An evaluation of geochemical fingerprinting for the provenancing of Scottish red ware pottery

Simon Chenery, Emrys Phillips and George Haggarty

SUMMARY

A geochemical study was undertaken to evaluate whether it was possible to accurately fingerprint Scottish, Post-Medieval and later red ware pottery sherds. The primary objective was to establish a set of criteria to distinguish between the pottery sherds, on both a site and regional basis, as an aid to provenancing. These preliminary investigations also utilised the British Geological Survey's national geochemical database of stream sediment analyses as an aid to predicting the potential clay source regions. The results of this study clearly demonstrate the potential power of this combined geochemical and statistical approach, and its application to archaeological site investigations.

Medieval Ceramics 25, 45–53, 2001

INTRODUCTION

Establishing the provenance or source of clay for pottery manufacture is a recurrent problem for many archaeological studies. Over the last few decades a number of observational techniques, *i.e.* thin section optical microscopy and instrumental techniques, including the geochemical characterisation of pottery sherds, have been applied to this problem. Previously, one of the most common and techniques was instrumental neutron activation analysis (INAA), in studies such as that on Tating Ware (Stilke *et al.* 1996) or Inscker and Tate, 1991 on Scottish medieval pottery. However, during the 1990's, the closure of many nuclear reactor facilities necessary for INAA has led to the use of other analytical techniques with some success, for example inductively coupled plasma – atomic emission spectrometry (ICP-AES) (Bruno *et al.* 2000).

This paper describes the results of a geochemical study of Scottish Post Medieval red ware pottery, which was undertaken to evaluate whether it was possible to accurately fingerprint pottery sherds as an aid to provenancing. The study utilised ICP-mass spectrometry (ICP-MS) which is a highly sensitive modern analytical technique and is compatible with the earlier used INAA. For a more detailed comparison between INAA and ICP-MS analytical techniques the reader is referred to Holmes (1997).

The suite of pottery sherds provided for analysis were selected from eleven archaeological sites, located within five geographical regions across Scotland (Fig. 1). These samples were divided into two groups. The first provided a training

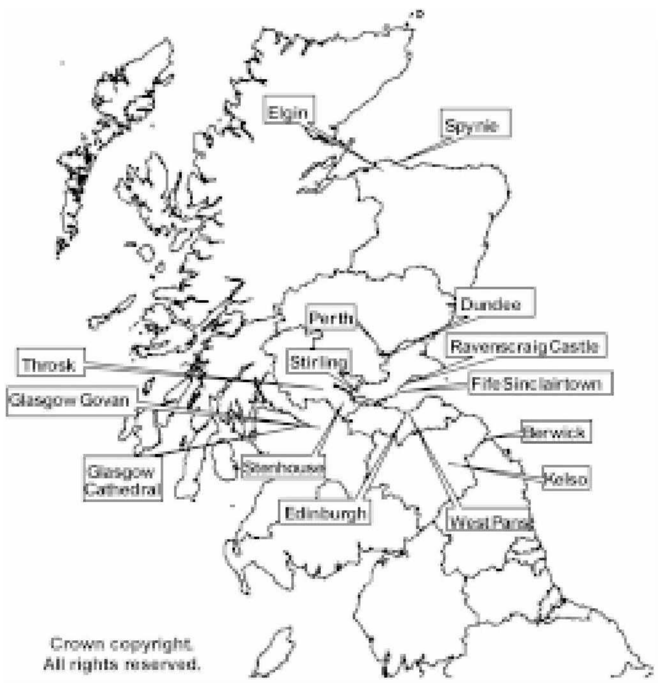

Fig. 1 Location maps of red ware pottery sites sampled or discussed in this study.

set which were used to establish a set of criteria for the fingerprinting of each site and/or region. These characteristics could then be used to provenance the second test group, which were initially supplied blind without any site specific or regional location details.

A number of statistical and graphical approaches have been applied to group the sherds on, in this case, the basis of their geochemical composition. To fully utilise the large amount of information generated by ICP-MS, emphasis has been placed on multi-variate techniques, such as factor analysis and discriminant analysis (Davis 1973; Adams 1995). The success of these statistical techniques for discriminating between pottery sherds from different localities was evaluated by applying them to the test samples. The degree of success could then be ascertained by the number of samples correctly assigned to a provenance or region.

The data were also compared with the British Geological Survey's national geochemical database to ascertain whether pottery production was from local or imported source materials.

ARCHAEOLOGICAL CONTEXT AND SAMPLE SELECTION

This multidisciplinary project involved Scottish Medieval archaeologists and ceramic historians (Medieval Archaeological Research Group), and analytical scientists at the British Geological Survey. The primary archaeological objectives of the project were: (a) to see if it were possible to differentiate between the iron-rich clays sourced from different major river systems in Scotland; and (b) to discriminate between a number of individual production sites within a single area. If the results of the pilot study were found to be favourable, MARG intended to design a much larger project on Scottish red ware pottery.

The pottery sherds were selected from five principal areas;

Group 1, Forth Basin - In the 17th and 18th centuries the Forth basin was the location of a number of large industrial potteries, brick and tile works. These industries started to utilise, on a large-scale, the abundant carseland clays present within the basin. Prior to this, pottery production was limited to a few small-scale potters working the local clay. During this period, the potters began to move from the vicinity of the larger towns, such as Stirling and Edinburgh, which were rapidly expanding beyond their medieval boundaries. For example, marriage documents from the first half of the 17th century give us the names of at least seven potters working in Potterrow just outside Edinburgh's city walls. However, by 1660 only a few clay pipe makers were still working in this area.

