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Pb Distribution in Bones from the Franklin Expedition: Synchrotron X-Ray Fluorescence and Laser Ablation/Mass Spectroscopy

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Pb distribution in bones from the Franklin expedition: synchrotron X-ray fluorescence and laser ablation/mass spectroscopy

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Abstract Synchrotron micro-X-ray Fluorescence has been used to map the metal distribution in selected bone fragments representative of remains associated with the Franklin expedition. In addition, laser ablation mass spectroscopy using a 25 μm diameter circular spot was employed to compare the Pb isotope distributions in small regions within the bone fragments. The X-ray Fluorescence mapping shows Pb to be widely distributed in the bone while the Pb isotope ratios obtained by laser ablation within small areas representative of bone with different Pb exchange rates do not show statistically significant differences. These results are inconsistent with the hypothesis that faulty solder seals in tinned meat were the principle source of Pb in the remains of the expedition personnel.

1 Introduction

In 1845, Sir John Franklin set out with two ships, the *Erebus* and *Terror*, to discover the Northwest Passage from the Atlantic to the Pacific oceans. The expedition, last seen by Europeans on July 28, 1845, vanished with the loss of all 129 participants. The many missions sent out to search for survivors and/or evidence for the cause(s) of the loss are reported in detail elsewhere [1–3]. Interest in the mission and investigations into the fate of the crew continues to this day [4].

The graves of three members (John Torrington, William Braine, and John Hartnell) of the expedition who perished in January 1846 were discovered on Beechey Island [3, 5, 6],

while scattered bone fragments found on King William Island were identified as the remains of crew who perished later in the expedition [7, 8] while attempting to escape overland after the presumed loss of both ships. While autopsies attributed the first deaths to pneumonia with evidence for tuberculosis [5], deaths later in the expedition may be attributed to other causes such as botulism [9]; Mays et al. [4] found no evidence of either scurvy or tuberculosis in remains believed to be those of H.D.S. Goodsir, assistant surgeon aboard HMS *Erebus* and identified severe dental infection as a possible cause of death. Subsequent detailed analysis of the Beechey Island remains [10] showed very high concentrations of lead (Pb) in bone, tissue, and hair samples from these individuals. These results were taken to be indicative of chronic Pb poisoning as one of the possible causes of the failure of the Franklin expedition. This hypothesis is supported by the discovery of high Pb concentrations in the bones recovered during foot surveys on King William Island [11–13]; Kowal et al. [14] identified solder used to seal tins of the canned meat used on the voyage as the probable source of the Pb and supported this hypothesis with a detailed study of Pb isotope ratios in the original solder from the tins and those found in bone samples from the expedition. The high Pb content of the bones and the agreement between the Pb isotope ratios in the bones and solder were taken to be evidence that Pb poisoning from the solder was a major factor in the Franklin disaster.

Farrer [15] has challenged this assertion citing the following.

The Pb and Pb isotope ratios must be shown to be different from those in similar expeditions and the environment.

The Pb and Pb isotope ratios $^{207}\text{Pb}/^{206}\text{Pb}$ in bone, hair, and other tissues must be examined since Pb has a different half-life in each case (around 20 years in bone versus 20–40 days in tissue).

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Other known sources of Pb on the expedition must be taken into account, including the Pb piping used on the ships.

Notman et al. [6] found no signs of Pb poisoning during an examination of the Beechey Island burials using portable radiologic equipment.

Electrolytic protection of Pb in the solder by tin and iron would have prevented Pb dissolution in the cans.

Farrer's first objection appears to have been addressed. Although there are no comparable data from similar expeditions, Kowal et al. [14] provide data from nineteenth century Inuit and caribou bone from King William Island showing much lower Pb concentrations and significantly different Pb isotope ratios, as well as showing different isotope ratios from solder from 1880 tins. The former result rules out local contamination as a possible Pb source.

The second statement is consistent with the existing literature on the mechanism and kinetics of bone Pb/bone blood exchange [16–23]. The long half-life of Pb in bone is especially relevant to an understanding of the Pb content of the Beechey Island burials, which occurred early in the expedition.

