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Research Article

Insights into biogenic and diagenetic lead exposure in experimentally altered modern and archaeological bone: Synchrotron radiation X-ray fluorescence imaging

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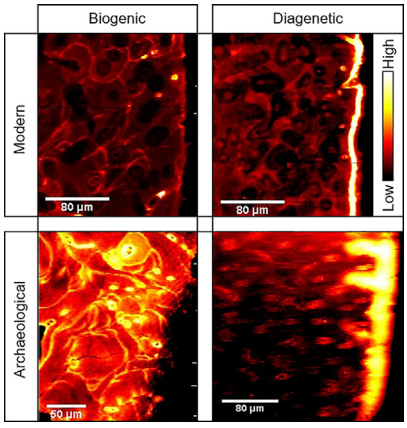
HIGHLIGHTS

- Pb contamination causes morbidity and mortality in past and present populations.
- Spatial patterns of bone Pb was measured in modern and archaeological samples.
- For modern bone Pb decreased in association with decreased Pb exposure.
- Different spatial patterning of Pb for biogenic vs. diagenetic uptake.
- Bones are under-utilized record of lifetime and postmortem Pb exposure.

GRAPHICAL ABSTRACT



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ABSTRACT

Bones represent a valuable biological archive of environmental lead (Pb) exposure for modern and archaeological populations. Synchrotron radiation X-ray fluorescence imaging (SR-XFI) generates maps of Pb in bone on a microstructural scale, potentially providing insights into an individual's history of Pb exposure and, in the context of archaeological bone, the biogenic or diagenetic nature of its uptake. The aims of this study were to (1) examine biogenic spatial patterns for Pb from bone samples of modern cadavers compared with patterns observed archaeologically, and (2) test the hypothesis that there are spatial differences in the distribution of Pb for diagenetic and biogenic modes of uptake in bone. To address these aims, this study used inductively coupled plasma-mass spectrometry (ICP-MS) and SR-XFI on unaltered and experimentally altered cadaveric bone samples (University of Saskatchewan, Saskatoon, SK) and archaeological bone samples from 18th to 19th century archaeological sites

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Skeletal microstructure
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Diagenesis
Biogenicity

from Antigua and Lithuania. Bone concentrations of modern individuals are relatively low compared to those of archaeological individuals. SR-XFI results provide insights into modern Saskatchewan Pb exposure with some samples demonstrating a pattern of relatively low Pb exposure with higher levels of Pb exposure occurring in bone structures of a relatively older age that formed earlier in life, likely during the era of leaded gasoline (pre-1980s), and other samples demonstrating a pattern of fairly consistent, low-level exposure. Results support hypotheses for the spatial distribution of Pb corresponding to biogenic vs. diagenetic uptake. Diagenetic Pb is mainly confined to the periosteal surface of each sample with some enrichment of cracks and sub-periosteal canals. This may be useful in the future for differentiating diagenetic from biogenic Pb accumulation, analyzing environmental contamination, and informing sampling strategies in archaeological or fossil bone.

1. Introduction

Given its grave and toxic health implications, its extensive exploitation by humans for millennia, and its environmental persistence, lead (Pb) is a significant contributor to morbidity and mortality among human populations (Lanphear et al., 2018; UNICEF and Pure Earth, 2020). Despite many government efforts to drastically reduce Pb exposure, it remains an important health concern worldwide, including in Canada (Juric et al., 2018; Ngueta et al., 2016; Safruk et al., 2017), especially with prevailing Pb pipe and paint infrastructure (Foley et al., 2011; O'Connor et al., 2018; Troesken and Beeson, 2003). The issue of Pb exposure has become an increasingly relevant topic in urban Saskatchewan, given concerns that a portion of residential water pipes rely on old lead-containing infrastructure and recent reports that Pb levels in tap water exceed the recommended limit of 5 μg/L (Health Canada, 2017).

Blood lead level studies primarily make up the Pb exposure literature on this topic (e.g., Egan et al., 2021; Health Canada, 2013; Safruk et al., 2017), though Pb has a relatively short half-life in blood (Rabinowitz et al., 1976). Bone represents a valuable, longer-term archive of Pb accumulation. During life, an estimated 90% to 97% of the total body burden of Pb is contained in the skeleton (Barry, 1975), with bones reflecting cumulative exposure on the order of years to decades. Given the propensity for skeletal remains to survive in the archaeological record, chemical analysis of Pb concentrations and Pb isotope ratios in archaeological bone can, in principle, provide insights into past Pb exposure and help contextualize exposure in modern populations. However, archaeological bone may also act as a post-mortem environmental archive of Pb exposure, diagenetically accumulating Pb from the burial environment that can overprint its lifetime (biogenic) signature (e.g., King et al., 2020; Wittmers et al., 2008).

