

The University of Surrey Ion Beam Centre

An EPSRC supported National Facility

The Ion Beam Analysis Laboratory

Report on the composition of two Pb samples

For Roger Webb, IBC

G469, Job No. 3172

22nd May 2012, C.Jeynes & G.W.Grime

Samples and Purpose of Analysis

Samples arrived 18th May 2012 from Roger Webb. One sample may be from the Jordan Codices (??), the other is a convenient "modern" control sample; we are looking for characterisation, both with 5 MeV alphas from ^{210}Pb disintegration and from trace element analysis using PIXE. The PIXE is reported here.

Conclusions

Large amounts of Sb and Sn are detected in the "old" sample, with strongly enhanced transition metal content and heavy chloridation of the surface. For more details see the Appendix.

Analysis

Data were collected using OMDAQ, and fitted with WiNDF. The particle detector was not used.

NDFv9.3e was used to fit the data (N. P. Barradas and C. Jeynes, "Advanced physics & algorithms in the IBA DataFurnace", *Nucl. Instrum Methods Phys. Res., Sect. B*, **266** (2008) 1875-1879).

Results

(For experimental setup and detailed results and discussion, please refer to the Appendix).

APPENDIX

Depth Profiling by Ion Beam Analysis

This work was done using a 2MV Tandetron accelerator from High Voltage Engineering Europe, commissioned summer 2002 at the University of Surrey Ion Beam Centre. This machine is capable of generating proton beams up to 4MeV and alpha particle beams of up to 6MeV ([Simon et al: Nucl.Instrum.Methods 2004: B219-220, 405](#))

Rutherford backscattering spectrometry (RBS) is an accurate, powerful and general thin film depth profiling technique typically carried out with 2 MeV He beams. Higher energy and proton beams are typically used for depth profiling thicker films, and for enhancing sensitivity to light elements with non-Rutherford elastic backscattering (EBS). Hydrogen can be depth profiled using elastic forward recoil spectrometry (FRS, also known as ERD: elastic recoil detection). Deuterium can also be depth profiled using nuclear reaction analysis (NRA) with a ^3He beam. Particle induced X-ray emission (PIXE) has little depth resolution but can unambiguously identify elements and analyse for trace elements with detection limits approaching $\mu\text{g/g}$. Particle induced gamma-ray emission (PIGE) is a form of NRA particularly valuable for lighter elements present in bulk materials at a trace level: F, Na, Al, Si.

The depth profiling beamline is equipped with a 6-movement goniometer from Arun Microelectronics Ltd, commissioned autumn 2002. This instrument is capable of loading entire 100mm wafers through a load lock, of channelling in arbitrary directions on a single crystal, and of high depth resolution (glancing beam incidence geometry). Both backscattering and forward recoil detectors are fitted. The target chamber has a base vacuum below 1 nbar.

The microbeam beamline was commissioned summer 2002. It has a magnetic quadrupole triplet lens and associated equipment from Oxford Microbeams Ltd, and can focus the beam to about 1 micron. The beam can be scanned over about 2mm giving trace and minor element mapping with PIXE and 3D depth profiling with RBS/EBS using the OMDAC and DAN32 software ([Grime & Dawson, Nucl.Instrum.Methods 1995: B104, 107](#)) which is based on the GUPIX code ([Blaauw, Campbell et al, Nucl.Instrum.Methods 2002. B189, 113](#)) Various sample stages are available including a cold stage, a goniometer, and a stage suitable for ion beam induced current (IBIC).

The external beamline was commissioned May 2004 and also has a magnetic quadrupole triplet with a thin window so that a focussed and scanned ion beam can be passed into air to analyse large, delicate or wet samples by PIXE, RBS/EBS and PIGE.

Depth profiles can be extracted automatically from RBS, EBS, ERD and NRA spectra using the Surrey IBA DataFurnace software ([Jeynes et al J.Phys.D, 2003: 36, R97, \[www.surreyibc.ac.uk/ndf\]\(http://www.surreyibc.ac.uk/ndf\)](#)). We have validated the accuracy of this code against a certified standard sample ([Boudreault et al Surf. Interface Anal. 2002: 33, 478](#)). The code is also validated by an international intercomparison ([Barradas et al Nucl.Instrum.Methods 2008: B266, 1338](#)). DataFurnace v9 ([Barradas & Jeynes Nucl.Instrum.Methods 2008: B266, 1875](#)), can also now handle PIXE data (with other IBA data) self-consistently ([Pascual-Izarra et al, Nucl. Instrum.Methods 2007: B261, 426](#)) and more correctly than GUPIX.

