Analysis of Ancient Pottery and Ceramic Objects Using X-Ray Fluorescence Spectrometry

A. E. Pillay,[1]* C. Punyadeera,[2] L. Jacobson[3] and J. Eriksen[1]

[1] Department of Chemistry, College of Science, Sultan Qaboos University, P.O. Box 36, Al Khoud, Postal Code 123, Sultanate of Oman

[2] Department of Chemistry, University of the Witwatersrand, P.O. Wits 2050, Durban 4000, South Africa

[3] McGregor Museum, P.O. Box 316, Kimberley 8300, South Africa

Archaeology has been called 'the science of the artefact' and nothing demonstrates this point better than the current interest displayed in provenance studies of archaeological objects. In theory, every vessel carries a chemical compositional pattern or 'fingerprint' identical with the clay from which it was made and this relationship is basic to provenance studies. The reasoning behind provenance or sourcing studies is to probe into the past and attempt to re-create prehistory by obtaining information on exchange and social interaction. This paper discusses the use of XRF spectrometry for the analysis of ancient pottery and ceramics to examine whether it is possible to predict prehistoric cultural exchanges. Copyright © 2000 John Wiley & Sons, Ltd.

INTRODUCTION

Archaeologists have long been concerned with the provenance of pottery and have evolved elaborate systems of classification based largely upon form and decorative styles.[1] The standard criteria used in the past to characterize potsherds from different geographical regions are the morphology (shape and size) of the vessel and the form of decoration.[2] While this approach is very useful for the classification of available materials, the fact that many of the people manufacturing pottery were mobile pastoralists suggests that a mixing of pottery was likely and therefore this typological method cannot be used to provide conclusive information on ethnic groupings.[3–8] In more recent years, such studies have been supplemented by determining elements or examining minerals which appear in the fired clays. Since provenance studies are aimed at identifying the sources of ceramic raw materials and finished items, or identifying the centers of production,[4,5] such assays may involve physical analysis[6,7] or chemical methods or a combination of both.[9,10] Sourcing usually depends on a combination of geochemical analysis and a detailed knowledge of regional geology.

Although the scientific analysis of pottery fabrics began in the 19th century,[11] it is only in the last decade that work of this type has been undertaken widely. It has been demonstrated[12] that a model combining analytical and archaeological information can provide significant information on social interaction and exchange which could not be derived from a visual stylistic examination of the artefacts alone. Chemical methods for 'geochemical fingerprinting' have emerged as a useful development in this area of study. Such a study bears the implicit assumption that the pottery produced in a particular area will carry a specific geochemical fingerprint. There are many analytical techniques which could be applied to the study of ceramics or pottery and the more important ones are compared below with XRF together with a discussion of certain aspects of their applications which directly concern archaeologists.

METHODS APPLIED IN STUDYING ANCIENT CERAMICS AND POTTERY

Petrological methods

A particularly valuable method of studying ancient ceramics is by examination of thin sections under the petrological microscope.[13] This involves the removal of a small fragment of pottery (10 × 10 mm) which is fixed to a glass microscope slide and ground with a diamond lap or with an abrasive powder until it is exactly 0.3 mm thick (see Ref. 13 for the detailed method). Most of the minerals are then transparent, and can be studied under a petrological microscope, an instrument equipped with optical refinements which allow the precise determination of mineral and rock inclusions. Since clay minerals are too fine-grained to be identified in this way, the study is limited to coarse inclusions, either naturally occurring in the clay or as an added temper. In this method, interest is focused on the potential clay sources rather than on the added temper. The mineralogy of the clays could also be studied by x-ray diffraction (XRD). The drawback, however, is that, when clays are heated to about 500 °C the clay minerals tend to be destroyed.[14]

Instrumental methods

Chemical analysis has found considerable application in the study of ceramics, particularly in problems of characterization, for different clay deposits can be distinguished

* Correspondence to: A. E. Pillay, Department of Chemistry, College of Science, Sultan Qaboos University, P.O. Box 36, Al Khoud, Postal Code 123, Sultanate of Oman.

by their chemical composition. In theory at least, any analytical technique can be employed. In 1908 Jenkins used the classical gravimetric method of silicate analysis to demonstrate that the briquetage from Iron Age saltworking on the Essex coast (UK) was made from local raw materials.[15] Today, such analysis is of little use as it is excessively laborious. However, such work can now be replaced by optical emission spectrometry (OES), x-ray fluorescence (XRF), neutron activation analysis, (NAA), particle induced x-ray emission (PIXE), atomic absorption spectrometry (AAS) and inductively coupled plasma (ICP).

OES involves taking a very small sample of pottery which is burnt between carbon electrodes. The light emitted is split by a system of prisms and the resulting spectrum photographed. The presence of different elements is represented by lines in specific places on the photographic plate and their intensity is proportional to the percentage of the element. The method, however, is not non-destructive, so samples cannot be re-analysed if necessary.

NAA however, is a non-destructive method which is receiving wide attention at present. Preliminary work has been carried out on various groups of Mediterranean pottery,[16] on Samarian ware[17] and on pottery from a number of sites in America.[18] Some of the drawbacks of this technique are that it is strongly dependent on the product half-life, hence turnover times are longer; it fails if the product is stable; a nuclear reactor is usually required; and it might not be adequately sensitive for light elemental analysis.[19]

AAS, although seldomly used by archaeologists, affords a means of elemental analysis that is less complex to carry out than some other methods and yields data that are more easily interpreted by non-specialists. The basic principle behind the technique is relatively uncomplicated. A hollow-cathode lamp (made of the analyte element) emits radiation of a specific wavelength characteristic of the analyte. This radiation is then absorbed by the sample solution and the absorbance is proportional to the concentration of the element of interest. Bower *et al.* described the usefulness of AAS in the archaeological analysis of ancient pottery.[20] However, AAS is not multielemental nor is it non-destructive, hence analysis becomes tedious and time consuming.

