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Archaeometallurgical residues from Molana Abbey, Co. Waterford (E001067)

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Abstract

Archaeological investigations at Molana Abbey produced two small blebs of decayed copper alloy, probably spills of casting metal fallen into the hearth, from a 'sooty' deposit on the floor of the cloister. This had been tentatively interpreted as representing scavenging of monastic fittings on disuse of the cloister at the dissolution.

Tentative analytical results from pXRF analysis suggest that the spills had been of a high-tin leaded bronze. Such a metal would have been employed in late medieval and early post-medieval periods mainly for the production of larger castings. The high tin content reported by the analyses of one of the blebs would be broadly compatible with medieval bell-metal, but it is uncertain to what degree this analysis reflects the original metal.

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Methods

The material described here derives from excavations at Molana Abbey, Co. Waterford, conducted by Eamonn Cotter.

All materials were examined visually with a low-powered binocular microscope and subsequently analysed using a handheld portable X-Ray Fluorescence instrument. Analysis employed a Bruker Tracer III-SD portable X-Ray fluorescence spectrometer (instrument belonging to the Department of Archaeology, Cardiff University, and the National Museum Wales). The instrument was operated with the Bruker 'yellow' filter (300µm Al + 25µm Ti), at 40kV and 9.60 µA, with a filament current of 189 µA, for 60s. The instrument was controlled by a PC running Bruker's *S1PXRF* software.

A very crude semi-quantitative calibration of the data was performed using a technique (Young 2015) employing a simple linear regression of data presented by Nicholas & Manti (2014) who analysed copper alloy standards using the same instrument and with the same operating conditions as for the present work. This calibration would not be expected to be fully valid for analysis of an irregular surface of weathering products, rather than smooth metal, hence it is not a fully quantitative approach. The calibration process uses the linear regression factor as a multiplier for the net peak area as report by Bruker's *Artax* software for the spectra exported from *S1PXRF* (Table 1).

Results

Description of residues

The two items have the visual properties of casting waste, probably small spills dropped into an ashy floor (quite likely the bottom of the hearth being used for melting the metals). They are not indicative of a precise process.

Two separate blebs of copper alloy decay products, each probably mixed with host sediment and ash, were investigated by hand-held portable XRF. Because of the nature of the material, a comprehensive quantitative analysis was not possible.

The two particles have essentially the same elemental composition, but in slightly different proportions (Figure 1). The analysis 'Molana A' shows much larger peak for copper, and correspondingly lower peaks for iron, zinc, lead and tin, than analysis 'Molana B'. For both samples the peaks for lead and tin are much larger than those for zinc. Indeed, the zinc content may be rather low. Neither spectrum shows peaks for arsenic or antimony.

The two analyses have been calibrated (Table 1) using an approximate calibration process intended for use on copper alloy metal, so which would not be expected to be capable of a good calibration of the present material, but this suggests that the main alloying elements are present in the two blebs in approximately the same proportions relative to each other – namely 1 part zinc to 9 parts tin to 4-5 parts lead. These alloying elements may comprise between 7% (Molana 'A') and 18% (Molana 'B') of the corroded metal. Taken together, these highly approximate numbers show that the metal in the spills was a quaternary alloy of copper and the relatively low zinc concentration suggests that the original metal was a leaded bronze. The zinc content appears too low for the term leaded gunmetal to be applicable, but zinc may be preferentially lost from such spills (both before and after cooling). Nonetheless the zinc content is sufficiently high to indicate that it was a component of the alloying system.

Distribution of residues

The material derives from a 'sooty' context, C21, lying on the floor of the cloister and below a layer of fallen roof tiles. It was suggested (Cotter 2015) that it might represent the result of scavenging of the Abbey fittings after the dissolution.

Interpretation

The composition of the original metal cannot be determined with certainty from the surviving materials.

Because of the irregular nature of the material only a very approximate analysis can be obtained by pXRF, and the calibration applied to the analysis here is only capable of a crude approximation to the actual composition. In addition to the poor quality of the analysis, there is uncertainty as to whether there have been any changes to the elemental composition of the spill during weathering (by preferential leaching, for instance). The composition of corroded casting spills is also unlikely to be completely representative of the original bulk metal being cast. Thus, at several levels, the analysis presented here is likely to be poor approximation to the original metal composition. Nonetheless, the similar ratio of the alloying elements generated for the two analyses, suggests that there may be some validity to the results and that some comment can be made. The data suggest that the original metal was a leaded bronze, probably with a relatively high tin content.