Previous researchers using element mapping techniques (e.g., synchrotron radiation X-ray fluorescence imaging [SR-XFI], laser ablation-inductively coupled plasma-mass spectrometry [LA-ICP-MS]) of archaeological bone microarchitecture have interpreted a heterogeneously distributed pattern of Pb with enrichment of cement lines and central canal surfaces to be indicative of biogenic exposure, and Pb enrichment originating at the periosteal or endosteal surfaces, cracks, or large pores to be indicative of diagenetic contamination (Swanston et al., 2012; Rasmussen et al., 2019). This validation study aims to test this by contrasting the spatial distributions of Pb in modern bone samples from contemporary Saskatchewanian individuals and the patterns observed in archaeological individuals from Antigua and Lithuania. It was hypothesized that the biogenic pattern of uptake from modern bone will be consistent with what has been interpreted as biogenic archaeologically, with an Pb microdistribution reflecting population patterns and individual life histories of anthropogenic Pb exposure. Among mature to elderly modern Saskatchewanian individuals, it was hypothesized that higher Pb exposure would have occurred decades earlier, prior to widespread efforts to phase out Pb, and that the biogenic microdistribution of Pb in bone would reflect this. Second, this study aimed to experimentally test whether there are indeed spatial differences for biogenic and experimentally induced diagenetic Pb exposure in bone, and whether these differences correspond with what has previously been observed and interpreted archaeologically or paleontologically. The null hypothesis is that the two processes would not produce different spatial patterns of enrichment; diagenetic Pb, if permeating through the entire bone sample, may potentially enter via large pores and bind to osteogenic proteins and hydroxyapatite minerals rich in the canals and cement lines, mimicking the so-called "biogenic" pattern.

1.1. Skeletal Pb uptake

Human cortical bone contains an exterior periosteal surface and an interior endosteal surface (Fig. 1). Layers of primary lamellae develop on these surfaces during growth, to be gradually replaced by secondary osteons (or Haversian systems)—the basic cylindrical structure of cortical bone. Secondary osteons contain concentric lamellae and a central (or Haversian) canal for neurovascular structures, all bound by a hypermineralized cement line, i.e., the interface between osteons and surrounding interstitial bone (Schaffler et al., 1987; Skedros et al., 2005). Bone constantly remodels throughout an individual's life, a process in which secondary osteons form following localized osteoclastic bone resorption events (Frost, 1969). These resorption spaces are gradually filled in by forming osteons, which continue to develop into mature osteons. Bone surrounding intact osteons may consist of interstitial fragments of primary lamellae or secondary osteon fragments that survived focal remodeling events. Bone turnover rates vary according to bone element, biological sex, age or stage in the life course, and other life history variables (Cho et al., 2006; Fahy et al., 2017; Recker et al., 2009), though the timescale of bone remodeling is not yet fully understood. Research tracking radiocarbon in bone collagen suggests that femoral turnover rates range from 1.5–3% to 3–4% for adult males and females, respectively (Hedges et al., 2007).

While Pb, as a multivalent cation, is believed to substitute for calcium (Ca) in the hydroxyapatite mineral of bone and teeth, this is not a simple substitution, and more research is needed (Montgomery et al. 2010: 211). Pb can also bind to non-collagenous proteins such as osteopontin and osteocalcin (Pemmer et al., 2013) that are especially rich along the osteon canal surfaces and in the cement lines. During life, Pb is typically only incorporated into actively mineralizing surfaces of bone; then, following localized osteoclastic remodeling activity of bone, Pb can be released back into the bloodstream, where it can intrinsically act as a source of Pb exposure and become reintegrated into newly formed bone once more (Rabinowitz, 1991). Pb is often mobilized from bone at an increased rate in disease states such as osteoporosis (Nash et al., 2004; Silbergeld et al., 1988), or during pregnancy and lactation (Gulson et al., 2016; Manton et al., 2003). Diagenetically, Pb in the burial environment may absorb onto bone surfaces, diffuse into bone, substitute for Ca and recrystallize hydroxyapatite, and precipitate new phases in bone (Dudás et al., 2016).

2. Materials and methods

2.1. Samples

Modern human mid-diaphyseal (bone shaft) femoral samples were acquired from 14 individuals donated to the Body Bequeathal Program