PIXE has also been applied to materials from the prehistoric period.[21] PIXE analysis relies on the detection of trace elements by means of their characteristic x-rays emitted during bombardment of the sample with a particle beam. PIXE limitations include: requirement for a particle accelerator; background problems due to bremsstrahlung; not cost-effective except if employed routinely; not suitable for light elemental analysis; and L/K interferences of heavy elements with transition metals and vice versa.[19]

The method ICP has not been as widely applied to provenance studies as NAA, PIXE or XRF. The method is an emission technique that uses a hot plasma and, although not non-destructive, is highly sensitive, multielemental and capable of detecting certain elements which might be beyond the detection limits of PIXE or XRF.[22]

XRF spectrometry (the method of choice in this paper) is one of the most widely used instrumental analytical techniques in industry today.[23] There are a number of reasons why this is so. The method is non-destructive and can be applied to solids, powders or liquids and even gases in some instances; it is applicable over a wide range of concentrations (from 1 ppm to 100%), giving good elemental coverage (atomic numbers 11–92); in exceptional cases it is also possible to determine F, O, N, C and B; it is precise and accurate (1–2%); and moreover it is a very rapid technique with data for up to 28 elements being obtained simultaneously in 2–3 min.[24] The principles of the method are well established.[25] Some of the drawbacks are that the instrumentation could be expensive (especially in developing countries) and it requires a well trained x-ray spectroscopist to set it up.[25]

PROVENANCE STUDIES

The standard criteria used to characterize archaeological artefacts (e.g. pottery) are morphological or stylistic. Although this approach is very useful, it is not easy to differentiate copies made elsewhere perhaps for the purposes of trade.[26] This is where provenance studies play a major role. The basic premise behind pottery or ceramic provenancing (sourcing) is straightforward. Theoretically, every vessel carries a chemical composition pattern or 'fingerprint' identical with the clay from which it was made. Hence it should be a simple matter either to source a vessel or pot to a specific clay bed or else, in the absence of known clays, to establish compositional groups such that the outliers or overlapping specimens from different sites can be determined.

In provenance studies, the objective is to correlate raw materials with a finished artefact. Because most raw materials and artefacts, especially pottery and clays, are compositionally complex, the comparisons are best accomplished by consideration of many properties or variables simultaneously, rather than one or several properties in sequence, in other words, as polythetic rather than monothetic classes. Such comparisons are often accomplished through a body of techniques called 'statistical analysis.'

Until recently, the general approach to the identification of composition types involved an initial arbitrary assignment of specimens to one or more 'common' types.[27] Simple statistical methods have then been applied to decide, for each element in sequence, which specimens belong to one or other of the common types. The statistical methods have been those dealing with single random variables, and account has not, therefore, been taken of all the available information, i.e. taking measured concentrations simultaneously for each specimen. Valuable progress has been made with this type of approach, but its limitations have become apparent within the last 3 years. Authors have increasingly stressed the need for more applied objective and powerful methods of multivariate statistical applications (cluster, principal component, discriminate factor, dendograms, non-linear mapping and correspondence analysis) in order to (i) define composition types directly from the raw analytical data without the need for arbitrary selection; and (ii) objectively assign specimens to composition types.[28–33] These techniques are of prime importance in analytical studies of pottery provenance.[27] This is not to say that the simpler, earlier approaches are of no value, and indeed situations arise where they are adequate.[34,35] Doran and Hodson have given a good general discussion of the basis and relevance of the many

available multivariate techniques to archaeological and other investigations.[36] In the case study discussed below, correspondence analysis was used in obtaining the relevant clusters.

XRF SPECTROMETRY AND CORRESPONDENCE ANALYSIS

The standard instrumentation, sample preparation methods and XRF procedures employed in studying ancient ceramics and pottery have been reported elsewhere.[37,38] To evaluate the cultural implications, the data from XRF spectrometry can be subjected to a special statistical technique called correspondence analysis. Correspondence analysis originated in France in 1977, and was considered to be the brainchild of Jean-Paul Benzecvi.[39] The name correspondence analysis is derived from the term 'analyse des correspondences' which means 'in a data set consisting of rows and columns, there is a close association between the elements of two sets,' in this case the rows and columns. Correspondence analysis belongs to the family of statistical techniques which simultaneously display the rows and columns of a data matrix in a low-dimensional space.[40]

In correspondence analysis, the total variation in the data matrix is measured by the usual chi-squared statistic for row–column independence and it is the chi-squared statistic which is decomposed along principal axes. To be more precise, it is a quantity called the inertia which is decomposed, which is equal to the chi-squared statistic divided by the grand total of the original data matrix. The parts of the inertia which are 'explained' or 'accounted for' by successive principal axes are called principal inertia and are usually expressed as a percentage of the total inertia.

In the context of multielemental analysis, the display in two dimensions may be interpreted as a map. Samples which are plotted close together are (in a certain sense) similar, and the elements plotted together are (using the term loosely) correlated. The simultaneous display of the rows (samples) and columns (elements) provides an insight into which samples cluster and also why they cluster. Correspondence analysis is thus an improvement on cluster analysis.[41–43]

ARCHAEOLOGICAL INTERPRETATION OF XRF DATA: A CASE STUDY

To appreciate the manner in which XRF data are employed in archaeological interpretations, a study undertaken to investigate the provenance of Iron Age pottery excavated in north-eastern South Africa could serve as a suitable case study. In this study 107 potsherds were investigated by XRF spectrometry for 24 oxides and elements: Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2, Fe_2O_3, Sc, V, Cr, Mn, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Mo and Pb. The numerical data for these determinations appear in full elsewhere.[37,38] For reasons given later, P_2O_5 was not considered in the treatment of the data.

These specimens originated from four sites: Mzonjani (coastal), Nanda (inland), KwaGandaganda (inland) and Emberton Way (coastal) (a map of the sites appears in Ref. 38). Nanda and KwaGandaganda lie on either side of the Mngeni River, about 5 km apart. Mzonjani and Emberton Way on the coast are about 20 km apart. The distance between the inland and coastal sites is about 50 km. Table 1 gives the period of occupation and symbols used to characterize the samples in the correspondence analysis plots below. The samples used in this particular study were excavated by standard archaeological methods from the four sites. Figure 1 depicts the characteristic styles and decorations, highlighting the different phases or tribes. Three sites, Mzonjani, Nanda and KwaGandaganda, were occupied at different times, in the 3rd, 7th and mid-8th centuries AD, respectively,[44–46] whilst the fourth site, Emberton Way, was occupied over the full-time period, albeit probably sporadically.[47] The sherds from the four sites were subjected to analysis to establish if it was possible to separate their pottery chemically and thus whether there was any contact between tribes from the inland and coastal sites.

Interpretations based only on the majors

Provenance studies comprise two steps: first the determination of trace metals in the potsherds and second the analysis of the chemical data thus obtained, in order to draw conclusions as to whether sherds are local to a site or introduced from elsewhere. Such information aids archaeologists to draw inferences relating to social or economic interactions. The data obtained from XRF spectrometry were subjected to correspondence analysis and the relevant sample and elemental plots are reflected in Figs 2–7 for the first three axes. In this study P_2O_5 was eliminated in the correspondence analysis plots owing to post-depositional contamination.

