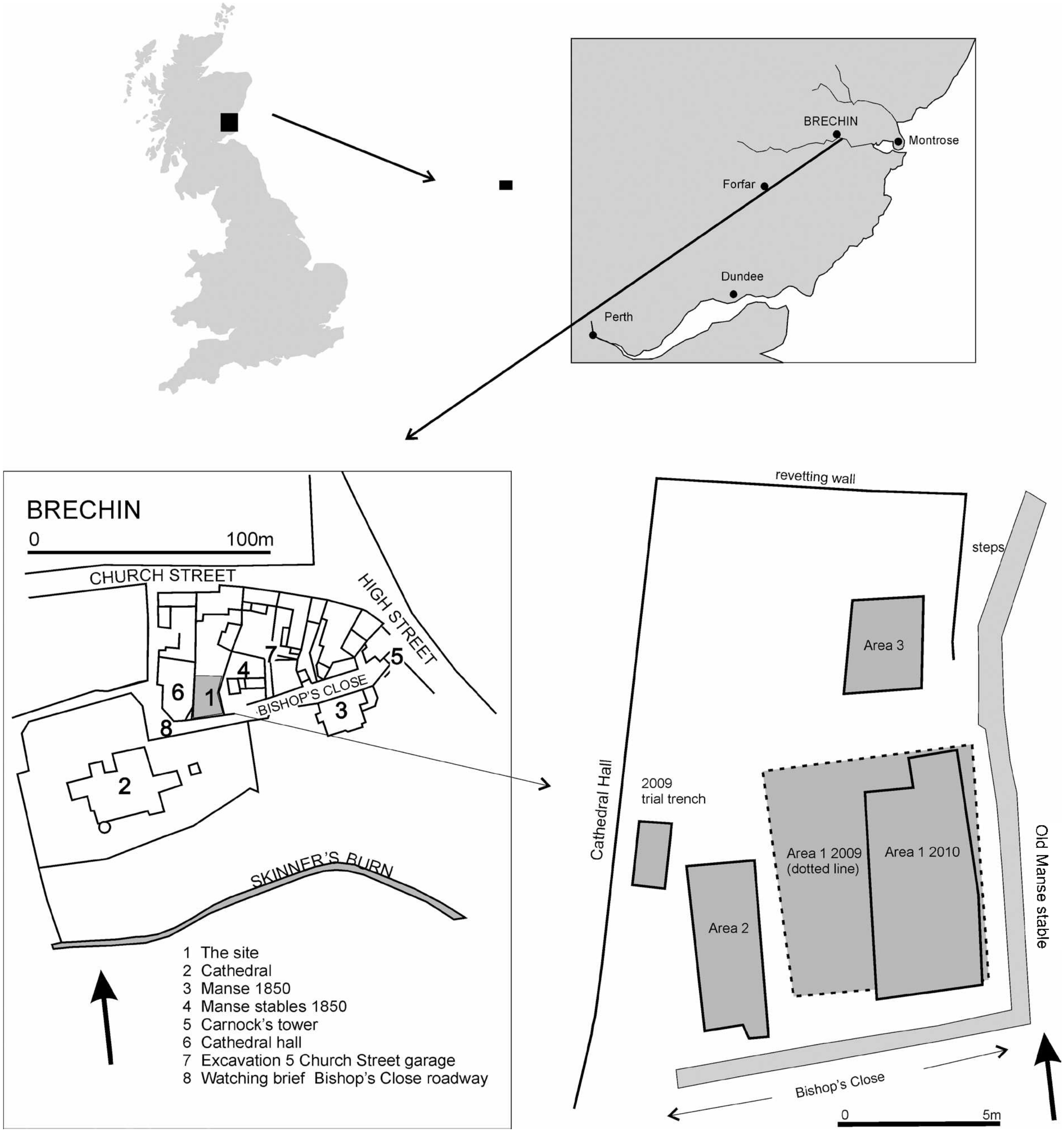

Figure 1

Brechin site location plan

After Murray and Murray 2011

A programme of ICP analysis on medieval pottery from Bishop's Close, Brechin

George Haggarty and Michael Hughes *

Summary

Eleven sherds of Scottish Redware from excavations in Bishop's Close, Brechin, Angus were chemically analysed using ICP. The sherds were chosen from a well dated midden layer (13th to 15th century) and the results suggest there is a markedly different signature visible when compared to previously sampled material from sites lying to the West of the River Tay.