Where the DataFurnace fit is *good* the fitted profile is *valid* (but not necessarily true!). In the analyses we will point out the limitations of the results due to counting statistics, finite energy and depth resolution, and other systematic errors. Profiles are always given as layer structures. We systematically use *Occam's Razor* ("minimise your assumptions") to be objective about how much information is really in the data: in particular the extracted layer structures tend to be as *coarse* as the data will allow, and the discontinuous profiles we always show are due to the finite energy and depth resolution of the technique and can be seen as an expression of these.

Complete data sets are archived and can be re-analysed on request. In particular, a rigorous statistical evaluation of the uncertainty of the depth profiles can be obtained with the Bayesian techniques natural to the DataFurnace implementation. We have an interest in accurate work with rigorous evaluation of uncertainties, and are always interested in joint publication.

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Samples and Purpose of Analysis

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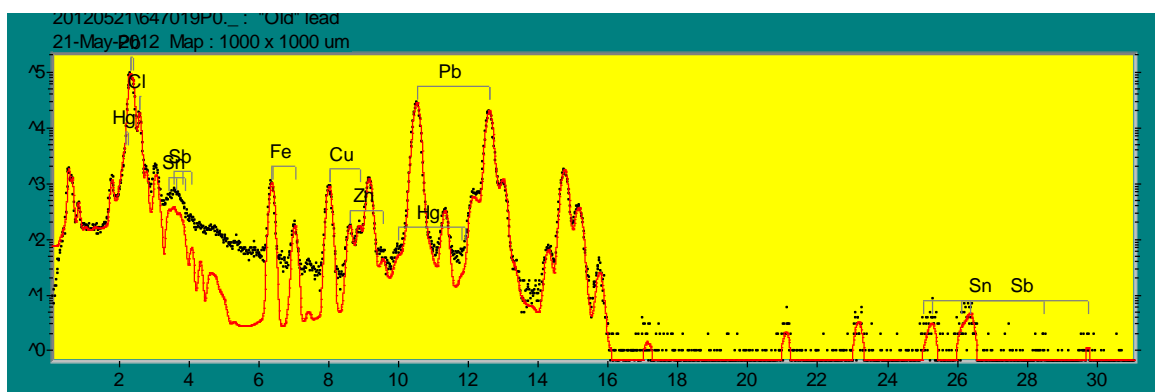
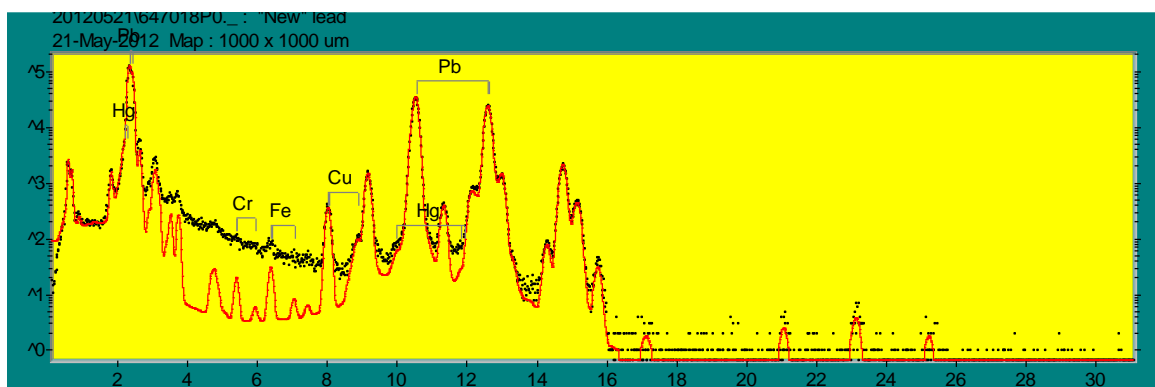
Analytical Conditions

2.530 MeV $^1\text{H}^+$, 21st May 2012. Beam current was ~500 pA, nominal beam size 2 μm .

The PIXE detector was at 45° to the beam in the IBM geometry. It had a filter of 130 μm Be.

Beam incident in a near-normal direction.