The chemical alteration of pottery buried in the soil is of considerable interest as it may affect the results and interpretation of provenance investigation, based on the elemental analysis.[48] Most authors who have investigated this problem in any detail have concurred with the

Table 1. The dating of the 107 sherd samples from the four excavated sites

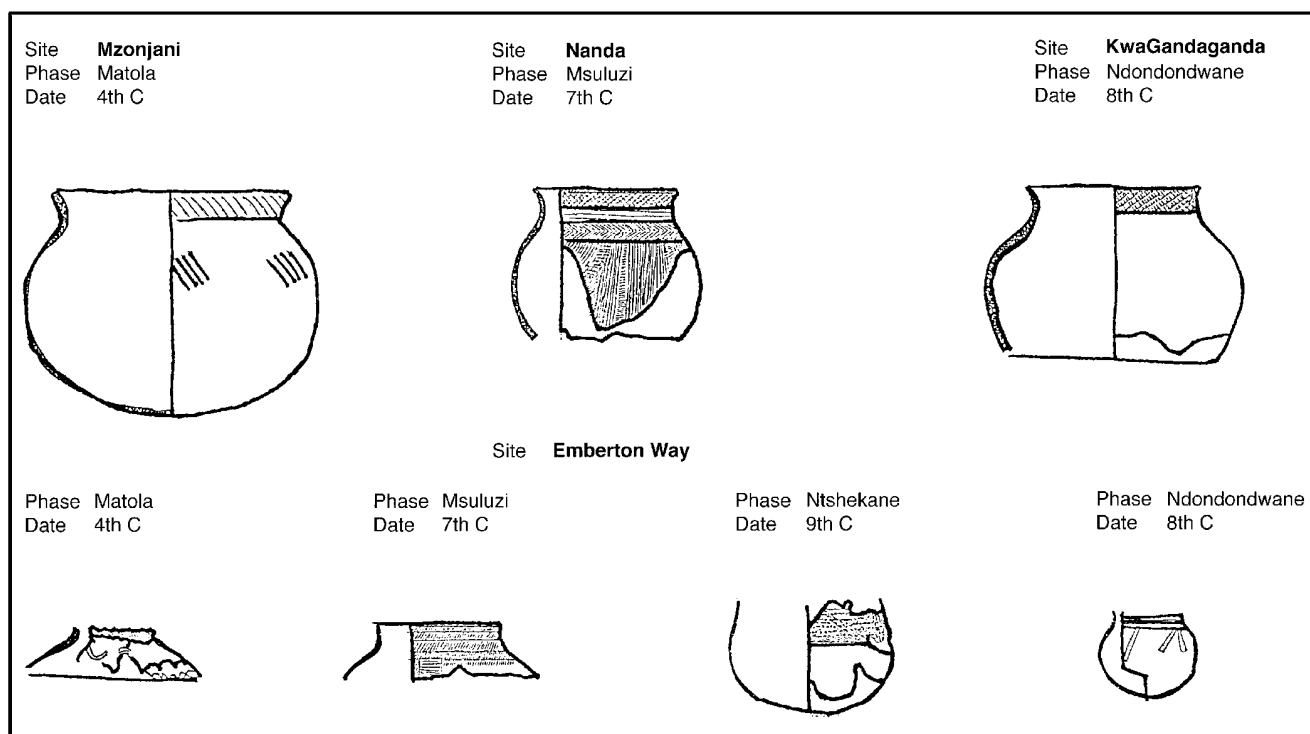| Site	Phase	Century (AD)	Symbol	No. of specimens from each site	
Mzonjani	Matola	4th	m	27	
Nanda	Msuluzi	7th	na	22	
Kwa Gandaganda	Ndondondwane	8th	ka, . . .; Ka, . . .	40	
Emberton Way	Matola	4th	Ma, Mb, Mc	3	18
Emberton Way	Msuluzi	7th	Na, Nb, Nc, Nd, Ne, Nf	6	
Emberton Way	Ntshekane	9th	ea, eb, ec, ed, ef, eg, eh, ej	8	
Emberton Way	Ndondondwane	8th	K	1	