Introduction (Figures 1 and 2)

In their conclusions to the Scottish Redwares monograph (Haggarty *et al* 2011, 68), the authors suggest that identifying a geographical source is crucial to the study of excavated medieval ceramic material; especially in ascertaining its movement, either in the form of trade or exchange. With this in mind Charles and Hilary Murray were approached to see if they would supply sherds of stratified redware pottery from the archaeological excavations they had carried out in Bishop's Close, Brechin. The site lay adjacent to the city's important cathedral (Murray and Murray 2011, 36–57). The eleven jug sherds chosen by them all derived from (phase 3 layer [28]) and were probably of local manufacture, being visibly indistinguishably from 95% of the total redware shard assemblage. Analysed were three decorated body sherds (RL27–29), three rims (RL30–32), two base sherds (RL 33–34) and single body sherds from layers [50G], [60C] and [60M] (RL35–37) respectively. The data produced was then compared with the Scottish redware data-base; presently held on a computer in the NMS ceramic store Granton and kept up to date by (GH).

The bottom level of the phase 3 midden was unusual for Scotland in that it produced from a relatively small area, a number of well dated coins, including three Henry III, English silver pennies, two of which date from (1247–1272) and one from (1280–1295), a silver halfpenny of Edward 1, (1280–1295) and a worn silver farthing of Edward 1 (1280–1307) (Thain 2011, 44–45). The midden mainly varied in depth between 700 and 900 mm. It had begun to develop in the late 13th or early 14th century and may have continued to be added to until sometime in the 15th, although most of the pottery is thought by the excavators to be from the 13th or 14th century (Murray and Murray 2011, 41). Results from other Scottish medieval ceramic assemblages suggest the almost total lack of ceramic cooking pots and may indicate a 14th century or later date.

But inductively-coupled plasma mass spectrometry (ICP-MS), thin section analysis, or other scientific techniques such as XRF, are not, and can never be the solution to all our medieval ceramic problems. It is essential that our excavated assemblages are also categorised visually against a good local or, preferably, national fabric reference collection in an effort to construct rigorous research strategies in a bid to make our ceramic reports of regional, national, or even international, significance. To this end the sampled sherds have been added to the national fabric reference collection. Presently this is held in the National Museums Scotland ceramic store at Granton.

Chemical analysis by Inductively-Coupled Plasma Atomic Emission Spectrometry and Mass Spectrometry

The analysis technique was the same as that applied for the Data-base of Scottish redwares, namely inductively coupled plasma spectrometry (ICP), using a combination of two instruments, Atomic Emission Spectrometry (ICP-AES) and Mass Spectrometry (ICP-MS) (Haggarty *et al* 2011, 5). Powdered samples for analysis were obtained from the sherds by drilling with a 2 or 3mm diameter tungsten carbide drill. In addition, the samples sent for ICP analysis included a Certified Reference Material (NBS679 Brick Clay produced by the US National Institute for Standards and Technology, Washington DC) spaced out in the analysis batch but without identification to the laboratory as such; these acted as analysis quality control samples. The analysis results on these control samples gave entirely satisfactory results. The powdered samples were analysed at Royal Holloway, Department of Earth Sciences, University of London, using their standard techniques for ICP-AES and ICP-MS.

