local background in pottery production during earlier phases of the Neolithic.

The clear geographical distributions of the four varieties presumably reflect production and mechanisms of distribution organized at a regional scale. There is very little geographical overlapping among the four varieties, suggesting that vessels did not travel very far from their production centre. There are some exceptions to this. For example, several fragments of Variety 1 have been found at the settlements of Pefkakia (in Thessaly) and at Slatino (upper Struma Valley, south-west Bulgaria).

Considering the scale of production and the relative percentages of the total amounts of decorated pottery, it appears that Variety 1 is by far the most dynamic and important production in its main distribution area—eastern Macedonia. In fact, Varieties 2–4 represent smaller percentages of the total amount of decorated ceramics in their respective distribution areas.

This feature, together with the fact that eastern Macedonia provides better conditions for detailed analysis (abundant material from systematically excavated sites, rich information from surveys and a relatively well-known geological context), led us to concentrate on Variety 1 for further technological analysis. The aim was to deal with matters of raw material management, such as provenance, the diffusion of ceramic products, the possible distinction of different workshops, and the socio-economic role that this specific ceramic group had in the Late Neolithic II.

Altogether, 195 samples were selected and analysed by NAA, following the above-described procedure, in attempts to answer the questions that arose during the stylistic study of this material. The samples originate from 14 sites shown in Figure 3 and from the site of Pefkakia (Fig. 2). The number of samples analysed from each site was proportional to the overall quantity of black-on-red pottery found at each site (see the last column of Table 4, below). Special emphasis was given to Kryoneri, as this is a reference site for this pottery ware, and it has a higher relative abundance of this ware than any other site in Macedonia or Thrace.

## THE STATISTICAL APPROACH

### *Variation matrix and total variation*

One way to estimate the existing geochemical variability in the compositional data for a set of ceramics is through the determination of their total variation, following the approach of Buxeda i Garrigós and Kilikoglou (2001). For this reason, a  $n \times n$  variation matrix  $T$  is generated, with  $n$  being the number of element concentrations, and  $\tau_{ij} = \text{var}\{\log(x_i/x_j)\}$  (Aitchinson 1986), the matrix elements, which present the variances of the element concentrations, being expressed as logarithmic ratios. In this way, all elements are used successively as a divisor in these ratios. The total variation of the data is then given by