The Forth basin satisfies one of the main objectives of the collaborative project, as it contains a number of individual ceramic production sites including West Pans [NT 371 736], Throsk [NS 903 868], Stenhouse [NS 880 824] and Fife Sinclairtown [NT 304 931]. These sites have been the subject of a number of recent archaeological excavations, as well as an ongoing documentary research program being undertaken by G. Haggarty (unpublished work-in-progress).

West Pans (WP - six training and three test samples) is a very complex and long lived ceramic manufacturing site. Production commenced in *c.* 1738 when an Edinburgh potter called Robert Pate petitioned the Council of Musselburgh for 20 guineas (which he received) prior to moving into the area. Slip decorated-type wares were being made using the local clay from at least *c.* 1748. West Pans was also the site of an 18th-century porcelain factory, as well as a number of 18th and 19th-century industrial pottery manufacturers which used both imported white and the local red clay.

Throsk (Th - six training and three test samples) is a very important 17th and 18th-century Scottish pottery production site. The potteries utilised the local estuarine clays and may have distributed their wares across Scotland. Substantial archaeological and documentary research on this ceramic industry has been published Caldwell & Dean (1992) and Harrison (2002).

Stenhouse (St - six training and three test samples) is an extensive pottery production site, containing evidence for large number of kilns that were excavated by the late Miss D Hunter (Hall & Hunter 2001). These authors concluded that the site is 15th or early 16th century in date and used the local red firing clay. The distribution area of Stenhouse pottery is unknown. However, one sherd with a distinctive Stenhouse-type facemask was recovered at Ravenscraig Castle in a post-1562 context (Laing & Robertson 1970).

Fife Sinclairtown (Fi - two training samples) is a small, recently excavated 19th and early 20th century pottery production site owned by J Buist & Sons. This site appears to have specialised in the production of Rockingham glazed teapots using both imported white Devon and local red clay (James *et al.* 1991). The source of the local clay was a number of pits located to the east of the pottery.

Group 2, Moray Firth – Two sites from the Moray Firth (Fig. 1), Elgin [NJ 2161 6289] and Spynie Palace [NJ 203 658], have been included in the present study.

At *Elgin* (El - three training and three test samples) there is very good evidence, as yet unpublished, for post-medieval pottery production within the town. This includes a few wasters as well as a good assemblage of post-medieval kiln furniture (B Lindsay pers. comm.). All the pottery used in this present study was excavated from features in the general area and believed to be post-medieval in date.

The pottery samples from *Spynie Palace* (Sp - three training samples) are all from stratified levels of a major archaeological excavation of an apparently high status palace (Lewis & Pringle 2002). However, examination of the pottery showed it to be extremely crude and lacking in the relative sophistication of the nearby Elgin material. This suggests that the pottery was locally produced. Although few red ware kiln sites have been found in Scotland, it is possible that the pottery was not being transported far and there may be many more production sites to be discovered.

Group 3, Tweed Basin – All the pottery sherds (Be - five training and three test samples) included within this group are from Berwick-upon-Tweed [NU 995 526]. The production site was located at Tweedmouth (now in the grounds of the Tower craft pottery) and used local clay. No detailed archaeological or documentary investigation has taken place. However the current owners have presented surface finds to English Heritage. These sherds (178 in total) indicate a post-medieval to early industrial date, with at least some being possible late 17th- century slip decorated ware. The latter were excavated by the Borders Burgh Archaeological Project from the Kelso area and may have originated from this site. Cruickshank *et al.* (in press) concluded that the slipwares from Kelso are distinct from those found at other production sites, both in Scotland and abroad.

Group 4, Tay Basin – Pottery from two sites from the Tay basin (Fig., 1), Dundee [NO 404 306] and Perth [NO 120 231], have been examined during the present study.

The pottery sherds from the *Dundee* site (Du - five training and three test samples) are probably late medieval and were taken from an archaeological excavation within the town. Laing (1974) interpreted the sherds as wasters and concluded that they provide proof of medieval ceramic production in Dundee town. However, the medieval ceramics held in the Dundee museum store have recently been reassessed and are now considered to be fragments of pipes associated with late industrial salt glazing (D Hall & G Haggarty pers. comm.).

At *Perth* (Pe - three training and three test samples), the large amounts of kiln furniture recovered from an archaeological excavation around Canal Street provide clear evidence for the local production of late red ware pottery (Blanchard 1979). Subsequently a medieval red ware kiln stand has been found in a excavation on the north side of town (D Hall pers. comm.).

Group 5, Clyde Basin – Archaeological evidence suggests that there was a post medieval pottery industry in the area of the old Calton in Glasgow which utilised the same clay source as the later industrial potters (Fleming 1923). Unfortunately, none of this material could be obtained for use in the present study. The sample sherds used came from excavations at Glasgow Govan [NS 553 659] and Glasgow Cathedral [NS 603 656] (Fig. 1).

The samples from *Govan* (GG - two training and two test samples) are from an archaeological excavation carried out on the site of the Moot Hill; a possible late prehistoric or early medieval meeting point. This artificial mound survived until the early 19th century when it was flattened to make way for a shipyard. The pottery (probably late-medieval) was recovered from the fill of the ditch circling the base of the mound.

The red ware sherds from Glasgow Cathedral (GC - two training samples) were recovered during an archaeological excavation within the nave and crypt of the cathedral (Driscoll in press). The present cathedral dates to the 13th century but the sherds are probably late medieval in age.