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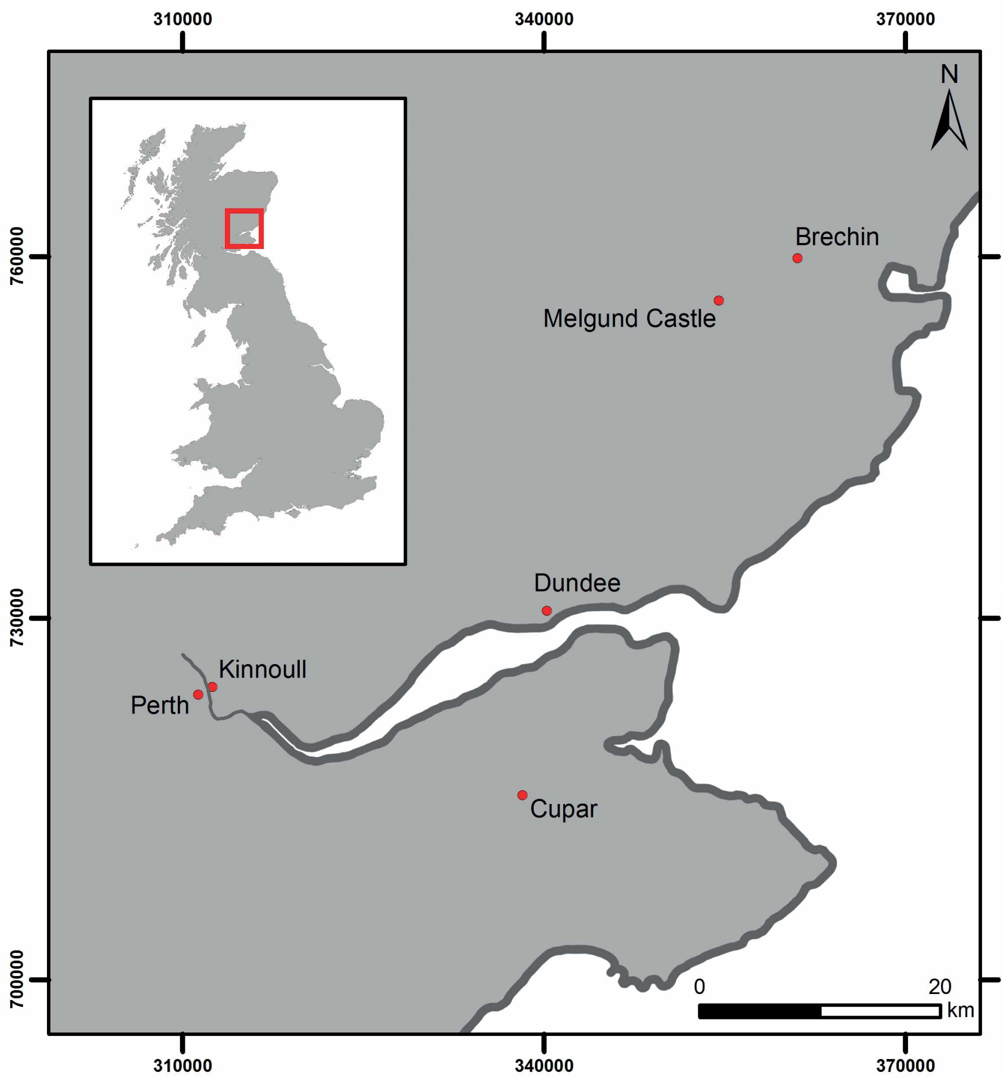

Figure 2
Map showing sites mentioned in the text

Results and discussion

The full results of the analyses are given in Table 1. Visual examination of the data showed a fairly similar chemical analysis for all sherds, which suggests one source.

Principal Components Analysis of the ICP results General aspects

Detailed interpretation of the ICP analyses was carried out with multivariate statistics, which simultaneously considers the concentrations of many elements in each sample. The multivariate statistics technique of Principal Components Analysis (PCA) was used (Manly 2005; Tabachnick and Fidell 2007). Descriptions of its application to archaeology have been given elsewhere (see for example, Baxter 1994 and 2003; Shennan 1997). The programme MINITAB version 16 was used with the 'PCA' procedure (Ryan *et al* 2005). The Excel file containing the original analysis data was read into MINITAB and natural logarithms were taken of all elements before subjecting the data to multivariate statistics – taking logs is regularly used in such applications. This pattern was followed in all the tests in this report; it differs from the approach used by Haggarty *et al* (2011) and Jones *et al* (2002–03) where the elements were scaled to aluminium. However the two approaches appear to produce very similar results (see Haggarty and Hughes 2013). Plots of pairs of the resulting principal components are effectively chemical 'maps' for the items analysed, and it would be expected that pottery made of the same clay to plot in the same part of the figure.