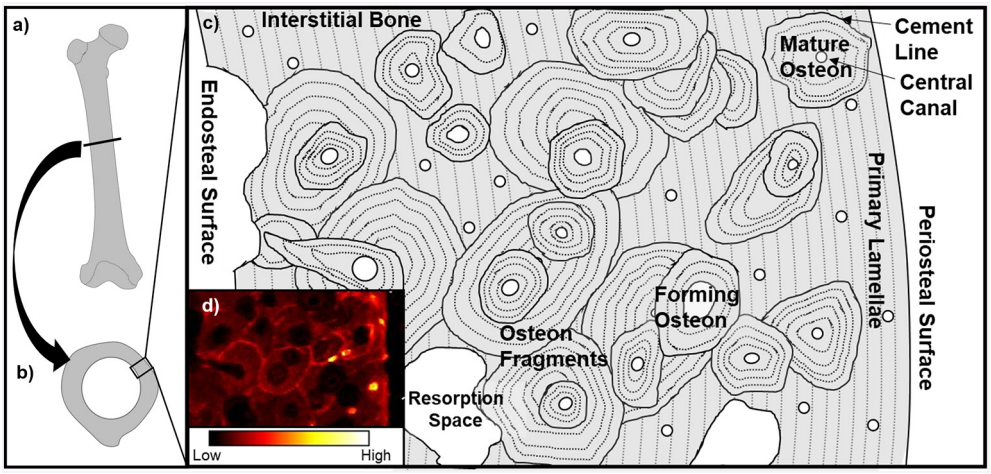

Fig. 1. Idealized schematic of a human femur (a), mid-diaphyseal (bone shaft) cross section (b), and cortical bone microarchitecture and remodeling in humans (c), with an SR-XFI map of Pb containing corresponding microarchitecture (inset; [d]). In the SR-XFI map inset, dark regions represent areas of low Pb uptake whereas bright red to yellow regions represent high Pb uptake. Note that in Pb map inset, the intensity of Pb does not necessarily correspond to age of structures. Age of structures can be relatively inferred on the basis of the microstructure superimposition; younger structures are superimposed on older structures, and interstitial and osteon fragments are relatively older structures. Swanston et al. (2018) provide a more thorough overview of timing inferences based on bone microarchitecture and calcium mineral density. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Department of Anatomy, Physiology, Pharmacology, University of Saskatchewan, Saskatoon, SK). This sample assemblage consisted of 8 males (aged 69–96) and 6 females (aged 53–97). The femur was selected for analysis because it reflects a longer turnover rate duration (Hedges et al., 2007), and thus a longer timeframe for lifetime Pb exposure. In keeping with the program anonymity standards, no information apart from age and sex were imparted for each individual. Biomedical ethics approval (BIO ID# 970) was obtained from the University of Saskatchewan.

Cortical bone samples from two archaeological individuals were also analyzed and compared with modern samples. One mid-diaphyseal fibular sample belonging to a 40–50-year-old male of European descent was acquired from a British Royal Navy Hospital Cemetery site in English Harbour, Antigua (c. 1768–1822), which represents a population with a documented history of high and sustained Pb exposure (Giffin et al., 2017). Pb was ubiquitous in the daily lives and industry of the British Royal Navy. In the Caribbean context, Pb in water cisterns and sugar and rum production equipment were likely contributors to the Pb burden of naval personnel (Varney et al., 2012). Previous analyses using SR-XFI, SR-X-ray absorption spectroscopy, and rare earth element (REE) concentrations (Choudhury et al., 2017; Giffin et al., 2017; Swanston et al., 2012) suggested that this sample was not significantly contaminated with diagenetic Pb.

An mid-diaphyseal femoral sample of cortical bone was also acquired from an adult female (1878–1939) entombed in an above-ground painted wooden coffin in the Tiškevičius (Tyskiewicz) stone family mausoleum in Kretinga, western Lithuania. This sample was selected to act as an archaeological example of pervasive diagenetic contamination with which to contrast the experimentally altered modern bone samples. It is presumed that the primary pathway of Pb diagenesis for this set of remains could be through leaded paint on the coffins in the mausoleum, increasingly mobilized by moist sea air.

2.2. Experimental diagenetic alteration

Mid-diaphyseal femoral cross sections approximately 5 cm in length were cut from cadavers using an autopsy saw. Diagenesis was experimentally simulated in half of each cadaveric sample by soaking the bone in an aqueous lead acetate ($Pb(CH_3COO)_2$) solution. This procedure aimed to mimic general mechanisms of Pb diagenesis caused by water in the depositional environment, including ion adsorption, exchange, and diffusion onto and into bone. The lead acetate concentration and the duration of the soak for this experiment was first determined through an ICP-MS pilot study on a cow femur; based on preliminary data, experimental conditions of a 200 μg/g (ppm) Pb concentration and a time period of seven days were selected because they resulted in a post-experimental bulk bone Pb concentration of 200 μg/g that was comparable with the bulk levels observed in the archaeological individual from Antigua also under study.

2.3. ICP-MS analysis of bone Pb concentrations

Bulk Pb concentrations were determined using 0.5 g of each cadaveric bone sample via inductively coupled plasma-mass spectrometry (ICP-MS). This portion of each sample was cut using a Buehler IsoMet low-speed saw using a diamond wafer blade. The blade was cleaned with 70% ethanol and rinsed with distilled water. The distilled water in the basket was changed between each sample to prevent trace element contamination between samples. Surfaces of samples were not abraded prior to analysis. Samples were ground into a powder using a Spex liquid nitrogen freezer mill (Lakehead University, Thunder Bay, ON). Components of the grinding apparatus were cleaned between samples with Sparleen 1 (powder) laboratory detergent in reverse osmosis (RO) water then rinsed thoroughly with RO water followed by a rinse with water further purified with a Millipore Synergy System. Components were dried manually with KimWipes. ICP-MS of the human cadaveric bone and diagenetically-altered cow bone was carried out at the Saskatchewan Research Council Environmental Analytical Laboratory using an Agilent 8800 ICP-MS with an Agilent ISIS discrete sampling system for sample introduction. The calibration is done using a linear curve fit produced by running standards run at 1 μg/L, 10 μg/L and 100 μg/L concentrations along with blank solutions. After the instrument is calibrated, a verification standard and blank are run every 10 samples and a blank subtraction was conducted when reducing the final data. Iridium (Ir) was used as an internal standard to monitor and correct for instrumental biases (Table S1 details additional ICP-MS parameters).