ANALYTICAL METHODOLOGY

The initial stages of the sample preparation involved cutting a 5-10 mm strip out of the centre of a sherd. This was used to make a thin section for petrographical analysis (Phillips 1998). The remaining material (up to 5 g in weight) was prepared for geochemical analysis using ICP-mass spectrometry. To avoid problems with the variable concentration of trace elements within the glaze, the latter was carefully removed by paring off using a stainless steel chisel (the glaze was retained for use in a possible future study). The whole surface of the remaining sample was lightly ground with a pure alumina grinding head to remove any surface contamination or alteration. The sherd was then crushed, ground to less than 30 mm and homogenised in an agate mill.

The solid pottery powder was accurately weighed into a PTFE test-tube and dissolved using a mixture of hydrofluoric, perchloric and nitric acids. The tube was heated until the sample was decomposed and the acids evaporated off. The dried material was then re-dissolved in a small amount of nitric acid and stored in a clean plastic bottle until required for analysis using ICP-mass spectrometry. For a more detailed account of the sample preparation methods for ICP analysis the reader is referred to Cook *et al.* (1997).

The samples were analysed for 45 elements: Lithium (Li); Beryllium (Be); Scandium (Sc); Titanium (Ti); Vanadium (V); Chromium (Cr); Cobalt (Co); Nickel (Ni); Copper (Cu); Zinc (Zn); Gallium (Ga); Arsenic (As); Rubidium (Rb); Strontium (Sr); Yttrium (Y); Zirconium (Zr); Niobium (Nb); Molybdenum (Mo); Silver (Ag); Cadmium (Cd); Tin (Sn); Antimony (Sb); Caesium (Cs); Barium (Ba); Lanthanum (La); Cerium (Ce); Praseodymium (Pr);

Neodymium (Nd); Samarium (Sm); Europium (Eu); Gadolinium (Gd); Terbium (Tb); Dysprosium (Dy); Holmium (Ho); Erbium (Er); Thulium (Tm); Ytterbium (Yb); Lutetium (Lu); Hafnium (Hf); Tantalum (Ta); Tungsten (W); Thallium (Tl); Lead (Pb); Thorium (Th) and Uranium (U) using a VG Elemental Plasma Quad 2+ ICP-mass spectrometer. A complete list of the data obtained is available from the lead author on request. The instrument was calibrated with solutions traceable to internationally recognised chemical standards. The data was validated with an extensive range of quality control samples. Quality control (QC) samples (reference materials, duplicate analyses and blanks) were also analysed, providing statistical information on the analytical quality and batch rejection criteria. No pottery reference materials were available; consequently the internationally recognised SCo-1 (Shale-Cody) and SDO-1 (Shale - Devonian Ohio) reference materials were used, with compiled concentrations taken from Potts *et al.* (1992).

All data-processing, graphical and statistical analysis were performed using commercial computer software packages (Excel™, Microsoft; Unistat for Windows 3™, Unistat, Ltd; Minitab 13™, Minitab Inc).

GRAPHICAL AND STATISTICAL ANALYSIS

The geochemical data obtained for the Scottish red ware pottery sherds have been analysed using a number of statistical and graphical techniques, ranging from the simple methods to sophisticated multivariate analysis. Each technique was evaluated to determine whether it provided new or corroborative information, allowing discrimination between sherds from the different archaeological sites.

Graphical analysis

The simplest interpretative method used was the bivariate (x-y) plot, with the plots of barium (Ba) versus strontium (Sr) (Fig 2) and barium (Ba) versus rubidium (Rb) providing the best discrimination between site groups. For example the sherds from Berwick-upon-Tweed (Be) are clearly distinguished by their low Ba and Sr concentrations from the Elgin pottery (El), which have much higher concentrations of these elements (Fig. 2). The more sophisticated log-element ratio plots (Fig. 3) are also extremely useful as geochemical data is not normally distributed and such diagrams expand the lower data values. Using these graphical methods a clear discrimination is achieved between the geographical groups of the training samples (see Figs 2 and 3). These plots also allow provisional assignment of the test samples to a particular region. The samples BS1, BS2 and BS3 possess Ba and Rb concentrations (Ba > 1000 $\mu g\ g^{-1}$, Rb > 160 $\mu g\ g^{-1}$) comparable to the known Elgin pottery sherds. The test samples BS7, BS8 and BS9 have Sr/Cr (log Sr/Cr ≤ -0.35) and Ba/Cr ratios (log Ba/Cr < 0.60) consistent with them forming part of the Berwick-upon-Tweed suite of pottery. However, samples BS16 to BS21 are more difficult to assign using these methods and may be derived from either the Dundee or Perth sites (see Fig. 2).

Multivariate statistical analysis

When performing multivariate statistics it is usual to normalise the data to ensure that elements with high concentrations and/or a large absolute variation, do not dominate the statistical processes. The conventional normalisation process of normal scoring

