Chemical Compositional Analysis of Prehistoric Pottery from Ratcliffe on the Wreake, Leicestershire

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Samples of Early Bronze Age, Middle Bronze Age and Iron Age pottery from various sites in the vicinity of Ratcliffe on the Wreake, found during archaeological investigations in advance of pipeline construction conducted by Network Archaeology Ltd, were submitted for thin section analysis by Ed McSloy (Vince 2007). Ten fabrics were identified, coded Fabric 1 to 10 (Table 1).

Table 1

REFNO	Action	TSNO	class	Subfabric	Location
48171	TS	V4231	POTTERY	1	Site 10
48337	TS	V4232	POTTERY	1	Site 10
48338	TS	V4233	POTTERY	2	Site 10
48383	TS	V4234	POTTERY	2	Site 10
48383	TS	V4235	POTTERY	2	Site 10
48383	TS	V4236	POTTERY	2	Site 10
48337	TS	V4237	POTTERY	2	Site 10
48283	TS	V4238	POTTERY	3	Site 10
48007	TS	V4239	POTTERY	4	Site 10
48022	TS	V4240	POTTERY	4	Site 10
54029	TS	V4241	POTTERY	5	Site 11
54033	TS	V4242	POTTERY	5	Site 11
095	TS	V4243	POTTERY	5	Site 11
54054	TS	V4244	POTTERY	6	Site 11
54096	TS	V4245	POTTERY	6	Site 11
54019	TS	V4246	POTTERY	7	Site 11
54022	TS	V4247	POTTERY	7	Site 11
65013	TS	V4248	POTTERY	8	Site 11
54019	TS	V4249	POTTERY	8	Site 11
54096	TS	V4250	POTTERY	9	Site 11
54096	TS	V4251	POTTERY	10	Site 11

This analysis indicated that one of the Iron Age sherds was probably a regional import, made from a self-tempered shelly clay of Middle Jurassic age, which neither outcrops locally nor could have been brought to the area as a result of glacial action. The remaining samples could either have been produced on a household or community level or made in a specialised community and exchanged with other settlements in the area. About half of the samples were tempered with angular fragments of acid igneous rock. This rock is probably the Mountsorrel granodiorite, which outcrops a few miles to the west of the site. To judge by the prevailing direction of ice flow and the post-glacial drainage of the area, it is unlikely that this rock could be found in local Wreake valley sands or gravels and no such rock fragments were noted in the fired clay used in these settlements (Vince, this vol, 00). To test whether this “Charnwood” fabric was produced locally by adding gravel collected elsewhere or whether the vessels themselves were imported to the area samples were taken for chemical compositional analysis, using Inductively-Coupled Plasma Spectroscopy (ICP-AES).

Methodology

Offcuts were taken from each sample and the outer surfaces of the sherd were mechanically removed, to a depth of c.1.0mm. The remaining block was then crushed to a fine powder and submitted to Royal Holloway College, London, where Inductively-Coupled Plasma Spectroscopy was carried out under the supervision of Dr J N Walsh, Department of Geology.

The frequency of a series of major elements was measured and expressed as percent oxides (App 1) and the frequency of a series of trace elements was measured in parts per million (App 2). The silica content of the samples was not measured but was estimated by subtracting the total measured oxides from 100%. The data were normalised to aluminium and these normalised values are quoted below except where explicitly stated.

Analysis

Post-Burial alteration

As a first step in the analysis a factor analysis was carried out on the dataset, including all measured elements. This analysis found five factors and a plot of the first against the second set of factor scores (Fig 1) indicated that there was one of the samples, Fabric 10, formed an outlier whilst two samples could be distinguished by their negative F2 scores. The remaining samples then formed a single cluster. However, further study revealed that within that cluster the samples from different sites could be distinguished. Those from Site 11 have high F2 scores and positive F1 scores. Those from Site 10 have negative F1 scores. The single sample from Site 13 has a positive F1 score and negative F2 score. Only the Site 12 sample cannot be distinguished, having similar F1 and F2 scores to the Site 11 samples.