$$vt = \sum_{ij} \frac{\tau_{ij}}{2n}$$



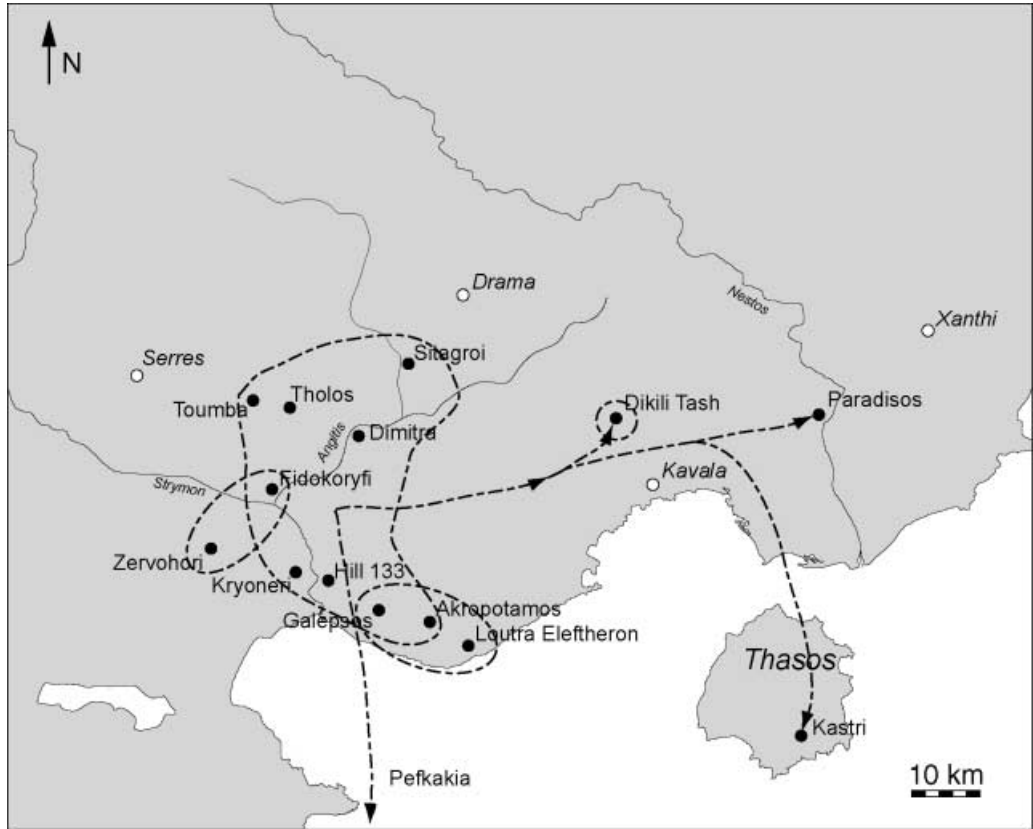


Figure 3 A map of eastern Macedonia, showing the sites from which samples came.

The sum  $\tau_{.s}$  of the variances in a particular column of the variation matrix gives the contribution to the total variation of the element  $s$ , which in this case has been used as divisor. Therefore a high ratio  $v_i/\tau_{.s}$  indicates low variability of the respective element (Buxeda i Garrigós 1999).

To study the variability of the entire assemblage, the variation matrices were calculated for a certain number of samples in each case randomly selected from the original data set. The idea is that the distribution of the total variations is related to the number of groups existing in the data set. In principle, this distribution can be interpreted in view of the number of groups to be expected in the data (Buxeda i Garrigós and Kilikoglou 2001).

#### *Mahalanobis distance and best relative fit*

A common approach to forming and defining groups in a compositional data set is to compare samples or groups of samples on the basis of a distance, in order to obtain a measure of similarity or dissimilarity. For this comparison, the Mahalanobis distance has been proved to be suitable in many cases, because uncertainties introduced in the data by natural inhomogeneities of the analysed material or statistical errors are taken into consideration (Bieber *et al.* 1976;

Beier and Mommsen 1994). However, Mahalanobis distance calculations require large groups. A similar, but simpler, distance, more suitable for small groups, is the squared Euclidian distance, weighted by the uncertainties that can be estimated from the standard deviations of the groups. In the case in which a sample  $n$  is tested for similarity to a group, the distance can be determined as follows:

$$d_{x,y}^2 = \sum_i \frac{(x_i - y_i)^2}{\sigma_i^2}$$

where  $x$  is the chemical composition of the sample,  $y$  is the average composition of the group and  $\sigma$  is the standard deviation of the group. This corresponds to considering only the diagonal of the estimated covariance matrix in the Mahalanobis distance.

Additionally, a best relative fit can be applied (Harbottle 1976; Beier and Mommsen 1994) to adjust for certain differences between two data sets. If, for example, there is a difference between two groups of samples in the amount of quartz or calcite that they contain, the one with the highest amount will exhibit systematically lower concentrations of trace elements, although the base clay is the same. With the application of a best relative fit, the variation induced by the temper materials can be corrected and the clay composition of a particular group of ceramics can be defined more precisely.

## RESULTS AND DISCUSSION

According to the approach outlined above, the variation matrix of the entire data set was calculated to obtain an estimate of the existing variability. The total variation was found to be 0.73, a value that, according to other similar case studies, appears to be on the low side. This value is comparable to compositional variability observed in pottery from production centres, and it is definitely lower than that observed in assemblages containing different fabric wares (Buxeda i Garrigós and Kilikoglou 2001). Therefore, we can assume that this value indicates a relatively homogeneous data set, representing broadly similar ceramic fabrics, produced from geochemically similar raw materials.