The bulk Pb concentration of the archaeological cortical bone sample from Antigua was previously determined with ICP-MS (Neptune, Thermofisher) at the Geological Sciences Department, University of Saskatchewan, Saskatoon, SK (detailed methods and results published

in Giffin et al., 2017; following laboratory procedures outlined in Stefanova et al., 2003; Jenner et al., 1990; Jackson et al., 1990).

The bulk Pb concentration of the archaeological bone sample from Lithuania was determined using solution ICP-MS (The Earth Resources Research and Analysis Facility [TERRA] of CREAIT, Memorial University, St. John's, NL) on a PerkinElmer Elan DRCII. Based on the method of Friel et al. (1990), five different multi-element solutions were used for external calibration (each containing a suite of different elements to correct for interferences) at concentrations aimed to be higher than the concentration of the samples analyzed. These solutions are analyzed at the beginning of the run, after a block of 8–10 samples plus calibration standards, and at the end. A blank solution is measured several times throughout the analytical run (beginning, after the calibration standards and at the end of the run) and a blank subtraction was conducted when reducing the final data. Sc, Re, Rh, and Th are used as internal standards to monitor for instrumental drift and matrix correction. The between assay variability was determined by comparing values from two internal standards, USGS T-143 and SRM1400, to the most probable or certified values (further parameters outlined in Table S1).

Pb concentration was also determined for the Lithuanian bone sample with a continuous raster along the sectioned surface from periosteum to endosteum via laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) using a Finnigan Element XR High resolution double focusing magnetic sector inductively coupled plasma mass spectrometer and GeoLas 193 nm excimer laser in the Micro Analysis Facility (MAF) in CREAIT at Memorial University, St. John's, NL. The LA-ICP-MS was tuned on the analysis days to maximum sensitivity and a ThO/Th below 0.5%. Standard-sample bracketing was carried out using NIST 610 as a calibration standard, and pressed pellets of SRM1400 (NIST Bone Ash, Pb = 9.07 ± 0.12 ppm) and SRM1486 (NIST Bone Meal, Pb = 1.335 ± 0.014) were used to determine Pb concentration accuracy throughout the analyses. The data presented are total Pb concentrations based on ^{208}Pb values and are based on a rolling average (n = 10) of the data points collected through the laser ablation raster (further parameters outlined in Table S2).

2.4. SR-XFI

To prepare all bone samples for SR-XFI, bone samples were sectioned into 1–2 mm thin sections using an IsoMet low-speed saw and a diamond wafer blade. No additional sample preparation was required. At the Advanced Photon Source (APS; Argonne National Laboratory, Lemont, IL) Sector 20-ID-B beamline, SR-XFI of the Lithuania individual was performed in August 2016 using a rapid scan mode and SR-XFI of the cadaveric bone and Antigua samples was performed in November 2019 and November 2020 (Table S3 outlines further parameters for each beamtime). It has been consistently demonstrated that confocal optics can optimize spatial resolution of element maps of bone by reducing the amount of fluorescence emitted from variable depths (Choudhury et al., 2016, 2017; Rauwolf et al., 2017). Confocal optics also enable optical, rather than physical, sectioning thereby minimizing the need for sample preparation steps such as grinding and polishing (Choudhury et al., 2016, 2017; Simpson et al., 2019). A polycapillary confocal optic was employed to reach a depth of 100–200 μm within each sample. Each sample was mounted onto a glass microscope slide with double sided tape, which was mounted onto a sample holder with double sided tape. The sample was placed in front of the beam with the periosteal surface of the sample oriented away from the detector. A 37 μm-thick sheet of aluminium foil was placed over the beam aperture to preferentially decrease Ca counts due to its lower photon energy. The scan areas for each sample were 2 mm × 2 mm, or 1.6 mm × 2.5 mm if the cortical envelope was thin, containing lots of trabeculae. Using multi-channel analysis (MCA), spatial data was simultaneously collected for Pb α and β, Ca, zinc (Zn), strontium (Sr), copper (Cu), and iron (Fe) to examine patterns of element localization for future research.

Scans were generated using ImageJ software with a Sector 20 input-output plug-in (Rasband, 1997–2018). A 0.5-pixel median filter was applied to improve the signal to noise ratio of images. A non-linear logarithmic calibration scale was used to normalize Pb counts. Brightness and contrast were adjusted to maximize visibility of bone structures enriched with Pb and ensure consistency between scans.

3. Results

ICP-MS results of bulk Pb for cadaveric bone are presented in Table S4. The procedural blank for Pb was <0.1 μg/L. Pb concentrations in the unaltered cadaveric bone samples range from 1.2 to 7.1 μg/g with a mean of 4.3 μg/g (±2.0). The mean Pb concentration for females is 3.5 μg/g (±1.9) while for males, the mean Pb concentration is 4.9 μg/g (±1.71).