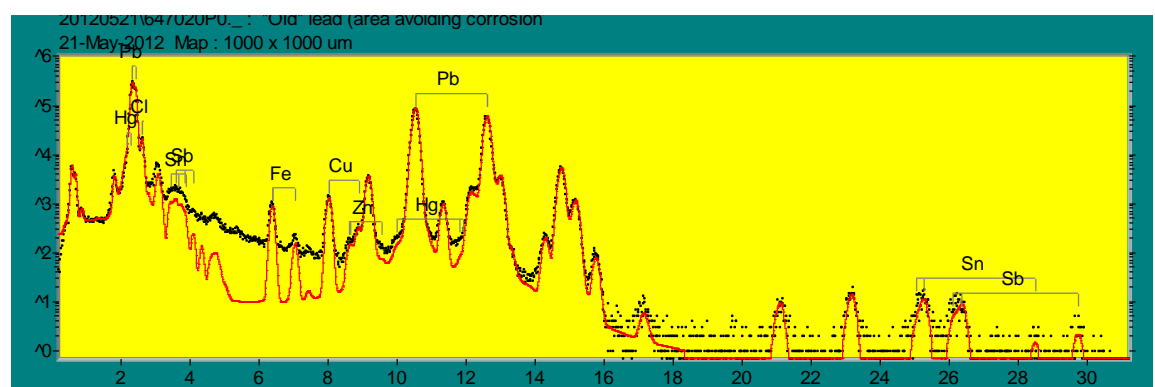
Results

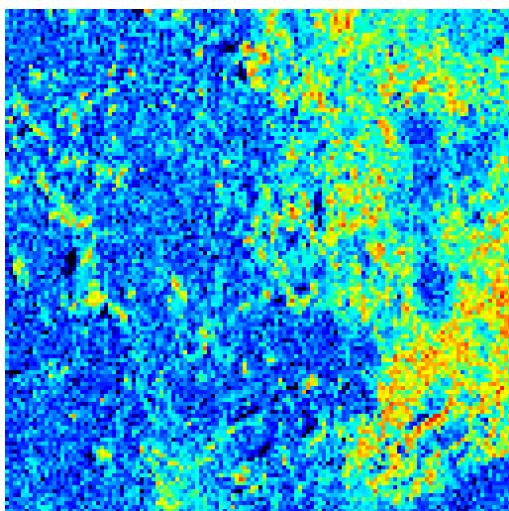


New lead

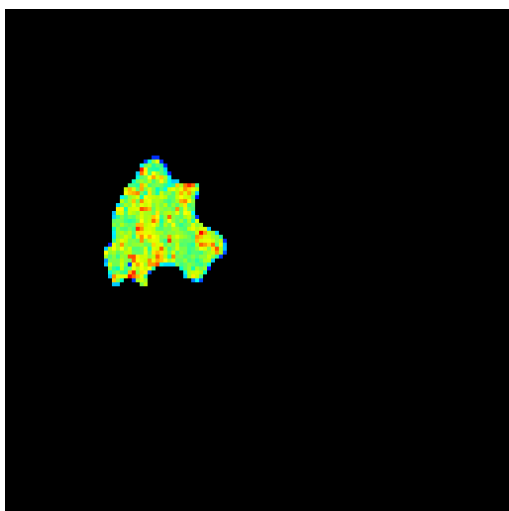
"Old" lead, full area

"Old" lead, selected area





Map of Cl signal: "Old" lead, full area

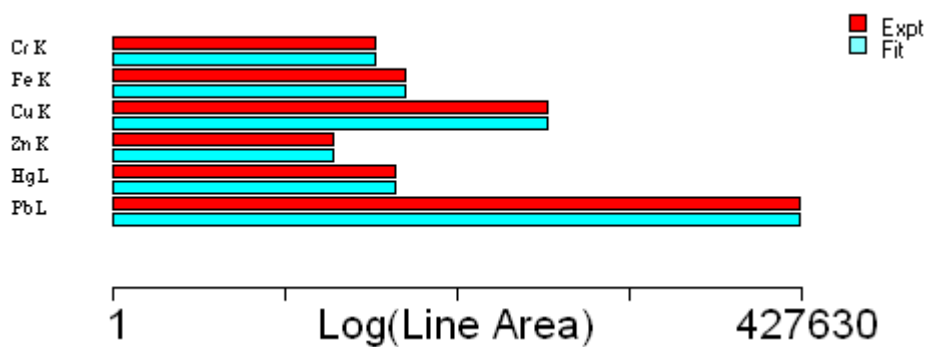


Map of Cl signal: "Old" lead, selected area

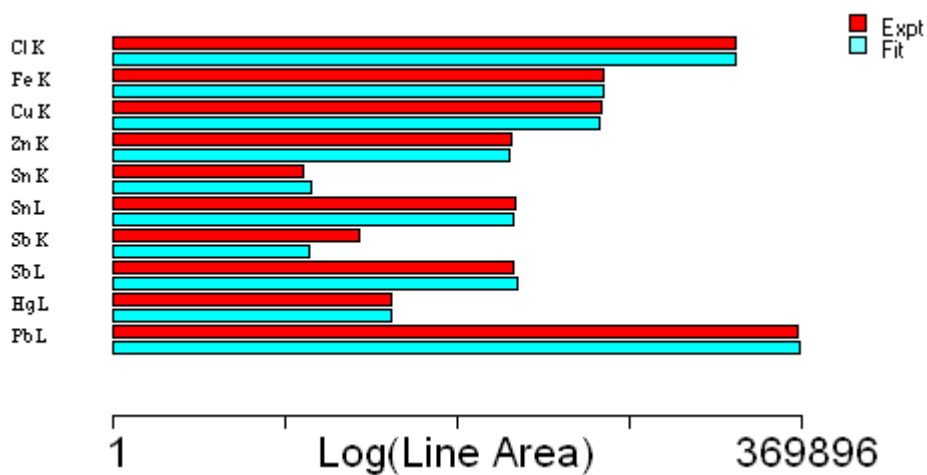
Table 1: Quantitative composition of lead samples

Sample	Parts per million (atomic)							
	Cr	Fe	Cu	Zn	Sn	Sb	Hg	Pb
"New" lead	212	377	6017	114	0	0	452	992830
"Old" lead	0	12695	14284	2921	3256	3760	433	962652
"Old" lead	0	5225	9726	887	4454	5899	438	973372

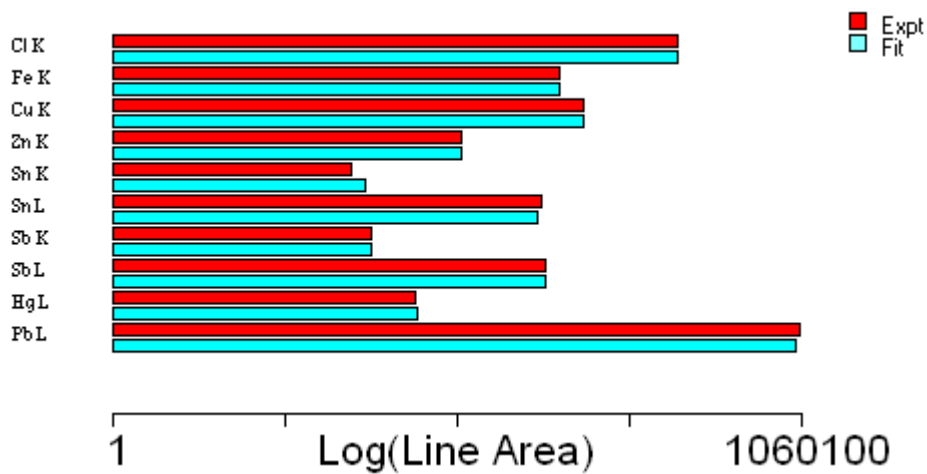
Sample	Uncertainties (ppm atomic)							
	Cr	Fe	Cu	Zn	Sn	Sb	Hg	Pb
"New" lead	87	79	144	78			131	1986
"Old" lead		178	200		326	376	121	2888
"Old" lead		89	117	63	223	295	96	1947



Sample#18: "New" lead



Sample#19: "Old" lead



Sample#20: "Old" lead

Conclusions

The fits to the data are good, so the confidence is good.

There appears to be a fixed "Hg" signal associated with the Pb: perhaps this is an extra line excited by the proton beam?