These groups cut across the fabric divisions and are either evidence for on-site production of all of the pottery, except for the Fabric 10 sample or, more likely for the contamination of the sherds after burial.

The data were therefore re-examined to determine which elements were responsible for the separation. Only two sites have enough samples for a comparison to be made. The samples from Site 10 contain more estimated silica, aluminium, potassium, titanium and zirconium than those from Site 11. All these elements are likely to have been present in resistant minerals such as quartz, clay minerals and feldspars, rutile and zirconium and in each case the difference in mean values is less than one standard deviation. Several elements are more frequent in the Site 11 than the Site 10 samples but to the same small degree: sodium; chromium; copper; lithium; nickel; scandium; vanadium; zinc and lead. However, the fact that there are more of these elements may indicate that some of these were affected by burial and they do include elements such as lead and zinc which can be mobile, depending on the soil chemistry. Finally, there are elements which are present in greatly enhanced levels on Site 11: iron (18%); magnesium (11%); Calcium (69%); phosphorus (15%); manganese (22%); barium (13%); strontium (50%); ytterbium (25%); lanthanum (14%); cerium (13%); neodymium (15%); samarium (23%); europium (25%); dysprosium (23%); ytterbium (16%); cobalt (15%). These elements probably group into three: those associated with iron; those associated with calcium and those associated with phosphorus. The largest differences are due to calcium-related elements (calcium and strontium, 50-69%); Iron, manganese and cobalt have similar enhancement levels (15-22%); as do the phosphorus-related elements (13-25%). Barium can substitute for strontium and calcium but its lower enhancement level in this case suggests that it is related to phosphorus.

Site 11 is under pasture on the top of a ridge of high ground whereas Site 10 is on lower ground, at the edge of the Wreake floodplain and was under the plough. Site 12 had a similar elevation and setting to Site 11 but was under the plough. The single sample from this site has similar levels of enhancement to those from Site 11, suggesting that the current land use is not responsible for the variations in burial conditions. Site 13 was situated half-way down a west-facing slope overlooking the river Soar. The one sample from this site has different levels of enhancement. The calcium-related elements are enhanced less than those from Site 11. The phosphorus-related elements are more enhanced than those from Site 11 and the iron-related elements are at similar levels to those in the Site 10 samples. Site 11 is also under the plough.

It seems, therefore, that three separate processes affected the samples after burial: enhancement or depletion of iron and associated elements; enhancement or depletion of calcium and associated elements and enhancement or depletion of phosphates.

Since phosphorus is mostly likely to have been present in the form of calcium phosphate a certain about of calcium and related elements were probably associated with the phosphorus but clearly not all. Phosphate-filled laminae were noted in one fabric, Fabric 1 from Site 10 but it is possible that phosphorus was also present in the acid igneous rock temper in the form of apatite. Phosphorus levels in the non-igneous rock-tempered samples are similar across all the sites but the difference in barium and rare earth levels is still seen.

Calcium levels are highest in the shell-filled regional import and in Fabric 9 which contains fossiliferous limestone inclusions. The levels in the remaining samples show no apparent correlation with fabric and do show a correlation with site.

The iron levels show a slight correlation with fabric, being present in higher levels in the non-igneous rock tempered wares, and cobalt levels are enhanced in Fabric 10, probably reflecting a difference in the potting clay. However, taking just the non-igneous samples of local origin there are enhanced levels in the Site 11 samples (or depleted levels in the Site 10 samples). Possibly iron panning is present in pores in the site 11 samples or possibly there has been some leaching of iron from the body (or inclusions) in the Site 10 samples. The site 12 sample has a higher cobalt level than any from Sites 10 or 11, suggesting that the correlation with iron is not the only factor involved in the cobalt enhancement.

The analysis therefore suggests that the differences between analyses of samples from different sites are due to post-burial alterations and are at such a high level in many cases that they mask any possible original differences between the samples. We must therefore omit the majority of measured elements from any attempt to investigate the original questions, of whether or not the igneous rock-tempered sherds were produced from the same clay as the others and whether or not the sites were supplied from different sources.

