Plasma spectrometry analysis (ICPS) of glazed floor tiles from the Cistercian nunnery of Haddington, East Lothian

M.J.Hughes

Introduction

Ten glazed floor tiles from the site of the Cistercian nunnery at Haddington, East Lothian were submitted to chemical analysis using plasma spectrometry (ICP) with the aim of determining their chemical relationship with tiles and pottery from other sites in the Scottish Redwares ICP database (Haggerty et al 2011).

ICP analyses and statistical investigation of the results

Samples of the body fabric of the tiles in the form of powder were obtained with a 2-3 mm solid tungsten carbide drill bits fitted in a low voltage jeweller's drill. The chemical analysis technique was inductively-coupled plasma spectrometry (ICPS) which gives a chemical fingerprint and thus information on its source, reflecting the clay from which it was made (carried out by the Department of Earth Sciences, Royal Holloway, University of London). The combined atomic emission and mass spectrometry versions of ICPS (ICP-AES plus ICP-MS) were applied, which analyse for all the major elements and a large number of trace elements in the body fabric. The results are given in Table 1, for a total of 47 chemical elements.

Visual scanning of the results and scatter plots of pairs of elements indicated that all the tiles had the same general chemistry. The average, standard deviation and coefficient of variation (which indicates the similarity of the analyses to each other) are also given in Table 1. The low coefficient of variation for many elements bear out this initial impression: sodium and potassium are about 3%; aluminium and other major elements and many trace elements including the rare earths are 6-7%; and other significant 'indicator' elements are around 10% (chromium, copper and caesium). Experience indicates that such percentages indicate a single common source for these ten tiles and scatter plots suggest some possible sub-groups:

Tiles S3, 4 and 10 group together with systematically lower concentrations of the measured elements; S1, 6 and 8 also appear as a possible subgroup with higher than average concentrations while the remainder S2, 5, 7 and 9 are close to the average concentration of the ten. Such differences most probably reflect the percentage of non-clay components in the matrix, very probably quartz - those with low element concentrations contain the highest percentages of temper of the ten. This may be the result of deliberate tempering or the natural variation within the local clay used for producing the tiles. There seems no systematic pattern in glaze colour among these possible sub-groups; they could represent production at different times or dug clay 'batches'. Stopford has proposed the identification of 'production groups' for decorated medieval floor tiles with common tile design and dimensions (Stopford et al 1991). Chemical analyses of medieval floor tiles from Bordesley Abbey, Warwickshire (Leese et al, 1989) and elsewhere has borne this out, showing specific chemical features for each group (perhaps a kiln 'batch') distinguished by slight chemical differences from other production groups. It may that all the Haddington tiles were produced at one period and that the analyses simply indicate day to day differences in the particular clay resources used, namely 'variations on a theme', including different percentages of temper.

Interpretation of the ICP analyses using Principal Components Analysis

Because ICP analyses for many elements, detailed interpretation was carried out with Principal Components Analysis (PCA), a form of multivariate statistics which simultaneously considers the concentrations of many elements in each sample (Afifi et al 2012; Baxter 1994; Orton and Hughes 2013, 175-183). As is common practice, logarithms were taken of all elements before subjecting the data to multivariate statistics.

Plots of the principal component scores are effectively chemical analysis 'maps' showing the relationship between the ceramics based on their chemical analysis alone, and ceramics made of the same clay will plot in the same part of the figure. For the statistical tests, 34 elements were selected: aluminium, iron, magnesium, calcium, sodium, potassium, titanium, manganese, lithium, nickel, scandium, vanadium, yttrium, zinc, chromium, cobalt, copper, rubidium, strontium, lanthanum, cerium, samarium, dysprosium, ytterbium, caesium, thorium, uranium, niobium, praseodymium, gadolinium, lutetium, terbium, thulium and holmium.

The analyses were compared using principal components with tiles analysed from local sites in the Scottish Redwares ICP database: Newbattle Abbey, Dirleton Castle, North Berwick nunnery and Dunbar Customs House (Haggerty et al 2011, fig.26, p.22). All five sites showed consistent but quite distinct chemical composition groups (Figures 1 and 2), although the two white slipped tiles analysed from Dunbar Customs House were very close in clay chemistry to the Haddington tiles (Figure 2). The horizontal spread of analyses from the different sites in Figure 1 (first principal component) mainly reflected the variations in percentage of temper in tiles from the same site. Tiles with higher alkalis (caesium, rubidium) and thorium, and lower transition metals (iron, zinc, copper and vanadium) and titanium appear towards the lower part of Figures 1 and 2 (i.e. characteristics of the Haddington tiles). Figure 2 plots the second and third components where the effects of temper are removed; it shows closer clustering of tiles from each site and that the Haddington and Dunbar tiles are chemically very similar and lie in the bottom right. Their characteristics are higher calcium, strontium and sodium and lower chromium, vanadium and thorium compared to those on the left of the Figure. They appear to have been made at the same place though these analyses alone do not indicate its location. Both are chemically unlike the ICP analyses of redware pottery and clays from Colstoun made by the late Alan Vince (analyses COL1A-S6 in the online ICP database, Vince 2010), which is slightly surprising given that Colstoun is c. 2 km from Haddington, but it may be that the geology of the area explains it - different rocks.

