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Hall, Allan, Ellam, Robert, Wilson, L., Pollard, Tony, and Ferguson, N. (2011) *Corrosion studies and lead isotope analyses of musket balls from Scottish battlefield sites*. In: Turbanti-Memmi, I. (ed.) *Proceedings of the 37th International Symposium on Archaeometry, 13th - 16th May 2008, Siena, Italy*. Springer, pp. 591-597. ISBN 9783642140770

<http://eprints.gla.ac.uk/48596/>

Deposited on: 21 January 2011

Corrosion Studies and Lead Isotope Analyses of Musket Balls from Scottish Battlefield Sites

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1 Introduction

The recovery and analysis of musket balls and other lead projectiles, with a particular focus on their morphology and distribution in the ground, is an important aspect of seventeenth to nineteenth century battlefield archaeology (Pollard and Oliver 2003). However, one factor significant to the analysis of musket balls has not been given due attention by archaeologists, namely the sourcing of lead for their manufacture. Lead isotopes provide a means of characterising sources of lead (Pollard and Heron 1996) and although there have long been concerns about the use of this technique in archaeology, especially in relation to mixing of metal sources (Knapp 2000), this method does offer the potential of characterising the nearly pure lead found in musket balls. The technique may therefore have an important role to play in the identification of specific sources of lead and thus provide a valuable insight into the supply of armies in the seventeenth to nineteenth centuries.

In any investigation of archaeological artefacts, scientific analysis must be undertaken with minimal destruction. The question therefore arose: Could lead isotope analysis be undertaken on the corrosion products thus minimizing the possibility of damage to the musket ball itself? Archaeological surveys carried out on two major battlefields of the Jacobite Risings in Scotland, Killiecrankie (1689) and Culloden (1746), have recovered significant numbers of musket balls, all of which show variable degrees of surface corrosion and are therefore ideal for

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this research. Not only will this research provide an important insight into lead sourcing during this period but will also, through the studies in lead corrosion, extend our understanding of lead survival in soil. Metallic lead is unstable in soils (Tylecote 1983) and lead musket balls will gradually corrode and dissolve in soil water. Once corrosion is complete or nearly complete, the ability to detect a lead musket ball using a metal detector, the only practical means of undertaking a systematic distribution survey (Pollard 2009), may no longer be possible. This is a major issue, not just for archaeological research on battlefields, but one that concerns the management and conservation of battlefield heritage as a whole.

2 Background

The Battle of Killiecrankie, 1689, is famed in Scottish history as the first battle of the Stuart Risings. This was to end in Jacobite defeat nearly 60 years later at the Battle of Culloden, close to Inverness, in 1746 after a series of unsuccessful campaigns stemming from political and religious upheaval (Duffy 2003). Fought along the main communication route from Perth into the Highlands, and within the enclosing landscape of the Pass of Killiecrankie, an army of *c.*4000 Government soldiers was to be defeated by *c.*2000 Jacobites, (Scots and some Irish). Although the basket-hilted broadsword and the older claymore may have been the Jacobite weapon of choice, firearms would have been used on both sides, in particular the flint-lock musket which, by 1689, would have replaced the unwieldy and less reliable matchlock musket (Pollard and Oliver 2003). At Culloden two distinct calibres of musket ball could be identified, allowing for the Brown Bess musket, predominantly used by the Government army, and the smaller French muskets, used by the Jacobites, to be distinguished in the assemblage. The same distinction cannot be made at Killiecrankie, where more variation in size was observed, thus making it more problematic to identify Jacobite from “redcoat” using the musket ball assemblage ($n = 67$) alone.