The archaeological cortical bone sample from Antigua has a bulk bone Pb content of 253.9 μg/g (Table S4; Giffin et al., 2017). The archaeological cortical bone sample from Lithuania had a bulk Pb concentration of 125 μg/g (Table S4). The procedural blank was only 0.0325 μg/g and the within assay variability of Pb concentration was 0.17% based on a sample replicate. The percent errors were 5.2% and 4.6%, respectively. LA-ICP-MS analysis of the Lithuania sample revealed that the outer periosteal edge had a Pb concentration of 1201 μg/g and the interior to endosteal edge had a mean of 63 μg/g. Both SRM 1400 (5 ± 4 ppm, 2σ, n = 5) and SRM 1486 (1.6 ± 0.8, 2σ, n = 7) gave measured Pb concentrations that were consistent with certified values.

In Pb fluorescence maps of modern bone samples (Fig. 2), cement lines and central canals of osteons tended to be enriched with Pb relative to concentric lamellar layers of osteons. Some samples (e.g., Fig. 2e, f, h, i) demonstrated homogeneity in Pb across osteons while in other samples (Fig. 2a, d, g), interstitial bone and fragments from previously remodeled (older) osteons were typically more enriched in Pb compared to intact younger osteons.

SR-XFI maps of experimentally altered cadaveric bone samples (Fig. 3b, d) consistently demonstrated a thick band of Pb enrichment along the periosteal edge of the sample. Fig. 3d exhibits Pb enrichment within an interior space. Images from diagenetically-altered samples exhibit Pb enrichment in small pores near to the periosteal surface; by contrast, these features were lacking in each image's unaltered counterpart (Fig. 3a, c). The Pb map of the Antigua sample (Fig. 3e) demonstrated vast heterogeneity, with cement lines and central canals of osteons and osteonal fragments disproportionately enriched with Pb. Certain osteonal structures are more enriched with Pb than others. Post-mortem cracks are visible on the Pb map as dark lines with no Pb signal. The Lithuania sample (Fig. 3f) demonstrates a remarkably high intensity of Pb at the subperiosteal edge of the bone sample. The Pb signal permeated past the subperiosteal surface via cracks and pores.

4. Discussion

4.1. Lifetime Pb exposure

The biogenic pattern of Pb uptake observed in the modern bone samples is consistent with general patterns observed in archaeological samples. Osteonal cement lines and central canal surfaces are disproportionately enriched with Pb relative to other structures. Based on observations from archaeological bone, it was hypothesized that the differential enrichment of osteons and interstitial bone of different "ages" would reflect individual histories of Pb exposure as influenced by population patterns of anthropogenic Pb use. Because the modern individuals sampled in this study consist of mature adults, and because bone can sequester trace elements for up to several decades, it was hypothesized that older structures were expected to exhibit relatively higher levels of Pb, and that the bone Pb concentrations and SR-XFI scans would reflect this.