Figure 1. Characteristic styles and decorations of pottery pieces from the early Iron Age, excavated in north-eastern South Africa.
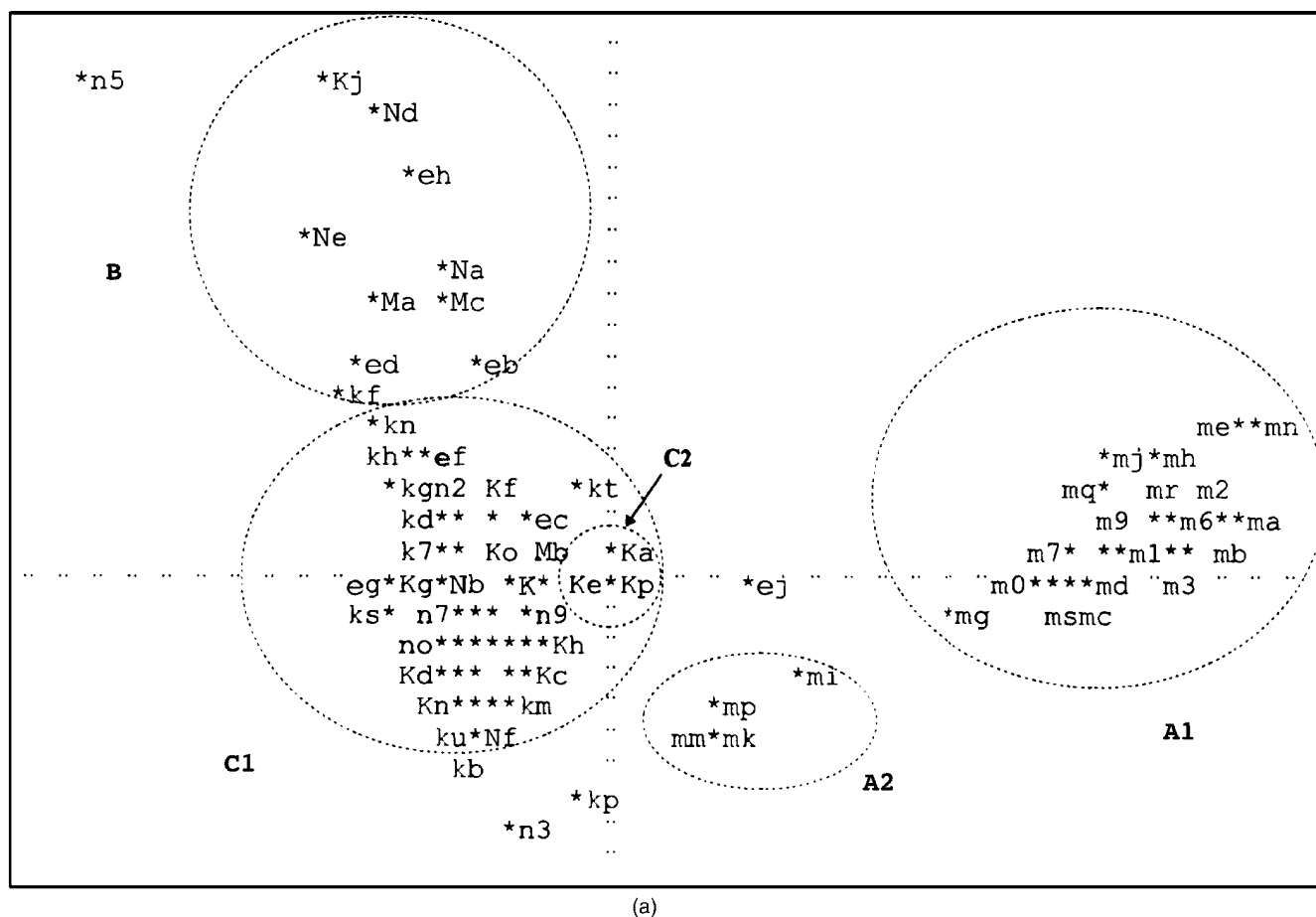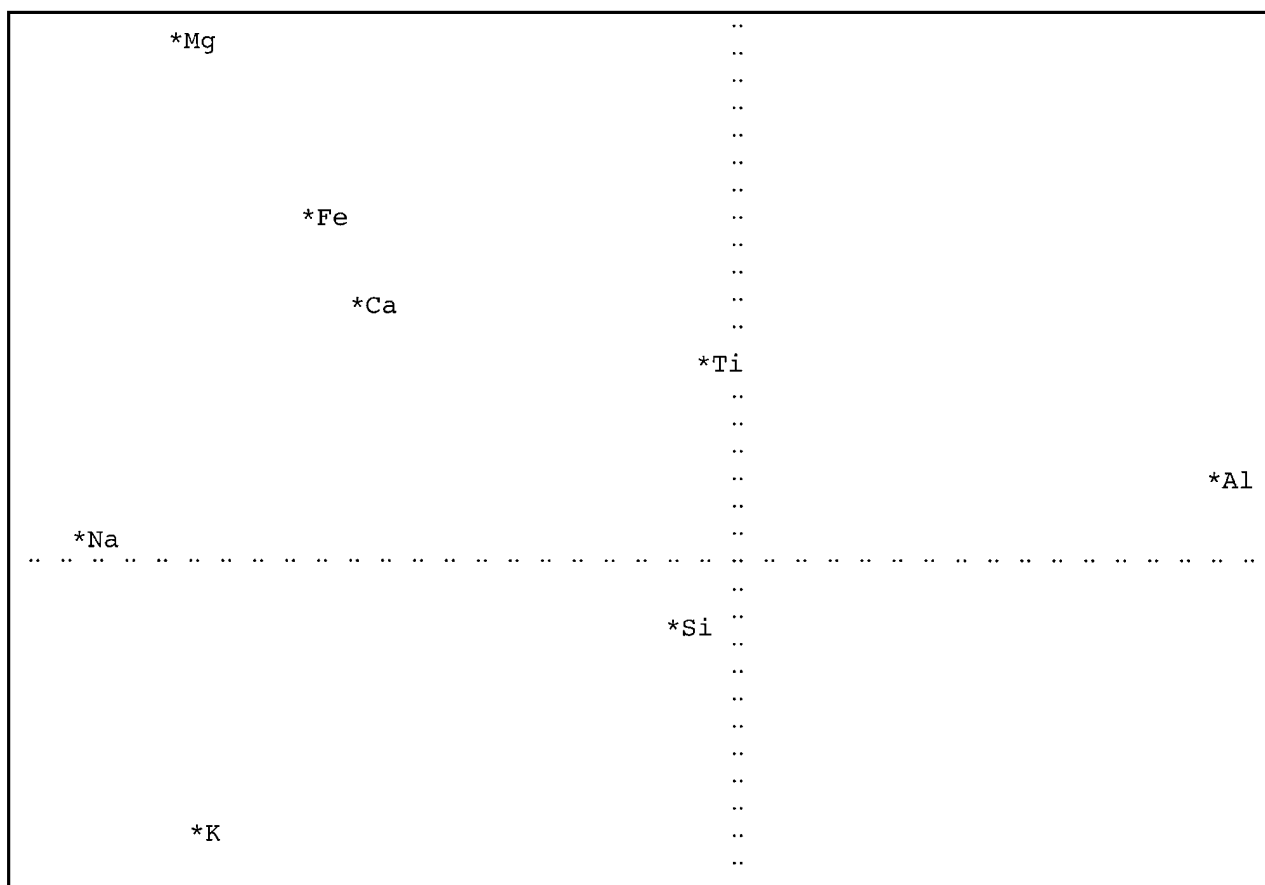

(a)

Figure 2. Correspondence analysis sample and elemental plots based on the oxides (axes 1 and 2), with a total inertia of 82.20%.
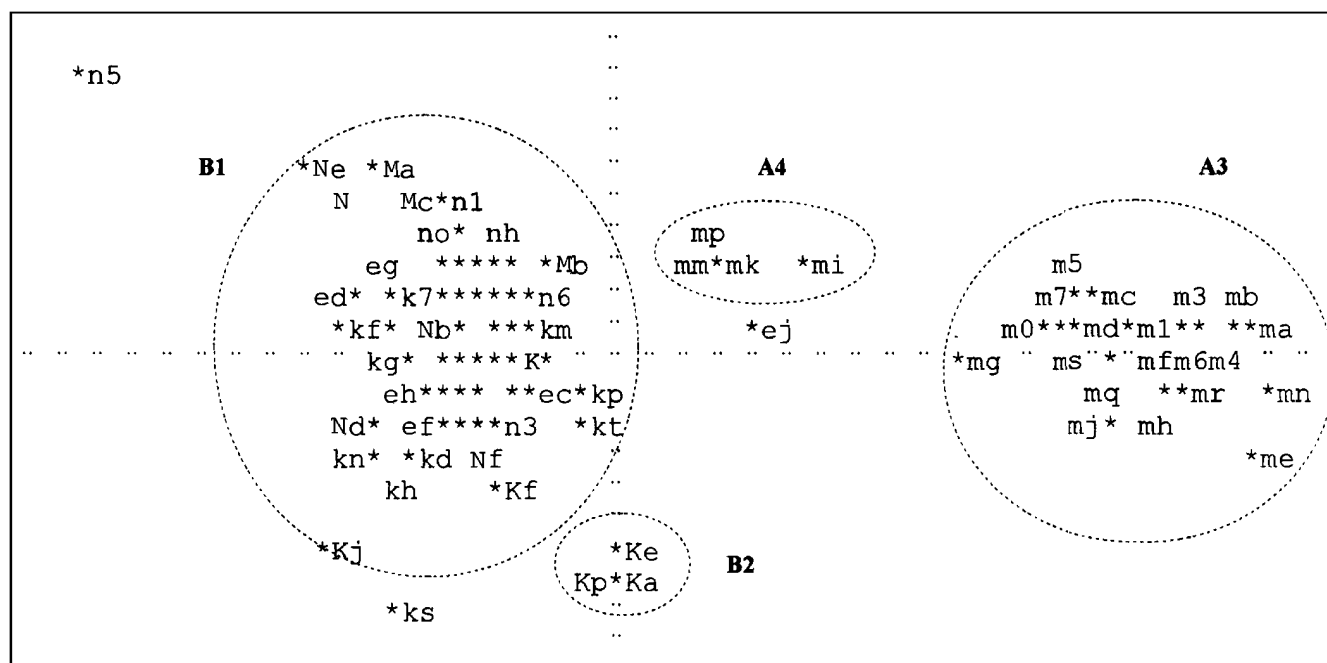
(b)