$$z_i = (a_i - x_i)/\sigma_i$$

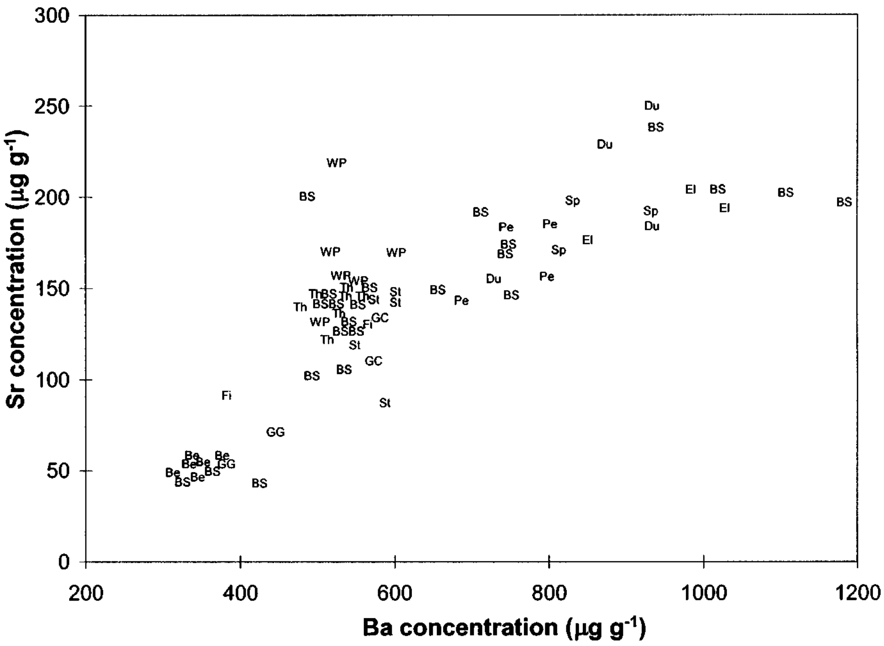

Fig. 2 Plot of Ba versus Sr concentration determined in Scottish red ware pottery coded for each of the eleven sites and the blind samples (BS). For full site codes see archaeological context. Plot demonstrates the discrimination, in particular, of samples from Berwick (Be) because of their low concentrations of these elements.

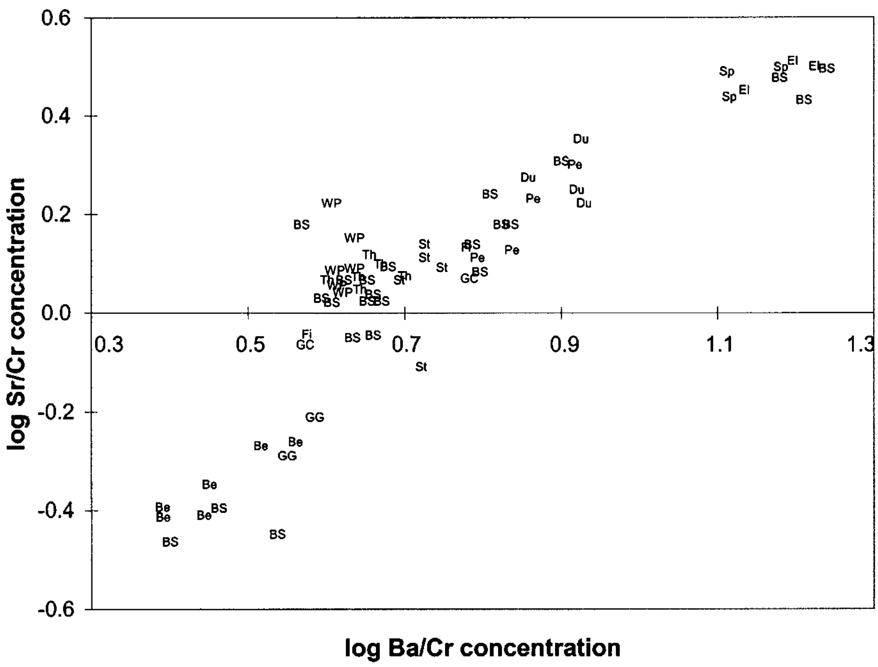

Fig. 3 Log plot of Ba/Cr versus Sr/Cr concentration ratios determined in Scottish red ware pottery, coded for each of the eleven sites and the blind samples (BS). For full site codes see archaeological context. This demonstrates the extra discrimination possible by this type of plot compared to simple two element concentration plots, in particular by region i.e. Berwick (Be); Spynie (Sp) and Elgin (El); Perth (Pe) and Dundee (Du).

has been used in this study, where z_i = normal-score, a_i = concentration for element i, x_i = the mean of concentrations for training set and σ_i = the standard deviation for the training set. Before conducting multivariate analysis the size of the data set (number of elements) was reduced to assist interpretation. Most multivariate methods aim to re-cast the data to maximise differences in order to highlight the underlying processes. Therefore, if variables (in this case the elements) are highly correlated in their statistical behaviour they will not aid in data processing. After inspection of a correlation matrix, one element (in bold):

La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y; **Nb**, Ti, Ta; **Co**, Ni; **Rb**, Cs; and **Zr**, Hf.

was chosen to represent each group of highly correlated elements identified during the first stage of the multivariate statistical analysis. The rare earth elements (La-Y) are commonly used in geochemical interpretation of geological materials. However, in the present study these elements did not provide any useful discrimination. Some of the other elements were also discounted: Cd, because of its poor precision in the quality control; Ga due to Ba interference; As due to a possible Cl interference and Pb because of possible glaze contamination. These problems may have been specific to the pottery samples analysed during this study and should not be considered generic.

The elements Li, Be, V, Cr, Co, Cu, Zn, Rb, Sr, Zr, Nb, Mo, Ag, Sn, Sb, Ba, La, W, Tl, Th and U were found to be the most robust and, therefore, used as normal-scored data in the multivariate statistical analysis.