It is likely that lead used for musket balls in these battles, with such wide political scope and support, came from mixed sources all over Europe. However, it is possible that some lead, especially that used by the Jacobites, came from special sources in Scotland (Fig. 1a); for example, Tyndrum which was exploited from 1741 and was captured in 1745 by Government forces (Wilson 1921); Strontian which was blockaded by the English navy in 1745 (Parsons 2008); and Leadhills/Wanlockhead where lead was recovered from at least the sixteenth century (Porteus 1876). Mining activity in Scotland was stimulated by exemptions from export duties on lead following the Union in 1707 (Downs-Rose 1994). While sourcing musket ball lead has thus far not been a major concern in historic battlefield research, the potential to identify some specific Scottish sources is important and stimulated this research project. It is particularly noteworthy that Tyndrum has been confirmed to have a distinctive lead isotope signature (MacKenzie and Pulford 2002) as the one result in the Rohl (1996) database indicates (Fig. 2b).

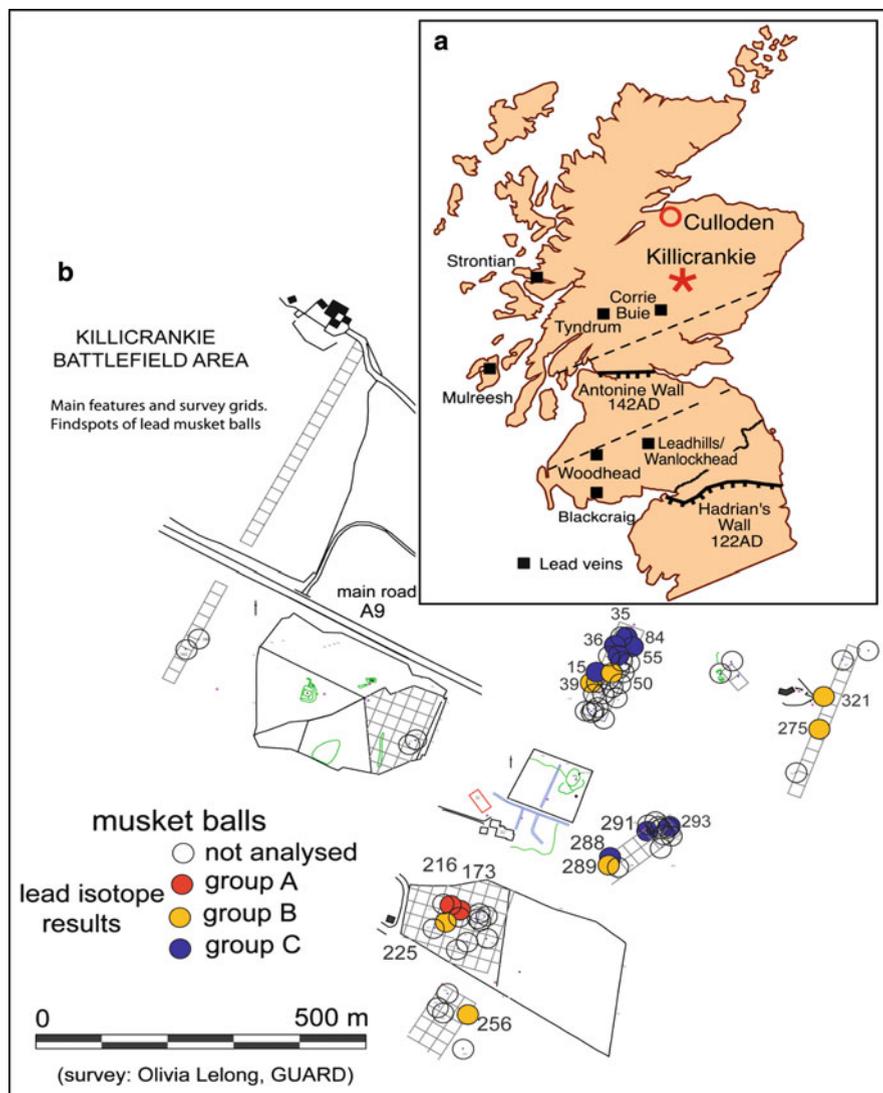


Fig. 1 (a) The inset map shows the location of the Killicrankie and Culloden battlefields and the major lead sources which were probably in production in Scotland during the eighteenth century. The Roman frontiers and the current England/Scotland border are shown for reference. The parallel *dashed lines* indicate the approximate boundaries of the Midland Valley of Scotland. (b) Killicrankie battlefield area showing the distribution of all musket balls recovered from survey grids. The analysed balls are numbered and colour-coded by provisional lead-isotope group (see Fig. 2a)

