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# X-ray fluorescence analysis of metal working waste and a pewter ring from Tintagel Castle

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Tintagel Castle  
Cornwall  
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pewter ring from Tintagel Castle

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## SUMMARY

A small number of objects recovered during the Tintagel Castle Research Project (TCARP2017) excavations in 2017 were sent to Fort Cumberland to determine whether they are associated with any metal working activity that may have taken place at Tintagel Castle. While some of the slag and crucible fragments are likely to be related to metal working activities, there are also a number of undiagnostic slags and fragments of technical ceramics. A small metal ring was found to be made from a lead dominated lead-tin alloy.

## CONTRIBUTORS

Dr. Florian Ströbele carried out the material analysis of the metal working waste and the ring.

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## INTRODUCTION AND BACKGROUND

A number of finds from the 2017 excavation at Tintagel Castle, North Cornwall, were sent to Fort Cumberland in order to be analysed and confirmed or refuted as potential evidence for metal working (Historic England 2015). Several pieces of potential slag, some sherds of technical ceramics and various pieces of burnt clay and some stone were among the finds. A lead alloy ring was also analysed in order to identify the alloy.

A report on metallurgical waste material from a previous excavation in the 1930s was published in 1988 (Bayley 1988). Besides various metal and bone small finds and burnt clay pieces, there were some objects that are identified as metal working waste: a crucible fragment, a tuyère fragment, three pieces of slag and a possible mould fragment. The tuyère fragment could not be assigned to a specific metallurgical process and the slag pieces were undiagnostic. The crucible sherd was unstratified. It showed vitrification on the outside, and XRF analysis did not yield any particular metal enrichment.

Another comprehensive report by Photos-Jones in Barrowman (2007, 268ff.) identifies industrial waste, identified as bloomery slag from iron smelting, and fuel ash slag. The overall comment on the slag analysis is inconclusive and indicates that some of the slag finds may be residual. Also, some fragments were identified as furnace lining, but could not be assigned to a specific process. The same is true for the crucible fragments.

The conclusion of these reports was that some metal working of an unknown type, but most probably small scale had been carried out at Tintagel Castle. The evidence for metal working on site is emphasized, but due to the small assemblage, no specific metal working process could be identified for certain.

An indication for base metal working is a leaded bronze sprue (RF 1040), which is excess metal from casting, found in the area of the steps (Batey at al. 1993). No production area was associated with this find.

During the excavations in 2017 a complex of three stone buildings: 092, 093 and 094 were investigated on the southern terrace. These were constructed on an artificial terrace made up of bedrock and soft ground: principally levelled midden material. Radiocarbon dating and other associated diagnostic artefacts indicate 3 broad phases of dating: Phase 1: 5<sup>th</sup> to 6<sup>th</sup> centuries AD, Phase 2: 7<sup>th</sup> to 9<sup>th</sup> centuries AD and Phase 3: 9<sup>th</sup> to 11<sup>th</sup> centuries AD (J Nowakowski, pers comm). All of the finds identified as potentially related to metal working come from secondary contexts as no clear evidence for an industrial structure such as a hearth or furnace was found *in-situ*.

## METHODS

XRF analysis is a fast and non-destructive method to gain knowledge on the chemical composition of most inorganic solid materials. The analysis is done by focussing an x-ray on the region of interest. These X-rays interact with the object and induce so called fluorescence or secondary x-rays. The secondary x-rays hit the detector of the device and are translated into an electronic signal.

Depending on the elements present, these secondary x-rays have distinctive energies and thus, all elements that are present can be identified. By means of model calculations (Fundamental

parameters) or by using a calibration curve based on various well known reference materials (standard based), the result, also called x-ray spectrum, can be evaluated and quantified. In a best case scenario, this allows very exact quantification that gives details about how much of each element (usually given in weight %) is present.

The XRF method is a surface sensitive analytical method; the x-rays do not penetrate the material. Depending on what kind of material is analysed, only information of the upper most layer (in the case of glass up to a depth of ~1.5mm, in the case of most metals only a few microns) is gathered. It might be necessary to remove corrosion products potentially present on the surface to expose the unaltered material. This manipulation is minimal and can be kept smaller than 1mm as the analysed area has only a diameter of 25µm.

However, most archaeological materials are not homogeneous. So in all cases where it is possible multiple spots on the object in question will be analysed to grasp the range of the materials' composition.