During the statistical treatment, some of the element concentrations were disregarded, for different reasons: As because of its known geochemical mobility; Hf, Tb, Zn and K because of some missing values; and Nd, Ni and Zr because of low counting statistics. Of the remaining element concentrations, La presented the lowest variation, with  $\tau_{La} = 0.85$ , making it the best candidate to represent only the natural variability of the data set. On the other hand, Ca ( $\tau_{Ca} = 6.82$ ), Cr ( $\tau_{Cr} = 1.29$ ), Na ( $\tau_{Na} = 1.38$ ), Sb ( $\tau_{Sb} = 2.56$ ), Sc ( $\tau_{Sc} = 1.29$ ) and U ( $\tau_U = 1.66$ ) showed higher variation. Therefore, for a principal component analysis (PCA) of the entire data set, the element concentrations were scaled by log-ratio transformation using the La concentration as the divisor. A plot of the first two principal components (Fig. 4) suggests one large compositional group, with only a few samples either forming small different groups or being chemical loners. This is an indication that the main body of the data should represent one large group, with a few smaller and chemically related groups.

Following the above-described approach, a series of variation matrices of 10 and 30 samples, respectively, were determined. These matrices were repeated, randomly, from the whole data set. In Figure 5, distributions of the total variation values are presented, each corresponding to 2000 different subsample sets. As could be expected, in the case of 30 samples the distribution is narrow (total variation values from 0.39 to 1.16, with a median of 0.72) and also more

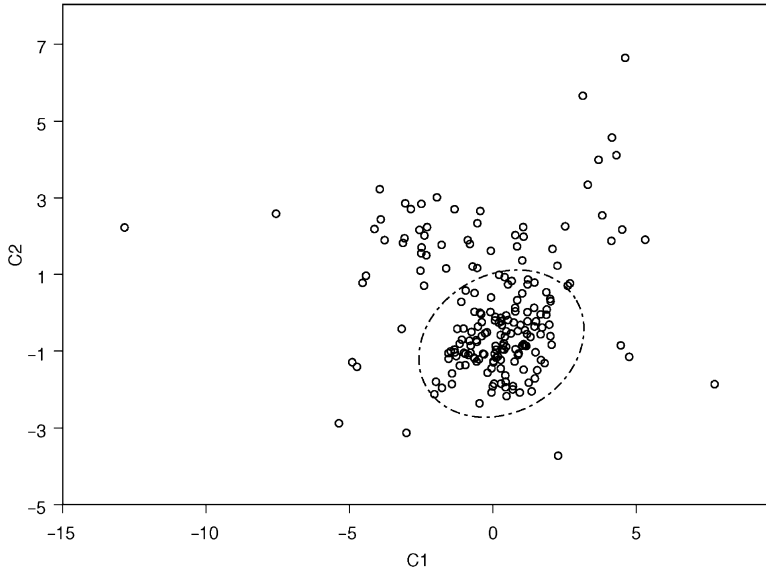


Figure 4 A plot of the first two principal components derived from PCA of all analysed samples.