Cluster analysis - There are many forms of cluster analysis, most of which fall into the category of unsupervised pattern recognition (*i.e.* no prior assumptions are made about grouping) and make use of the degree of 'similarity' between objects. When using geochemical data this 'similarity' is usually quantified as some measure of the distance between samples in multivariate space. The different forms of cluster analysis may produce different results. Therefore, there is no single correct result, with the success of the clustering process being dependent upon the information being sought (Adams 1995). Consequently, a number of forms of this type of analysis were tried. Hierarchical clustering, using the single linkage method and the Euclid distance as a measure of similarity proved to be the most successful, the graphical results are shown in Fig. 4. From this dendrogram it was possible to provisionally assign some of the test samples to

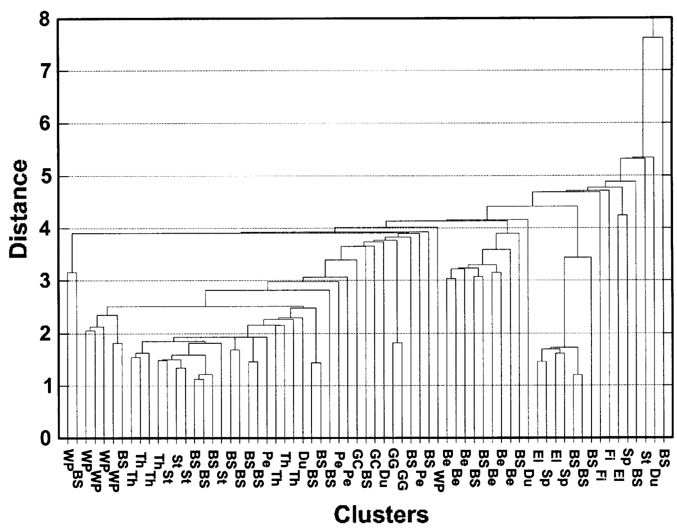

Fig. 4 A dendrogram resulting from cluster analysis of Scottish redware pottery coded for each of the eleven sites and the blind samples (BS). For full site codes see archaeological context. The cluster analysis was performed using hierarchical clustering, the single linkage method and the Euclid distance as a measure of similarity.

particular regional groups, in particular: samples BS11 and BS12 to West Pans; samples BS13, BS14 and BS15 to Stenhouse; samples BS7 and BS8 to Berwick; and samples BS2 and BS3 to either Elgin or Spynie.

The K-means algorithm was another cluster method used to analyse the data. In this technique, a certain amount of predefined information is given, including how many clusters are required (in this case the eleven sites), with one training sample being used to 'seed' each cluster. This technique is, therefore, a form of supervised pattern recognition. The results of K-means clustering were, however, disappointing and led to significant mis-assignment, even of the samples belonging to the training set. Consequently, no useful information was obtained using the K-means cluster technique. A possible reason for the failure is the production of more clusters than sites due to chemical composition differences within sherds from a single site. This seems highly likely if pottery was produced over a period of time and from different batches of raw clay even from a single source.

Factor analysis – This method of data analysis is a form of unsupervised pattern recognition. The first stage in factor analysis is to decide how many factors are required to describe the data. The number of factors should not be confused with the number of sites, as the factors will reflect underlying causes of variation in the data. For example, the variation in the data may be caused by elements being absorbed onto the surface of clay minerals, or the presence of an accessory mineral phase which contains a large concentration of otherwise exotic element. The number of factors may be chosen by first performing a principal components analysis (PCA). This manipulates the data in such a way that a new series of variables (factors) are produced. The first will account for the maximum amount of variance in the data, the second the next most significant and so on. Using a scree plot (Adams 1995), five factors were found to be significant, with the amount of variance explained by the model being shown in Table 1. In particular, the percentage of the total explained by each factor and the cumulative total as each factor is added.

The next stage of the factor analysis is the application of a Varimax rotation. This process aids meaningful interpretation as the new axes are rotated relative to the sample space. This is not the only form of rotation that

Table 1 The amount of variance explained by the factor analysis model. Specifically, the percentage of the total explained by each factor and the cumulative total as each factor is added.

Factor	Eigenvalue	% total for factor	Cumulative %
1	4.84	23.1	23.1
2	3.66	17.4	40.5
3	2.91	13.9	54.4
4	1.87	8.9	63.3
5	1.25	6.0	69.2

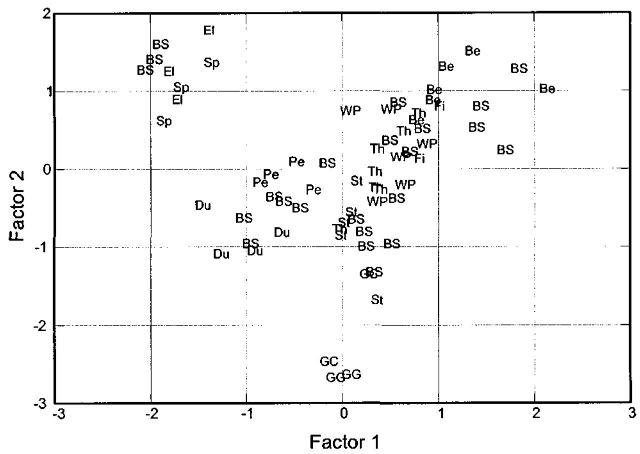

Fig. 5 A plot of Factor 1 versus Factor 2 sample scores from a five factor analysis using Varimax rotation, an unsupervised pattern recognition method. These factors demonstrated best discrimination between the Forth basin geographical group and the other regional groups.

might be considered, but is applied here as it frequently produces good results with geochemical data. The simplest way to represent the results of the factor analysis is to plot the factor scores against each other, as shown in Fig 5.

The application of factor analysis to the Scottish red ware data allowed test samples BS1, BS2 and BS3 to be assigned to Elgin, samples BS20 and BS17 to Dundee, BS16, BS 18, BS19, BS20 to Perth and sample BS9 to the Berwick-upon-Tweed site. More importantly, the factor matrix also provides an indication of which elements are related to which factors; for example, Factor 1 was dominated by a positive correlation with Cr and strong negative correlations with Ba, Rb and Sr. These correlations indicate why these elements provided a clear discrimination between the Scottish red ware pottery sites on the bi-variate plots.

