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Microchemical Journal xx (2005) xxx – xxx

MICROCHEMICAL
JOURNAL

www.elsevier.com/locate/microc

Inductively coupled plasma-mass (ICP-MS) and atomic emission spectrometry (ICP-AES): Versatile analytical techniques to identify the archived elemental information in human teeth

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Received 18 January 2005; received in revised form 1 April 2005; accepted 3 April 2005

Abstract

Human dental enamel is composed of sequentially calcifying growth layers that can provide an archival record of temporal changes such as past pollution events and changes in elemental nutrition. Human teeth and bones alike are mainly made out of calcium and a phosphorous rich crystalline building block called hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$]. Divalent cations such as Zn^{2+}, Pb^{2+}, Sr^{2+}, and Mg^{2+} can replace isovalent calcium sites, and phosphate and hydroxyl sites can substitute with anions, such as carbonate and fluoride, respectively. In this investigation inductively coupled plasma-atomic emission (ICP-AES) and mass spectrometry (ICP-MS) was used to determine lead, zinc, and strontium concentrations in deciduous teeth from contemporary populations from Solís, Mexico and Kalama, Egypt and permanent teeth from Bronze age Tell Abraq, United Arab Emirates and the 18th century New York African Burial Ground (NYABG) from Lower Manhattan. The concentration of lead in children's teeth from a semi-urban village in Egypt (ranged from 162 to 2.6 μg g^{-1}; $n=10$) and NYABG individuals (range 112–1.2 μg g^{-1}; $n=6$) showed the elevated lead levels while the ancient population from Tell Abraq had the lowest level (1.34 to 0.03 μg g^{-1}; $n=10$). Lead isotope ratios (i.e., $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$) of above individuals' teeth were measured using ICP-MS to discern their domicile. Zinc and Sr concentrations of teeth reflect the diet, nutritional and environmental history of individuals. The versatility of ICP-AES and ICP-MS as trace metal analytical techniques in unraveling elemental information embedded in hard tissue, like teeth, is demonstrated.

Keywords: Inductively coupled plasma-atomic emission (ICP-AES) and mass spectrometry (ICP-MS); Human teeth; Zinc; Lead; Strontium; Isotopes

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1. Introduction

Teeth are valuable bioarchives of information about the organism. They can provide information about development, nutrition, and physiological stress, exposure to disease, pollution and residential mobility. Unlike bone, teeth tend to be more resistant to remodeling or resorption. Dental hard tissues, in particular enamel and dentine, begin developing during the sixth week in utero, and then teeth in each jaw become the deciduous teeth that are later replaced by the permanent teeth [1]. Divalent cations such as lead, zinc, cadmium, and strontium, particularly interact and replace isovalent calcium sites in the hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] in enamel matrix of dental tissue resulting in a permanent record that can indicate the past exposure [1–3]. In addition anions carbonate (CO_3^{2-}) and fluoride (F^-) can replace the anionic sites like phosphate (PO_4^{3-}) and hydroxyl groups (OH^-) in the bioapatite matrix, respectively [3]. As stated by Losee et al., in 1974, a minimum of 41 elements are incorporated into the enamel tissue when the teeth are developing and frequently below the atomic number 60 (Nd) [4]. The atom size, charge density is a factor influencing the substitution of elements incorporated into the enamel during development. These alterations are reflected in teeth and can provide clues about

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0026-265X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.microc.2005.04.002

the environmental chemical changes, nutritional, and physiological changes that happened during an individual's lifetime. Thus, dental tissue is an excellent biomonitor, one suitable for nutrition and/or pollution studies [1,5–7].

Mineralized dental tissue includes enamel, dentin, and inner pulp cavity, an often thin layer of cemented tissue visible at the root zone cementum [8]. Enamel is mostly inorganic, mineralized material that covers the crown of the tooth. The inorganic matrix of enamel is composed of hydroxyapatite. Calcium content in the enamel ranges from 34 to 39 (% w/w); organic content is little as ~1% by weight and very dense with a mean density of 3.0 g cm^{-3} [9,10]. Dentin is biologically more active than enamel, is composed of smaller apatite crystal, and tends to be less densely packed than enamel. Dentin is richer in organic content (~22% w/w) than enamel tissue and contains 10% water [4,8]. Cementum is a thin layer of calcified tissue, much like bone in its relative calcification and turnover properties, which cover the tooth root. As its name implies, cementum forms an attachment between the tooth and its bony socket. Pulp cavity tissue is the most biologically active, containing nerve and blood tissues, which facilitate communication between dental tissue and the rest of the body and obtain nutrients from the body [2,8].