The third observation suggests that there were other Pb sources on the ships. There was extensive Pb piping aboard the ships and M'Clintock [2] reports finding Pb sheeting as part of the cargo of a boat, which was apparently being dragged overland by members of the expedition. In addition, the high levels of Pb in the hair samples reported by Kowal et al. [14] would be better indicators of environmental exposure to Pb rather than ingestion [24], and may be indicative of Pb from sources other than the solder.

Elements such as Sr and Pb are incorporated in bone during remodeling [19] and are taken to be indicative of diet and Zn might be included as dietary indicator [20]. Modern Pb values vary widely but concentrations in the order of 3 to 30 ppm might be expected [21]. The levels reported in remains from the Franklin expedition are consistent with neurological effects which may have contributed to the failure of the mission [9, 22, 23]. However, anomalously high Pb was not uncommon in the eighteenth and nineteenth centuries [24–27]. Thus, the essential question is whether the Pb bone isotope ratios reported by Kowal et al. [14] could be achieved in the space of a few years at most if the sole Pb source on the expedition was from the tins and was sufficient to swamp preexisting Pb isotope ratios. The existing literature suggests a longer time interval would be required.

In reference to Kowal's reliance on isotope ratios [14], Farrer [15] points out that isotope ratios may be used to exclude possible sources but cannot identify specific sources with certainty citing [29], where ratios around 0.847 for $^{207}\text{Pb}/^{206}\text{Pb}$ are reported for samples from several sources around Turin, virtually identical to those from the tins [14].

The last two of Farrer's arguments are weak. Notman et al. [6], using portable X-ray equipment, would not have

detected Pb in the ppm range. In addition, the solubility of Pb would be greatly enhanced if chloride ion was present, since formation of PbCl^+ would make the Pb electrochemically active.

Kowal et al. [28] have suggested that the variability in their isotope ratio results may be due to the presence of Pb from exposure previous to the Franklin mission and that the bulk analytical techniques used further masked any minor contributions from Pb exposure before the expedition.

This study, accordingly, has as its principle objective: to determine if interrogation of small regions within bone samples from the Franklin expedition using micro X-ray Fluorescence and small spot laser ablation analysis will yield Pb results consistent with Kowal's [14] assertion that the excess Pb is primarily due to dissolution from the tins.

Synchrotron micro-X-ray Fluorescence Analysis (SXRF) is a technique, which has been shown to be effective for interrogation of bone [30, 31] to elucidate the spatial distribution of Pb, and other metals, within the bones; here our expectation is that an influx of new Pb would appear as an enhanced Pb signal in the regions that exhibit the most rapid uptake, such as the trabecular (spongy) bone. Second, we compare isotope ratio data obtained by small spot laser ablation mass spectroscopy to examine isotope ratios in different limited areas within individual bones. Local isotope ratios, especially those obtained from mineralized cortical bone, that differ from the tin solder ratios would be indicative of multiple (nontin) lead sources.

Inductively coupled plasma mass spectroscopy may be used to investigate isotopic ratios at concentrations as low as picograms per gram [32]. Laser ablation mass spectroscopy provides an alternative technique for isotopic analysis of solid samples [33] with a sufficiently small analysis area as to be essentially nondestructive; this technique has low detection limits, the parts per million range can be realized easily [34].

Given the long half-life of Pb in bone ($t_{1/2}$ 20–40 years for compact bone) and the comparatively small volumes involved in the remodeling process it should be possible to detect isotope ratios in areas representative of pre-voyage Pb deposition and/or Pb from sources other than solder during the exploration (such as Pb in drinking water in contact with Pb piping) using techniques capable of producing reliable analysis of small, restricted areas within the available bone samples.

If the hypothesis that Pb from faulty solder in the tinned meat taken on the voyage lead to increased Pb in the bones of the expedition members, increased Pb should be found at the bone margins and within the spongy (trabecular) portion of the bone where the kinetics of exchange are most rapid. This hypothesis would be strengthened if there were significant differences in Pb isotope ratios throughout the bone.

2 Experimental

XRF imaging was obtained from one Beechey Island bone sample (vertebra from the John Hartnell burial, January 1846) and two fragments of tibia from the King William Island fragments (presumed death date 1848, collected in 1983). The Beechey Island material, recovered from burial in permafrost would contain more of the organic portion of the bone than the King William Island material which had been exposed on the surface for over a century. In addition, XRF images were obtained for a $820 \times 150 \mu\text{m}$ segment of a tooth recovered from the Stirrup Court Cemetery, Township of London, Ontario, Canada [35]. This is a mid-nineteenth century cemetery, and provides material contemporaneous with the Franklin expedition.