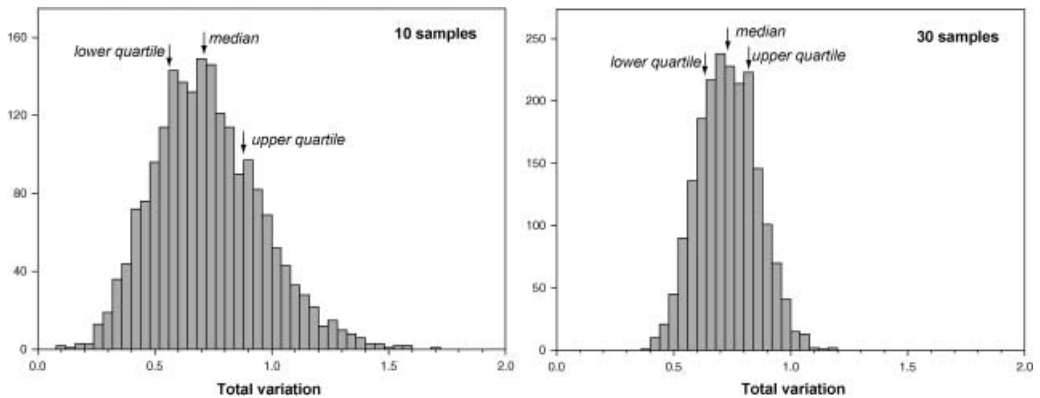


Figure 5 Distributions of the total variation values of sets of 10 and 30 samples randomly selected from the entire data set. Each distribution has been formed by 2000 values.

balanced in terms of low and high values. In the case of 10 samples, the distribution is broader (total variation values from 0.12 to 1.70), but here also the median of 0.71 is considerably close to the actual total variation of the entire data set. The distribution presents a clear tail to the higher values, because in the case of 10 samples, a loner (or outlier) with a different chemical composition has a stronger influence on the total variation. Nevertheless, the distribution is considerably small compared to other ceramic assemblages, indicating a large group of samples with relatively homogeneous chemical composition (Buxeda i Garrigós and Kilikoglou 2001).

Table 1 Average values and standard deviations for chemical Group A ( $n = 136$ ) before and after a best relative fit factor was applied

	Group A (raw data)			Group A (best relative fit)		
	Average	s.d.	s.d. (%)	Average	s.d.	s.d. (%)
As	10.3	9.5	93	10.2	9.2	89
Ba	569	112	20	568	117	21
Ca (%)	2.1	1.6	75	2.1	1.8	85
Ce	93	6	6.4	92	3	3.1
Co	20.4	2.2	11	20.4	1.8	8.6
Cr	98	8	8.3	98	6	6.4
Cs	12.7	1.9	15	12.7	1.7	14
Eu	1.63	0.09	5.7	1.63	0.06	3.4
Fe (%)	5.39	0.47	8.8	5.37	0.34	6.3
Hf	5.63	0.69	12	5.63	0.80	14
K (%)	3.06	0.30	9.8	3.06	0.32	10
La	42.2	2.6	6.2	42.1	1.2	2.9
Lu	0.46	0.04	7.8	0.46	0.03	6.5
Na (%)	1.27	0.19	15	1.27	0.22	17
Nd	50	8	16	50	8	16
Ni	49	20	41	49	20	40
Rb	172	12	7.2	172	9	5.1
Sb	1.37	0.42	30	1.36	0.40	29
Sc	20.4	1.3	6.2	20.4	0.7	3.2
Sm	8.35	0.54	6.5	8.32	0.24	2.9
Ta	1.59	0.12	7.4	1.59	0.10	6.4
Tb	0.99	0.11	11	0.99	0.09	9.5
Th	19.2	1.4	7.3	19.1	0.8	4.2
U	5.11	0.91	18	5.09	0.88	17
Yb	3.65	0.26	7.2	3.64	0.18	5.1
Zn	153	14	9.4	152	10	6.7
Zr	234	34	15	233	35	15

On the other hand, sets of particular combinations of 10 or 30 samples, which provided the lowest total variation values, are assumed to represent typical samples with membership in the core groups or to represent subgroups from specific production locales.

