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

Ellen Webb, Dulasiri Amarasiriwardena*, Socheata Tauch, Ethan F. Green, Joseph Jones, Alan H. Goodman

School of Natural Science, Hampshire College, Amherst, MA 01002, USA

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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

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

* Corresponding author. Tel.: +1 413 559 5561; fax: +1 413 559 5448.
E-mail address: dula@hampshire.edu (D. Amarasiriwardena).

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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 non-