XRF maps of the elemental concentrations in the bone and tooth samples were obtained at Brookhaven National Laboratory (BNL) National Synchrotron Light Source (NSLS) beam line X26A (details for this beam line and software used may be found at <http://www.bnl.gov/x26a>). This beam line is a scanning X-ray microprobe facility. It provides monoenergetic X-ray beams with energies from about 4 to 28 keV. The samples were used as received at BNL. X-ray focusing mirrors are used to produce a beam size at the sample with dimensions of $7 \mu\text{m}$ in the vertical and $10 \mu\text{m}$ in the horizontal. The X-rays are detected with both energy dispersive multielement germanium and silicon-drift detectors. Detection limits are Z dependent and are around 1 fg for Pb, iron (Fe), copper (Cu), and zinc (Zn). Maps are made by accumulating data point-by-point as the sample is moved past the beam spot. The intervals between points were determined by the size of the maps and available analysis time at the NSLS and were in the region of 30–50 μm . The dwell times were usually around 2–3 s. While SXRF can be made quantitative when calibrated using suitable standards, the variable density within teeth makes results obtained in this way semi-quantitative. Concentration values were estimated by comparing the unknown spectra to those obtained from a National Institute of Standards and Technology Standard Reference Material 1944, New York/New Jersey Waterway Sediment and from a specially prepared standard of 1200 ppm lead acetate in a plaster-of-Paris matrix. Pb concentrations found from integrating data over the area of the maps were generally consistent with bulk measurements reported by Kowal et al. [10]. In one case the value found from the map was much lower than the bulk measurement. This result shows that the lead concentration varies on a micro scale from point-to-point in the bone. Since Pb is the focus of this work quantitation has been attempted only for this element.

Note that since the Pb L_{α} emission line overlaps the arsenic K_{α} X-ray emission line the presence of Pb was confirmed by tuning the excitation energy below that used to excite the Pb L_{α} . Each of calcium Ca, Fe, Pb, Cu, and Zn

Fig. 1 Rep representative bone fragments (a) tibia from King William Island (1848), (b) vertebra from Beechey Island (1846), and (c) vertebra mounted in X-ray beam; the light spot on the bone indicates the region of the XRF map. Regions characteristic of compact and trabecular bone as well as onne Harversian canal are shown

were detected in all of the bone samples in addition Br was detected in the King William Island sample.

A fragment of tibia representative of the King William Island remains, fragments of the Hartnell vertebra, and the experimental set-up showing the approximate area studied for the Hartnell vertebra are shown in Fig. 1.

The laser ablation ICP/MS (inductively coupled plasma/mass spectroscopy) was carried out at the Great Lakes Institute for Environmental Research Metals Laboratory at the University of Windsor, Windsor Ontario using a ThermoElectron Model: X7-II ICP/MS with a Quantronix Model: Integra C Type: Ti:sapphire based laser. The 25 μm diameter circular spot was analyzed, with one analysis per second while the sample was moved at 5 μm per second for 15 minutes. ^{203}Tl and ^{205}Tl mass standards were included in each run to ensure accurate assignment of the Pb isotopes. No effort has been made to obtain quantitative concentrations in the absence of exactly matched standards and problems associated with the variable density of the substrate. Pb isotope ratios are sometimes used for source identification; in addition, they allow direct comparison with Kowal's [14] results.

One bone sample collected at the King William Island site, and hence representative of deaths presumed to be no earlier than 1848 was a tibia fragment supplied by Kowal (Fig. 2). Three laser scans were carried out, one on the outside, one in the middle and one in the interior of the bone. Two samples from the Beechey Island burials (1846), a fragment of radius (John Torrington), and clavicle (William Braine) also supplied by Kowal, were similarly analyzed.