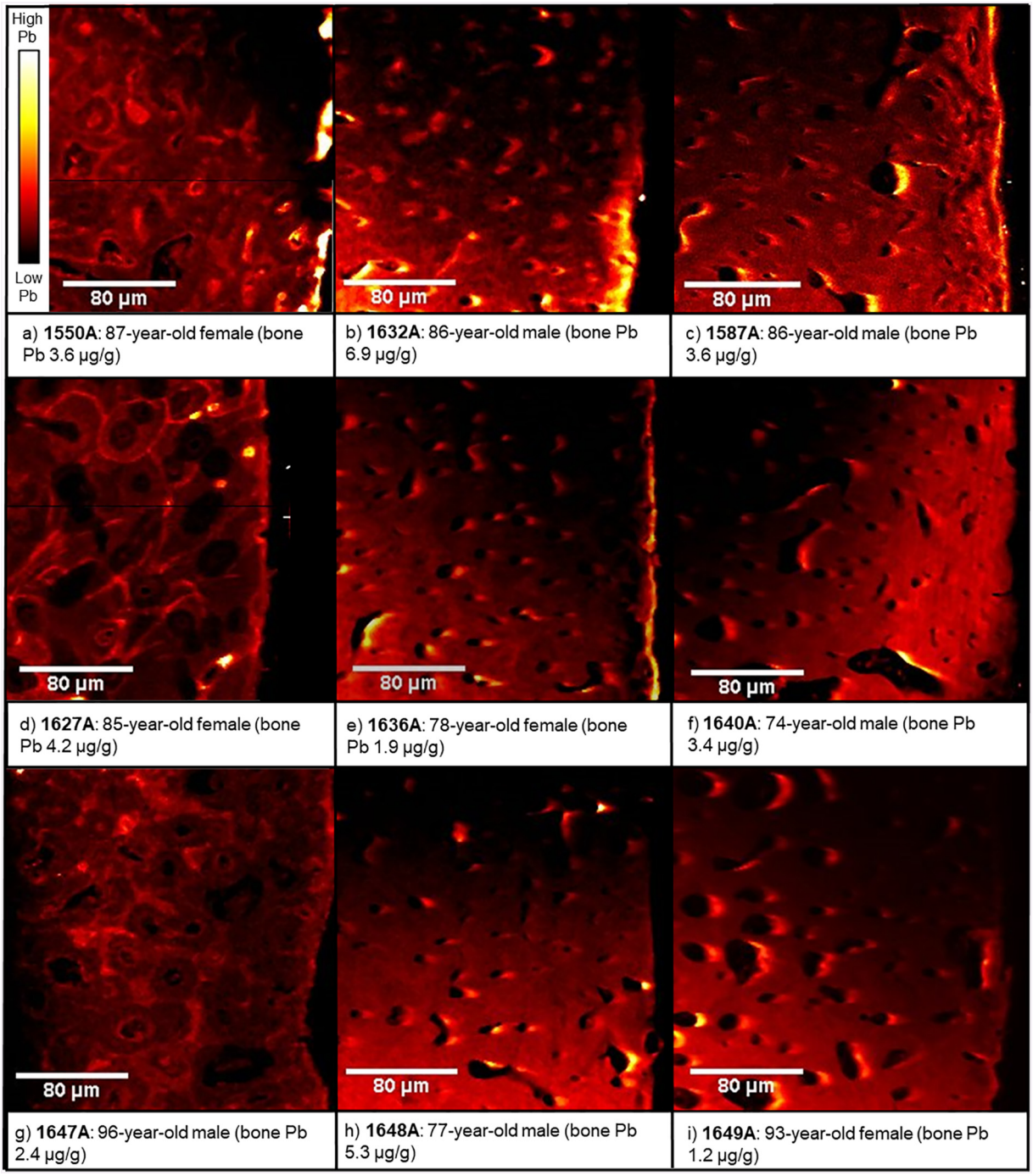

Fig. 2. SR-XFI maps of biogenic Pb microdistributions in bone samples from modern cadaveric bone. Images in left column scanned in November 2019; scans central and right columns scanned in November 2020 (Table S3).

From the 1920s, tetraethyl lead was a common additive to gasoline and was only prohibited for on-road vehicles in Canada in 1990 (Nriagu, 1990; Health Canada, 2013: 20). This had toxic health implications for the general public in the 20th century (Boeckx et al., 1977; Zhang et al., 1994) though its prohibition has drastically reduced atmospheric Pb levels (Shotyk et al., 2016). During this time, Pb was also widely used in plumbing infrastructure (pipes, fittings, solders), which can gradually contaminate residential drinking water (Health Canada, 2013; Lytle and Schock, 1996; Safruk et al., 2017). Degraded leaded paint and contaminated soil particles would have also contributed to household dust (Lanphear and Roghmann, 1997; Health Canada, 2013). Studies on non-occupationally exposed Canadians dating to, or immediately postdating, the era of higher Pb use found that modern bone Pb concentrations ranged from 8.47 to 29.8 µg/g (Gamblin et al., 1994; Kowal et al., 1991; Samuels et al., 1989). Comparatively, the mean bone Pb concentration of 4.3 µg/g (± 2.0) observed among these modern Saskatchewan individuals marks a relative temporal decrease in Pb exposure. This decrease in bone Pb mirrors temporal trends observed in blood Pb levels of Canadians (Bushnik et al., 2010; Health Canada, 2013; Safruk et al., 2017).

Fluorescence maps of modern bone samples also indicate overall low Pb exposure, exhibiting either a relatively homogenous Pb pattern in which all structures exhibit similar intensities of Pb fluorescence, or Pb enrichment mostly occurring in mature osteons and interstitial and osteon fragments. The former pattern indicates consistent low-level Pb exposure throughout the duration of bone remodeling. Individual

