Ancient Monuments Laboratory Report 3/96

TECHNICAL ANALYSIS OF THE RIPON JEWEL

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Summary

Non-destructive analysis of the gold-silver-copper alloys used to make this seventh-century artefact was carried out using energy-dispersive X-ray analysis in a scanning electron microscope. Three levels of gold purity were identified, with the most silver-rich alloy being used at the back of the artefact. The foils and an area of possible cement or filler material were also examined by this method. The existence of some silver-rich foils were confirmed, but these may have been mercury-gilt originally. The identity of the cement or filler remains unknown. The garnets were investigated using a refractometer, absorption spectroscopy and non-destructive X-ray fluorescence analysis. The resulting data are compared with the results of similar work on contemporary artefacts, with some discussion about the origins of the materials.

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Technical analysis of the Ripon Jewel

Catherine Mortimer

The compositions of some of the components of the Ripon Jewel were determined, at the request of the York Archaeological Trust. The Ripon Jewel is a gold roundel decorated with a gold cloisonné design which has red gemstones, amber and ?decayed glass settings (shown approximately life-size in Figure 1). The inner circumference of the artefact has a twisted beaded wire design. Stylistically, it is likely to be a seventh-century Anglo-Saxon artefact. Although it was found during the 1977 excavations in the gardens of the Old Deanery, 50m north-east of Ripon Cathedral, it has its closest parallels in the south-east of England.

It is of interest to determine how many different alloys were used to make the artefact, and whether particular alloys were used for certain components. The compositions used in this artefact can be compared with those used in seventh-century artefacts from other locations (*eg* Hawkes et al 1966), to see if any regional patterning is discernable; gold artefacts are rare in the north of England at this time, and this artefact may have been imported from the south or south-east of England. Furthermore, it is thought that gold coins may have been the source of the alloys used in gold artefacts made in England at this time. There was no English coinage at the time, so the alloys used in this artefact should be compared with those used in contemporary coinage in France (*eg* Kent 1972).

The settings can also be studied analytically. The compositions of the decorative foils which underlie the garnets were investigated, as some of the foils were noted to be more silvery than golden. The ?glass inlay and an area of possible cement of filler which underlies one of the amber inlays were examined. A gemmological study of the 'garnets' (some of which may not be garnets but other red stones) was carried out to investigate the reasons for the different colours observed by the conservator, ranging from red to purple.

Methods

Non-destructive analysis of the metal components was required, so energy-dispersive X-ray (EDX) analysis was carried out in a scanning electron microscope (SEM). The Jewel was prepared for analysis by placing it in a specially tailored conductive mount, made with Plastazote foam covered with aluminium tape (Figure 2). This was attached to the sample table with further aluminium tape and silver dag. The electron beam should not rest for long on the amber as unacceptable heating and therefore burning of the surface may result, so narrower strips of aluminium were placed over the amber inlays; these strips also served as locating points, allowing navigation between different areas of the Jewel without resting on the garnets too long, since these too may be sensitive to heating. The SEM allows selection and analysis of very small areas of the artefact; for instance, at magnifications of around 1000x, discrete areas of about 100 μ x100 μ could be selected (NB there are 1000 microns (μ) in a millimetre).

Cell walls and beading. Many of the cell walls and some of the beads of the filigree design were found to be heavily abraded and flattened on their top surfaces. It is not clear whether some of this occurred in antiquity (eg during manufacture or over-zealous cleaning during use) or whether it is all due to burial and post-deposition effects. Gold alloys are often so soft that abrasion can occur very easily, but conservation techniques on this sort of material use the softest possible tools. If this flattening is recent, it may have had the useful effect of removing the top surface from areas which might otherwise have been depleted in silver and copper (therefore apparently enriched in gold), due to corrosion during burial.