Figure 2. (*continued*).

Figure 3. Correspondence analysis sample plot based on the oxides (axes 1 and 3), with a total inertia of 65.10%.

view that phosphate absorption is a post-depositional definite phenomenon.[49–51] In 1993, Bollong *et al.* noted that sherds that had been found on the surface had lower bulk phosphorus contents than buried sherds.[52] They suggested that phosphorus had been leached from the surface of the sherds during weathering. Freestone *et al.* in 1994 concluded that elevated P_2O_5 concentrations in archaeological pottery may not be taken as an indicator of use.[48] It is

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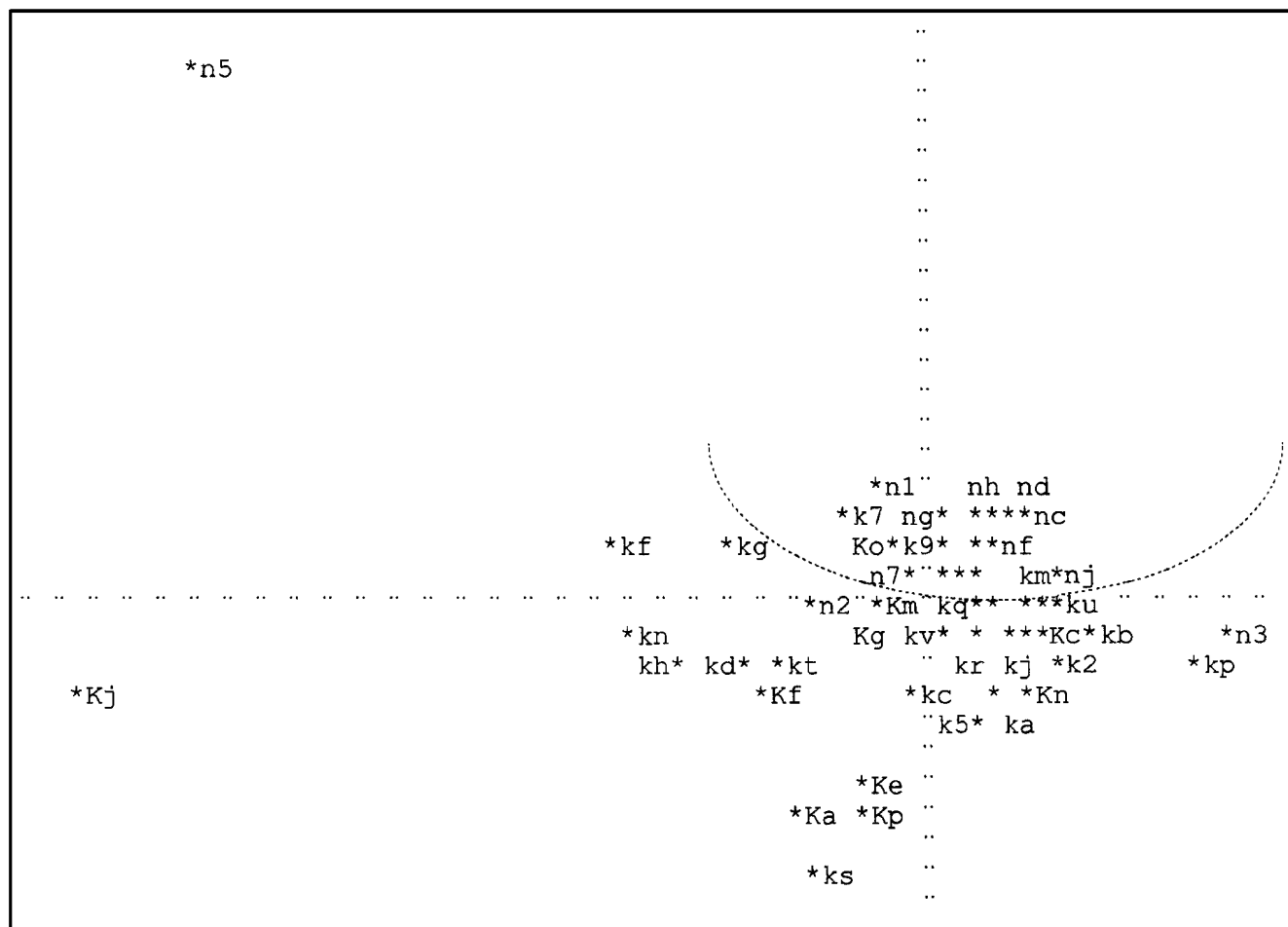
Figure 4. A sub-cluster of the correspondence analysis sample plot shown in Fig. 2(a).

primarily a reflection of the depositional environment and the microstructure of the pottery and does not necessarily reflect absorption of fats or other organic substances by the pottery fabric during use. In this study, P_2O_5 was eliminated in the correspondence analysis plots, for the aforementioned reasons.

A combination of all the major oxides (Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2 and Fe_2O_3) produced a sample plot based on the first two axes [Fig. 2(a)] with a total inertia of 82.20%. (Note: in Figs 2–7 asterisks mark the exact spot; overlapping samples are not shown.) The corresponding plot of the oxides is shown in Fig. 2(b) [only the elements are shown in Fig. 2(b)].

The m samples from the Matola phase form two discrete clusters (A1 and A2) without any overlap and load heavily on aluminium [Fig. 2(b)]. The Matola phase samples (Ma, Mb and Mc) from Emberton Way show no link to the Mzonjani site, but appear to fall into two clusters, one centered on Emberton Way (cluster B) and the other on the inland samples from Nanda and KwaGandaganda (cluster Cl).