Enamel layers grow much like tree rings: about 4–6 nm of enamel are laid down each day and then a new layer is secreted. Enamel growth starts at the tip of the tooth with subsequent layers building outwards and then downwards toward the tooth root. Tooth enamel calcifies during early development (4 months in utero) and reflects physiological exposure beginning with the deciduous incisors and first molars that commence calcification during the second trimester through the complete calcification of the wisdom teeth (permanent third molars) at the age of 18–25 years, making teeth an excellent hard tissue for environmental pollution and nutrition studies [1,8].

Inductively coupled plasma-atomic emission (ICP-AES) and mass spectrometry (ICP-MS) are versatile and mature elemental analysis techniques [11,12]. Both methods are used for analysis of biological materials [11] including teeth [13,7]. ICP-MS is not only a sensitive elemental detector but provides isotopic abundance information [14–17].

Teeth are particularly valuable for lead source identification because tooth lead indicates exposure over several years, from before birth to tooth loss [18] in contrast to blood and body tissue lead, which has a short residence life of 4 to 6 weeks [19]. Lead is a toxic element that has been used since antiquity [19]. Lead mimics the chemistry of calcium and is easily incorporated into calcifying tissues. Nearly 70% of lead in children is stored in the skeletal system, and the biological half-life of lead can reach 30 years. Lead levels in the blood are good indicators of current exposure and are physiologically active, while lead levels in hypomineralized tissue such as bone or teeth appears to be an inert but good indicator of cumulative exposure [19]. ^{208}Pb, ^{207}Pb, and ^{206}Pb are decay products of the ^{232}Th and ^{235}U, and ^{238}U series, respectively, while ^{204}Pb is a primordial lead isotope. Hence, radiogenic lead isotopic abundances (^{208}Pb, ^{207}Pb, and ^{206}Pb) vary depending upon geologic formations and the concentration of parent nuclides present in those areas [20]. Potential lead sources have been determined using isotopic ratio analyses of blood and gasoline [20,21], air [21], teeth [18,22–24] calcium supplements [16], and other contributors to childhood lead poisoning [6,17]. In this paper, lead isotope ratios were measured by quadrupole ICP-MS, and these ratios were used to trace the domicile of individuals from Kalama, Egypt; Solís, Mexico; the New York African Burial Ground (NYABG); and Bronze Age Magan who lived in the area of present-day Tell Abraq, UAE.

The purpose of this investigation was to determine lead, strontium and zinc concentrations in teeth by ICP-AES and ICP-MS and to investigate whether any lead isotope variations existed among deciduous Egyptian and Mexican teeth and permanent teeth from Bronze Age Magan and the individuals recovered from the New York African Burial Ground.

2. Experimental methods

2.1. Dental samples

Thirty-three tooth samples were used for this study, including seven deciduous teeth from Solís, Mexico, and 10 deciduous teeth from Kalama, Egypt. The teeth from these two locals were initially collected as a follow-up to a longitudinal study of the effects of marginal nutrition [25,26] under the international "Nutrition Collaborative Research and Support Program on Nutritional Intake and Function" (Nutrition CRSP) funded by United States Aid for International Development (USAID).

Solís, Mexico is an agricultural community located 170 km northeast of Mexico City. The staple diet is corn grown in the valley. By contrast, Kalama, Egypt, is a semi-urban area located on the southeast side of the Nile River Delta and 19 km north of Cairo [25].

Among the archeological samples, 10 adult permanent teeth came from the Bronze Age site of Tell Abraq, possibly ancient Magan, located in the United Arab Emirates (UAE). The site of Tell Abraq dates to approximately 2200 BC and was occupied around the fall of the Akkadian Empire and the construction of the Tower of Babel by Sumerians [27,28]. Located east of Bahrain, Tell Abraq is believed to have been a seaport and trading culture in the Arabian Gulf, a region of fishing villages and full-scale agriculture [27].