These flattened areas are in any case better for analysis, as they approximate more closely to the ideal areas for quantitative EDX analysis, that is, solid, flat, polished surfaces, parallel to the surface of the sample table. However, the results of quantitative analyses even on flattened areas rarely totalled more than 95%, and were often less than 90%, suggesting that the areas used were not perfect for this method. Small peaks from iron, silica and calcium were also noted in most EDX spectra, suggesting the presence of corrosion products or soil on the surface; these were usually calculated to be of the order of 0.1% or 0.2%, in quantitative analyses. Further preparation of the surface was not allowed so the results of analyses (including Au, Ag, Cu, Fe, Si and Ca) were normalised to 100%. The non-normalised analytical totals are also noted, because this allows an assessment to be made of the accuracy of the analyses. Analyses with analytical totals of less than 75% were not used. The percentages were initially calculated to one decimal place, but this may give rather too flattering an impression of the accuracy and precision attained using the methods described above and figures to the nearest 0.5% were thought to be more appropriate.

Decorative foils. Three of the garnets were removed, using acetone to soften the adhesive (HMG-cellulose nitrate) which had been used to keep them in position. This exposed the foils at the bottom of the cells, although traces of HMG were noticeable at the edges of the foils. The geometry of the artefact and of the equipment meant that it was difficult to focus the beam on the foils in these positions. Tilting the artefact towards the X-ray detector and masking off the neighbouring cell walls using aluminium or carbon tape showed some improvement, reflected in a slightly larger number of X-rays reaching the detector, but many of these were aluminium or carbon X-rays.

In a small number of cases, the edge of a foil could be seen between the garnet and the cell wall, sometimes extending up to the level of the top of the cell wall or of the garnet. In these cases, the surrounding cell walls and garnets were masked off, leaving only the foil exposed. This masking was achieved by placing a double-sided adhesive carbon tab so that a hole pierced through it was directly above the area to be analysed. Again, the top surfaces of some of these foils had been abraded and flattened, presenting rather more suitable areas for quantitative EDX analysis. However, SEM examination at high magnifications showed that the foils were often porous, due to corrosion.

Neither of these methods of masking are perfect, and only small gold, silver and copper peaks were recovered during EDX analysis of the foil. The analytical totals achieved were correspondingly very low (rarely over 20%), and it is sensible only to suggest whether the foils were gold-rich or silver-rich, rather than give normalised results from these analyses.

Possible inlays and deposits. The nature of the four inner inlays is not known and these are now

very corroded. Previously X-ray fluorescence (XRF) on this area had shown that sodium, potassium and iron were present and it was suggested that this inlay had been a soda glass which had decayed. Further qualitative EDX analysis was carried out in the SEM on one of the ?glass areas. X-ray diffraction (XRD) analysis was performed on a small sample taken from one of the ?glass inlays using a diffractometer with cobalt radiation and a silicon detector; the sample was powdered with an agate mortar and pestle and mounted on a specimen holder consisting of a flat single crystal of silicon to reduce background scatter. EDX analysis was carried out in the SEM on the SEM on the same piece, to confirm the identifications made using XRD.

A powdery material was visible on top of the gold foil under amber 4 and this was qualitatively analysed by EDX in the SEM.

Garnets. The three red stones which were released from their setting in attempts to analyse the underlying foils were examined with transmitted and polarised light to look for anisotropy (different refractive indices at different orientations) and for inclusions. Subsequently, a further nine stones were released from their settings and the twelve stones then available were then submitted to a range of standard gemmological tests. The colour was noted, refractive indices were calculated using a refractometer, strong lines were noted in absorption spectra using a hand spectroscope and, for five examples, detailed absorption spectra were recorded in the 750 to 300nm wavelength range, using a UV spectrometer. Non-destructive XRF was carried out under vacuum on six stones and the major peaks present were noted. Density or specific gravity measurements which could also have been useful, were not possible, as the stones were too small. Suitable equipment for X-ray diffraction of the stones was not available.

Results

Cell walls. Quantitative EDX analysis was carried out on 23 areas of the gold cloisonné framework and the beaded wires. Six areas on the back of the artefact were also analysed. The results (Table 1) were compared with results of EDX analyses on seven gold-silver and gold-copper standards, carried out under the same analytical conditions, which gave good agreement with the stated compositions.