In order to define groups of geochemically similar samples, initial groups were selected on the basis of PCA and total variation. From these initial groups, samples were added or removed by using the weighted Euclidean distance, as described above. This procedure was repeated until stable groups were established. As expected from the PCA and the total variation considerations, a large core group was formed. In Table 1, the average values and standard deviations for Group A ( $n = 136$  samples), calculated for the raw data and transformed data using the best relative fit, are presented. The total variation of this group is 0.42, with Sc and Th as elements with the least variation, with both  $\tau_{Sc}$  and  $\tau_{Th}$  showing a value of 0.48. The highest variations were again presented by Ca ( $\tau_{Ca} = 4.90$ ), Sb ( $\tau_{Sb} = 1.27$ ), Na ( $\tau_{Na} = 0.96$ ) and U ( $\tau_U = 0.87$ ), whereas the increased variation of the Cr concentration, which was observed in

the entire data set, disappeared ( $\tau_{Cr} = 0.49$ ). Variation of Ca can often be attributed to variation of the calcite content that occurs either as part of the natural clay or in the form of temper added to the clay paste. Higher calcite results in lower trace element concentrations for all of the elements, and the effect is normally indicated by a relative fit factor clearly above 1. However, this was the case for only a few samples. Therefore, a few samples with Ca concentrations of approximately 5% were selected for additional mineralogical examination using X-ray diffraction (XRD) and scanning electron microscopy (SEM) to assess the firing temperatures of these sherds. It was determined that the microstructure developed in all of the sherds was compatible with firing temperatures well above 900°C (Tsitsoni *et al.* 2005). At these temperatures, and taking into account the fine nature of the ceramic materials, high-temperature Ca-rich mineral phases should be expected rather than original calcite (Maniatis *et al.* 1981). The XRD results present, however—apart from diopside, which was assumedly formed during the firing after the decomposition of CaCO<sub>3</sub>, plagioclase contents—were clearly higher, compared to samples with lower Ca content. Although plagioclase could have developed as a high-temperature mineral phase, the variation in the Ca content is more likely attributed to the varying plagioclase contents of the original raw materials. The high variation of U is probably related to the high degree of mobility of this element in underground waters, in combination with the fact that U is elevated in the soils within the study area (Stavropodis and Pournis 1971). In any case, the high standard deviation is mainly caused by only a few samples with particularly high concentrations.

Three smaller groups were defined, which were compositionally similar to Group A but which could be distinguished on the basis of particular elements. Group A-V1, which comprised four samples, presented significantly smaller concentrations of most of the rare earth elements (REE), Hf, Sc and Ta, but higher concentrations of Ca and to a lesser extent, Cr (Table 2). This significant difference in Ca has an effect on the colour of the ceramic bodies of Group A-V1, as they appear buff compared to the dark red of the typical black-on-red ceramics. Group A-V2 comprises four samples that have higher concentrations of Cr, Sb and U. Finally, the two samples that form Group A-V3 have the highest U values. All these differences could be principally explained with varying content of accessory minerals, or in the case of Group A-V1 with a dilution effect caused by the inclusion of non-plastic tempers. Therefore, these three subgroups are most likely related to Group A, given the geochemical similarity of these samples to Group A pottery. In other words, these subgroups are assumed to represent pottery production in the same area as Group A.

Apart from the main group and the three related subgroups, three additional groups were identified (Table 3), indicating that black-on-red ceramics were produced apparently with different raw materials. If these chemical groups are compared to their provenance, it seems likely that they represent local production groups (Table 4). The discriminant analysis plot of Figure 6 illustrates the chemical distinction among the four groups. Judging from the mean and standard deviations presented in Tables 1 and 3, all groups appear to be statistically tight, indicating either chemical uniformity of raw materials within extensive areas or organized productions from geographically specific clay beds. It is worth noticing that the total variations of the three small groups were smaller compared to Group A: 0.20 (Group B), 0.31 (Group C) and 0.39 (Group D).