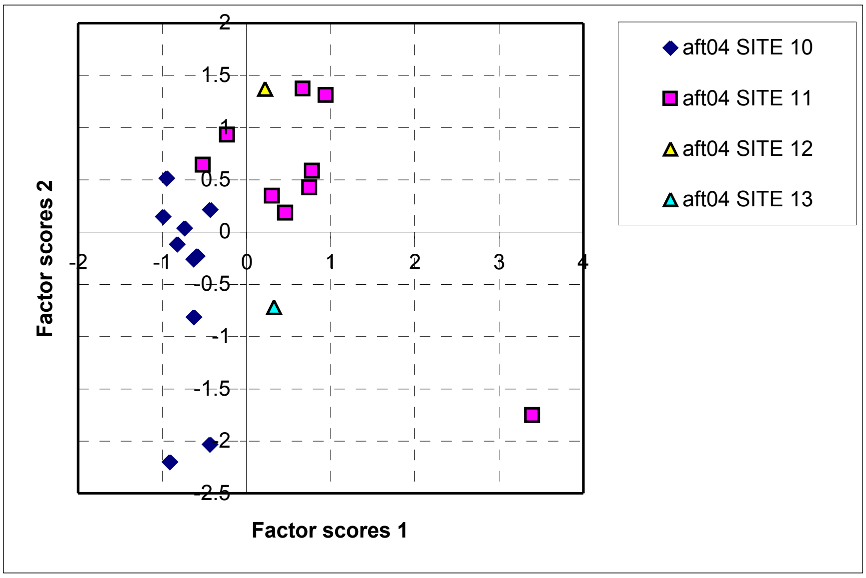

Figure 1

Comparison of igneous-rock-tempered and other fabrics

Using a similar methodology to that employed to study the post-burial alteration of the samples, the mean values for each element were compared for the “local” and “local or Charnwood” groups.

The local samples have higher levels of manganese (10%) and nickel (15%). Nickel is not an element apparently affected by burial whilst manganese is.

The possible Charnwood samples have higher levels of magnesium (13%); sodium (39%); phosphorus (21%); barium (21%) and strontium (26%). The similar level of enhancement of phosphorus, barium and strontium suggests that all entered the samples through the same route but given the evidence for post-burial alterations in phosphorus and related elements this cannot be used to explore the character of the parent clay. The enhanced magnesium rate is due to a single sample, which also has a high sodium level. It is possible that magnesium is present in these samples, at least in part, in the form of ferromagnesian silicate minerals (e.g. pyroxenes and amphiboles, perhaps in this case hornblende or biotite). In either case, both the magnesium and sodium are likely to be present in the igneous rock temper itself and therefore give no clue as to the origin of the clay.

A factor analysis was therefore carried out using those elements with least evidence for post-burial alteration and excluding both magnesium and sodium. This analysis found three factors. Examination of the factor scores shows that there is no correlation of these scores with the find locations nor with the age of the samples.

The two flint-tempered samples have negative F2 scores and positive F1 scores which distinguish them from the remaining samples. The main contributing elements appear to be low potassium and high titanium. Two outliers were distinguished by their F1 or F2 scores, the Fabric 3 sample (Late Bronze Age, igneous rock-tempered), which has a negative F1 score and one of the two Fabric 4 samples (Late Bronze Age, igneous rock and quartzose sand tempered) which has a negative F2 score.

All of the Fabric 2 samples (Early Bronze Age, quartzose sand tempered) and one of the Fabric 7 samples (Iron Age, quartzose sand tempered) have high F3 scores. These scores appear to be due mainly to high zirconium values and to a lesser extend high nickel and titanium scores. These elements are probably present in the sand fraction but the samples of fabric 5, which has a mixture of igneous rock and rounded quartzose sand inclusions, have low F3 scores, as do the other igneous rock-tempered samples (Fabrics 3, 4 and 6). The Fabric 6 samples, which have no rounded quartzose sand, also have the lowest F3 scores.