Geological studies of mining areas have mainly been concerned with the characterisation of minerals and understanding their origin. This contributes little directly to archaeological and historical interests. Nevertheless, archaeologists

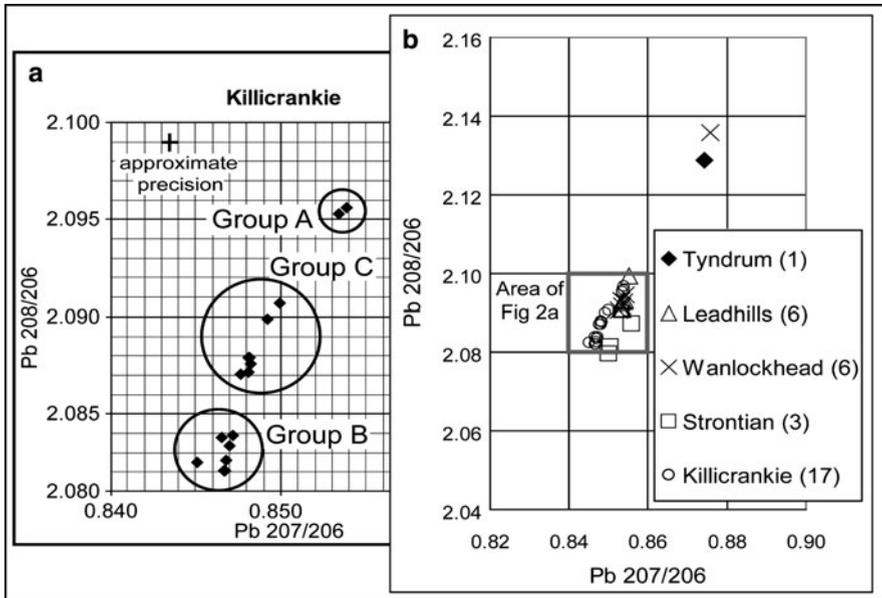


Fig. 2 (a) Lead isotope results showing three provisional groups of musket balls; the groups are very scattered on the battlefield (See Fig. 1b). (b) The Killicrankie musket ball results compared with data for Scottish mines (four) from Rohl (1996)

and historians have to turn to geological expertise in order to help establish the availability of lead in particular regions and fortunately this basic geological knowledge is now available. All known lead sources in the UK were incorporated into the lead isotope database of Rohl (1996), but the question remains as to which mines were in production in the seventeenth to nineteenth centuries.

3 Methods

Three non-destructive approaches have been used to investigate musket ball corrosion products:

3.1 Theoretical Computational Equilibrium Thermodynamics

This was used to understand the corrosion process and predict corrosion products. Geochemical modelling was undertaken using Geochemist's Workbench (Bethke 1996) and has the *ultimate aim* of estimating the lifetime of lead musket balls in the soil vadose zone. Analyses of soil-solution from battlefield sites is required for the

model and this was undertaken on Culloden soil-solution using ion chromatography and total inorganic carbon-total organic carbon (TIC-TOC) methods.

3.2 *Analyses of the Corrosion Products*

Powder X-ray diffraction spectrometry and scanning electron microscopy with energy dispersive X-ray analysis was used to determine the mineralogical and chemical components in the corrosion products. Both of these techniques can be used directly on musket balls without modification of the corrosion surface.

3.3 *Lead Isotope Analyses*

Non-destructive or more exactly, “minimally-invasive” analysis of the lead-rich corrosion layer was undertaken using a laser ablation ICP-MS. Errors estimated for Pb 208/206 and 207/206 are: ± 0.001 .

