pXRF Analysis of a Bronze Age Metalworkers Hoard

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Introduction

Throughout Britain, Bronze Age hoards are commonly found, often by metal detectorists and amateur archaeologists. These hoards consist of intentional depositions of tools such as axe heads, daggers, and spearpoints, as well as metal fragments such as waste material from the casting process. Often tools from the middle and late bronze age are found in the context of hoards rather than settlements, though there are notable exceptions (Hamon, 2008). For this reason, it is difficult to state why these hoards were deposited, though primary theories are that they are for safekeeping (presumably to be returned to a later date) or ritual dispositions of some kind (Radivojević, *et al.* 2019). Bronze age hoards have typically been categorized by either the intention of deposition or the morphologies of tools found within them. More recently, studies have focused on categorization by the metal composition that the fragments are made from. Thanks to the advent of new analytical methods within the past few decades, much more information can be extracted from these finds (Bottaini, *et al.* 2016, pp. 345). Work in this field has been able to show the provenance of metal sources from hoards as well as show patterns of use and reuse through evidence of recycling. In this paper, the results of a late Bronze Age hoard found near Henfield, West Sussex analyzed using a portable x-ray fluorescent scanner (pXRF) are discussed. The hoard consisted of a palstave axe head (Figure 1) and 17 metal fragments, one of which was determined to be a casting jet (Figure 2), and the remainder either ingot fragments or casting waste (Figure 3), which were found together as an assemblage (Clark, 2021). The goals of this analysis were twofold. The first was to determine if the palstave is of the same composition as the fragments, or if the fragments may have come from a variety of different castings by comparing their chemical composition. The second was to provide preliminary data to guide further analysis that can provide a clearer picture of provenance and use.

Figure 1: Palstave Axe (Clark, 2021)

Figure 2: Casting jet (Clark, 2021)

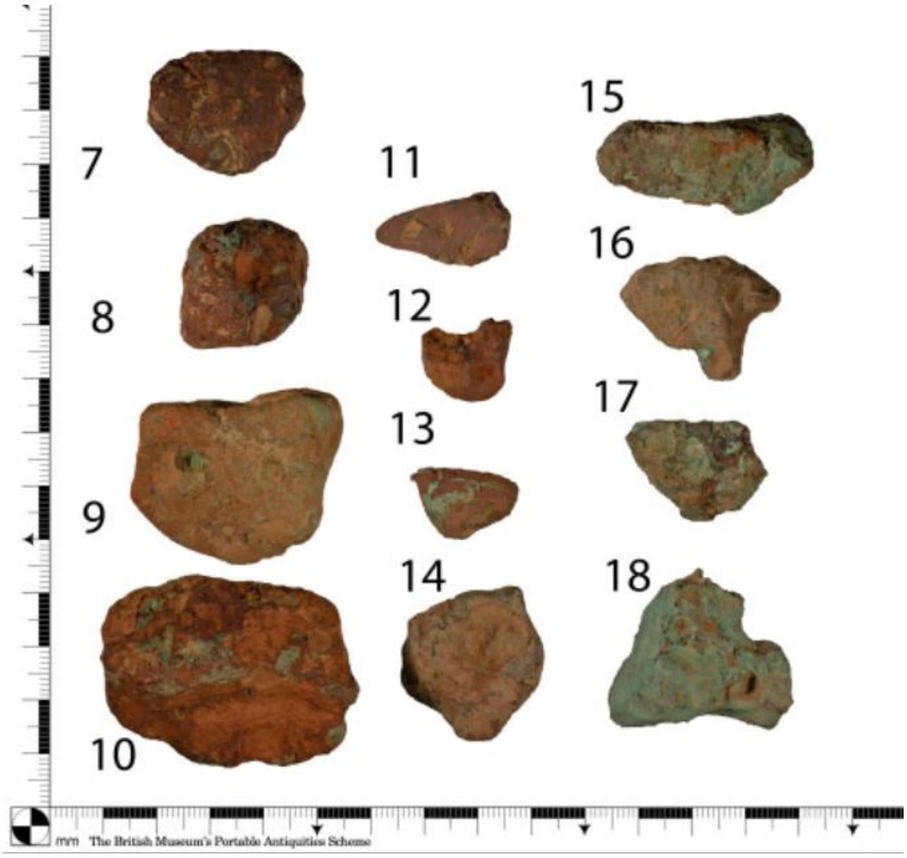

Figure 3: Casting waste ingots (Clark, 2021)