This analysis therefore confirms that Fabric 1, which is tempered with angular flint, was probably produced from a different clay from the remainder but is ambiguous about the source of the igneous rock tempered samples, since all of the differences in composition between these fabrics and the others can be explained in terms of the added temper rather than the clay itself.

Comparison of Fabric 10 and Other Shell-tempered wares

The ICPS sample of Fabric 10, which contains a mixed shell fauna which suggests the use of middle Jurassic shell marl, was compared with samples of similar shelly wares of Iron Age, Saxon and medieval date from Cambridgeshire and Lincolnshire. A preliminary factor analysis of this data allowed all of the late Saxon and medieval samples to be excluded, leaving samples of Iron Age data from Yorkshire and Cambridgeshire.

All of these samples are from consumer sites and so cannot be used to pinpoint an actual production site. Five factors were found and the first two place the Fabric 10 sample with those from Cambridgeshire rather than those from Yorkshire (Fig 2). This separation is due to a high F1 score, which is due to higher rare earth element values. Omitting the rare earths, which as we have seen can be affected by burial, only three factors were found and the Fabric 10 sample has scores for all three factors which do not allow it to be separated from either group. However, the cobalt and nickel values are outside the range found in the Yorkshire samples (Fig 3).

This analysis therefore favours a Southeast Midlands source for Fabric 10 and shows that it is similar in composition to samples from various sites in northwest Cambridgeshire (Great Gidding, Hamerton and Stow Longa).