The majority of the Emberton Way samples form a cluster (B) cross cutting the different phases of the site (e.g. Ma, Ne and eb), thus indicating that they were probably locally made [Fig. 2(a)]. However, cluster B tends to load highly on Fe_2O_3 and CaO. Figure 3 represents a sample plot based on axes 1 and 3 (a corresponding elemental plot appears in Ref. 43 and has not been shown). From

Fig. 3, it is apparent that two KwaGandaganda samples (Kj and Kf) belong to cluster B1 (note: a Q-test was performed to establish that these samples Kj and Kf belong to cluster B1). These two particular specimens could in fact indicate a possible trade or social link between the two sites, since Emberton Way was sporadically occupied between the 4th and 8th centuries.[47] A few samples in cluster B1 overlap with the bulk of the KwaGandaganda and Nanda samples and this could indicate that they were made from similar clay beds to those used in the inland sites (Fig. 3). However, three samples (Ka, Ke and Kp) stand out, and sample n5 is isolated from the rest of the groups and could well reflect a different clay source, perhaps resulting from an import to Nanda from elsewhere, possibly further inland.

It was found that the SiO_2 concentration in sample n5 is relatively low compared with the rest of the samples.[43] Owing to the low SiO_2 concentration, sample n5 is pulled further away from cluster C [Fig. 2(a)]. Sample Kj, which ostensibly clusters with group B, pulls away (downwards) considerably from the group and coalesces with group B1 (Fig. 3, when axis 3 is considered). The outlier ej falls close to cluster A2 [Fig. 2(a)] and A4 (Fig. 3) and could represent a coastal source which is closer in chemical composition to Mzonjani than Emberton Way. In addition, axis 3 (Fig. 3) suggests the existence of a sub-cluster (B2) adjacent to group B1. Furthermore, Fig. 3 shows clearly that there are two main clusters, both mixed, with
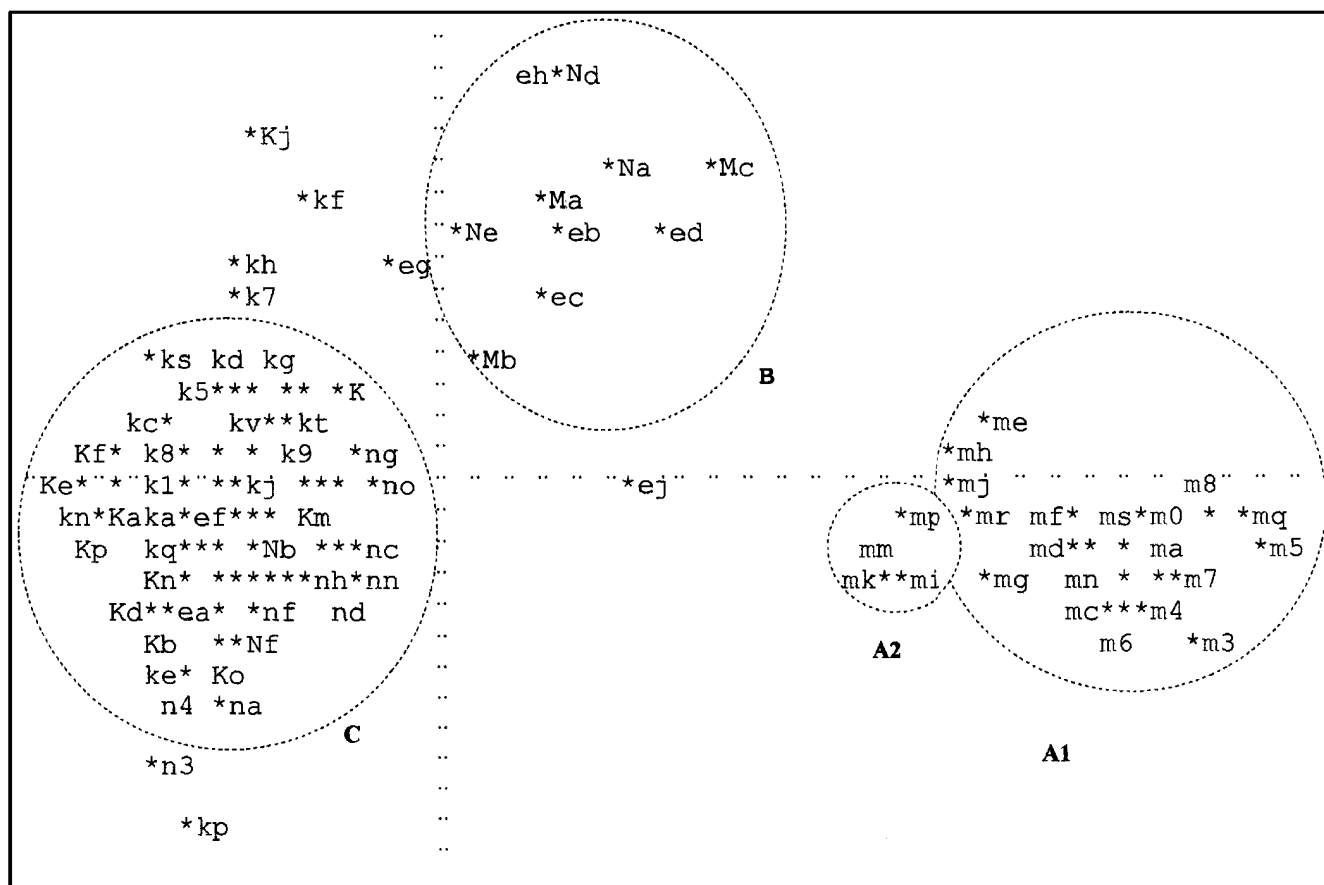
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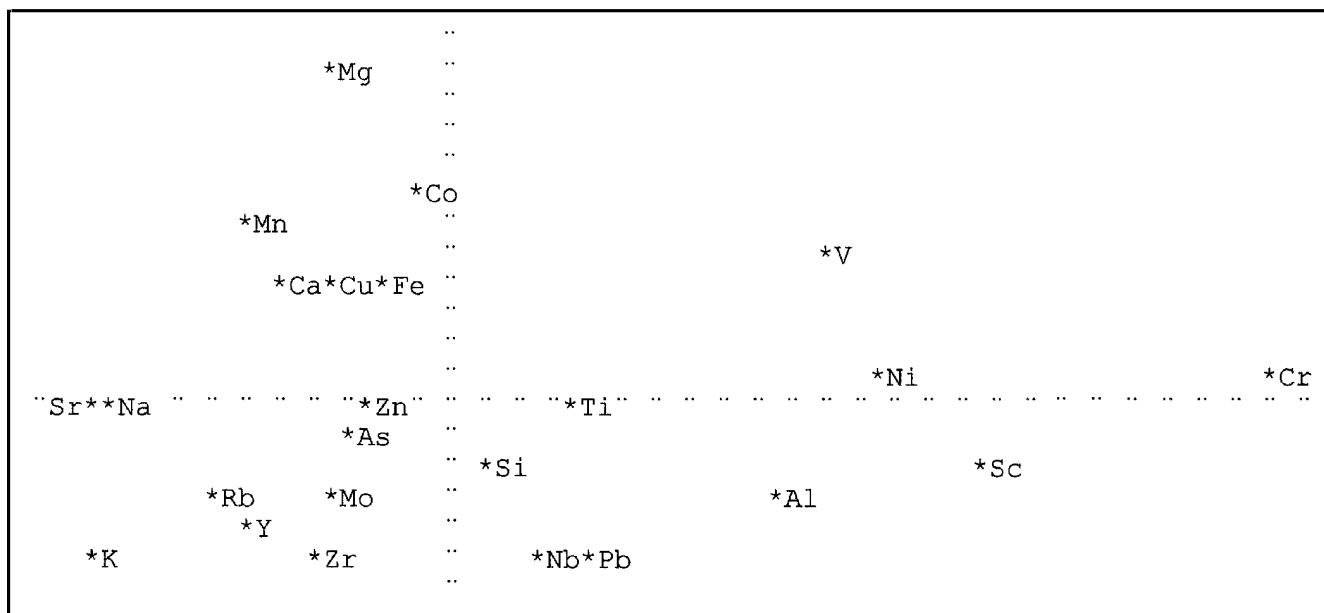
(b)