The alloy compositions recovered by this analysis are comparable with compositions recorded from other artefacts of this period (eg Hawkes et al 1966). Silver values range from c. 9.5% to c. 24.5% and copper values range from c. 1.0% to 2.5%. The remainder was gold, with the traces of iron, silica and calcium detected attributable to corrosion products and soil (see above).

The analytical method used is likely to produce rather inaccurate and imprecise values, but there does seem to be some clustering within the compositional dataset, when the silver values are considered. The beaded wire and three areas of the cloisonné and filigree design were shown to be rather lower in silver (9.5-11.5%) than other areas on the front of the artefact (14%-19.5%). The back plate has the highest silver content (24.5%) of any of the areas analysed. Thus it could be suggested that at least three different ranges of gold alloy compositions were used to make this artefact. The next logical step would be to suggest that three batches of gold sheet were used, but the quality of the data is not adequate to support this.

Foils. As indicated above, it was not possible to get accurate results from the foils in situ, but

EDX analysis of masked areas did confirm that the foil under garnet 1e was silver-rich and those under garnets 2c and under amber 4 were gold-rich. The foil under garnet 4e seems to have a silver:gold ratio of c. 1:1. On close inspection, the spectra from the foils under amber 4 and garnet 4e appear to have very small mercury peaks present.

These analyses confirm the observations made during conservation studies that some of the foils appear to be relatively silver-rich, but suggest further that some of these silver-rich foils may originally have been mercury-gilded. Where a foil is gold-rich but has a detectable mercury peak, it is possible that it is a mercury-gilded silver-rich foil, but that the gold layer is sufficiently thick and intact to shield the silver content from detection. However, these are all surface analyses on material which is likely to be deeply corroded, to judge from the heavy pitting visible at high magnifications. Further sampling would be necessary to confirm this.

Possible inlays and deposits. XRD analysis of a sample from the possible glass inlay indicated that the sample was not very crystalline; most glass is amorphous (not crystalline). The small peaks that were visible in the XRD spectrum fitted the standard patterns for silver metal and silver chloride (Figure 3). Silver and chlorine were also prominent in the bulk EDX analysis of the sample, but some spot EDX analyses carried out also showed silica, aluminium, phosphorous, calcium, manganese and iron (Figure 4), which suggest the presence of a silicate, one which must be non-crystalline (because it was not detected in the XRD analyses). The silver and chlorine are present as contaminants; silver chloride is a common silver corrosion product.

The results of analysis do not allow an unequivocal identification, but the inlay could have been a glass. On the basis of the XRD and EDX analyses, the sample is unlikely to be any of the white substances used as inlays in Anglo-Saxon jewellery which have been identified analytically, *eg* shell, bone, ivory, magnesite or cristobalite (La Niece 1987).

The EDX analysis of the suggested cement or filler material on top of the gold foil under amber 4 showed that the area was rich in silver, presumably in the form of silver salts, which had been leached from nearby cell walls and foils. It is possible that analysis of the organic components present would indicate whether the silver salts are found in combination with backing materials, such as beeswax, which might have been used in manufacture (Shearman 1993), but this would require sampling.

Garnets. There are several types of garnet, defined by their chemical compositions. Garnets are silicates combined with various sorts of metal ions, notably aluminium, iron, manganese, magnesium and calcium. The different types of garnet are defined by their divalent ions, thus almandine is the most iron-rich form, $Fe_3Al_2(SiO_4)_3$, and pyrope, $Mg_3Al_2(SiO_4)_3$, is magnesium-rich. Chromium may also be present as a colourant in pyropes. Grossular garnets (calcium-rich) and spessartite garnets (manganese-rich) are also known. However, these are theoretical compositions and in nature garnets are very rarely composed of only one variant. Stones with compositions which can be interpreted as mixtures of almandine and pyrope are commonly used in archaeological artefacts, but other gemstone types are also encountered.