Finally, 6 samples of adult permanent teeth are included from the 18th century New York African Burial Ground (NYABG) in lower Manhattan. The burial ground's excavated portion yielded 419 skeletal remains; the largest nonindigenous North American bioarchaeological population studied to date. Analysis of these remains provides a view of enslaved African life in the colonial North. For example, individuals included in this study exhibit skeletal evidence of nutritional stress (diplotic expansion) and work stress (hypertrophy, enthesopathy, and advanced osteoarthritis) [29,30]. Of the included individuals, four adults (Burials 47, 266, 340 and 367) had culturally modified teeth (CMT), i.e., intentionally chipped or filed anterior teeth. This practice has been linked to African-born individuals in other Diasporan burial contexts [31]. Non modified teeth used in this study are from children and represent that subset of the population most likely born in the Americas.

2.2. Tooth preparation

Whole tooth samples were soaked 24 h in distilled deionized water (DDI, 18 MΩ cm^{-1}) and cleaned with an acid-cleaned toothbrush to remove any debris. They were subsequently soaked in a 1% (w/v) papain solution to dissolve any lingering protein material. After three rinses in DDI water, the teeth were immersed in 3% (v/v) hydrogen peroxide for 30 s, and finally rinsed thoroughly with DDI water several times for 10 min, and allowed to dry overnight in a clean hood. Tooth samples were weighed, ground to powder using mortar and pestle, and weighed again before the digestion (depending on the tooth type and size, they ranged from 0.009 to 0.735 g).

2.3. Evaluation of the digestion procedure

Mineral acids like nitric acid and hydrochloric acid mixtures are frequently used for digestion of bones and teeth [32]. In this study, powdered teeth samples were pre-dissolved in 2 mL of sub-boiled HNO_3 (Optima, Fisher Scientific, Pittsburgh, PA) overnight at room temperature, and then the partially digested solution was heated to dryness in an acid-cleaned Teflon beaker on a hot plate. An aliquot of 0.2 mL of trace metal grade concentrated hydrochloric acid (ACS trace metal analysis grade, Fisher Scientific, Pittsburgh, PA) was added to the digestion mixture. This procedure was repeated with additional aliquots of 2 mL sub-boiled HNO_3 and 0.2 mL volumes of concentrated hydrochloric acid until it used up a total volume of 10 mL of sub-boiled HNO_3 and 0.8 mL of concentrated hydrochloric acid. Finally, 1 mL of 30% (v/v) concentrated H_2O_2 was added, and the solution was allowed to cool down to room temperature. The digested solutions were diluted with DDI water to 5 to 10 mL final volumes. National Institute for Standards and Technology (NIST) Bone Ash standard reference material (SRM-1400) was used for the evaluation of the recovery of analyte elements. Furthermore a 500 μg Y spike was added to the 150 mg bone ash samples and digested as discussed previously and the recovery of Y was evaluated by ICP-AES.

2.4. Digested teeth samples

Digested samples were diluted to 5 mL and 10 mL based on sample mass. Samples 0.100 g or above were diluted to 10 mL and samples 0.09 g or below were diluted to 5 mL with deionized water. Further dilutions were done so that the analytical solutions were within the calibration range during the ICP-AES and ICP-MS analysis.

2.5. Elemental analysis

The determination of Ca, Fe, K, Mg, Mn, Sr, and Zn concentrations was done by ICP-AES (Perkin Elmer, Optima 2000DV, Shelton, CT), and Pb concentration in bone ash was measured using ICP-MS (Perkin Elmer, Elan 6000, Shelton, CT). Calibration function for the ICP-AES spectrometer was generated using a multi-element standard with a suite of elements having concentrations ranging from 10 to 0.1 μg/mL in 1000 μg/mL calcium and 2% (v/v) sub-boiled