Visual comparison of the Haddington analyses against those of redware pottery from East Lothian, including kiln sites at Portobello, Morrison's Haven, West Pans, Stenhouse and Throsk, and consumer sites of Edinburgh Cannongate and Chambers St (used in testing of pottery from Niddrie Burn, Edinburgh: Haggerty and Hughes 2013) showed no chemical similarities – the Haddington tiles had significantly less iron, chromium and aluminium but more calcium.   Neither were the Haddinton tiles chemically like pottery from the kiln site at Coupar, and consumer sites: Melgund Castle; Perth High Street, Canal Street and Kinnoul A and B; and Brechin (Hughes 2014).

Further tests were carried out to compare the tile analyses against those of tiles from four known Dutch tile kilns whose data were in the Scottish redwares database, namely Amsterdam, Dordrecht, Haarlem and Utrecht (Figure 3). This indicated that the Haddington, Dunbar and Dirliton Castle tiles had chemical compositions consistent with their being Dutch: the Haddington tiles were closest in chemistry to tiles from Amsterdam, but slightly different to those from Haarlem and Utrecht. The Dunbar and Dirliton tiles were consistent with Dordrecht material. All these groups were clearly chemically distinguishable from the Scottish-produced tiles from Newbattle and North Berwick.

Conclusions

All the tiles have very similar clay chemistry in body fabric, indicating a common source. Some chemical sub-groups appear to be present, but with no clear link to glaze colour or other physical characteristics may simply reflect different natural quartz temper in the original dug clay. Comparison with ICP analyses of tiles from local sites in East Lothian shows a close link with two white slipped tiles from Dunbar Customs House, but distinct differences to pottery from the nearby production site at Colstoun, and pottery from other East Lothian sites, the Forth Valley and Perth areas. Further investigation confirmed the Haddington tiles as being of Dutch origin, and of the available chemical analyses, they were closest in chemistry to tiles produced at Amsterdam.

References

Afifi, A., May, S. and Clark, V.A., 2012, *Practical Multivariate Analysis, Fifth edn.*, CRC Press, Taylor and Francis, Boca Raton FL

Baxter, M. 1994. *Exploratory Multivariate Statistics in Archaeology*. Edinburgh University Press, Edinburgh.

Haggerty, G., Hall, D. R. and Chenery, S., 2011, *Sourcing Scottish Redwares*, Medieval Pottery Research Group Occasional Paper 5.

Haggarty, G. and Hughes, M., 2013, The medieval and later pottery from Niddrie near Edinburgh, *Medieval Ceramics*, **33**, 55-71

Hughes, M., 2014, Plasma spectrometry analysis (ICP) of Scottish Redware and other pottery from the City Chambers (PEX63) and Atholl Place (PE55) in Perth, unpublished report

Leese, M.N., Hughes, M.J. and Stopford, J., 1989, The chemical composition of tiles from Bordesley: a case study in data treatment, in S.Rahtz, and J. Richards, (eds.) *Computer Applications and Quantitative Methods in Archaeology,* British Archaeological Reports Int. Series **548**, 241-249

Orton, C. and Hughes, M., 2013, *Pottery in Archaeology* 2nd edn, Cambridge University Press, Cambridge

Stopford, J., Hughes, M.J. and Leese, M.N., 1991, A scientific study of medieval tiles from Bordesley Abbey, near Redditch (Hereford and Worcester). *Oxford J. Archaeol.* **10**, 349-360.

Vince, A., 2010. *Medieval Pottery Research Group (2010) Alan Vince Archive* [data-set]. York: Archaeology Data Service [distributor] (http://archaeologydataservice.ac.uk/) (doi: 10.5284/1000382).

Table and Figure captions

Table 3. Full list of ICPS (inductively coupled plasma spectrometry) analyses of the tiles from Haddington.

Figure 1. Principal Component Analysis comparing the ICPS results on the Haddington tiles with those of local tiles in the Scottish Redwares ICP database: Newbattle Abbey, Dirleton Castle, North Berwick nunnery and Dunbar Customs House analysed in this project. Plot of first and second principal components. The horizontal axis plots the first principal component (containing 41% of the variation in analysis of all the pottery), and the vertical the second principal component (a further 25%). The samples fall into very distinct groups by tile location; the slight separation of the Haddington tiles into sub-groups is detectable.