Canonical Discriminant Analysis (CDA) - is probably the most powerful multivariate statistical technique for the assignment of test samples to known sites. This is primarily because the technique is a form of supervised pattern recognition using the *a priori* knowledge of all the training data set. Elements used in this modelling were the same as those used for the previous analytical methods. However, Ag and Sb were eliminated as factor analysis had shown that these elements did not significantly contribute to modelling.

CDA is similar to factor analysis in that it relies on an underlying principle components analysis to create a new set of multivariate axes from normalised data. However, the aim of CDA is to maximise the separation between known groups and CDA was first performed on the training data set. The result was complete separation between the regional sites, with 93% of variance accounted for in the first 3 factors. The CDA coefficients were then applied to both the normalised training set and the normalised test data set to produce a set of scores.

An example of a plot of CDA factors 1 versus 2 is shown in Fig 6. Factor 1 provided the best separation between the

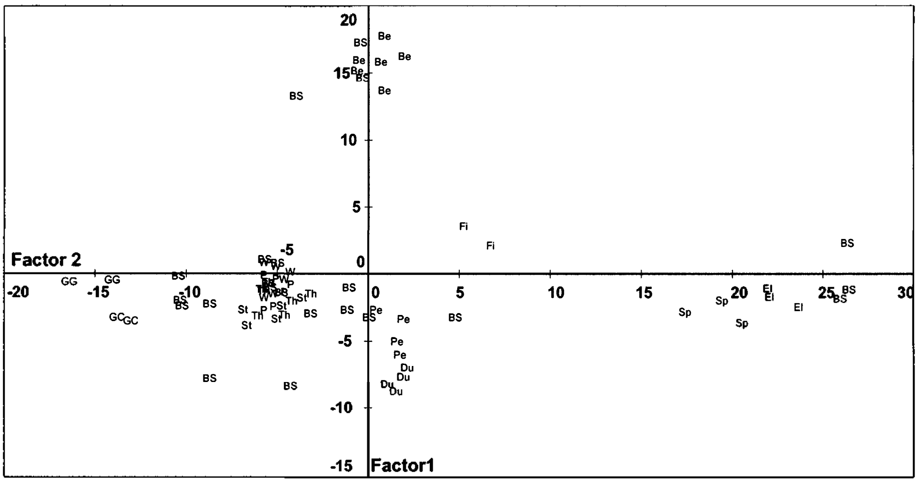

Fig. 6 A plot of Factor 1 versus Factor 2 sample scores from a canonical discriminant analysis (CDA), a supervised pattern recognition method. These factors demonstrated best discrimination between the Forth basin geographical group and the other regional groups.

Elgin/Spynie and Glasgow sites. In contrast, Factor 2 clearly separated pottery sherds from the Berwick and Perth/Dundee sites. Both factors 1 and 2 proved to be successful in separating the Fife samples from the other regional sites. Factors 3 and 4 were useful in distinguishing between the Forth sites of Stenhouse, Throsk and West Pans. CDA was also applied to the test samples and resulted in the following assignments: BS1, BS2 and BS3 to Elgin; BS4, BS5, BS6 and BS11 to Throsk; BS7, BS8 and BS9 to Berwick-upon-Tweed; BS10 and BS12 to West Pans; BS13, BS14, BS15, BS22 and BS23 to Stenhouse; BS16, BS17, BS18 and BS20 to Dundee; and finally samples BS19 and BS21 to the Perth site.

Although CDA is a powerful '*a priori*' statistical technique it is limited by the quality of the training data set. In the current study although the 'training set' used well researched material, the sample size for each site was typically small (five) and in some cases extremely small (two). This small sample size may give rise to problems with the CDA statistical analysis and distort results (Baxter 1994 and Hope 1968). To minimise this possibility five samples per site should be considered the minimum in future studies and ten or more preferred if possible.

RESULTS OF STATISTICAL ANALYSIS OF THE SCOTTISH POTTERY DATA

To make the final assignment of the test samples to individual archaeological sites and geographical regions the results of all of the statistical techniques were collated into a single table (Table 2). The most weight was given to the results of Canonical Discriminant Analysis as this was a supervised pattern recognition technique, making full use of the multi-element data set by manipulating that data set to maximise the differences between sites. This process resulted in the correct assignment of nineteen out of twenty-three pottery samples to their true site of origin, with a further two more sherds being assigned to the correct geographical group. Only two samples were assigned to both the wrong site and regional group, having erroneously been assigned to Stenhouse (Forth) rather than Govan (Glasgow). This error may, at least in part, be due to the very small size of the

Table 2 Summary of sites assigned to blind test samples (BS) by different statistical and graphical methods in comparison with actual site.