Use and Limitations of X-Ray Fluorescence

X-ray fluorescence is an analytical method which involves irradiating an object with x-rays, and measuring the resulting fluorescence that occurs. X-ray fluorescence analysis works similarly to how we perceive colours in the visible light spectrum. Materials, by nature of their chemical composition, either reflect or absorb portions of the visible electromagnetic spectrum. The portions which are reflected are perceived by our eye as the colour of that specific material. Fluorescence on the other hand is caused by EM radiation that is absorbed and re-emitted in the form of photons. When X-rays interact with a material, they contain enough energy to remove electrons from individual atoms, resulting in a high-energy, unstable ionized form of the atom. To return to equilibrium, an electron from a higher energy orbital will replace the one that was removed, which results in an energy differential that is emitted as X-ray fluorescence. The energy signature of this fluorescence is distinct for each element. Because of this, the fluorescence measured is not affected by molecular structure, and will only correspond to ratios of individual elements (Jenkins, 1984, Horiba Scientific, no date). pXRF analysis is useful because it is a relatively fast and simple method to gain compositional insights into materials. Since it is non-destructive, it is often the main method available to test objects which are displayed in museum collections (Arnoldussen *et al.*, 2022), or where permissions to alter the objects are not available, as is the case in this analysis. However, pXRF is limited to penetration of only a few hundred micrometres (Šatović *et al.*, 2013, as cited in Nørgaard, 2017), and therefore can only provide the composition of the surface of the material. As is common with bronze objects which have spent thousands of years buried, the surface is often a corrosion layer (Scott, 2002). For this reason, to obtain the composition of the core of an object, a scan must be taken of a cut or polished section (Nørgaard, 2017). The pXRF manual (Jiangsu Skyray Instrument Co., 2014) also states that rough surfaces may cause aberration in the data, which makes scanning corroded bronze surfaces challenging. For this reason, it is useful to measure multiple areas of a rough-surfaced object. XRF analysis is useful for the identification of the major elements of an object, however more in-depth questions such as determining provenance or specific techniques used in crafting will require the use of XRF in conjunction with other methods such as electron microscopy, hardness tests, or isotopic analysis (Nørgaard, 2017, pp. 120).

Methods

To gain a comparative understanding of the surface composition of the Henfield hoard fragments, each was scanned using a Skyray Instruments Explorer 3000 pRXF. The pXRF was positioned within a benchtop stand and remained stationary throughout sampling. Before scanning the hoard fragments, the pXRF scanner was tested using the provided reference disk with a known element composition to verify that the scanner was calibrated correctly. Table 1 shows the measured values compared to the manufacturer-listed values for the reference disk. The reference material composition was determined to be within the expected error margins, verifying correct operation of the pXRF.

Table 1: Reference material measured vs. expected values

Element	**Measured Content**	**Measured Error**	**Expected Content**	**Expected Error**
Cr(PPM)	45.5	±0.85	45.1	±1.9
As(PPM)	16.3	±0.08	17	±1.2
Br(PPM)	1390.5	±1.19	1430	±80
Cd(PPM)	147.9	±0.38	146	±5
Hg(PPM)	10.6	±0.14	9.9	±0.8
Pb(PPM)	68.8	±0.30	69.7	±2.5

The Explorer 3000 comes with pre-configured analysis profiles to target specific groups of elements. Since the hoard was identified as copper alloy materials, the copper alloy detection profile was selected. Fragments 5,7,10 and 14 were withheld for museum display and thus were not scanned. Fragments 3 through 17 were scanned on the top and bottom of each object, targeting areas with the least amount of patina (Figure 4). Where necessary, foam was used to position the fragments so that the angle of incidence of the X-ray was as close to 90 degrees as possible (Figure 5). Fragment 2, the casting jet, due to its irregular shape was scanned on 2 sides as well as the top. The palstave was scanned on all sides, with additional scans on sections of the left and right sides where the metal was scraped and appeared to reveal the raw metal under the corrosion layer (Figure 6).