The corrosion products on the surface of the "Old" lead sample are associated with chlorine, with enough Cl to give 42 nm equivalent thickness on average in the analysed area. Note that the quantity of Cl is very non-uniform and thus it will be much thicker in some areas.

The "Old" and "New" lead samples are quite different, with the "Old" sample having 0.1at% Zn and significant quantities of Sb and Sn. The corrosion products (chlorides) on the "Old" sample probably contain lots of transition metals (Fe, Cu, Zn) since these are reduced in the selected area. Note that the heavy metals (Sn, Sb) are *increased* in the selected area, as expected from extra absorption in the L lines (not much weight is given to the K lines which have a very high statistical uncertainty).

Table 2: Quantitative composition of lead samples

Sample	NaCl equiv. thickness	Parts per million (atomic)						
	nm	Fe	Cu	Zn	Sn	Sb	Hg	Pb
"New" lead	0	377	6017	114	0	0	452	992830
"Old" lead	42	12695	14284	2921	3256	3760	433	962652
"Old" lead (selected area)	25	5225	9726	887	4454	5899	438	973372

Sample	Uncertainties (ppm atomic)						
	Fe	Cu	Zn	Sn	Sb	Hg	Pb
"New" lead	79	144	78			131	1986
"Old" lead	178	200		326	376	121	2888
"Old" lead (selected area)	89	117	63	223	295	96	1947