Table 1

Details of the pottery and full analysis results on all the sherds from Bishop's Close, Brechin analysed in this project by inductively coupled plasma spectrometry (ICP-AES and ICP-MS)

Al2O3	aluminium	P2O5	phosphorus	Sc	scandium	Rb	rubidium	Cs	caesium	**rare earth elements**							
Fe2O3	iron	MnO	manganese	Sr	strontium	Zr*	zirconium	Tl	thallium	La	lanthanum	Eu	europium	Er	erbium		
MgO	magnesium	Co	cobalt	V	vanadium	Nb	niobium	Pb	lead	Ce	cerium	Gd	gadolinium	Tm	thulium		
CaO	calcium	Cr	chromium	Zn	zinc	Mo	molybdenum	Bi	bismuth	Pr	praesodymium	Tb	terbium	Yb	ytterbium		
Na2O	sodium	Cu	copper	Y	yttrium	Cd	cadmium	Th	thorium	Nd	neodymium	Dy	dysprosium	Lu	lutetium		
K2O	potassium	Li	lithium	Ba	barium	Sb	antimony	U	uranium	Sm	samarium	Ho	holmium				
TiO2	titanium	Ni	nickel	As	arsenic												

The results from Al2O3 to MnO inclusive are given as the oxide, in weight percent; all the rest are given as the element, in parts per million.

* The zirconium results were not used in the statistical tests since the laboratory indicated possible incomplete dissolution of this element from the powder sample.

sample	layer/identity	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	P2O5	MnO	Co	Cr	Cu	Li	Ni	Sc	Sr	V	Zn	Y	Ba	As	Rb	Zr*
RL 27	28 decorated sherd	17.2	7.35	2.48	2.16	1.91	3.39	0.78	1.42	0.1	21	107	30	45	66	16	262	102	100	29	1058	16	109	188
RL 28	28 decorated sherd	14.2	6.15	1.98	3.01	0.92	3.67	0.62	1.6	0.07	16	83	21	60	45	14	154	98	70	26	725	9	130	113
RL 29	28 decorated sherd	19.8	7.98	2.46	0.7	1.4	3.43	0.98	1.33	0.05	23	141	29	55	60	17	203	141	141	19	857	51	121	249
RL 30	28 rim sherd	19.6	6.57	2.55	1.26	1.78	3.14	0.97	0.6	0.14	30	119	20	57	63	18	183	123	84	27	1094	12	93	284
RL 31	28 rim sherd	20.2	9.88	3.11	2.29	1.4	3.85	0.89	1.72	0.13	28	147	49	58	85	20	249	121	133	29	1148	16	129	232
RL 32	28 rim sherd	20.1	7.95	3.56	1.28	1.5	3.79	0.99	0.87	0.08	31	151	56	75	85	22	156	148	123	29	1126	20	133	207
RL 33	28 base sherd	17.9	6.97	2.88	1.81	1.66	3.05	0.91	0.61	0.08	28	126	30	60	71	19	190	123	115	32	1195	18	99	285
RL 34	28 base sherd	19.5	9.75	3.33	1.51	1.47	3.61	0.89	0.47	0.16	37	140	54	74	91	21	175	130	126	31	1118	14	129	218
RL 35	midden 586	17.9	7.24	3.13	1.2	1.38	3.34	0.88	1.11	0.1	30	142	38	60	75	20	143	129	115	25	1031	8	114	208
RL 36	60C	13	6.6	1.99	3.22	0.77	3.66	0.55	2.22	0.07	18	90	27	66	45	15	237	112	80	24	803	34	138	98
RL 37	60M	19.9	9.74	3.63	1.47	1.28	3.76	0.9	0.71	0.11	35	160	56	77	94	22	175	146	130	30	1094	12	145	214