Figure 4: Examples of targeted areas for scans

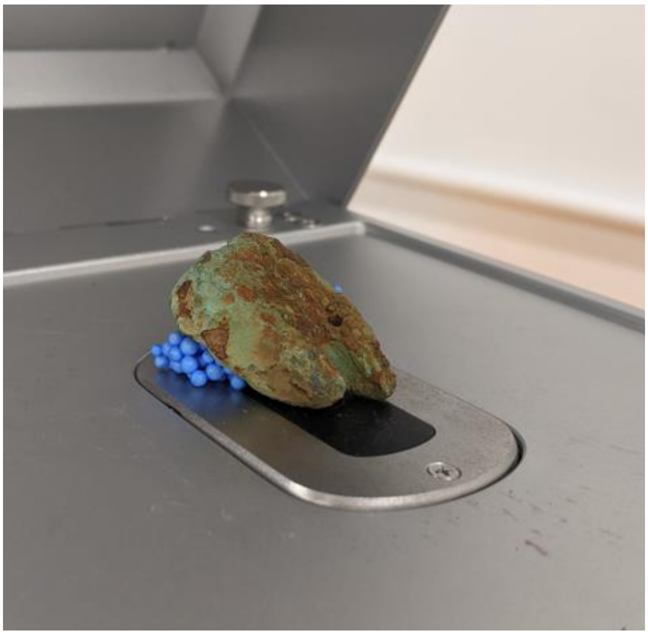

Figure 5: Foam was used to adjust angle of X-ray

Figure 6: Areas of palstave which show bare metal

Results and Discussion

The results of the pXRF scans showed that all the objects in the hoard were copper-tin alloys, with relatively low impurities. Table 2 shows the average elemental composition for the metal scraps and bun ingot fragments, excluding fragment 12. Fragment 12 was excluded as it is an outlier, the only one which was composed primarily of iron. All items had trace elements commonly found in late Bronze-Age hoards (Hamon, 2008, Needham, Lease, Hook and Hughes, 1989). The results also show that the compositions of the corrosion layers among the fragments are not homogenous and suggest that the objects were not from a single source but may have been collected in phases and deposited at a later time. This substantiates the hypothesis that the palstave axe head is of an earlier date than the rest of the fragments (Clark, 2021). Table 3 shows the primary elemental composition of each fragment. The values shown are the average composition of the scans taken on each side. Based on the differences in composition, they can be categorized into 4 distinct groups shown in Table 4. Group 2, 3 and 4 fragments all display a measurable presence of lead, supporting the hypothesis that these are likely from the late Bronze Age to early Iron Age (Arnoldussen *et al.*, 2022, pp. 10-11). High lead content, such as displayed in fragment 2, may also suggest evidence of recycling of bronze however it has been shown that surface pXRF measurements can exaggerate lead content by as much as 30%, so this cannot be concluded without further testing (Tylecote *et al.*, 1977; Pernicka *et al.*, 1990, p. 272; Mangou and Ioannou, 1998, p. 98, as cited in Orfanou and Rehren, 2015).

Table 2: Average elemental composition across all fragments (excluding fragment 12)

Element	Average Content
Al(%)	1.33
Si(%)	0.49
Cr(%)	0.02
Mn(%)	0.03
Fe(%)	5.80
Co(%)	0.05
Ni(%)	0.18
Cu(%)	82.23
Zn(%)	0.45
Sn(%)	0.27
Sb(%)	0.19
Pb(%)	0.89

Table 3: Main elements by fragment number

Fragment	Cu %	Error	Sn %	Error	Fe %	Error	Pb %	Error
2	90.35	±0.12	0.51	±0.01	1.08	±0.01	5.27	±0.05
3	95.31	±0.09	0.16	±0.00	1.80	±0.01	0.04	±0.00
4	85.53	±0.10	0.25	±0.00	11.60	±0.02	0.25	±0.01
6	71.30	±0.12	0.21	±0.00	23.37	±0.04	0.67	±0.01
8	87.67	±0.09	0.15	±0.00	9.27	±0.02	0.58	±0.01
9	91.40	±0.10	1.07	±0.01	3.62	±0.01	0.59	±0.02
11	94.87	±0.09	0.20	±0.00	1.87	±0.01	0.27	±0.01
12	9.60	±0.07	0.19	±0.00	86.11	±0.09	0.31	±0.00
13	96.56	±0.09	0.10	±0.00	1.08	±0.01	0.03	±0.00
15	93.85	±0.10	0.18	±0.00	2.95	±0.01	0.05	±0.00
16	93.76	±0.09	0.16	±0.00	1.90	±0.01	0.06	±0.00
17	82.12	±0.10	0.15	±0.00	13.38	±0.02	0.64	±0.01

Table 4: Grouping of fragments by similar elemental composition

Group #	Fragment	Cu %	Error	Sn %	Error	Fe %	Error	Pb %	Error
Group 1 (High Cu, low Fe & Pb)	3	95.31	±0.09	0.16	±0.00	1.80	±0.01	0.04	±0.00
	13	96.56	±0.09	0.10	±0.00	1.08	±0.01	0.03	±0.00
	15	93.85	±0.10	0.18	±0.00	2.95	±0.01	0.05	±0.00
	16	93.76	±0.09	0.16	±0.00	1.90	±0.01	0.06	±0.00
Group 2 (High Cu, low Fe, high Pb)	2	90.35	±0.12	0.51	±0.01	1.08	±0.01	5.27	±0.05
	9	91.40	±0.10	1.07	±0.01	3.62	±0.01	0.59	±0.02
	11	94.87	±0.09	0.20	±0.00	1.87	±0.01	0.27	±0.01
Group 3 (High Cu, Fe and Pb)	4	85.53	±0.10	0.25	±0.00	11.60	±0.02	0.25	±0.01
	6	71.30	±0.12	0.21	±0.00	23.37	±0.04	0.67	±0.01
	8	87.67	±0.09	0.15	±0.00	9.27	±0.02	0.58	±0.01
	17	82.12	±0.10	0.15	±0.00	13.38	±0.02	0.64	±0.01
Group 4 (Low Cu, High Fe)	12	9.60	±0.07	0.19	±0.00	86.11	±0.09	0.31	±0.00