Analytical details:

Device: Bruker M4 Tornado

Atmospheric conditions: Vacuum

Acceleration voltage: 50kV

Anode current: 200mA (400mA for the SF5016 metal ring)

Filter: blank (630µm Al for the SF5016 metal ring)

Analysis time: 200s per spot (live time)

## RESULTS

The metal ring SF Nr 5016 (751) rubble collapse north of wall (577)/(556) building 094

This object was analysed to identify the alloy. XRF analysis of the object yielded large quantities of lead and tin as well small amounts of copper and iron. Unfortunately, the object seems to be completely corroded (Fig. 1), thus, a quantitative evaluation of the original alloy is no longer possible. From the composition of the corrosion products, the original ring may have had a composition of between 50%Pb + 50%Sn and 70%Pb + 30%Sn.



*Fig 1. SF 5016. The ring is heavily corroded, no quantitative evaluation of the results was possible.*

The lead-tin alloy pewter can be copper free or have up to several per cent of copper. The ring has only traces of copper that are most likely lower than 0.1%. Again, exact quantification is not possible due to the condition of the object. The detected iron is likely to come from the environment (soil) as this element is usually not present in pewter.

Although local tin has been mined throughout the centuries in Cornwall (Gerrard 2000) it is not possible to confirm whether the ring is made from Cornish tin material. It is corroded too heavily and the necessary data that might answer the question (Tylecote et al. 1989, Haustein et al. 2010) could not be obtained by the method used for the analyses.

## The metal working waste

### *Slag*

The slag was assigned to the standard categories outlined in the Historic England Archaeometallurgy guidelines (Historic England 2015). Slag is a by-product from many metallurgical processes, formed when some of the metal oxidises and reacts with gangue, furnace or hearth linings, or crucibles.

The slag fragments were washed through a sieve, and the debris was checked for hammerscale (a type of smithing waste) with a magnet. No hammerscale was detected. Two of the more compact slag pieces may be from iron working, but due to the small size it's difficult to assign them to a process (smelting or smithing); however (779) is possibly from iron smelting.

**(751) 26-07-17, north of building 094, rubble collapse N of (577), phase 2** undiagnostic. Smelting or smithing slag typically has a high iron content ( $\text{Fe}_2\text{O}_3$ ) of 40 to 60 wt%, whereas the iron content of this particular piece is only ~13 wt% and thus, far too low to necessarily indicate a metal working process.

**(783) SF 931, building 094, fill of hearth (782), phase 1:** undiagnostic. Although this piece has a high iron content ( $\text{Fe}_2\text{O}_3$ : ~65 wt%) it is very light in weight due to its high porosity



and foam like texture. No flow textures that would be indicative of smelting slag could be observed.

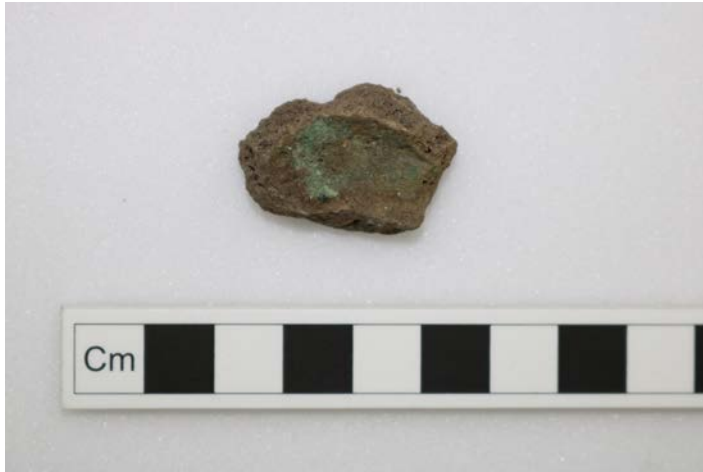
**(779) 06-08-17, area of building 094, rubble retaining wall, phase 1** Several small pieces show the texture of a completely molten and solidified silicate (Fig 2). The outside surface is very smooth and of fluid shape. The piece contains some bubbles and a few, very small inclusions, which mostly look like small fragments of shale and sometimes quartz under a microscope. This piece is likely to be derived from iron smelting, although this does not confirm iron smelting on site, as considerably larger amounts of slag would be expected in such circumstances.



*Fig 2. (779) 06-08-17. Note the very smooth surface of the broken bubble at the bottom of the piece of slag.*

### *Crucibles*

**(324) SF 5051, building 094, midden, phase 1:** is confirmed as a crucible fragment, used for casting copper alloys. The green mineral on the inside is a copper corrosion product (Fig 3). The analysis also yielded small amounts of zinc. On the outside, only minor amounts of copper and zinc are present. No remains of intact metal droplets or prills were found on the fragment.



*Fig 3. (324) SF 5051. The inside of the crucible fragment has green copper corrosion, consistent with the use of the crucible for base metal working.*

**(551) SF 5062, middle terrace, possible phase 1** the glaze-like outer surface does not show any enrichment of metal at all. The concave inside surface however is enriched in zinc. This is what would be expected from a crucible that was used for base metal processing. No remains of metal droplets were found on the fragment (Figs 4 and 5).