Table 1
ICP-MS and ICP-AES operating parameters

ICP-MS operating parameters (Perkin Elmer, Sciex Elan 6000)		
Forward power/kW	1	
Ar gas flow rates/L min^{-1}		
Coolant	15	
Auxiliary	1.2	
Transport gas	0.7 to 1.0	
Spray chamber/ nebulizer	Scott/cross Flow Nebulizer	
Measurement conditions	Quantitative analysis	Isotope ratio analysis
Dwell time/ms	50	100
Sweeps/reading	10	50
Readings/replicate	1	1
Replicates	6	6
Isotopes measured (*m*/*z*)	^{208}Pb	^{208}Pb, ^{207}Pb, ^{206}Pb, and ^{204}Pb
Internal standard (*m*/*z*)	^{209}Bi	
ICP-AES operating parameters (Perkin Elmer, Optima 2000DV)		
Forward power/kW	1.45	
Ar gas flow rates/L min^{-1}		
Coolant	15	
Auxiliary	0.2	
Transport gas	1.2	
Read delay/s	75	
Replicates	3	
Spray chamber/ nebulizer	Scott/cross flow nebulizer	
Analyte wavelengths (nm)		
Zn (II)	206.200	
Fe (II)	238.204	
Mn (II)	257.610	
Al (I)	396.153	
Sr (II)	232.235	
Ca (II)	317.933	
Na (I)	589.592	
Mg (I)	285.263	

nitric acid (Optima Grade, Fishier Scientific, Pittsburgh, PA). Calcium, Sr, Mg, and Na were measured separately using single elemental standard solutions having concentrations ranging from 10 to 0.1 µg/mL. All standards were prepared using dilution of 1000 µg/mL stock standard solutions (Spex Certiprep Standards, Metuchen, NJ). The ICP-AES operating conditions and wavelengths used are shown in Table 1.

A series of lead standards (100, 10, 1, 0.1 ng/mL) in 2% (v/v) sub-boiled nitric acid were prepared by serial dilution of 1000 µg/mL Pb stock solution (Spex Certiprep Standards, Metuchen, NJ).

2.6. Lead isotope analysis

A 50 ng mL^{-1} National Institute for Standards and Technology-Common Lead Isotope Standard (NIST 981) solution in 5 µg mL^{-1} calcium matrix was used for the correction of mass discrimination biases. A 2% (v/v) nitric acid solution in 5 µg mL^{-1} calcium was used as a blank. Lead isotope ratio $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ measurements were done with ICP-MS and the mass discrimination biases were frequently corrected with NIST 981 standard solution during the analysis. The instrument operating conditions are shown in Table 1.

3. Results and discussion

3.1. Evaluation of the acid digestion procedure

The total digestion of bone ash (~150 mg) and human dental tissue was achieved with an $HNO_3/HCl/H_2O_2$ mixture, and elemental recoveries were validated with NIST-1400 Bone Ash SRM material. Digested samples were clear and colorless after dilution with distilled deionozed water. The dissolved bone ash SRM and human dental tissue were analyzed for Ca, Fe, K, Mg, Mn, Sr, Y and Zn by ICP-AES, and Pb was measured using ICP-MS. The recoveries obtained for lead, zinc, strontium, iron, manganese, magnesium, potassium and calcium in the bone ash SRM are shown in Table 2. Successful recoveries (>94%) of Ca, Mg, Sr, Pb, and Zn were achieved (see Table 2). The Y spike percent recovery was very good (99±2%, $n=4$). This method was used to determine Ca, Sr, Pb, and Zn in the human tooth samples used in this study.

Table 2
Recoveries of trace elements from bone ash standard reference material (SRM NIST-1400)

Element	Concentration ($\mu g\ g^{-1}$)		%ΔE
	Found	Certified	
Pb	9.21±0.13	9.07±0.12	+1.54
Zn	179±4	181±3	−1.10
Sr	247±5	249±7	−0.8
Fe	568±7	660±27	−14
Mn	14±1	(17)	−17.6
Mg	0.684±0.012%	0.684±0.013%	0
K	161±21	186±8	−13.4
Ca	40.36±0.63	38.18±0.13	+5.71

$$\%\Delta E = \frac{\text{Found} - \text{Certified}}{\text{Certified}} \times 100.$$

$n=7-8$.