Figure 5. Correspondence analysis sample and elemental plots based on 24 elements and oxides (axes 1 and 2), with a total inertia of 65.60%.

a number of sub-clusters and prominent outliers. Cluster B [Fig. 2(a)] contains two KwaGandaganda sherds whilst the Nanda/KwaGandaganda clusters (C1 and C2) pertain to a number of Emberton Way sherds. In addition, small sub-clusters are apparent but have not been shown.

In an attempt to assess the interrelationship in clusters C1 and C2 [Fig. 2(a)], the data were once again subjected to correspondence analysis omitting groups A1, A2 and B and some specimens belonging to Emberton Way (Fig. 4). This map reflects a more detailed plot using only the k and n samples. Note the tendency for the samples to segregate
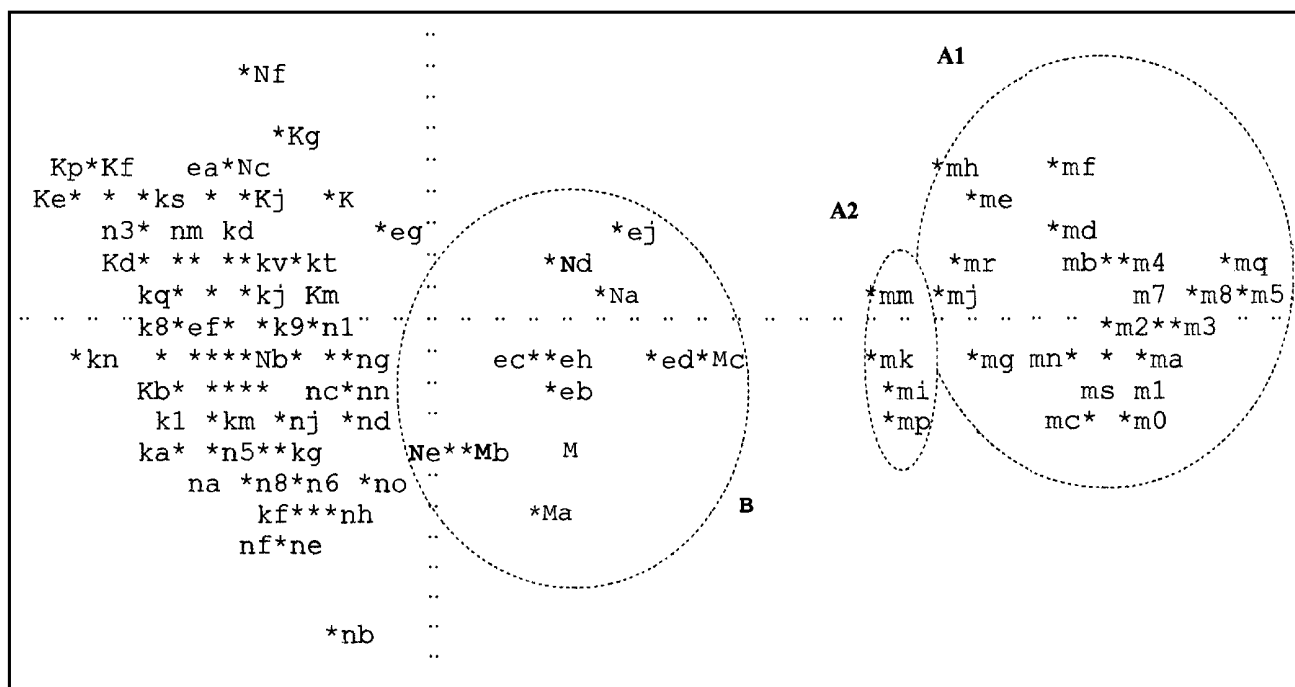
Figure 6. Correspondence analysis sample plot based on 24 elements and oxides (axes 1 and 3), with a total inertia of 56.00%.
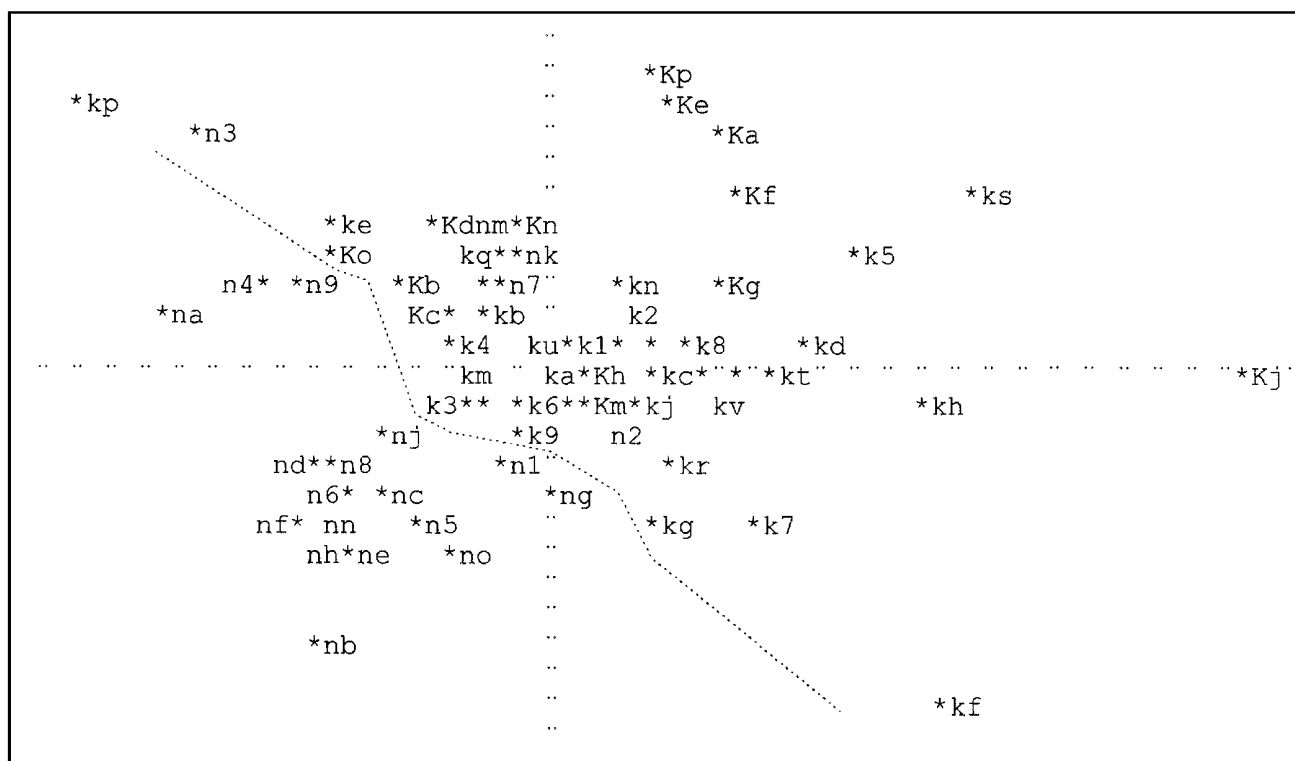