It is apparent from the number of samples belonging to Group A and the number of sites that the samples come from that this group represents the main body of production and the distribution of the black-on-red pottery in eastern Macedonia. Group A contains all samples from Kryoneri, Dimitra, Hill133, Toumba Serron, Sitagroi and Tholos (Table 4). As can be

Table 2 Average values and standard deviations of chemical subgroups of Group A

	Group A-V1 (n = 4)			Group A-V2 (n = 4)			Group A-V3 (n = 2)		
	Average	s.d.	s.d. (%)	Average	s.d.	s.d. (%)	Average	s.d.	s.d. (%)
As	10.4	4.0	39	8.1	3.4	43	9.3	7.8	84
Ba	650	90	14	594	70	12	939	198	21
Ca (%)	6.5	3.0	47	4.0	0.9	23	1.2	0.4	37
Ce	82	2	2.3	90	7	8.3	94	4	4.1
Co	19.8	3.0	15	20.2	1.6	7.8	22.5	0.3	1.3
Cr	115	6	5.1	121	12	9.7	90	0	0.5
Cs	10.9	0.7	6.4	13.3	1.5	11	13.4	2.8	21
Eu	1.40	0.04	3.2	1.64	0.10	5.9	1.65	0.04	2.6
Fe (%)	5.27	0.25	4.7	5.62	0.50	8.8	5.79	0.45	7.7
Hf	4.21	0.24	5.8	4.05	0.26	6.5	5.60	0.53	9.5
K (%)	3.18	0.61	19	3.15	0.27	8.5	2.55	0.08	3.1
La	37.4	1.6	4.3	40.7	3.6	8.8	41.2	2.4	5.8
Lu	0.38	0.02	5.8	0.41	0.05	12	0.41	0.01	2.2
Na (%)	1.04	0.02	1.6	1.04	0.14	14	1.30	0.04	2.9
Nd	47	9	20	45	3	6.1	58	–	–
Ni	69	13	19	60	3	4.6	31	–	–
Rb	166	2	1.5	173	12	7.2	166	11	6.4
Sb	2.77	1.69	61	2.79	0.42	15	1.47	0.28	19
Sc	17.9	1.1	6.2	20.0	1.3	6.5	20.0	0.1	0.7
Sm	7.17	0.30	4.2	8.20	0.68	8.3	8.69	0.02	0.2
Ta	1.28	0.06	4.5	1.41	0.07	5.1	1.51	0.08	5.2
Tb	0.93	0.10	11	0.96	0.02	2.6	1.04	0.07	6.2
Th	18.4	0.5	3.0	19.3	1.6	8.4	18.9	1.8	9.7
U	5.09	0.71	14	8.78	0.82	9.3	14.50	1.13	7.8
Yb	2.92	0.16	5.5	3.36	0.26	7.6	3.43	0.29	8.5
Zn	148	10	6.6	168	13	7.9	154	2	1.4
Zr	178	30	17	196	56	29	300	3	0.9

seen in Figure 3, all of these sites form a geographical cluster located in the valley of the rivers Angitis and Strymonas. Also, approximately half of the samples analysed from Akropotamos, Fidokoryfi and Zervohori, all three on the periphery of this cluster (Fig. 3), belong to Group A. Taking into account most of the central sites of the cluster and the rich alluvial clay deposits in the valley are assigned to Group A, it is safe to assume that this group represents the local black-on-red production. The importance of Group A is apparent from the perspective that all samples from the distant sites of Kastri on Thasos Island, Pefkakia in Thessaly and Paradisos in the extreme east are also assigned to this group, indicating inter-regional distribution from the main production area.

A second area of production seems to be the coastal zone, represented by Loutra Eleftheron, whose samples cluster exclusively in Group B, and Akropotamos with Galepsos, which share their samples with Group A. The clays from this production area are more calcareous than those of Group A, but contain no significant macroscopic differences in terms of appearance. However, there are small stylistic differences in the decorative motifs that suggest a different production group.