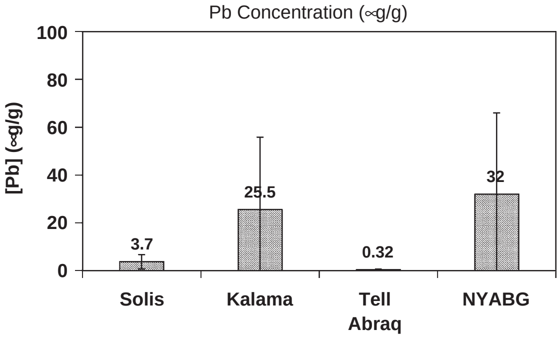

Fig. 1. Lead concentration in teeth among individuals from Solis, Mexico; Kalama, Egypt; Tell Abraq, United Arab Emirates (UAE), and New York African Burial Ground (NYABG).

3.2. Elemental analysis of deciduous and adult teeth

The elemental analysis results demonstrate some differing concentrations of Pb, Sr, and Zn among the various population groups. The elemental concentration variation within the groups is also great, as illustrated by large confidence intervals.

3.2.1. Lead concentration

Large variations in Pb concentrations were found within the investigated study cohorts (see Fig. 1 and Table 3).

Lead concentrations in two groups, Kalama, Egypt, and NYABG were high enough (>100 µg g^{-1}) to indicate potential lead contamination [2]. The highest lead concentration was found amongst deciduous teeth of the children

Table 3
Total concentrations of Pb, Zn, and Sr in dental tissue in four population groups

Sample (n)	Concentration →	Pb ($\mu g\ g^{-1}$)	Zn ($\mu g\ g^{-1}$)	Sr ($\mu g\ g^{-1}$)
Kalama (10)[a]	Average[b]	25.5±30.3	472±382	143±25.3
	Max and min range	161.8–2.6	1643–71	247–106
Solis (5)[a]	Average	3.7±3.0	112±29.9	39.4±26.3
	Max and min range	9.0–1.0	140–98.2	76.6–41 ($n=4$)
NYABG (6)[c]	Average	32±42	150±51	242±88
	Max and min range	112.2–1.2	252–58.1	343.3–85.5
Tell Abraq (10)[c]	Average	0.32±0.28	168±23	2197±309
	Max and min range	1.34–<0.03	243–104	3347–1551

[a] Contemporary population: deciduous (primary) teeth.
[b] Average concentration±CI (confidence interval, 95%).
[c] Ancient population: permanent teeth.

from Kalama, Egypt (maximum and minimum range: 162–2.6 μg g^{-1}), followed by teeth from the NYABG (maximum and minimum range: 112–1.2 μg g^{-1}), indicating ingestion of lead during childhood in these groups. The very large variation in both groups may reflect differences in ingestion during tooth calcification. The range of variation in Kalama may reflect different opportunities for lead ingestion in this semi-urban community, including lead rich auto exhaust, lead glazed ceramics and lead in household paint and dust. Four individuals from the NYABG who appear to have been born in Africa (with modified teeth) have lower tooth lead concentrations (range: 1.2–15.3 μg g^{-1}, $n=4$). The lead concentrations among the NYABG teeth were found to be highest among those individuals (with non-modified teeth) who were believed to be born in New York (NYABG B-405 and B-304 had lead level 112 and 48 μg g^{-1}, respectively). This is interesting considering the sources of pollution in New York City compared to West Africa during the 1700s when these individuals were believed to have lived. Potential contamination may have originated from anthropogenic sources, such as drinking water from leaded pipes, or some individuals may have had access to Caribbean rum stored in leaded vats during shipping or temporary stays at Caribbean islands [30].