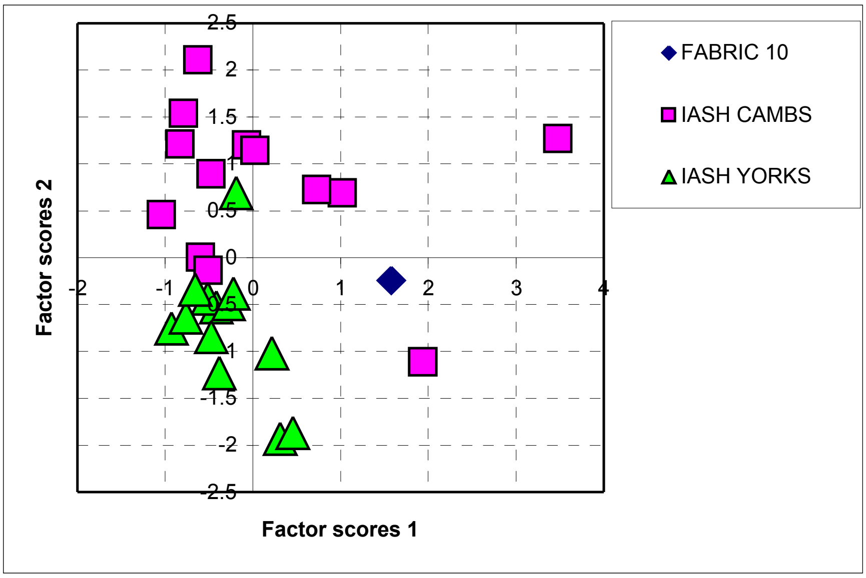

Figure 2

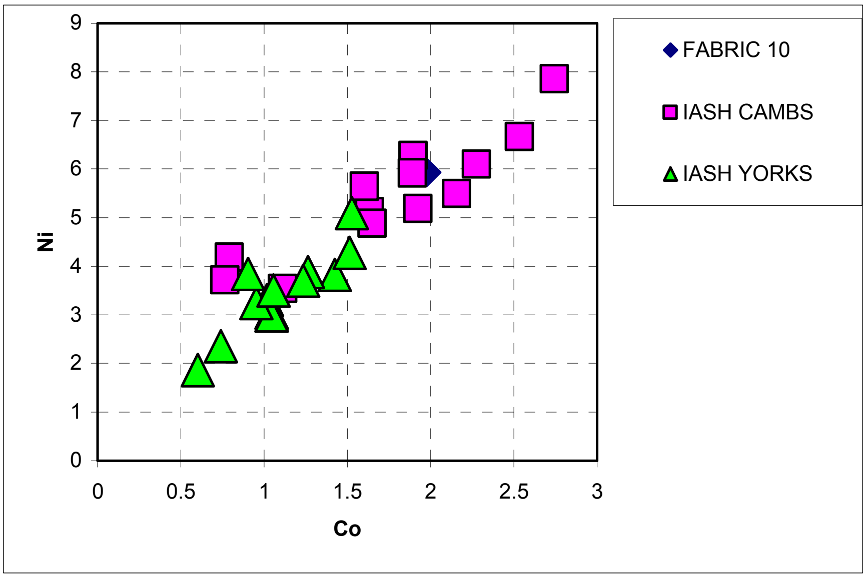

Figure 3

Conclusions

Chemical analysis of samples of Early Bronze Age, Middle Bronze Age, Late Bronze Age and Iron Age pottery from sites near Ratcliffe on the Wreake, Leicestershire, is consistent with the results of thin section analysis.

In the Early Bronze Age, two groups of pottery can be distinguished, the first is tempered with angular flint and the second with a rounded quartz sand. Chemical differences between the groups suggest that they come from different sources and the flint temper, which is absent from all the other samples, indicates that this group is non-local, although the thin section analysis does suggest that both groups were made using boulder clay.

The Middle Bronze Age is represented by a single sample of Fabric 3, which contains angular igneous rock fragments, and is a very similar fabric to Fabric 6, which is Iron Age. The two fabrics come from different sites which have been affected by burial in different ways. However, even when only non-mobile elements were considered, the ICPS data separate the fabrics.

The Late Bronze Age is represented by two samples of Fabric 4, both from Site 10. This fabric is tempered with angular igneous rock and rarer sandstone and the ICPS data places these samples with other igneous rock-tempered fabrics (3, 5 and 6).

The Iron Age is represented by a series of fabrics which contain rounded quartz sand (Fabric 7), sometimes with other inclusion types, such as fossiliferous limestone (Fabric 9) or clay pellets (Fabric 8), as well as by fabrics with igneous rock inclusions, with and without rounded quartz sand (Fabrics 5 and 6 respectively). There is no clear-cut separation in the ICPS data between samples with igneous rock inclusions and those without and there are chemical differences between Fabrics 5 and 6. These, however, probably reflect the chemical composition of the igneous rock (higher in sodium) and the presence of inclusions within the quartzose sand which are rich in potassium, titanium, phosphorus, chromium, cobalt and lead. Since these samples mostly come from the same site, Site 11, the presence of enhanced phosphorus and rare earth elements in the sandy samples (including Fabric 5) may reflect the original composition rather than post-burial alteration.

Finally, a single sample of a shell-filled fabric, identified in thin section as being probably of Middle Jurassic origin, was matched with samples of Iron Age shelly ware from consumer sites in northwest Cambridgeshire and shown to be distinguishable from visually and petrologically similar Iron Age shell-tempered wares from sites in Yorkshire which were probably made from clays of similar age.

Bibliography

Vince, Alan (2007) Petrological Analysis of Prehistoric Pottery from Ratcliffe on the Wreake, Leicestershire. AVAC Reports 2007/63 Lincoln,

Appendix 1 ICPS Data for Major Elements (Percent Oxides)