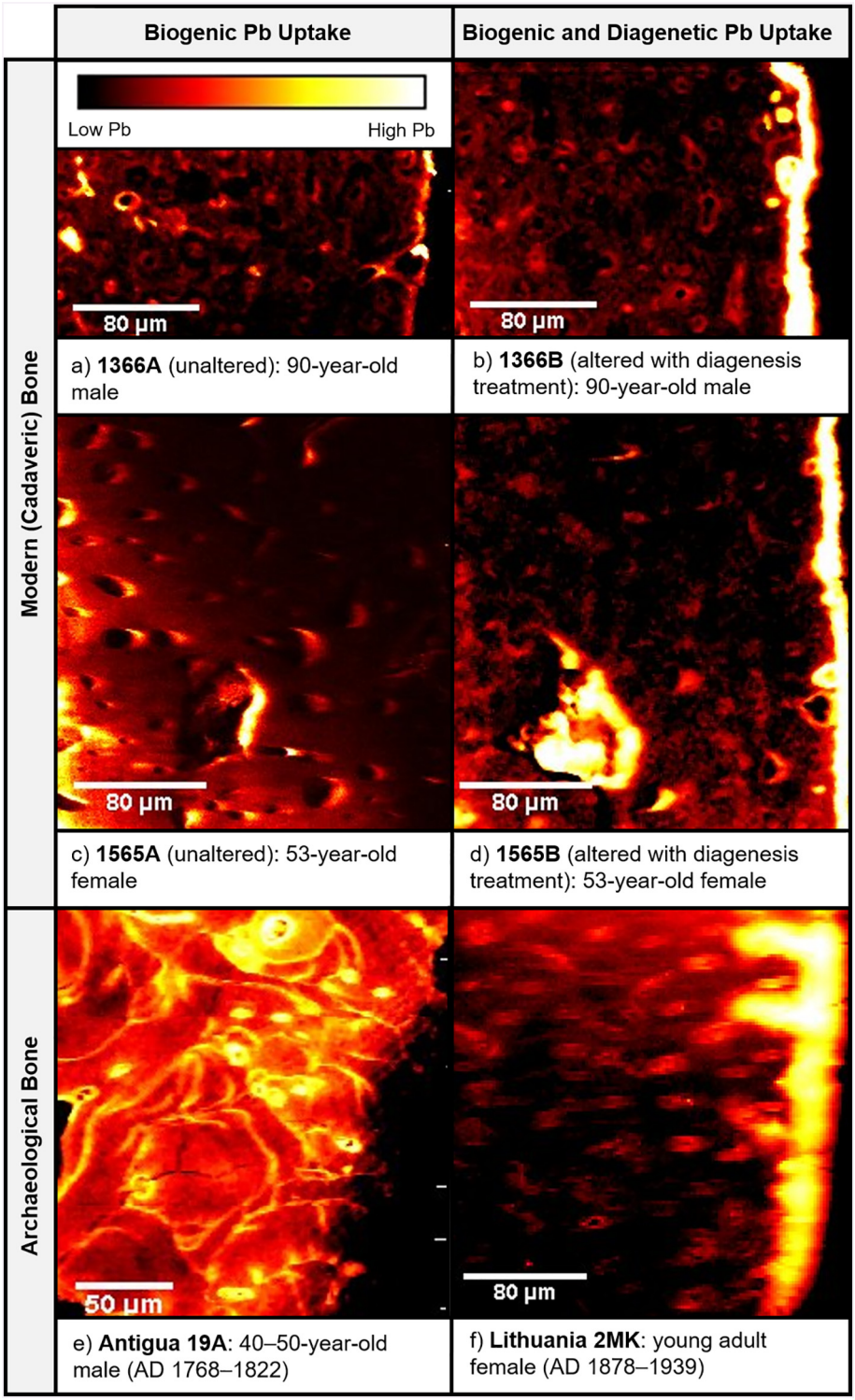

Fig. 3. SR-XFI maps representing biogenic and diagenetic Pb in modern and archaeological bone.

variation in remodeling rates may mean that these samples reflect a shorter period of time (years as opposed to decades). Additionally, the kinetics of Pb between bone and blood (Rabinowitz, 1991) mean individuals exposed to Pb earlier in life can be intrinsically exposed to Pb mobilized from bone, a portion of which may, in turn, become reintegrated into bone once more. The latter pattern, involving enrichment of structures corresponding to earlier periods in life, confirms the hypothesis that Pb exposure was higher in the past for these individuals. Individual 1366 (Fig. 3a) shows evidence of higher enrichment within single structures, possibly reflecting specific events of elevated Pb exposure. It is difficult to determine whether these events stem from extrinsic or intrinsic sources of Pb exposure though the higher intensity of fluorescence in these structures potentially suggests the former.

The microdistribution of Pb in archaeological bone samples also exhibited variation related to individual Pb exposure and anthropogenic Pb use by the population. Within the individual from Antigua, both newly formed and mature bone structures were highly enriched with

Pb, suggesting that this individual was exposed to high Pb levels over his lifetime. This is consistent with the sample's bulk Pb concentration of 253.9 μg/g—approximately a sixtyfold increase from the mean concentration observed in the modern samples. In this Caribbean British Royal Navy context, higher levels of Pb exposure likely occurred via occupational (industrial) exposure and consumption of rum distilled from sugar cane juice which were processed using leaded equipment (Handler et al., 1986; Varney et al., 2012). The sample from Lithuania exhibits evidence of comparatively lower biogenic Pb enrichment of internal bone microarchitecture. Cultural pathways of Pb exposure at this time occurred through ammunition, utensils, food containers, paints, pigments, glazes, glazes, solders, beverages, water catchments, and plumbing (Lessler, 1988; Montes-Santiago, 2013; Warren, 2001).

4.2. Confirming the spatial distribution of biogenicity vs. diagenesis

Diagenesis of bone represents both a prevailing concern for the field of archaeological bone chemistry, and an opportunity to study environmental toxicity. Like many trace elements, diagenetic Pb cations in the depositional environment may become mobilized by water and adsorb onto bone surfaces or enter bone via diffusion, pores, cracks, and other spaces, where it may substitute for Ca in the Ca(I) or Ca(II) positions in hydroxyapatite mineral and ultimately recrystallize the hydroxyapatite (Dudás et al., 2016; Hedges and Millard, 1995; Keenan, 2016). Methods of identifying element diagenesis are therefore critical. SR-XFI results support our hypothesis that diagenetic and biogenic Pb uptake result in different spatial patterns of accumulation. Through comparison of unaltered modern bone sections with corresponding diagenetically-altered modern bone sections, this study has demonstrated that in both modern and archaeological bone, diagenetic Pb is typically confined to the periosteal surface of bone and small, subperiosteal pores. One exception is seen in Sample 1565B (Fig. 3d) that demonstrated diagenetic Pb enrichment of residual soft tissue contained within a resorption space. Archaeologically, the Lithuania sample exhibited signs of diagenetic Pb also pervading into bone via post-mortem cracks.