sample	layer/identity	Nb	Mo	Cd	Sb	Cs	Tl	Pb	Bi	Th	U	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
RL 27	28 decorated sherd	4.3	0.4	0.16	0.6	5.4	1	270	0.18	11.6	2.7	48	90	10.7	45	8	2	6.3	1.1	5	1	2.9	0.48	2.7	0.44
RL 28	28 decorated sherd	7.2	0.8	0.14	2.8	6.2	6.6	7924	0.19	12.5	3.2	43	83	9.7	40	7.1	1.5	5.7	1	4.6	0.9	2.6	0.41	2.37	0.38
RL 29	28 decorated sherd	17.8	2.7	0.1	2.4	6.6	2.9	2615	0.11	14.2	4.3	41	76	8.4	33	5.6	1.3	4.3	0.7	3.5	0.7	2	0.34	2.34	0.32
RL 30	28 rim sherd	17	0.5	0.1	1	6.6	1.2	554	0.06	11.8	2.8	55	142	11.3	46	7.7	1.9	6.4	1.1	4.7	0.9	2.7	0.44	2.46	0.4
RL 31	28 rim sherd	13.4	0.5	0.19	1	6.9	1	88	0.19	12.6	3	56	103	12.2	51	8.8	2.1	7	1.2	5.1	1	2.8	0.48	2.58	0.42
RL 32	28 rim sherd	18	1.8	0.09	1.9	7.7	2.8	2486	0	13.8	3.2	58	106	12.7	53	9.1	2	7.2	1.3	5.3	1	2.8	0.5	2.5	0.4
RL 33	28 base sherd	17.1	0.5	0.16	0.8	6.6	1	187	0.19	12.3	2.9	55	104	12	50	8.7	2.2	7	1.2	5.4	1.1	3.1	0.51	2.89	0.48
RL 34	28 base sherd	16.8	0.3	0.09	0.9	7.5	1.1	163	0.13	12.8	3	58	126	12.7	52	9.1	2.2	7.4	1.3	5.5	1.1	3	0.5	2.77	0.45
RL 35	midden 586	14.9	0.6	0.08	1	6.7	1.7	1144	0.05	12.4	3.1	48	90	10.6	44	7.6	1.6	6	1	4.5	0.9	2.4	0.39	2.17	0.35
RL 36	60C	6.5	2.8	0.04	1.1	6.7	1.1	215	0	12.2	3.9	41	80	9.3	39	6.8	1.4	5.4	1	4.3	0.9	2.4	0.4	2.29	0.36
RL 37	60M	17.9	0.3	0.14	1.1	7.8	1.4	565	0.06	13.3	2.8	59	107	12.9	53	9.2	2.1	7.4	1.3	5.4	1.1	2.9	0.48	2.64	0.43

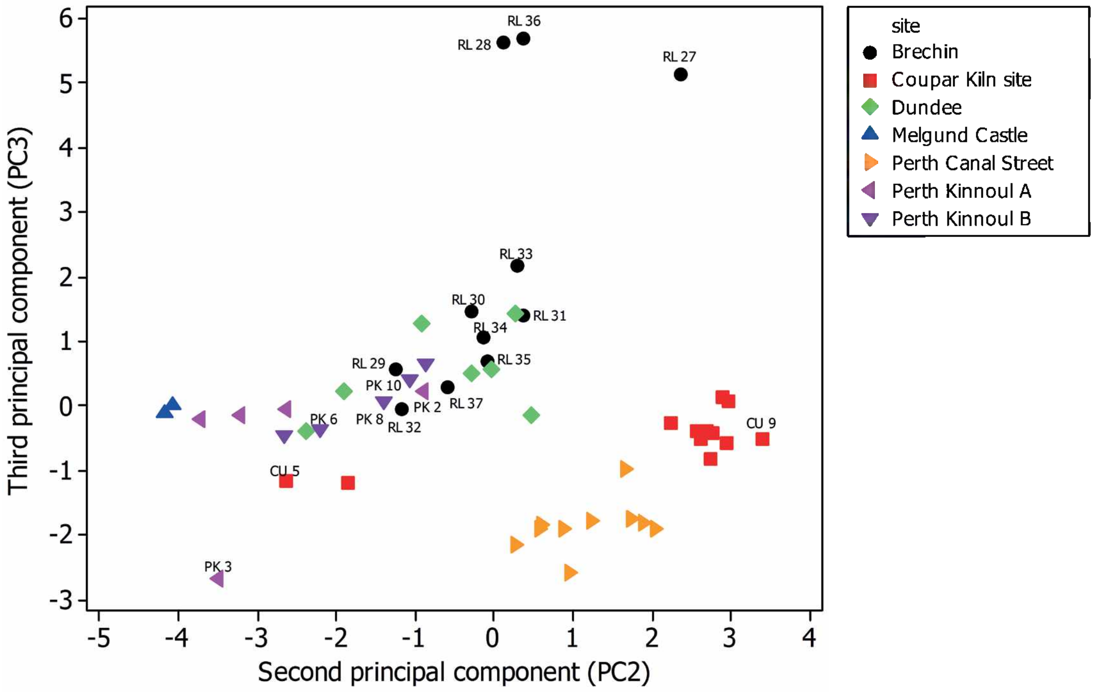

Figure 3
Graph showing the plot of the second and third Principal Components arising from ICP analysis of the redware pottery from Bishop's Close, Brechin analysed in the project, combined with pottery from six other sites in the local area, including the kiln sites (Cupar) and probable kiln site (Perth Canal Street) based on 28 chemical elements. The symbol type and colour indicates the site, while the annotation alongside the symbol is the analysis number (see Table 1 for key). The Brechin and Dundee sherds overlap, together with some Perth Kinnoull A and B, while the Perth Canal Street possible kiln material and Cupar industrial kiln sherds are clearly different in clay chemistry.