The lowest levels of Pb (0.32±0.28 μg g^{-1}, 95% CI, $n=10$) were found among teeth from the Bronze Age Magan population in Tell Abraq, UAE. The ratio of average lead concentration between ancient and contemporary populations ($[\mathrm{Pb}]_{\mathrm{ancient\ (Tell\ Abraq)}}/[\mathrm{Pb}]_{\mathrm{contemporary\ (Kalama)}}$) is 0. 0125, and was consistent with similar comparisons (i.e., ancient to contemporary) reported in the literature [2]. In order to make a comparison of lead concentrations between ancient and contemporary cohorts, Fergusson and Purchase reported $[\mathrm{Pb}]_{\mathrm{ancient}}/[\mathrm{Pb}]_{\mathrm{contemporary}}$ ratio of <1 (i.e., 0.001 to 0.53) [2]. A study done on ancient 17th century Hopi Indians, revealed dental lead levels of 7.0 μg g^{-1}, while contemporary Hopi Indians had levels of 27.6 μg g^{-1} [2]. Natural lead levels do not tend to change drastically over time, and this increase is most likely attributable to an increase in leaded gasoline and the use of other lead-based consumer products and the resulting environmental contamination. The concentration of lead levels in the air in prehistoric times was 0.4 ng m^{-3} while contemporary average background lead levels in the air has risen to 10 ng m^{-3} even in rural America [19]. The low levels found in the Tell Abraq teeth may be significant in this respect. Among a variety of reported studies on ancient teeth [2], the Tell Abraq teeth had the second lowest mean lead concentration. In a review of lead in ancient teeth, Fergusson and Purchase [2] reported that Peruvian teeth (pre industrial, 4500–5000 bp) were found to contain the lowest quantity of lead (average 0.11 μg g^{-1}; max and min range 0.23–0.04 μg g^{-1}). The average concentration found among the Tell Abraq teeth (0.32 μg g^{-1} range: 1.34–<0.03 μg g^{-1}) is pretty close to the reported Peruvian teeth concentrations. Ancient peoples living in Tell Abraq were exposed to some, but very little, lead technology and in a pre-industrial society such as this one it is likely that the primary source of lead ingested was derived from underlying soils and bedrock rather than pollution sources [33].

The five tested deciduous teeth of Solís children contained an average quantity of 3.7 μg g^{-1} of lead, ranging between 1.0 and 9.0 μg g^{-1} of lead. Surprisingly, Solís had a much lower lead concentration than would be expected, although the people in Solís are more likely to use pottery made with lead-based glaze for cooking [17], eating and storing foods and beverages. The low levels of lead in the Solís teeth samples tested here might be the result of high calcium intake by these individuals. In the processing of corn for use in tortilla preparation, *cal* [a crude mixture of calcium hydroxide (slacked lime, one of the major ingredients), calcium oxide, and calcium carbonate] is added to increase the efficiency of corn digestion before making *massa* (dough). High calcium intake through tortilla consumption can decrease lead incorporation in the dental tissue due to the substitution of calcium in lead sites of the hydroxyapatite matrix of teeth.

3.2.2. *Zinc concentration*

As shown in Table 3 and Fig. 2, the highest concentration of zinc (472±382 μg g^{-1}, 95% CI, $n=10$) was found among Kalama children's whole teeth, followed by teeth from the Tell Abraq (168±23 μg g^{-1}, 95% CI, $n=10$) and teeth from NYABG (150±51 μg g^{-1}, 95% CI, $n=6$) individuals (see Fig. 2 and Table 3).

The children's teeth from Solís, Mexico, had the lowest amount of zinc (112±30 μg g^{-1}, 95% CI, $n=5$). A study done in Norway reported a mean Zn concentration of 144.5±1.6 μg g^{-1} ($n=2747$) for whole primary (deciduous) teeth [35]. Cutress reported a median zinc level of 210 μg g^{-1} (range: 126–276 μg g^{-1}) and 145 μg g^{-1} in permanent and primary tooth enamel, respectively [34]. The zinc levels of Tell Abraq individuals are not as high as would be expected given the frequent consumption of seafood by members of this ancient fishing community who lived on the Arabian Gulf [27]. The concentration of zinc in the Solís teeth (average 112 μg g^{-1} range: 98–140 μg g^{-1}) indicates that zinc intake and

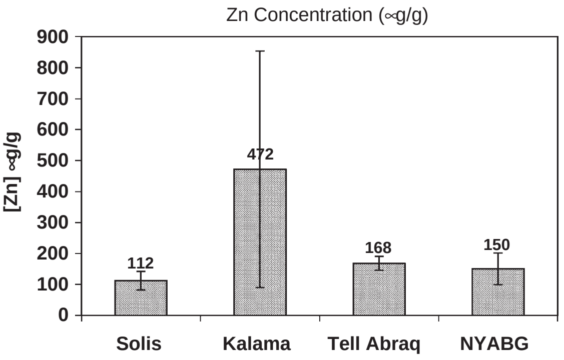

Fig. 2. Zinc concentration in teeth among individuals from Solis, Mexico; Kalama, Egypt; Tell Abraq, United Arab Emirates (UAE), and New York African Burial Ground (NYABG).