Through several types of analysis (Table 2), all the available stones were shown to be garnets, of three different types.

The colours observed in natural light were described (by Steve Kennedy, Gem Testing Laboratory) as orange, red and mauve. These broadly agree with the colours observed by Erica Paterson in her conservation notes on the stones when they were in situ, orange and red stones

being described by her as 'red', and mauve stones as 'purple', with one exception, 4e, which was described as orange by Steve Kennedy but as '?purple' by Erica Paterson. When placed in its setting, the colouration of the underlying foil may cause some confusion about the true colour of a stone. Such colour descriptions of course can only be subjective, but garnets (almandine, pyrope, spessartite and grossular), spinel and ruby are often found with these sorts of colours.

Measurement of the refractive index showed a range of values, from 1.746 to above 1.81 (the maximum reading on the refractometer); this means that the stones cannot be spinel (which has values of 1.712-1.736) but they could possibly be grossular garnet, *eg* hessonite (1.738-1.745), spessartite garnet (1.795-1.815) or ruby (1.766-1.774). Almandine and pyrope garnets have values of 1.75 to above 1.81 and 1.73-1.75 respectively, with the division between the two types of garnet being set at 1.75 rather arbitrarily, in view of the known compositional continuum between them (Rouse 1986, 39).

Absorption spectroscopy showed strong lines at 505, 525 and 575nm in the six mauve/purple stones and a broad absorption band between 520 and 620nm for the orange/red stones. These are characteristic of almandine and pyrope respectively, the former being the lines for iron and the latter for chrome. Iron must also be present in the pyropes, but its peak is swamped by the chromium signal; there is however a suggestion of a peak at around 505nm in the absorption spectrum for one of the pyrope garnets (3b). A reference spectrum for hessonite was run, and shown to be quite different to the spectra from the orange/red (pyrope) stones. The spectra found in spessartite garnets have strong lines at 432, 424 and 412nm, relating to the manganese content of this type of garnet, but these lines can be difficult to see as they are at the violet end of the visible light spectrum. The presence of manganese in the mauve/purple stones tested by XRF may suggest the presence of a small amount of spessartite.

XRF showed silicon and iron in all six stones analysed, but there were much higher levels of chrome in the three orange stones tested than in the three mauve stones tested; chrome-rich pyrope garnets are well-known and the chrome gives these stones their orange or brownish colouration. Peaks for aluminium and magnesium were not recorded during XRF analysis, as the relevant X-ray peaks (K α) are at too low an energy (1.487kV and 1.254kV respectively) to be detected accurately, even under vacuum.

It was noted that the mauve/purple stones also tend to have more inclusions in them. Some of these are needle-like and these are probably in the form of rutile crystals, which are common in almandines but rare amongst pyropes. The patchy anisotropy which was observed in some of the orange/red stones is probably due to strain, and does not indicate that they are not garnets at all (*ie* ruby).

Hence all of the stones belong to the pyrope/almandine series, with six of them being more pyrope-like than almandine-like. The slightly different colouration observed within the group of pyrope stones examined may relate to the presence of different proportions of chrome.

Discussion

This analysis of the Ripon Jewel allows it to be placed in a wider context. It is widely thought that gold artefacts of the sixth and seventh centuries were made by melting down gold coinage, particularly Merovingian, but also Byzantine. As some of the coins are dateable to the reigns of particular kings, the relationship between the composition, usually discussed as the gold fineness, and the date of the coins has been examined (Kent 1972). Three different series of Merovingian

coins were investigated, showing that there were three different standards of purity, the highest being the 'high Provençal' and the lowest being those from outside Provence, but with a general trend downwards in each case - from consistently above 85% gold in the last two decades of the sixth century to well below 50% gold in the second half of the seventh century. On the basis of the coins found at Sutton Hoo and Crondall, it has been suggested that many more coins from outside Provence were available than other types, so that the 'extra-Provençal' standard is the most appropriate in assessing the likely date of artefacts of this period. It is however highly likely that small numbers of earlier coins or small numbers of Provençal coins would have been included in the melt, which would lead to the suggestion of a misleadingly early date for manufacture being estimated on the basis of artefacts by their composition can only be an estimate and one which quite often gives what seems to be too early a date.