In the high medieval to early post-medieval periods leaded bronze as used for a variety of purposes, most

commonly as a casting metal for larger objects according to Blades (1995), and to a much lesser extent in sheet metals and wire. It was not the main casting metal for smaller castings (dress accessories for instance), nor for use in wrought materials. The blebs lack the arsenic and antimony commonly encountered in castings for large pieces of tableware (ewers, jugs etc.; Dungworth & Nicholas 2004). The composition reported for the bleb with the higher levels of alloying elements ('Molana B') is not far from that of some medieval bells (Audy &Audy 2008 cite pre-17th century bells having tin contents below 12%), but bells would typically be made from metal with a lower lead and slightly higher tin content than suggested by the present analyses. In the lack of any certainty over how the measured estimate of composition of these weathered blebs might compare to the actual composition of the original metal, however, it important to avoid over interpreting these results.

Discussion

The analyses must be taken solely as being broadly indicative of the nature of the original metal. Nonetheless a relatively high-tin leaded bronze is suggested. Such a metal would be most likely to be from, or for a larger casting (it is not possible to determine from these materials whether an object was being created afresh, or whether the activity was simply recycling). It is not inconceivable that the source (or purpose) of the metal might have been a bell, if the more tin-rich of the compositional estimates is close to that of the original metal. It is possible that the context, as originally suggested by Cotter, represents recycling of monastic fittings at the dissolution, but the level of precision offered by the analyses precludes such a firm conclusion. However, had the activity been the casting of small domestic or dress items, then it would have been much more likely that the metal employed would have been zinc-rich.

Further work

Although it is possible that the blebs contain fresh metal hat might yield further information upon analysis, the degree of alteration on the outside of the blebs suggests that this is unlikely. Accordingly, no further analysis of the blebs is recommended.

The blebs should ideally be deposited along with the site archive. They will need suitable storage to ensure they do not degrade further.

References

AUDY, J & AUDY, K. 2008. Analysis of bell materials: tin bronzes, *China Foundry*, **5**, 199-204

COTTER, E. 2015. Interim report on archaeological excavations at Molana Abbey, Ballynatray Demesne, Co. Waterford. Unpublished Report.

DUNGWORTH, D. & NICHOLAS, M. 2004. Caldarium? An antimony bronze used for medieval and post-medieval cast domestic vessels. *Historical Metallurgy,* **38**, 24-34.

NICHOLAS, M & MANTI, P. 2014. Testing the applicability of hand held portable XRF to the characterisation of archaeological copper alloys. *In* J. Bridgland (ed) *ICOM-CC 17th Triennial Conference Preprints, Melbourne, 15–19 September 2014*. Paris: International Council of Museums.

YOUNG, T.P. 2015. Analyses of copper ingots from St Michael's Mount. *GeoArch Report 2015/03*. 63pp.