Figure 2. Plot of the second and third Principal Components from the same results as Figure 1. The Haddington and Dunbar tiles are chemically very similar and lie in the bottom right. The third principal component contained 16% of the variation in analysis of all the pottery).

Figure 3. Plot of the second and third Principal Components comparing the Haddington and other Scottish tiles against analyses of four Dutch kilns: Amsterdam, Dordrecht, Haarlem and Utrecht.

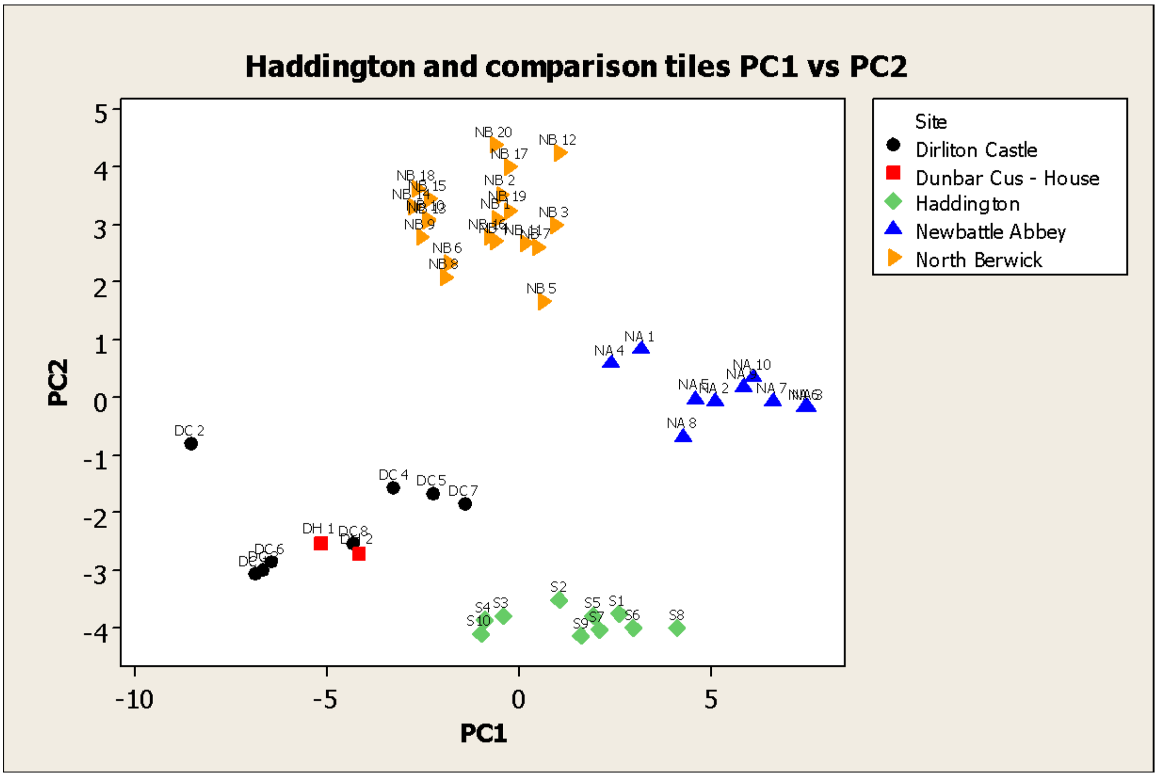

Figure 1

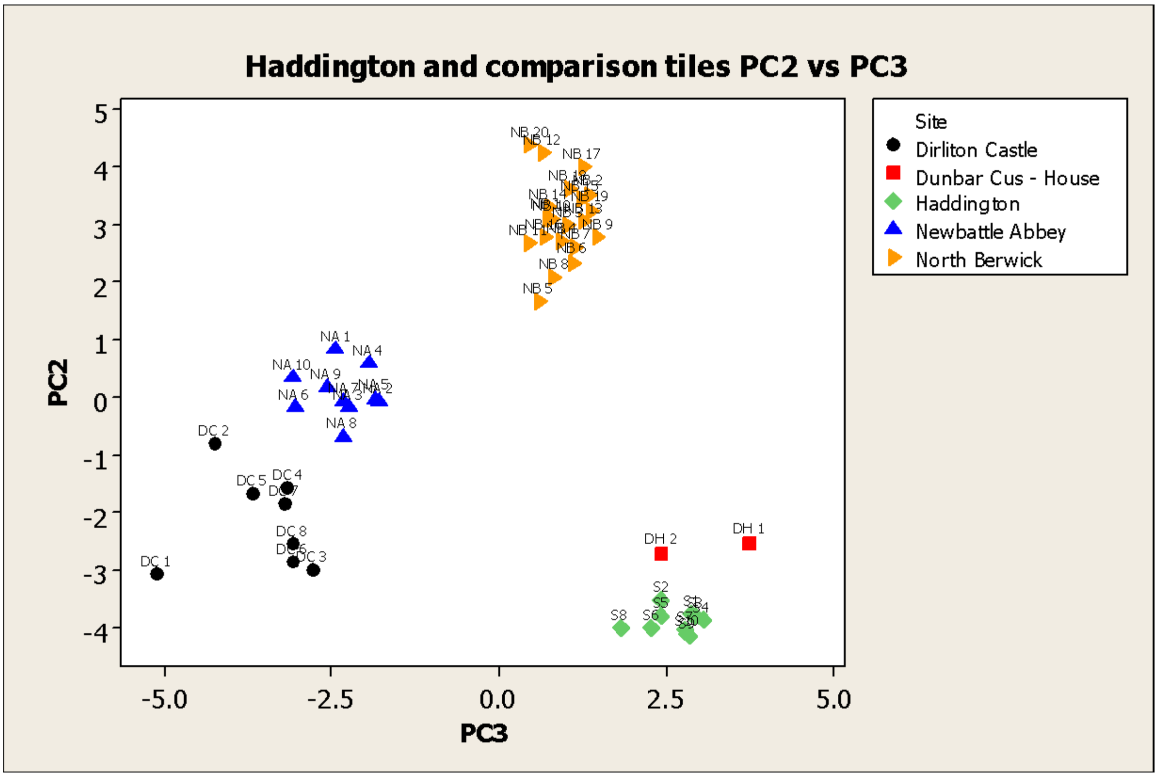

Figure 2

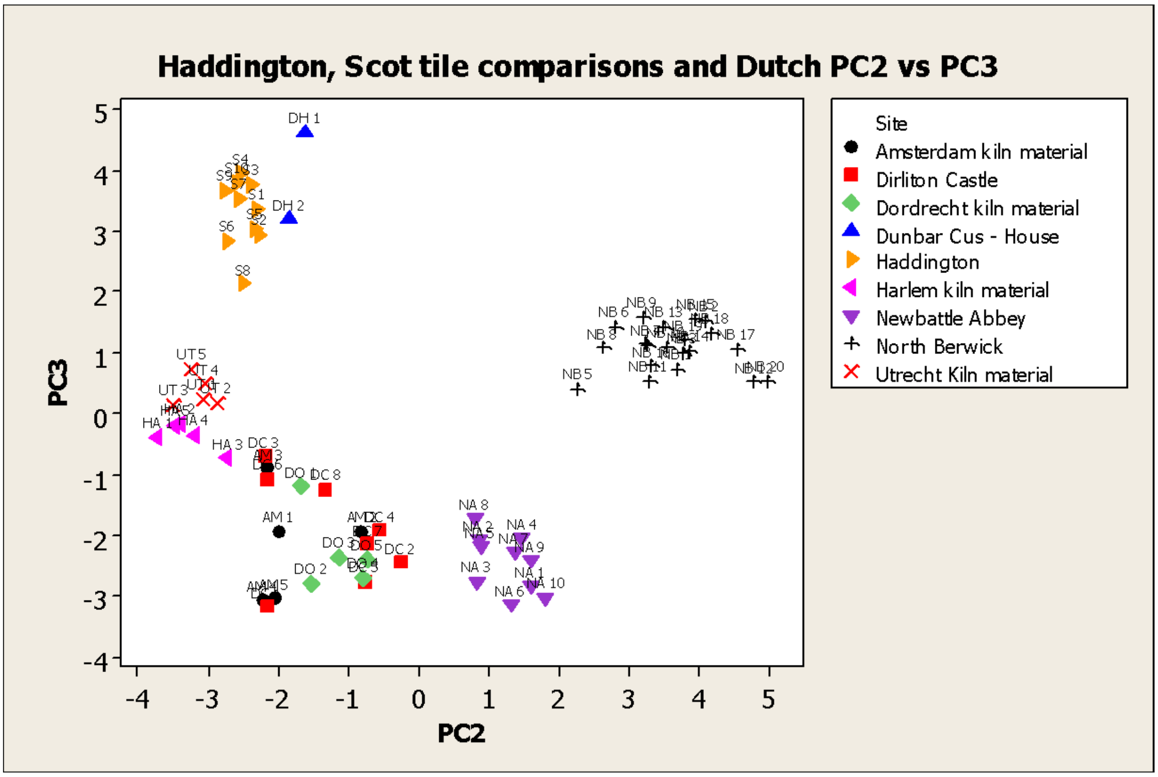

Figure 3