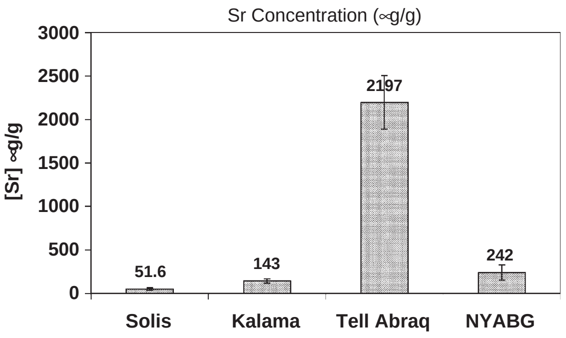

Fig. 3. Strontium concentration in teeth among individuals from Solis, Mexico; Kalama, Egypt; Tell Abraq, United Arab Emirates (UAE) and New York African Burial Ground (NYABG).

subsequent absorption are perhaps difficult for the residents living in Solís. Fosse and Justesen in 1978 showed that zinc levels below 90 μg g^{-1} in children's teeth might be an indication of marginal zinc availability [36]. Although zinc uptake levels are similar between Egyptian and Mexican children, the diets in Mexico provide more phytate, an antagonist of zinc absorption, which could account for the lower concentration of zinc found in the Mexican teeth. The much higher concentration of zinc found in Egyptian teeth may be due to consumption of yeast-leavened breads that may have facilitated the zinc availability. N-CRSP study findings also demonstrate that the prevalence of inadequate zinc intake was greatest for Mexicans, followed by Kenyans, and least for the Egyptian population [26].

3.2.3. Strontium concentration

Strontium, is a primary diagenic source with no reported biological function [37] perhaps accounting for the higher concentration of strontium found in Tell Abraq (2197 ± 309 μg g^{-1}, 95% CI, $n = 10$) and New York African Burial Ground (NYABG) teeth (242 ± 88 μg g^{-1}, 95% CI, $n = 6$) than in the other two groups (see Fig. 3 and Table 3). Diagenesis is a concern for teeth from a burial ground such as Tell Abraq and the NYABG, but not for the Egyptian and Mexican teeth since these were collected upon exfoliation. On the other hand, strontium occurs in the environment and quantities in bone and teeth vary depending upon geographical origin. Typically plants contain more strontium than animals, thus the bone and teeth of herbivores tend to contain more strontium than the bone and teeth of carnivores. This is due to strontium fractionation or “discrimination” along the trophic level from plants to herbivores to carnivores [37]. The lowest concentration of Sr was found among the deciduous teeth from Solís (39.4 ± 26.3 μg g^{-1}, 95% CI, $n = 5$). This could partly be due to consumption of calcium-rich tortilla made from alkaline treated (with *cal*) corn as described in the previous section.

3.3. Lead isotope ratio measurements

A plot of $^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ in Fig. 4 demonstrates several distinct clusters: one for the Kalama (K) teeth (five out of nine Kalama deciduous teeth samples) and another for the common lead standard (NIST-981), while the New York African Burial Ground (NYABG-N; n = 4), Tell Abraq (T; $n = 4$) and Solís teeth (S, $n = 3$) had three very closely clumped yet rather discernable lead isotope ratio clusters (see Fig. 4). As expected triplicate analysis of three bone ash (BA) samples (NIST-1400) formed a single cluster. The center of Fig. 4 shows that the NYABG and Tell Abraq teeth have clusters having rather similar isotope ratios, an indication that outside factors not yet established may have affected the results. As illustrated in the left bottom quadrangle of Fig. 4, few individuals of Kalama, Solis, NYABG had unique lead isotope ratios that did not belong to any of the previously discussed clusters. The reason for this is presently unknown.