Sample	Bivariate graphs	Hierarchical cluster analysis	K-means cluster analysis	Factor analysis	Canonical discriminant analysis	Actual
BS1	Elgin		Elgin	Elgin	Elgin	Elgin
BS2	Elgin	Elgin or Spynie	Elgin	Elgin	Elgin	Elgin
BS3	Elgin	Elgin or Spynie	Elgin	Elgin	Elgin	Elgin
BS4					Throsk	Throsk
BS5			Throsk		Throsk	Throsk
BS6			Throsk		Throsk	Throsk
BS7	Berwick	Berwick	Berwick		Berwick	Berwick
BS8	Berwick	Berwick	Berwick		Berwick	Berwick
BS9	Berwick		Berwick	Berwick	Berwick	Berwick
BS10					West Pans	West Pans
BS11			West Pans		Throsk	West Pans
BS12			West Pans		West Pans	West Pans
BS13		Stenhouse	Stenhouse		Stenhouse	Stenhouse
BS14		Stenhouse	Stenhouse		Stenhouse	Stenhouse
BS15		Stenhouse	Stenhouse		Stenhouse	Stenhouse
BS16	Dundee or Perth			Perth	Dundee	Dundee
BS17	Dundee or Perth		Dundee	Dundee	Dundee	Dundee
BS18	Dundee or Perth			Perth	Dundee	Dundee
BS19	Dundee or Perth		Perth	Perth	Perth	Perth
BS20	Dundee or Perth		Dundee	Dundee	Dundee	Perth
BS21	Dundee or Perth		Stenhouse	Perth	Perth	Perth
BS22			Stenhouse		Stenhouse	Govan
BS23			Stenhouse		Stenhouse	Govan

training set provided for the Govan (two samples) and Clyde basin (four samples) sites. Furthermore, G. Haggarty and D. Hall (pers. comm.) have both suggested that these sherds may have indeed originated from the Stenhouse area.

COMPARISON OF POTTERY COMPOSITION WITH BGS GEOCHEMICAL DATABASE

Since the early 1970's the British Geological Survey has been conducting a national Geochemical Baseline Survey of the Environment (G-BASE). This survey measures the concentrations of a wide variety of elements in stream sediment, soil and water samples at a density of approximately one per square kilometre. For the sediments, the samples are of the finer fraction (less than 150 microns) and are internationally recognised as being representative of local geology and geochemistry. Of particular relevance to the current study, this fine fraction usually contains a high proportion of clay and minor mineral phases, which are likely to be included within the final manufactured pottery. Data for this area was produced using the analytical technique DC Arc - Atomic Emission Spectrometry. The BGS has a number of survey programs that continue over many years. To ensure comparability of data over time and advances in analytical techniques the laboratories have detailed quality assurance and quality control schemes.

The Elgin, Spynie, Dundee and Perth sites are all located within the East Grampians region of the G-BASE. Data for this area is available in the form of maps created using Geographical Information Systems (GIS) (British Geological Survey 1991). Elemental concentrations for all G-BASE sites, within 5 km of the archaeological sites, were extracted from the master ORACLE database for use in the present study. The average concentrations of the elements Ba, Cr, Rb and Sr in pottery analysed from the Elgin, Spynie, Dundee and Perth sites were then compared with the range of concentrations of these elements in the G-BASE (Table 3). The Elgin and Spynie archaeological sites have been considered together as these geographically close sites can not be separated on the scale of the G-BASE data.

The compositional variations within the pottery geochemical data are also recognisable in the G-BASE dataset and, therefore, are believed to reflect regional changes in source clay composition. In particular, there is a decrease in Ba concentrations from Elgin/Spynie through Dundee to Perth, with the pottery data falling within the recorded range of Ba for these areas in the G-BASE dataset. Furthermore, pottery from the Elgin/Spynie sites contain a higher Rb and lower Cr concentrations than sherds analysed from the Perth and Dundee sites (both of which have similar values), with a similar variation also being recognised in the G-BASE dataset. The broad similarity in Sr concentrations in pottery sherds from all three sites is also reflected in the stream sediment geochemical data. In detail, pottery from the Perth site does exhibit a slightly lower Sr content suggesting that the source clay may have been derived from a lower Sr region to the west of Perth recognised on the single element G-BASE map for this area.

Table 3 A comparison between the composition of Scottish red ware pottery from Spynie/Elgin, Dundee and Perth and geochemical survey (G-BASE) stream sediments from within 5 km of the archaeological sites.

Location	Ba (ppm)	Cr (ppm)	Rb (ppm)	Sr (ppm)
Elgin/Spynie pottery	971	64	181	194
Elgin/Spynie G-Base	1300-2000	32-80	100-300	268-376
Dundee pottery	822	107	118	192
Dundee G-Base	560-920	132-276	<41-72	268-435
Perth pottery	748	109	125	169
Perth G-Base	<360-920	132-404	<41-72	268-435

CONCLUSIONS

The present study has clearly demonstrated that it is possible to geochemically fingerprint Scottish red ware pottery and predict, with a high degree of certainty, on both the geographical regional and the site specific level the origin of the pottery sherds. The division of the pottery samples into a training set (whose site of origin was known) and test group has proved a successful means of avoiding any bias in the assignment process. The pottery sherds were analysed using ICP-MS geochemical analytical technique, which is becoming increasingly widely available. A variety of graphical and statistical techniques were then applied to these data to provide a basis on which to assign the test samples to a regional site. Some techniques, such as log-element ratio plots, are perhaps more common in geochemistry than archaeology, but show the synergy of the two disciplines. The supervised pattern recognition method of canonical discriminant analysis proved to be the most successful technique. Errors in assigning the test samples are considered to result from the small size of the training set for a particular site, which should ideally contain at least five samples. Initial results suggest that the comparison of pottery chemical data with the British Geological Survey's national geochemical database (G-BASE) may provide a useful tool in the location of potential sources of raw clay materials.

Acknowledgements

The authors would like to thank the many Scottish archaeologists and museum staff who provided material for this collaborative study and, in particular, Derek Hall and

David Caldwell for helping drive the project. We are indebted to Historic Scotland for funding this work and Olwyn Owen for believing in its success. We would also like to acknowledge the help of two former members of BGS, Phil Green for extracting the G-Base data and Nigel Ruckley for bringing together the Scottish pottery experts with the BGS geoscientists. This work is published with the permission of the Director, British Geological Survey, Natural Environment Research Council, UK.