The high percentages of iron in the group 3 and 4 fragments were unexpected. Typically, the iron content in metal from bronze-age hoards ranges from 0.5% to 2-3% (Gutiérrez Neira *et al.,* 2011, Arnoldussen *et al.*, 2022). Iron is found in higher concentrations in the corrosion layers of bronze (Leisner and Buchwald, 1990), but not in the degree found in the group 3 and 4 fragments. A possible explanation is that these are waste materials from deliberate slagging during the smelting process to remove impurities, however, the higher concentration of copper in these fragments makes this implausible. If these were simply discarded bits of slag, we would expect to see very little copper in them, and likely the presence of other impurities in higher concentrations (Cradock and Meeks, 1987, pp. 187-190). Another possible reason is that these fragments were deliberately enriched with iron. However, high iron content makes bronze alloys difficult to hammer and cast, and Cradock and Meeks (1987) proposed these types of ingots may have been produced as a form of currency based on the context of ferruginous copper ingots which have been found. These examples are uncommon, however, with only one coming from Britain (Sutherland, 1955, as cited in Cradock and Meeks, 1987), which makes these fragments worthy of further analysis, namely SEM examination and further testing to verify the composition of the core metal, as pXRF has been shown to inflate relative iron composition (Orfanou and Rehren, 2015, pp. 391-393).

The palstave's composition, shown as average composition from all surfaces scanned in Table 5, did not correspond to any of the groupings of the fragments found with it. Notably, the results displayed an extremely high tin content. There are examples of high tin-content axe heads which have been found in Scotland (Coles, 1970), though they are not nearly as high as the Henfield palstave. It has also been theorized that some Bronze Age tools were deliberately tinned (Meeks, 1986). However, these typically display a silvery surface appearance, which we do not see in the Henfield axe. The most likely explanation is the overrepresentation of tin content at the corrosion layer of bronze (Williams and Roberts, 2024). This has been attributed to a combination of "tin sweating" which can occur during casting, the tendency for tin to aggregate in the corrosion process (Scott, 2002) and some degree of error that is typically found with pXRF measurements, all of which have been well documented (Meeks, 1986, Nørgaard, 2017, pp. 113, Orfanou and Rehren, 2015, pp. 391-392). As previously discussed, the levels of lead and iron shown in the palstave are likely also higher than the core metal due to the corrosion layer.

Table 5: Palstave elemental composition

Element	Avg. Content	Avg. Error
Al(%)	1.52	±0.08
Si(%)	0.45	±0.01
Cr(%)	0.07	±0.00
Mn(%)	0.13	±0.01
Fe(%)	12.11	±0.05
Co(%)	0.10	±0.00
Ni(%)	0.67	±0.01
Cu(%)	34.70	±0.09
Zn(%)	0.43	±0.00
Sn(%)	48.79	±0.06
Sb(%)	0.41	±0.00
Pb(%)	0.51	±0.01

Conclusion and Future Research

The pXRF results suggest that the fragments of the Henfield hoard are likely from several different production sequences and possibly periods, with group 3 and 4 likely being of a later period. It was hypothesized that the palstave was of earlier origin, however, due to the likely overrepresentation of tin in the measurements due to the corrosion layer, it is not possible to confirm through this analysis. Composition analysis with a more sophisticated XRF tool of a polished area of the palstave would be able to verify the true content of the core metal, however this analysis would be destructive. Nonetheless, these results merit further study, particularly the high iron content group 3 and 4 fragments, as this composition has rarely been documented in Britain.

Questions of provenance and evidence of recycling are similarly not adequately addressed through this pXRF analysis alone. Though compositional ratios of trace elements can yield insights into metal sources and the number of times it has been resmelted (Bray and Pollard, 2012), the margin of error associated with pXRF on the corrosion layer makes this impossible. In conjunction with XRF, the Henfield hoard would benefit from further, more sophisticated analytical techniques such as lead isotope analysis and examination of the metallurgical structure under an SEM.

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