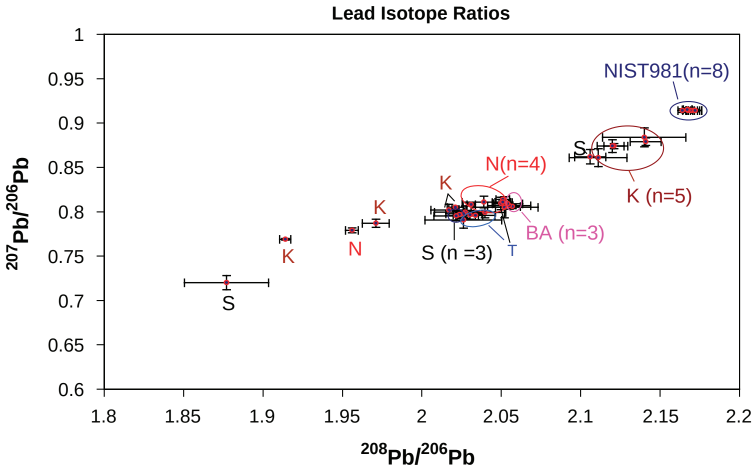

Fig. 4. Lead isotopic ratio composition ($^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$) among individuals from Solis, Mexico (S); Kalama Egypt (K); Tell Abraq, United Arab Emirates (UAE) (T); and New York African Burial Ground (N) including lead isotopic composition of Bone Ash-SRM-NIST 1400 (BA) and Common Lead SRM-NIST 981.

The interpretation of lead isotope signature is often complicated by contributions from different lead sources from the environment (i.e., air, food, mines and bedrock, and water) [24]. Even within a tooth the lead isotope signature varies from enamel to dentine. Enamel encapsulates an early record of individual's lead exposure while the dentine tissue has the capability to communicate with body fluids through dentinal tubules [2] therefore dentine could provide the evidence of an individual's most recent lead exposure. Lead isotopic information derived from enamel and dentine therefore could offer evidence of in utero exposure and exposure during the early childhood, respectively [24]. It should be considered that variations and similarities in lead isotopic ratios within a country might oversimplify the larger trends of a region. In a preliminary study such as this one, the number of the teeth analyzed may not have been large enough to make definitive statements about natal home or potential sources of lead contamination for the population. However, such isotopic information obtained from a much larger sample pool can be used together with other supportive evidence to allow for a more complete establishment of the individuals' country of origin and exposure to anthropogenic lead sources.

4. Conclusions

The study demonstrates that ICP-MS and ICP-AES techniques are versatile analytical approaches for gathering and identifying the nutritional, paleodietary and pollution histories of individuals living in ancient and contemporary times through the elemental information archived in calcified tissue such as human teeth. A satisfactory acid digestion approach to ICP-MS and AES elemental (Ca, Mg, Sr, Pb, and Zn) analysis of dental tissue was validated. The lowest lead levels were found among the ancient population of Magans who lived in the area of present-day Tell Abraq while the most elevated lead levels were present among the children of Kalama, Egypt, perhaps due to leaded gasoline use there. The trace metal Pb, Zn, and Sr composition of teeth reflects the diet, nutritional and environmental history of individuals. Along with other supporting archeological and historical evidences, lead isotope ratio analysis of teeth by ICP-MS can provide information about the potential sources of lead pollution and clues about individuals' domiciles.

Acknowledgements

We would like to thank the National Science Foundation (NSF)—Collaborative Research in Undergraduate Institutions Program (CRUI, Grant # DBI-9978793) for funding this research project, and to acknowledge the financial support of the Undergraduate Biological Sciences Education Program of the Howard Hughes Medical Institute (HHMI #71100-503803) and of the Kresge Foundation to Hampshire College. This study was also made possible by the assistance of individuals from Solis, Mexico and Kalama, Egypt that participated in diverse studies in their communities. Special thanks also go to Kristen Shrout for laboratory assistance.

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