Whole samples were introduced to the ablation cell of a New Wave UP-213 laser system and supported on “plugs” of quartz wool. The laser, which is a frequency-quintupled Nd-YAG, was used to ablate Pb from the sample with a beam diameter of 5 μm . Ablated material was transported from the cell with a flow of Ar gas to a modified ICP-MS cyclonic spray chamber which was used to mix the sample material with a stream of Tl introduced from an Apex-Q desolvating nebuliser. The Pb-Tl mixture was then transported to the ion source of a Micromass IsoProbe MC-ICP-MS. Pb-isotope ratios were determined on 3 blocks of 20 5-s integrations while the laser beam was rastered over approximately $100 \times 100 \mu\text{m}$ squares, allowing a second pass to begin if the analysis time (5 min) required. No physical damage to the sample surface was discernable with the naked eye or the microscope optics of the laser system. Data quality was assessed by analyzing NBS981 Pb wire mounted in epoxy resin on a microscope slide. During the course of this study, this standard gave $^{208}\text{Pb}/^{206}\text{Pb} = 2.1688 \pm 18$ and $^{207}\text{Pb}/^{206}\text{Pb} = 0.91521 \pm 38$ (2 s.d., $n = 5$) which compare with the “triple spike” values of 2.16771 ± 10 and 0.914750 ± 35 (Galer and Abouchami 1998).

4 Results

4.1 *Theoretical Computational Equilibrium Thermodynamics*

Analysis of Culloden soil solution indicated this is a relatively corrosive environment, with a high chloride content and acidic pH. The theoretical calculations undertaken by simulating lead interaction with soil solution demonstrated that at

the Culloden battlefield site, there would be an initial period of lead dissolution, due to the corrosivity of soil solution. The model indicates however that while some mass would be lost from the musket balls, they would not dissolve completely. Instead they are likely to reach a thermodynamic equilibrium after approximately 170 years, whereupon lead carbonate minerals (cerussite, PbCO_3 and hydrocerussite, $\text{Pb}_2(\text{OH})_2\text{CO}_3$) are predicted to precipitate. These are typical lead corrosion products found in archaeological contexts and form a protective barrier layer which can prevent further corrosion. While the musket balls may not be lost to the archaeological record entirely, the mass loss predicted may be significant for this particular battlefield.

4.2 *Analyses of the Corrosion Products*

X-ray diffraction confirmed that cerussite is the major corrosion product as expected where rainwater with dissolved CO_2 is the main corrosive agent in soil.

4.3 *Lead Isotope Analyses*

Preliminary lead isotope analyses confirmed that the corrosion-layer lead can be used as a proxy for the lead metal of the musket ball with comparative results for Pb 208/206 and 207/206 better than ± 0.001 , i.e. within estimated analytical precision. This involved analysis of the metallic lead core and corrosion layer on a sliced section of a musket ball. Further analyses was undertaken only on corrosion surfaces.

The systematic results ($n = 17$) of balls selected to be representative of the size range (spanning pistol balls to musket balls) of the Killicrankie (Fig. 1b) archaeological assemblage ($n = 67$ of an estimated potential total of *c.* 1,000 fired) indicate provisionally on visual examination, that there are three groups of musket balls with similar lead isotope ratios (Fig. 2a). The overall range of data from Killicrankie compared with the UK Pb-isotope database of Rohl (1996) does not point to a single source; the detailed comparison with the Rohl (1996) data for Scotland is given in Fig. 2b.

5 Conclusion

It is confirmed that lead isotope analysis of lead corrosion products offers a means of characterising lead-rich archaeological materials and that this can be undertaken non-destructively using the laser ablation method.

Analyses of 17 representative musket balls from Killicrankie indicate that there are potentially three groups with significantly different isotopic ratios. However, understanding the significance of the groups and their distribution on the battlefield will require consideration of other archaeological data.

In order to recognise specific sources of lead used in the manufacture of musket balls recovered from Scottish battlefield sites, there is a need for historical information on Scottish lead production and also a more appropriate lead isotope database for historic lead sources, building on that of Rohl (1996) to include early European sources.

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