Principal Components Analysis of the ICP results on Bishop's Close, Brechin, pottery together with comparative analyses from the Scottish Redware ICP Data-base

Statistical tests were carried out by combining the results on the Brechin sherds with a selection of comparative pottery analyses of production and consumer sites drawn from the Scottish Redware ICP Data-base. Unfortunately to date little ICP analysis has been carried out of redwares in the region. Sites and samples chosen for comparison were: the kiln site at Cupar (sample number code CU1-12; NGR NO 377 143); and consumer sites: Dundee (DU1-7; NO 404 306); white trailed slip decorated redware sherds from Melgund Castle (MC1-2; NO 546 563); Probable Industrial Kiln Material from Perth Canal Street (PC1-10; NO 118 233); and Perth Kinnoull A and B medieval sherds (PK12-5 and PK6-10 respectively; NO) 123 232) (Figure 3). The analyses of the major elements were missing from the medieval Dundee samples so the comparison was made omitting all the major elements in the Brechin sherds and comparative material.

A representative selection of the elements analysed was used in all the tests on the Redwares employing Principal Components Analysis, omitting elements which may be subject to leaching during burial or tend to show poor correlation with other elements. The elements selected include: titanium, lithium, chromium, cobalt, copper, zinc, nickel, vanadium, scandium, yttrium, rubidium, strontium, caesium, lanthanum, cerium, samarium, europium, niobium, neodymium, praseodymium, gadolinium, dysprosium, holmium, erbium, ytterbium, lutetium, uranium and thorium (28 elements). The zirconium results (Zr*) were not used in the statistical tests since the laboratory indicated possible incomplete dissolution of this element from the powder sample.

Principal components analysis on the combined dataset showed that the first principal component was correlated positively with all elements, a very common finding in studies of archaeological and historic ceramics, and is an approximate measure of 'total element concentrations'. It reflects the percentage of diluting temper in the body fabric (natural or added, often quartz silt or sand). Pottery with higher concentrations of elements (*ie* with more positive values on that component or axis in a plot) represents fabrics with less quartz temper. One major difference in chemistry between the analyses of these groups of pottery is therefore simply the total concentration of elements, which is a measure of the proportion of diluting temper. There was significantly more variation in temper proportion among the Brechin sherds than those from the comparison sites, which showed decreasing degrees of variation in temper proportions in the medieval Dundee and Kinnoull A and B sherds; then the Perth Canal Street (Blanchard 1979, 75), and finally the Industrial Cupar kiln site (Martin and Martin 2002, 12–25), showed the least variation of all. The variation due to temper proportions in the Brechin and other sites is almost certainly due to the deliberate inclusion of temper such as quartz, which contains very low amounts of chemical elements apart from silica and therefore acts as a simple diluent in the clay fabric. The first principal component (not plotted) accounted for 46% of the variation in composition, and was correlated positively with the concentrations of all the elements – *ie* it is a 'dilution' effect. Brechin sherds RL34, 32 and 37 contained the highest concentrations of elements in 0all the Brechin and comparison sherds (*ie* had the least amount of temper). On the other hand sherds RL28, 29 and 36 had the most temper in the Brechin sherds, though two Cupar kiln sherds (CU5 and 9) and two Perth Kinnoull A (PK 2 and 3) showed significantly more temper was present, as did other Dundee sherds. This is in line with current evidence which suggests in Scotland the earlier the redware the more temper was introduced to the body.