*Fig 4. (551) SF 5062. The outside of the crucible fragment has a bright, shiny, glaze-like surface. This vitrification usually occurs when technical ceramics come into contact with fluxes like fuel ash.*



Fig 5. (551) SF 5062. The side view shows the shape of the rim of the crucible (top of image).

**(774) SF 5063, outside southern wall (553) of building 093, 'seaweed' context**

**(774), phase 1:** The identification of SF 5063 as a crucible is uncertain. The inside of this piece is very rough (Fig 6). A dark brown crust has formed on the inside. Where this has broken away, a light grey, slightly yellowish fabric can be seen. The texture of this sherd is very coarse and the ceramic mass is heavily grogged. The outside is heavily weathered. Although the analysis of this piece yields traces of copper, zinc and lead, identification as a crucible is not certain because the surface is poorly preserved.



Fig 6. (774) SF 5063. The fabric of this ceramic sherd is very coarse. No indication of direct metal contact could be found on the inside of the sherd.

*Furnace / hearth linings*

Pieces of fired clay with vitrified surfaces can be produced by many burning processes. Those from metallurgical processes are more likely to be reduce-fired grey or black on the inside surface and may have adhering slag. Again it's not possible to assign the fragments from Tintagel to a metallurgical process as the assemblage is small; however the inner surfaces are reduced-fired (dark colour) so involvement in metal working is possible.

**(552) 11-07-17, building 094, cleaning below turf, phase 3:** The black inner surface is porous and vitrified, whereas the reverse side is burnt red. There are no traces of base metals, and the iron content is low. As there are no clear indications that this was connected to metallurgy, it is otherwise undiagnostic.

**(555), outside SE wall (556) of building 094, midden (555), phase 1** had two samples: **09-08-17** and **'daub or furnace lining'**: undiagnostic.

**09-08-17** has only traces of copper and low iron content and is probably not connected to metallurgy. It has a higher calcium and phosphorous content than the other pieces of ceramic examined, and it is possible that a small amount of bone ash was used as temper.

**(555), outside SE wall (556) of building 094, midden (555), phase 1**

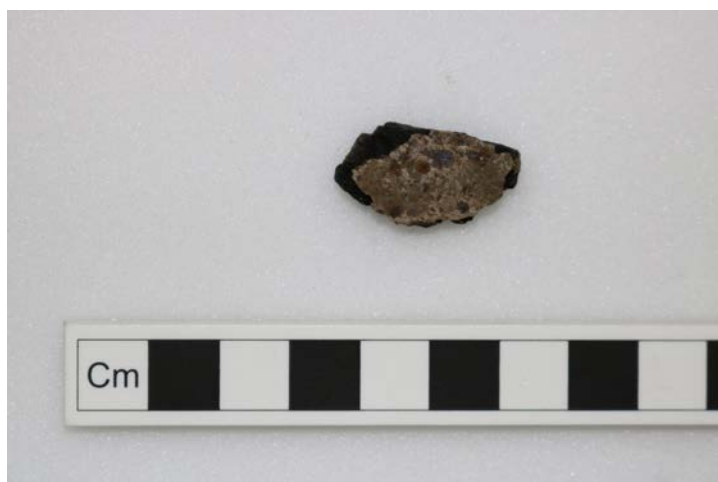
The piece dated labelled **'daub or furnace lining'** was not analysed due to lack of original contact surface. It look similar to the 'wall' side of SF5086 from (562), but is burnt at less oxidizing conditions, as it has a less intense reddish colour.

**(562) SF 5086, north of northern wall (577) of building (094), phase 2/3:** This piece of lining has a black slagged surface and is burnt red on the reverse. There are numerous imprints of plant material that show tempering of the clay with organic material. The slagged surface is vitrified and has a high iron content that implies the piece being part of a metallurgical structure, such as a hearth or furnace for iron working. Only traces of base metals are present so this fragment was not associated with copper related metallurgy.

## Others

The following material could not be related to metal working. Some of it is geological, and some of the samples were identified as heated clay that could be connected with a domestic hearth or any other heating event. One of the samples is calcined bone.

**‘Shale’ (324) SF 5050, surface of midden SE corner of building 094, phase 1:** There were several small fragments in the bag labelled ‘shale’. One of them is shale but there are two fragments that have a black break and a whitish, powdery surface (Fig 7). These pieces are slightly curved. These yield strong signals of calcium and phosphorus and are most likely burnt bone.



*Fig 7. (324) SF 5050. While the outer surface is white and soft, the inside seems to be more brittle and heavily carbonised.*

**(320) 10-08-17, ‘Stone within hearth features’, building 094, hearth [343], phase 1:** three are quartz, and one is a magmatic rock, probably originating from local dykes that run from the east of Tintagel through the village and continue a few miles south (de La Beche, 1856).