With this in mind, the values for the Ripon Jewel can be considered. Most of the parts analysed had gold contents in the 80-90% range. Even allowing for a few percent surface enrichment and any inaccuracy due to surface preparation, this would imply a date before 625 - in fact, if the extra-Provençal standard is used, the date would have to be before 610. The back of the artefact was shown to have a lower gold content (72%). This might be taken to suggest a manufacture of the whole artefact could not have taken place before coinage with this purity was used, *ie* after 610 if the extra-Provençal standards are used or after 640 if the other standards were used. If the jeweller had available sheets of gold of various purities, low purity gold sheet may have been selected for the back of an artefact, if it (and its more silvery colour) would not be visible.

There are relatively few gold artefacts from this period outside the south, especially the south-east of England. It is therefore difficult to make any statement about regional patterning in compositions. More detailed analyses, including trace element data, might show some regional patterning, but this would require sampling of a large number of objects and gold artefacts tend to be more carefully curated than some others.

The nature of the ?glass inlay is still unclear. Arrhenius notes that glasses were amongst the other inlays sometimes found on garnet cloisonné artefacts (Arrhenius 1985,36-38), but with the results achieved here one cannot, in this case, say more than glass may well have been used. The lack of lead in the EDX analysis may be significant, if it reflects the original composition. Enamels would normally contain substantial amounts of lead, so the suggested glass inlays must instead have been made from a soda-lime-silica glass, probably small flat pieces chipped into shape. However, it is not clear why soda-lime-silica glass should have decayed so thoroughly, as it is usually well-preserved in most types of burial context. More analytical work could perhaps be carried out on this subject, if further sampling were possible.

Further sampling might throw light on the subject of organic-rich fillers around or under the foils, garnets and amber, but the post-excavation experience of this artefact allowed plenty of scope for modern contamination so sampling strategies would have to be very carefully considered. On the foils themselves, further analysis, using destructive sampling methods such as slicing tiny amounts from their edges, is less likely to give useful results because of the evidence for deep corrosion. Non-gold foils have been noted elsewhere, normally mercury-gilt originally, even if this gilding is not now clearly visible.

Garnets used in Anglo-Saxon jewellery are likely to have been chosen for their ability to be cleaved, as were garnets in Merovingian jewellery (Arrhenius 1985, 31). This is not a typical

feature of garnets available commercially nowadays, which means that it is not appropriate to try to associate the garnets found in ancient jewellery directly with garnet sources in use today. Instead the appropriate type of geological formations (ones in which rock-forming processes were carried out at great heat and pressure) should be sought. Arrhenius grouped Scandinavian and central European garnets by their X-ray diffraction values (*op cit*, 27-29). On the basis of this, she suggested garnet sources in Bohemia were probably used for much Western European garnet jewellery of this period, although Austria and even the Black Sea area were also cited as possible sources for some of the garnets (*op cit*, 34-36). Garnets from Bohemia include almandine and pyrope/almandine of various colours, so the Ripon Jewel garnets could well be from these sources.

References

Arrhenius B 1985 Merovingian garnet jewellery, emergence and social implications (Stockholm)

Brown P D C and Schweizer F 1973 'X-ray Fluorescent Analysis of Anglo Saxon Jewellery' Archaeometry 15(2); 175-192.

Hawkes S C, J M Merrill and D M Metcalf 1966 'X-ray Fluorescent Analysis of some Dark Age Coins and Jewellery' *Archaeometry* 9; 98-138.

La Niece S 1988 'White inlays in Anglo Saxon Jewellery' in Slater E A and Tate J O (eds) *Science* and Archaeology, Glasgow 1987 (Proceedings of a conference on the application of scientific techniques to archaeology Glasgow, September 1987), British Archaeological Reports British Series 196(i); 235-246

Kent J P C 1972 'Gold standards of the Merovingian coinage AD 580-700' in Hall E T and Metcalf M (eds) *Methods of chemical and metallurgical investigation of ancient coinage* Royal Numismatic Society, London; 69-74.