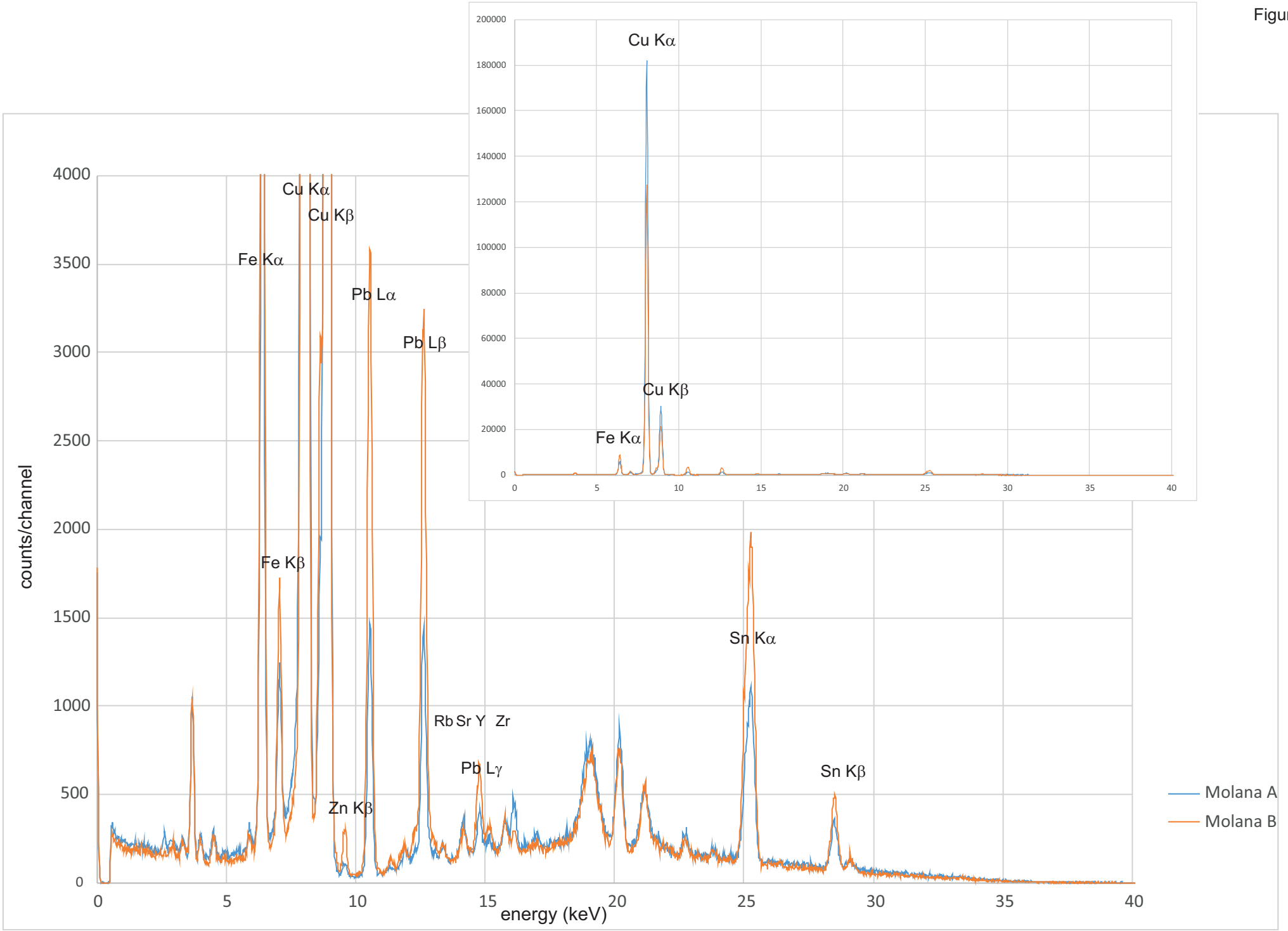
Figure Captions

Figure 1: XRF spectra for analyses of the two blebs. The inset shows the entire spectrum; the major diagram shows the detail of the lower peaks.

Table 1: tentative calculation of approximate elemental compositions from XRF spectra. The calibration has only been applied to the elements likely to have been present in the copper alloy spill, as opposed to the substrate.

Line		Net peak area		Adjusted net peak area		calibration	Raw wt%		Norm wt%		Ratio to Zn		
		Mol A	Mol B	Mol A	Mol B		Mol A	Mol B	Mol A	Mol B	Mol A	Mol B	
Al	K12	148	136	246	225								
Si	K12	112	197	186	326								
K	K12	655	476	1089	788								
Ca	K12	6306	6260	10487	10365								
Ti	K12	1135	1105	1888	1830								
Cr	K12	188	79	313	131								
Mn	K12	851	810	1415	1341								
Fe	K12	46893	74972	77983	124130	0.00001773	1.4	2.2					
Ni	K12	524	348	871	576	0.00001789	0.0	0.0					
Cu	K12	1683991	1170404	2800491	1937819	0.00001759	49.3	34.1	93.2	82.0			Cu
Zn	K12	12810	24207	21303	40079	0.00001231	0.3	0.5	0.5	1.2	1	1	Zn
Sr	K12	2550	1817	4241	3008								
Zr	K12	1428	1783	2375	2952								
Mo	K12	951	453	1582	750								
Rh	K12	8533	7951	14190	13164								
Rh	L1	532	90	885	149								
Sn	K12	19308	37045	32109	61335	0.00006914	2.2	4.2	4.2	10.2	8.5	8.6	Sn
Sn	L1	9	216	15	358								
Sb	K12	61	324	101	536	0.00009543	0.0	0.1	0.0	0.1	0.0	0.1	Sb
Sb	L1	40	1	67	2								
Ba	K12	263	54	437	89								
Ba	L1	54	1	90	2								
Pb	L1	15082	38036	25081	62976	0.00004250	1.1	2.7	2.0	6.4	4.1	5.4	Pb

Figure 1


counts/channel
energy (keV)
Cu Kα
Cu Kβ
Fe Kα
Pb Lα
Pb Lβ
Fe Kβ
Sn Kα
Rb Sr Y Zr
Pb Lγ
Zn Kβ
Sn Kβ
Molana A
Molana B

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