**(774) 27-07-17, ‘slag/haematite’, mid terrace, outside southern wall (553) of building 093, ‘seaweed’ context (774), probably phase 1:** the bigger piece is a magmatic rock or dyke that also could be local. The smaller piece has a reddish appearance on one side and a grey appearance on the other. There are some small slate fragments. The material is comparable to that from context 787 (SF 936), see below.

**(787) SF 936, ‘burnt clay’, building 094, upper hearth (785), phase 1:** undiagnostic. Red burnt clay with small fragments of slate. There are some minor (<1mm) particles of charcoal. Material like this could come from any domestic or workshop fireplace.

**(750), ‘industrial’, building 092, rubble collapse east of south western wall (598), phase 2** undiagnostic. This appears to be debris that has been sintered together by some calcareous mineral precipitation during burial. The red powdery mineral that is attached to some of the smaller pieces is an iron mineral, most probably goethite of geological origin.

## DISCUSSION

Based on the analysis, it can be stated that metal working took place to a small extent at Tintagel Castle. As only a small number of finds related to metal working were identified, and no dedicated metal working site has been found at Tintagel Castle yet, it is likely that only local, small scale production and secondary metal working such as smithing or repair works was carried out. Three different types of industrial waste were found during the 2017 excavations at Tintagel Castle (crucible fragments, furnace / hearth lining and slag).

The analytical results for the crucibles indicate the working of base metals. As discussed by (Dungworth (2000, 2001) metal impregnation of technical ceramics found with chemical analysis can indicate whether base or precious metals were being worked, but cannot be used to determine the exact composition of the alloy that has been processed; unfortunately no metal prills or droplets survived on these crucibles. As metallurgical crucibles are a type of specialist equipment, that are (usually) not found far away from their respective place of use or “working context”, and so the possibility of that small scale base metal working took place at Tintagel Castle at an early period (that is, during phase 1) is high.

The slag pieces do not give much information, as they are small and few in number. Due to the lack of clearly identifiable shapes, discrimination between hearth slag and tap or furnace slag, the first being typical for smithing, the latter for smelting, is difficult. The only piece of slag that can clearly be associated with iron smelting is (779) found in made ground which was sealed below track 791 located mid terrace between buildings 093 and 094. Fuel ash slag, as well as hearth lining, is not necessarily indicative of a metallurgical process, as both may form in any fireplace, no matter if it is domestic or industrial.

As the only fragment that from the uncertainly dated (probably phase 1) context (774) is not necessarily a crucible, no definitive dating evidence for the metalworking can be drawn from the finds of the 2017 excavations.

## CONCLUSIONS

For the reasons explained above, the results of the analysis from this report are in good accordance with the results from earlier analyses (Photos-Jones in Barrowman 2007; Bayley 1988), indicating small scale copper alloy working at the site. The small amount of evidence for iron working found so far is not sufficient to indicate iron working at the site however. None of the metal working activity can be dated closely to a particular phase of.

## REFERENCES

Barrowman, R C, Batey, C E, Morris, C D 2007. *Excavations at Tintagel Castle, Cornwall, 1990-1999*. Reports of the Research Committee of the Society of Antiquaries of London 74.

Batey, C, Sharpe, A, Thorpe C M 1993. ‘Tintagel Castle: archaeological investigation of the Steps area 1989 and 1990’. *Cornish Archaeol* 32, 47-66.

[Bayley, J 1988. \*Technological Finds from Tintagel\*. Ancient Monuments Report 195/88.](#)

Beche, H, de la 1856. *Coast from Tintagel to Newquay; Padstow, Camelford, St. Columb, the Mining Districts of Bodmin, Lostwithiel* Geological Survey of England and Wales 1:63,360 geological map series [Old Series]. British Geological Survey.

Dungworth, D 2000. 'A Note on the analysis of crucibles and moulds'. *Historical Metallurgy* 34(2), 83-86.

[Dungworth, D 2001. \*Metal Working Evidence from Housesteads Roman Fort, Northumberland\*. Centre for Archaeology Report 109/2001.](#)

Gerrard, S 2000. *The Early British Tin Industry*. Charleston: Tempus Publishing Inc.

Haustein, M, Gilles, C, Pernicka, E 2010 'Tin Isotopy – A new method for solving old questions'. *Archaeometry* 52, 816-832.

Historic England 2015 *Archaeometallurgy: Guidelines for best practice*.

Tylecote, R F, Photos-Jones, E, Earl, B 1989 'The composition of Tin Slags from the south-west of England' *World Archaeology* 20, 434-445.



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