Table 3 Average values and standard deviations of chemical Groups B, C and D. Significantly different values appear in bold

	Group B (n = 18)			Group C (n = 6)			Group D (n = 5)		
	Mean	s.d.	s.d. (%)	Mean	s.d.	s.d. (%)	Mean	s.d.	s.d. (%)
As	12.0	5.0	42	7.6	2.7	36	18.5	15.8	86
Ba	652	190	29	582	30	5.2	491	84	17
Ca (%)	4.4	1.1	25	1.2	0.2	15	2.6	1.2	47
Ce	91	4	4.4	<b>177</b>	5	2.8	92	3	3.5
Co	16.6	1.7	10	20.4	1.4	6.9	20.9	1.4	6.7
Cr	96	5	5.7	<b>194</b>	33	17	210	24	11
Cs	10.9	0.5	4.4	11.7	2.8	24	15.5	2.3	15
Eu	<b>1.46</b>	0.07	5.0	1.64	0.07	4.1	1.69	0.07	4.1
Fe (%)	4.73	0.21	4.5	5.22	0.43	8.2	5.29	0.41	7.7
Hf	5.34	0.41	7.6	6.23	1.07	17	5.69	0.70	12
K (%)	2.85	0.20	7.0	2.93	0.18	6.2	3.36	0.14	4.1
La	40.4	1.7	4.2	40.7	1.3	3.3	41.5	1.6	3.9
Lu	<b>0.37</b>	0.03	8.4	0.45	0.03	7.2	0.48	0.01	3.0
Na (%)	1.19	0.08	7.1	1.33	0.39	29	1.24	0.28	22
Nd	45	4	9.5	41	3	8.2	43	6	13
Ni	50	19	37	41	8	20	–	–	–
Rb	169	11	6.4	174	9	4.9	<b>204</b>	8	3.7
Sb	2.26	0.59	26	1.14	0.20	18	1.44	0.31	22
Sc	<b>16.9</b>	1.0	5.8	<b>40.0</b>	3.1	7.7	<b>42.1</b>	2.0	4.7
Sm	<b>7.48</b>	0.36	4.9	7.83	0.33	4.2	8.33	0.27	3.2
Ta	1.44	0.09	6.1	1.58	0.11	7.0	1.53	0.07	4.3
Tb	0.82	0.06	6.9	0.85	0.04	4.6	0.97	0.11	12
Th	20.5	0.8	3.9	<b>36.3</b>	1.9	5.3	19.8	0.6	2.8
U	5.06	0.53	10	4.56	0.58	13	5.10	0.46	9.1
Yb	<b>3.05</b>	0.22	7.2	3.61	0.21	5.8	3.77	0.07	1.8
Zn	147	19	13	146	10	6.6	160	15	9.4
Zr	213	34	16	238	32	14	–	–	–

The third group (Group C) represents two sites in the central/western part of Strymonas Valley—Fidokoryfi and Zervohori. Although both sites have samples that can be assigned to Group A, the existence of the distinct Group C indicates a local production as well. Finally, samples from Dikili Tash are equally divided between Group A and Group D, which is exclusive to this site. These findings again suggest the existence of local production in Dikili Tash, coexisting with the imports from the valley area.

The general view has been that one black-on-red tradition exists throughout eastern Macedonia, and that this pottery-making tradition shares the same technological and, in broad sense, stylistic characteristics. This is supported by the first results of the scanning electron microscopy examination of representative samples (Tsirtsoni *et al.* 2005). However, we now know that pottery production took place in at least four geographical areas (Fig. 3) and that whatever chemical variability exists originates only from the nature of the local raw materials.