TSNO	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O	TiO2	P2O5	MnO
V4231	14.25	7.79	0.54	0.81	0.21	1.49	0.62	1.53	0.053
V4232	16.6	8.11	0.49	0.83	0.23	1.68	0.72	1.26	0.063
V4233	17.07	9.73	1.23	1.09	0.1	2.11	0.75	0.88	0.165
V4234	17.49	8.87	1.54	1.03	0.28	2.72	0.72	0.52	0.286
V4235	17.84	9.35	1.57	0.94	0.27	2.76	0.73	0.93	0.142
V4236	16.94	7.69	1.52	1.06	0.27	2.56	0.67	0.24	0.202
V4237	14.05	6.57	1.25	1.12	0.27	2.29	0.63	0.58	0.11
V4238	15.43	5.84	2.78	1.23	1.18	3.11	0.59	0.73	0.105
V4239	15.86	7.28	1.4	1.17	0.88	1.96	0.62	1.55	0.036
V4240	17.41	5.56	0.95	0.87	0.38	2.24	0.74	1.4	0.019
V4241	14.35	10.55	1.32	1.95	0.38	1.72	0.53	1.25	0.222
V4242	12.6	10.05	2.09	2.26	0.48	1.89	0.46	1.37	0.133
V4243	15.14	6.37	1.52	1.44	0.62	2.24	0.55	2.33	0.117
V4244	16.83	11.64	1.65	2.92	0.85	1.97	0.59	1.41	0.237
V4245	18.55	11.18	1.72	2.56	0.82	1.99	0.63	1.29	0.207
V4246	10.94	7.75	0.93	1.64	0.33	1.67	0.42	1.14	0.061
V4247	12.49	8.27	1.32	1.37	0.35	1.51	0.47	0.82	0.107
V4248	14.59	10.12	1.67	1.12	0.34	1.95	0.58	0.59	0.387
V4249	15.24	11.21	1.58	1.5	0.47	1.69	0.59	1.3	0.269
V4250	14.2	8.58	1.61	4.79	0.26	1.8	0.56	0.72	0.124
V4251	12.14	7.34	1.03	20.94	0.13	1.28	0.49	0.91	0.103

Appendix 2 ICPS Data for trace elements (parts per million)

TSNO	Ba	Cr	Cu	Li	Ni	Sc	Sr	V	Y	Zr*	La	Ce	Nd	Sm	Eu	Dy	Yb	Pb	Zn	Co
V4231	475	106	29	58	61	14	49	135	24	68	37	70	39	8	1	4	2	25	94	13
V4232	451	114	30	58	65	15	50	149	27	83	40	79	42	8	2	5	3	25	93	15
V4233	802	111	38	43	122	16	52	136	26	119	31	69	34	8	1	5	3	23	116	18
V4234	630	119	48	109	87	17	78	154	26	107	38	82	40	8	1	5	3	22	164	24
V4235	722	125	46	108	102	17	80	145	25	101	39	78	41	8	1	4	3	18	163	21
V4236	497	114	37	98	77	17	81	148	26	105	40	97	42	8	1	5	3	17	114	20
V4237	637	96	31	104	87	13	58	110	22	77	31	62	33	6	1	4	2	20	107	16
V4238	658	76	27	94	62	13	119	90	22	72	28	58	30	6	1	4	2	13	167	15
V4239	735	97	35	76	52	16	116	142	31	78	34	65	37	8	2	5	3	21	135	11
V4240	732	106	22	108	39	15	138	106	24	86	44	94	45	8	2	4	2	20	111	11
V4241	738	101	34	75	71	16	227	143	39	63	45	89	49	11	2	7	3	25	142	19
V4242	954	86	27	78	44	14	210	120	33	69	40	81	43	10	2	5	3	18	139	15
V4243	2,163	96	27	76	60	15	157	120	30	75	45	96	47	8	2	5	3	23	83	19
V4244	787	104	34	104	79	17	283	165	37	76	40	76	43	9	2	6	3	21	111	19
V4245	1,032	117	37	101	75	19	219	153	35	77	43	85	46	9	2	6	3	17	111	20
V4246	565	78	23	45	50	11	175	106	24	41	32	66	34	7	1	4	2	20	101	15
V4247	567	87	34	139	71	13	149	113	34	73	38	79	41	9	2	6	3	22	118	16

V4248	663	103	33	85	64	16	85	140	34	77	42	95	46	10	2	7	3	21	156	24
V4249	719	110	38	99	108	17	194	132	42	72	50	107	54	12	2	7	3	26	146	28
V4250	653	92	38	98	60	15	143	130	32	71	41	83	44	10	2	5	3	23	140	16
V4251	452	76	27	63	72	12	301	81	50	81	42	91	47	14	3	8	3	17	78	24