BIBLOGRAPHY

Adams, M. J. 1995, Chemometrics in Analytical Spectroscopy. *Royal Society of Chemistry Analytical Spectroscopy Monogr* Cambridge **216**.

Blanchard, L. 1979, Perth Enters The Lists. *Scottish Pottery Society Archive News* 4, Edinburgh **75**.

British Geological Survey, 1991, *Regional geochemistry of the East Grampians area*, British Geological Survey, Keyworth, Nottingham, UK.

Bruno, P., Caselli, M., Curri, M. L., Genga, A., Striccoli, R. & Traini, A. 2000, Chemical characterisation of ancient pottery from south of Italy by inductively coupled plasma atomic emission spectroscopy (ICP-AES) statistical multivariate analysis of data. *Analytica Chimica Acta* **410**, 193-202.

Caldwell, D. and Dean, V. 1992, The pottery industry at Throsk, Stirlingshire, in the 17th and early 18th century. *Post-Medieval Archaeol*, **26**, 1-46.

Cook, J. M., Robinson, J. J., Chenery, S. R. N. & Miles, D. L. 1997, Determining cadmium in marine sediments by inductively coupled plasma mass spectrometry: Attacking the problems or the problems with the attack? *Analyst*, **122**, 1207-1210.

Cruichshank *et al.*, (in press).

Davis, J. C. 1973, *Statistics and Data Analysis in Geology*. John Wiley and Sons. New York, 550.

Driscoll, S.T. 2002, Excavations at Glasgow Cathedral 1988-97. *Society for Medieval Archaeol Monogr* **18**.

Fleming, J. A. 1923, *Scottish Pottery*. Glasgow.

Hall, D.W. and Hunter, D. 2001, The Rescue Excavations of some Medieval Redware Pottery Kilns at Stenhousemuir, Falkirk between 1954 and 1978. *Medieval Archaeol* **45**, 97-168.

Harrison, J. G. in press, The Pottery at Throsk, Stirlingshire *c*1600 – 1800; Context Links And Survivals. *Proc Soc Antiq Scot*.

Holmes, L. J. 1997, *Application of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to the Chemical Analysis of Ancient Ceramics*. unpublished Ph.D. thesis, University of Manchester.

Inscker, A. and Tate, J. 1991, Neutron Activation analysis of Scottish Medieval Pottery: A Grain Size Study. In P. Budd, B. Chapman, C. Jackson, R. Janaway and B. Ottway (eds.), *Archaeological Sciences* 1989, Oxbow Monogr **9**, Oxford, 69-75.

James, H., Turnbull, G. & Mechan, D. 1991, *The Excavations at Sinclairtown Pottery Kirkcaldy*. Kirkcaldy.

Laing, L. & Robertson 1970, Notes on Scottish Medieval Pottery. *Proc Soc Antiq Scot* **102**, (1969-70), 146-154.

Laing, L. 1974, Medieval Pottery in Dundee Museum. *Proc Soc Antiq Scot* **103**, (1970-1), 169-177.

Lewis, J. & Pringle D. 2002, Spynie Palace and the Bishop of Moray History Architecture and Archaeology, Edinburgh Proc Soc Antiq Scot Monogr Ser **21**.

Phillips, E. R. 1998, *The petrography and micromorphology of a suite of Scottish Medieval pottery sherds*. British Geological Survey, Technical Report, **WG/98/13**.

Potts, P. J., Tindle, A. G. & Webb, P.C. 1992, *Geochemical Reference Material Compositions: Rocks, Minerals, Sediments, Soils, Carbonates, Refractories and Ores Used in Research and Industry*. Whittles Publishing, Caithness, 313.

Stilke, H., Hein, A. & Mommsen, H. 1996, Results of Neutron Activation Analysis on Tating Ware and the Mayen Industry. *Medieval Ceram* **20**, 25-32.

Simon Chenery, British Geological Survey, Nicker Hill, Keyworth, Nottingham, NG12 5GG, UK
Emrys Phillips, British Geological Survey, Murchison House, West Mains Road, Edinburgh EH9 3LA, UK
George Haggarty, 8 John Street, Portobello, Edinburgh EH15 2EE, UK

Résumé

Afin de déterminer s'il etait possible de tracer précisement l'origine des tessons post-médiévaux d'Ecosse, une étude géo-chimique a été mise en œuvre. L'objectif premier était d'établir une liste de critères pour distinguer l'origine des tessons à la fois à l'échelle régionale et sur un site particulier. Ces études préliminaires utilisent la base nationale de données géo-chimiques des sédiments de rivières (British Geological Survey) permettant de prévoir l'origine de l'argile. Les résultats de cette étude démontrent le pouvoir potentiel de cette approche combinant la géo-chimie et la statistique, et leur application dans l'étude des sites archéologiques.

Zusammenfassung

Eine geochemische Studie wurde erstellt, um festzustellen ob es möglich ist, schottische spätmittelalterliche und spätere Rotware-Keramikscherben genau zu bestimmen. Die Hauptaufgabe war, eine Reihe von Kriterien für die Herkunftsbestimmung von Scherben sowohl auf lokaler als auf regionaler Ebene aufzustellen. Die Voruntersuchungen benutzten auch die nationale geochemische Datenbank für Flußsand-Sedimentanalyse des British Geological Survey als eine Hilfe, die mögliche Herkunft des Tones zu bestimmen. Die Resultate dieser Studie zeigen deutlich die potentielle Stärke dieser kombinierten geochemischen und statistischen Annäherung und deren Anwendung auf archäologische Untersuchungen.