To test intrabone variations in Pb isotope ratios, the data collected from three regions (outer, middle, and interior of bone) were compared using a Kruskal–Wallis one way analysis of variance (ANOVA) on ranks because the data were not normally distributed. No intra-bone differences

Fig. 2 Summed X-ray spectrum from the Beechey Island vertebra (11846)

were detected for any of the isotope ratios ($p = 0.110$). Therefore, the average Pb isotope values from each bone scan, which contained over 1,000 sampling points per bone, were used to compare Pb isotope values between individual bones. A Kruskal–Wallis ANOVA on ranks was followed by Dunn’s test in instances for which the Pb isotope values from the bones of men who died in 1846 ($n = 6$) differed from those of men who died in 1848 ($n = 3$) or from tin can solder ($n = 10$). The isotope ratios for tin can solder were calculated from data presented in Kowal et al. [14].

3 Results and discussion

A SXRF spectrum obtained from the Hartnell vertebra (buried 1846 on Beechey Island) is shown in Fig. 2. This result is typical of those obtained from all the bones reported here and illustrates the ability to collect information for many elements during a single measurement.

The SXRF maps obtained from selected bone fragments from the Franklin expedition are shown in Figs. 3a–c; the SXRF maps of the tooth (Stirrup Court mid-1800s) are shown in Fig. 3d. Individual metals are displayed using a color scale based on the maximum concentration of the metal; the scale is not normalized in such a way as to allow direct comparison of the concentrations of different metals. While it has been suggested that a detailed study of the Haversian canals in bone may provide a chronology of Pb accumulation [36], the existing literature [16–23] on the kinetics of Pb/bone exchange make it clear that the Pb distribution patterns within bone will provide a realistic chronology of uptake. The significance of the distribution of other metals must be uncertain, though the Beechey Island materials (Fig. 3a) were from bodies buried in the permafrost and so would yield more reliable information.

Elements other than Pb that appear in Fig. 3 are of minor interest. The Ca images show the densest bone regions and are useful for this reason; the elements bare passing mention. Fe probably indicates blood, and Cu may be suggestive of inflammation [37]. Zn is a normal trace component of periodontium [38] and bone, and is presumed to have a role in bone formation. It has been found associated with osteons and Haversian canals [36]. The King William Island (Fig. 3c) fragment is rich in Br, which might reasonably be associated with a marine diet [39].

The results do show a general, unambiguous Pb enrichment, consistent with previous observations. All the Pb maps show this metal to be widely distributed throughout the samples with no local enrichment, which might be indicative of increased ingestion. In addition the semiquantitative SXRF analysis of the Pb concentration yielded results between 100 and 200 ppm.

In the tooth from Stirrup Court (Fig. 3d), Pb was found in the cementum region, which is defined by the Zn image [40]. This result is also demonstrative of the ability of synchrotron SXRF to produce element maps in hard tissue and helps show the extent to which Pb is ubiquitous in bone contemporary with the Franklin material.

The wide distribution and high concentrations of lead in the measured bones is indicative of a long-term exposure before the start of the expedition. The uptake of Pb in bone is known to be slow [28] and exposure to Pb solely during the expedition is inconsistent with our observations. Pb ingested during the expedition would be expected to appear close to the bone surface and possibly in trabecular bone. We also note that examination of a bone section obtained from the Royal Naval Hospital in Antigua at the Canadian Light Source showed lead distributions similar to the observations reported here [31].

Fig. 3 XRF maps of regions from (a) Beechey Island vertebra (1846), (b) King William Island tibia (1848), (c) lateral side view of King William Island tibia (1848) and (d) tooth from Stirrup Court (mid-1800s). The areas mapped were: (a) vertebra 2×2 mm, (b) tibia 8×12 mm, (c) lateral tibia 2×3 mm, and (d) tooth 150×820 mm. The approximate regions for the laser ablation scans are shown on the King William Island Ca image

Table 1 shows the isotope ratios in the outer, middle and inner scans in individual bones given the different kinetics involved in each portion of the bone this result is consistent with a lifetime Pb uptake from the same or very similar sources. This is especially true of the middle of the bone scans which are in the densest portion of the bone which is most resistant to exchange with new Pb.

Table 2 presents a comparison of the pooled Laser ICP/MS isotope ratios for all samples surveyed. The very small volumes interrogated by the laser ablation show small but statistically significant differences from the ratios reported by Kowal et al. [14]. The differences may be due to the small sampling volume used. There is, more importantly, no statistically significant difference between different regions within individual bone fragments nor between bones for the Beechey Island remains and the later more heavily weathered King William Island material.