La Niece S 1988 **

Rouse J D 1986 *Garnet* (Butterworth's Gem Books)

Shearman F 1993 'Excavation, examination and conservation of Anglo-Saxon jewellery from Bosshall Ipswich' in *The Conservator* 17; 26-33.

		Normalised values*					Average non-	
Area		Au%	Ag%	Cu%	Others	No. of analyses	analytical total	
cell walls	Cloison border, inside	78.0	19.0	1.5	Fe	2	78.0	
	Cloison border, outside	82.5	15.0	2.0		2	87.7	
	Cloison, zig-zag (2b)	87.0	11.0	1.5		2	93.5	
	Cloison, zig-zag (4e/f)	80.5	17.0	1.5	Fe	2	89.5	
	Framing amber 3	89.5	9.5	1.0		2	88.6	
	Framing amber 4	77.5	19.5	2.0	Fe	2	92.4	
	Border, inside filigree section 1	84.5	14.0	1.5		3	94.0	
	Border, inside filigree section 4	87.0	11.0	2.0		2	89.9	
beaded wire		84.5	11.5	2.5	Fe	6	98.5	
back plate		72.0	24.5	2.0	Fe	6	85.5	

Table 1	EDX anal	vses of	gold a	allovs o	n the	Ripon	Jewel
		,	Dv -w •				

*Au, Ag and Cu are given to nearest 0.5%, other elements are noted as present where calculated to be more than 0.1%.

Au = gold, Ag = silver, Cu = copper, Fe = iron

Garnet no.	Colour	Refractive index	Inclusions	Hand spectro- scope ID	UV curve	EDX*	Final ID
1b	Orange	1.75	none	not clear	na	Cr Fe	orange pyrope
3c	Orange	1.75	none	not clear	na	Cr Fe	orange pyrope
3f	Orange	1.748	crystals	not clear	na	na	orange pyrope
3g	Orange	1.746	none	not clear	pyrope	Cr Fe	orange pyrope
4	Orange	1.75	none	not clear	pyrope	na	orange pyrope
3b	Red	1.75	crystals	ругоре?	ругоре	na	red pyrope
3a	Mauve	1.793	needles	almandine	na	na	pyrope/almandine
4a	Mauve	>1.81	needles	almandine	na	Fe Mn	pyrope/almandine
4c	Mauve	1.792	needles	almandine	almandine	Fe Mn	pyrope/almandine
4f	Mauve	>1.81	needles	almandine	almandine	na	pyrope/almandine
4g	Mauve	1.783	crystals	almandine	almandine	Fe Mn	pyrope/almandine
4d	Mauve	>1.81	needles	almandine	na	na	pyrope/almandine

Table 2: Identification of garnets

* Major peaks only noted.

na = not analysed, Cr = chrome, Fe = iron, Mn = manganese

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Figure 1: Schematic diagram of Ripon Jewel. The amber inlays are numbered 1-4, from top clockwise; the garnet inlays are numbered 1a, 1b, 1c etc. from top right quadrant (top of), clockwise.



Figure 2: Method of preparing the Jewel for SEM and EDX analysis; cross-section



Fig 3: X-ray diffraction pattern of deposit from Ripon jewel

The standard pattern in red, (4-783) is silver (metal) and displacement of our pattern relative to it would suggest the sample is impure and has other material dissolved in it. The green pattern (31-1238) is silver chloride, AgCl, chlorargyrite. However it is not a very good fit but elemental analysis is in agreement.



Figure 4: SEM-EDX analysis of ?glass sample from inner inlay of Ripon Jewel, showing carbon (C), oxygen (O), aluminium (Al), silicon (Si), phosphorous (P), sulphur (S), chlorine (Cl), silver (Ag), calcium (Ca), manganese (Mn) and iron (Fe) peaks.