These findings are promising for the field of bioarchaeological and paleontological trace element analysis. Due to the susceptibility of bone to trace element diagenesis (Budd et al., 2000; Montgomery et al., 2010: 203), Pb isotope studies of skeletal remains often rely on dental enamel, though enamel is not always impervious to diagenetic contamination (King et al., 2020). This study showed that bone, even exposed to Pb diagenetically, may still be of utility when regions of diagenetic contamination can be successfully identified. Element mapping techniques including SR-XFI can be used to identify regions biogenic and diagenetic Pb accumulation, and potentially act as a visual guide for recovering biogenic information from bone. SR-XFI can be coupled with synchrotron radiation X-ray Absorption Spectroscopy (SR-XAS) techniques to further confirm the nature of Pb in regions suspected as being biogenic or diagenetic. SR-XFI could also be used to inform sampling regions for LA-ICP-MS, in which microsamples of a bone or tooth sample can be extracted to assess element concentrations or isotopic analysis.

4.3. Limitations and potential future directions

Absolute quantification of Pb concentrations within regions of interest is not currently possible with SR-XFI when working with thick three-dimensional samples (e.g., bone), as self-attenuation of X-ray photons may occur, and as a result, the underestimation of absolute Pb counts. Given the sensitivity of using samples from human cadavers and the time restrictions of limited synchrotron beamtime, the sample size of this study was smaller than ideal and thus, caution should be exercised when considering these results in the larger population context. Additionally, while these modern samples are from individuals who likely lived in Saskatchewan toward the end of their lives, long-term residential and occupation information was not available. When drawing comparisons of bulk Pb concentrations across sample groups, it is also important to consider the different facilities, procedures, and spectrometers used to analyze the archaeological vs. modern bone samples (Table S1).

It could be argued that by exposing the bones to a Pb solution for a short period of time, the artificial diagenetic treatment in this study would not adequately mimic diagenesis. However, SR-XFI maps from experimentally altered modern bone and diagenetically-altered archaeological bone are similar, both containing a pattern of periosteal diagenetic enrichment, and sometimes entry via large pores or cracks. Another difference between the experimental conditions of this study compared with natural diagenesis is that this study used cut bone sections, rather than intact whole bones, which could alter pathways of Pb accumulation and diffusion. As an exploratory, proof-of-principle study, this study was restricted in the range of diagenetic variables tested, both in terms of Pb concentration and duration of exposure. Experimental studies (e.g. Von Endt and Ortner, 1984; Nicholson, 1996; Person et al., 1996; Nielsen-Marsh and Hedges, 1999; Trueman et al., 2004; Harbeck and Grupe, 2009; Fisk et al., 2019; Krajcarz, 2019) and analyses from archaeological contexts (e.g. Elliot and Grime, 1993; Hedges et al., 1995; Nielsen-Marsh and Hedges, 2000; Berna et al., 2004; López-Costas et al., 2016) revealed that diagenesis is affected by factors including temperature, pH, site hydrology, soil type, bone type, and bone porosity. Future experimental studies can implement a more longitudinal perspective, and potentially control for these other factors in examining the extent of Pb diagenesis in bone.

5. Conclusions

Bone represents a valuable, albeit under-utilized, record of long-term Pb exposure. Examining Pb in bones from modern and archaeological populations can provide insights into changing patterns of environmental Pb toxicity through time. Using ICP-MS and SR-XFI on modern cadaveric and archaeological bone samples, this study sought to (1) examine the microdistribution of Pb within modern bone samples, contrasting the biogenic pattern of modern bone with patterns observed in archaeological material, and (2) assess whether there are different spatial patterns of uptake for biogenic and diagenetic Pb exposure. ICP-MS results show that the modern individuals analyzed in this study experienced comparatively lower Pb exposure relative to individuals from decades and centuries ago. SR-XFI maps both confirm that the presumed 'biogenic' Pb pattern interpreted archaeologically is compatible with biogenicity, and provide insights into individual histories of Pb exposure. Comparing unaltered and experimentally altered bone samples with archaeological bone samples supports the initial hypothesis that biogenic and diagenetic Pb exposure result in visually distinct spatial patterns of uptake.

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CRediT authorship contribution statement

Rachel Simpson: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Writing – original draft, Writing – review & editing, Visualization, Project administration. **Tamara L. Varney:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Ian Coulthard:** Investigation, Writing – review & editing. **Treena Swanston:** Investigation, Writing – review & editing. **Vaughan Grimes:** Investigation, Writing – review & editing. **T. Jessica A. Munkittrick:** Investigation, Writing – review & editing. **Rimantas Jankauskas:** Resources,

Writing – review & editing. **David M.L. Cooper:** Conceptualization, Methodology, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.148144.

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