The results of both the Synchrotron XRF and Laser ICP/MS data are consistent with significant Pb exposure prior to the 1845 expedition.

4 Conclusions

The micro-X-ray fluorescence Pb maps show small local variations in Pb concentration; however, the Pb distribution is essentially uniform as might be expected from lifetime Pb ingestion. There is no evidence for a sudden massive increase in Pb during the latter part any individual's life.

There is no significant difference between the Pb isotope ratios throughout individual bones. The known kinetics of Pb uptake in bones clearly indicate that this result can only be achieved as a result of very long exposure to lead sources having the same or very similar isotope composition. The pooled results show no internal isotope differences

Table 1 Lead isotope ratios (mean $\pm$ SE) for three regions within each bone: inner, middle, and outer. Mean ($\pm$ st. dev.) ratios from individual bone scans (782 to 1220 scans per bone) provide information about the low variability in isotope ratios within and among the samples. Data from all three regions within each bone type were pooled to compare

overall differences within bones since there were no differences among sampling regions ($p = 0.11$). One-way ANOVA failed to detect differences among the three types of bone (p values shown in bottom row)

Bone type	Region	Lead isotope ratio		
		207/206	208/206	208/207
Tibia (1848)	Inner	0.817 $\pm$ 0.132	2.088 $\pm$ 0.428	2.577 $\pm$ 0.453
	Middle	0.844 $\pm$ 0.112	2.123 $\pm$ 0.356	2.532 $\pm$ 0.384
	Outer	0.839 $\pm$ 0.127	2.189 $\pm$ 0.410	2.630 $\pm$ 0.451
Radius (1846)	Inner	0.778 $\pm$ 0.611	1.861 $\pm$ 1.324	2.337 $\pm$ 1.941
	Middle	0.800 $\pm$ 0.098	2.006 $\pm$ 1.378	2.517 $\pm$ 1.560
	Outer	0.812 $\pm$ 0.147	1.994 $\pm$ 0.658	2.501 $\pm$ 1.005
Clavical (1846)	Inner	0.701 $\pm$ 0.129	1.922 $\pm$ 0.343	2.466 $\pm$ 0.456
	Middle	0.803 $\pm$ 0.091	1.898 $\pm$ 0.236	2.307 $\pm$ 0.319
	Outer	0.818 $\pm$ 0.185	2.093 $\pm$ 0.343	2.590 $\pm$ 0.417
Pooled data	Inner	0.796 $\pm$ 0.010	1.966 $\pm$ 0.048	2.473 $\pm$ 0.053
	Middle	0.817 $\pm$ 0.008	2.023 $\pm$ 0.034	2.471 $\pm$ 0.038
	Outer	0.823 $\pm$ 0.008	2.092 $\pm$ 0.036	2.578 $\pm$ 0.037
<i>P</i> value		0.110	0.196	0.193

Table 2 Summary of statistical analyses for Pb isotope ratios presented. Means followed by different lowercase letters are significantly different (p values reported in bottom row)

Year of burial	Source	Sample size (# of scans)	Isotope ratio					
			207/206		208/206		208/207	
			Mean	SE	Mean	SE	Mean	SE
1846	Beechey Is. 1	3	0.799 b	0.007	1.967 ab	0.024	2.47 ab	0.032
1846	Beechey Is. 2	3	0.804 b	0.003	1.978 b	0.007	2.47 b	0.009
1846	Beechey Is. avg.	6	0.802 b	0.004	1.972 b	0.01	2.47 b	0.017
1848	King William Is.	3	0.833 a	0.003	2.132 a	0.008	2.58 a	0.009
Tins	Kowal et al. [14]	10	0.845 a	0.0003	2.085 ab	0.0008	2.46 b	0.0006
<i>p</i> value			0.044		0.011		0.042	

but there is a small but statistically significant difference from Kowal's data in the Beechey Island material; this result reflects the small volumes interrogated by our methods.

The distribution of Pb and Pb isotopes in both the well preserved Beechey Island remains and in the extensively weathered King William Island material fails to support the hypothesis that the principle source of Pb in the bones was the defectively soldered tins.

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