Figure 7. A sub-cluster of the correspondence analysis sample plot shown in Fig. 5(a).

except for a few overlaps. As the two sites are very close to each other but were occupied at different times, this simply means that they must have both exploited one or more common clay sources.

Interpretation based on all 24 elements and oxides

This total analysis brings together all the major, minor and trace elements into one analysis. The resulting sample plots are shown in Fig. 5(a) for the first two axes and Fig. 6 for axes 1 and 3. The elemental distribution plot appears in Fig. 5(b) for axes 1 and 2 (the elemental plot for axes 1 and 3 appears in Ref. 43 and has not been shown).

The sample plots show a strong resemblance to those based only on the majors. A clear separation of Mzonjani samples from the others was observed. An apparent sub-cluster (A2) can be proposed but it is doubtful if it has any real meaning in this context.

The other coastal site, Emberton Way, has mixed results. Whereas most of the samples in Fig. 5(a) tend to form their own cluster (B), there are a number of significant outliers from this cluster which show interesting associations. The main Emberton Way cluster probably represents pottery made at the coast but the outliers are likely to have different origins. First, sample ej occupies a solitary space [Fig. 5(a)], which indicates that it originates from a different location to that of the known samples; whether far or near it is impossible to say. Sample ej appears, from the evidence of the third axis (Fig. 6), to be closer to the inland samples than Emberton Way itself and it is possible that it forms part of the large diffuse cluster of inland samples. From Figs 5(a) and 6 this inland cluster contains unequivocally five samples (K, ea, ef, No and Nf) from Emberton Way, thus demonstrating clearly that these sherds, although found at the coast, originate from the inland clays. The two inland sites show an interesting pattern. When the inland samples are analysed separately from the coastal site (Fig. 7), it becomes clear that although close in chemical composition, the samples do, with a few exceptions, display separate characteristics. With the exception of five samples (n2, n3, n7, nk and nm), from Nanda, the samples form two distinct clusters (Fig. 7). As these sites were occupied some 300 years apart,[44] the overlaps do not indicate trade or the movement of vessels but rather the fact that the potters from these two sites, which are situated close to one another, must have exploited a number of common clay sources. Figure 5(b) shows that the coastal sites, Emberton Way and Mzonjani, load heavily on metals which are characteristically found in beach deposits of that area.

The above results display very interesting archaeological interpretations. In order to examine these further it will be necessary to refer to the clusters in terms of their cultural affinities.

Prehistoric cultural affinities

Although differences exist between the correspondence analysis plots of the majors and all 24 elements and oxides, there are definite trends which provide evidence of socio-economic links.

Based on all 24 elements and oxides, all four sites discussed date from the early Iron Age and cover four distinct phases. The earliest phase, Matola, is found at Mzonjani[44] and at Emberton Way.[47] The chemical evidence from both sites is that Matola sherds were only made on the coast.

This accords well with the observations of the archaeologists that the Matola phases are only known from coastal areas. The vegetation of the coastal area is coastal forest and is rich in plant foods. This, together with the availability of sea foods, meant that it was unnecessary for these communities to move inland.[53] Matola sites are also known from other localities along the coast but no evidence is available yet to prove that there was much interaction between sites.

The next phase, Msuluzi, is represented by samples from Nanda and Emberton Way (note that Emberton Way is a multi-phase site). At this point, archaeologists now suggest that coastal resources were being exploited by people from inland sites.[47] The analytical evidence shows that three Msuluzi phase sherds from Emberton Way (Fig. 6, Nb, Nc and Nf) must have been made inland. This means that Msuluzi people were going to the coast, probably to harvest shellfish, and took along with them at least some of the pottery they needed, making the rest at the coast.

The single Ndondondwane sherd (K) [Fig. 5(a)] from Emberton Way shows the same pattern, i.e. an inland origin. The Ntshekane phase samples mainly occur at Emberton Way but some show a dual origin. As shown in Fig. 5(a), most of these sherds originate at the coast with two exceptions (ea and ef, possibly three if one includes 'eg') coming from inland.

The overlaps of the Emberton Way sherds with the inland sites suggest that this inland area must have been a favoured region for settlement. It provided flat valley bottoms for settlement, fertile alluvial soils for crops and abundant water. Speculations from such data could indicate that the other archaeological sites on the coast in the vicinity will also show such links.

CONCLUSION

It has been demonstrated that the chemical characterization of ancient pottery by XRF spectrometry can reveal new insights into archaeological interpretations. It has been shown that Iron Age specimens which were found on a coastal site can reflect an inland origin. Such interpretations cannot be ascertained by the visual inspection of vessels alone, particularly when vessels are similar in decorations. From work of this nature it is possible to establish experimentally the socio-economic links between inland and coastal tribes.

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