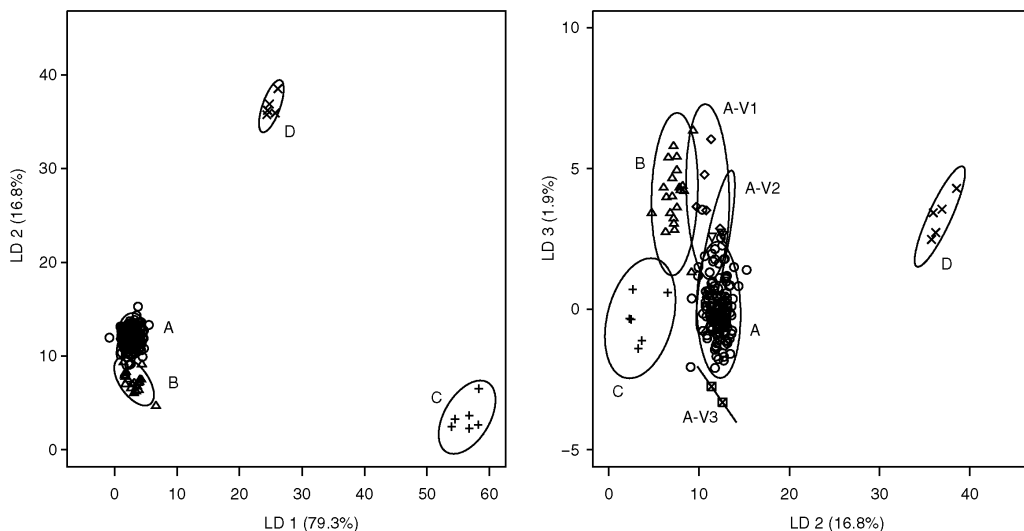


Figure 6 A discriminant analysis plot of the groups formed after the statistical analysis. In the left-hand plot, Group A and the three subgroups have been considered as one. In the right-hand plot, they are kept separate, but they still show separation from Groups B, C and D. Ellipses indicate  $2\sigma$  boundaries.

Table 4 Summary of analysed samples, sites and compositional groups

	A	A-V1	A-V2	A-V3	B	C	D	Loner	Total
Akropotamos	4	1			5				10
Dimitra	20							1	21
Fidokoryfi	3					4		1	8
Gianitsa								1	1
Galepsos	7				3				10
Kastri	9				1(?)				10
Kryoneri	49 + 4(?)	3 + 1(?)	3					4	64
Hill 133	10								10
Loutra Eleftheron					8 + 2(?)				10
Dikili Tash	4				1		5	1	11
Pefkakia	3								3
Paradisos	4				1				5
Sitagroi	9 + 1(?)								10
Toumba Serron	5			2				3	10
Tholos	7		1						8
Zervohori	2					2			4
	136 + 5(?)	4 + 1(?)	4	2	18 + 3(?)	6	5	11	195

A large number of clay samples have also been collected from the area and analysed raw and after firing (Malamidou *et al.* in press). The analytical data derived from clays were compared to the ceramic groups, either straightforwardly or assuming all possible mixing combinations, but no chemical match was achieved. One possible explanation is that because the sedimentation



in the area is very high, the surface clays collected are very recent, given that the Neolithic horizons occur metres below the surface.

From the 195 samples included in the programme of analysis, 11 could not be assigned to any of the established groups and have to be considered as chemical loners. Two of these 11 samples have chemical profiles that are extremely different from those of Groups A–D and they definitely represent different raw materials. The rest, although not so distinct, were removed from consideration in the analysis because their inclusion would only serve to increase the standard deviation of the groups, without providing any new information on their geographical or chemical composition. When further analyses take place, these samples will be re-examined.

## CONCLUSIONS

Chemical patterning by NAA of black-on-red Neolithic pottery samples analysed from eastern Macedonia resulted in the identification of four distinct groups, each of which represents a distinct production area. The main production area for black-on-red pottery proved to be the valley of the rivers Strymon and Angitis. Pottery from this area was transported to Thessaly (south) and Thasos Island (east).

The pottery production in the four geographical areas had common technological and, in a broader sense, stylistic characteristics. This suggests that the know-how in the Neolithic pottery-making societies of eastern Macedonia was widely spread and shared. It remains to be seen whether this standardization existed in other areas of Macedonia.

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