It was more useful to consider the plot of the second and third components (PC2 and PC3) in which by definition the 'diluting' effects extracted with the first principal component play no part. The element scandium contributed very little to the position of the samples in Figure 3; it is closely associated with the element aluminium, which indexes the clay mineral component of a clay fabric, and indicates that the second and third components of Figure 3 show real differences in the chemistry of the clay component between the pottery sherds rather than the temper effect. The second and third components contained a further 15% and 11% respectively of the chemical variation, a cumulative total of 73% of the chemical variation in the pottery samples were therefore summarised in just these three components. Figure 1 showed a pronounced grouping of samples by site, indicating an internal consistency in chemical composition for the sherds in each of the site groups, some of which overlapped. The Cupar kiln and Perth Canal Street form non-overlapping clusters of sample points in the lower right, the Cupar samples being the more compact, indicating a very consistent clay source was used. All the sites except Cupar lie on the Arbuthnott–Glenlee Formation, wacke sandstone type rock and so it would be expected that the local clays at most sites would be similar in clay type, but contrast with clays at Cupar which is on Stratton Group Old Red Sandstone (Haggarty *et al* 2011, table 1, p.36). The fairly close plotting of the Cupar Kiln and probable kiln material from Perth Canal Street suggests the use of a similar clay type for both groups of pottery.

The Canal Street and Cupar sherds differ from the clay type used for the Brechin, Dundee and Perth Kinnoull groups. The latter three groups show definite overlaps: Brechin and Dundee sherds show the greatest overlap and seem to be chemically indistinguishable. Three of the Perth Kinnoull B sherds (PK6, 8 and 10) also overlap with them as does one Perth Kinnoull A (PK2). The Brechin, Dundee and these Perth Kinnoull sherds all appear to belong to the same chemical group, indicating a common geological clay source for all these sherds. The remaining Perth Kinnoull A and B sherds seem to form another closely-related chemical group towards the lower right of Figure 3, together with the two sherds from Melgund Castle which appear very similar to each other chemically. Although earlier statistical tests found no difference between the two Perth Kinnoull groups (Haggarty *et al* 2011, 49) it seems the two site groups each contain members of two slightly different chemical groups.

Three of the Brechin sherds are separated from the rest in Figure 3, occurring in the top right. Sherds RL28 and 36 are very similar chemically, and could well be from the same kiln batch, while RL27 is slightly different. Inspection of the analyses however shows that all three only have small differences from the rest of the Brechin sherds in titanium, and the trace elements chromium, copper and vanadium. This could be caused by the presence of some minor minerals in the three, which otherwise do not differ in their clay chemical characteristics from the rest of the Brechin sherds.

Summary and conclusions

Plasma Spectrometry (ICP) analyses on redware pottery from Bishop's Close, Brechin were interpreted by principal components analysis, following the approach used for the major project on Scottish redware (Haggarty *et al* 2011). The pottery would appear to derive from one clay source, and comparison with ICP analyses in the Data-base of Scottish redwares suggests a commonality with medieval pottery from Dundee, and some medieval pottery from Perth Kinnoull A and B. The Brechin material however contrasts as one might expect, significantly in clay chemistry with pottery from the probable kiln material from Perth Canal Street and sherds sampled from the clay used at the Cupar industrial pottery production site. The results also show that Kinnoull 1 and 2 shard material recovered from the east bank of the River Tay have nothing in common with pottery from the town of Perth; which confirms the results of earlier work (Haggarty *et al* 2011, 48). Finally there is an undoubted lacuna in the ICP data for the area between Perth, Dundee and Aberdeen which needs addressing.

Acknowledgments

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Résumé

Onze tessons de poterie rouge écossaise provenant de fouilles réalisées à Bishop's Close, Brechin (Angus), ont fait l'objet d'une analyse chimique par ICP. Les tessons ont été choisis dans une couche d'ordures bien datée (13e au 15e siècle) et les résultats suggèrent une signature très différente de celle d'échantillons antérieurs de matériaux provenant de sites à l'ouest de la River Tay.

Zusammenfassung

Elfe Scherben von Redware (Keramik aus rotem Ton) aus Ausgrabungen in Bishop's Close, Brechin, Angus, wurde mit Hilfe der AES-Analyse (Atomemissions-Spektralanalyse) chemisch untersucht. Die Scherben wurden aus einer gut datierten Abfallhaufen-Schicht ausgewählt (13.–15. Jahrhundert), und die Ergebnisse deuten darauf hin, dass eine deutlich unterschiedliche typische chemische Zusammensetzung vorliegt, wenn man sie mit dem vorher beprobten Material aus Fundstätten westlich des River Tay vergleicht.