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Methodological strategy for the analysis of human dental enamel by LA-ICP-MS

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Abstract

The application of LA-ICP-MS to human dental enamel usually follows a methodological procedure that starts with the vertical sawing of the tooth in order to obtain a flat surface. However, the inner enamel can be accessed in archaeological teeth that are fractured for natural, taphonomic reasons, which reduces further damage to archaeological specimens by cutting them. This paper analyzes the differences in the counts of trace elements by laser ablation–inductively coupled plasma–mass spectrometry between a cut and broken surface from the same teeth. Results show that the two surfaces do not produce statistically different readings, which extends the possibility to apply this methodological procedure to archaeological remains that cannot be sectioned, and therefore reducing the amount of damage effected to important specimens.

Keywords: Laser ablation; Human teeth; Inner enamel; Trace elements

1. Introduction

During the last decade or so, laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) has seen increasing use as an analytical tool to detect trace element concentrations in a variety of materials. In archaeology, LA-ICP-MS has been used on ceramics, glass, metals, obsidian and semiprecious stones (Speakman and Neff, 2005). Overall, ‘‘LA-ICP-MS has become one of the most exciting new fields of research in material science’’ (Speakman and Neff, 2005:1). Its ability to target specific areas has been useful in the analysis of temporal variation in the elemental composition of human teeth (Cox et al., 1996; Budd et al., 1998; Lee et al., 1999; Lochner et al., 1999; Dolphin et al., 2005).

Human teeth develop over time (Hillson, 2002), with appositional layers deposited in onion-like fashion (Kang et al., 2004). Dental enamel is first laid down at the dentin-enamel junction just below the cusps or incisal margin of the crown, and deposition of enamel gradually continues toward the cemento-enamel junction that at the time of completion of the crown formation will represent the boundary between crown and root. This means that the earliest enamel to form can be found at cusp level and the latest toward the root. The enamel is very resistant to diagenetic contamination; nonetheless, the external surface may incorporate contaminants from the burial environment.

At present, several features distinguish laser ablation analyses on human remains from other archaeological and geological applications. One problem is that matrix-matched hydroxyapatite standards so far have not been developed to calibrate elemental concentrations in enamel or bone. Since hydroxyapatite constitutes about 97% of human dental enamel (Hillson, 2002), the development of a standard for hydroxyapatite is an important goal of an ongoing research. Matrix matching of standards to actual specimens is important, because ablation volumes and laser–sample interactions can affect the ICP-MS signals in unpredictable ways. In practice, however, many of these effects can be estimated using samples

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of known concentrations, and we believe that proper standard correction factors enable us to acquire useful compositional data in the absence of matrix matching. Another set of problems relates to sample preparation, and this is what concerns us in the present paper.

To avoid contamination and in order to expose the inner enamel, the method of sampling human teeth consists of sectioning the tooth along its vertical or horizontal axis. This is usually accomplished with a low speed diamond blade (or similar), and the tooth is usually treated chemically or simply washed and sonicated with distilled, deionized water to remove potential contamination from the sawing process (Cox et al., 1996; Budd et al., 1998; Lee et al., 1999; Lochner et al., 1999; Kang et al., 2004; Dolphin et al., 2005). This approach produces a homogeneous, flat surface, but it requires both an Isomet low speed blade (which not every lab may have on hand), and more importantly, the permission to cut or otherwise alter the tooth. While LA-ICP-MS is essentially non-destructive in that it leaves an imperceptible mark on the ablated surface, sectioning of the tooth is obviously destructive and may reduce the chances that permission for analysis will be granted by museums or governmental institutions. Even though very little mass is removed by the diamond blade, gluing the two halves back together after the analysis does not restore the tooth to its original size and morphology.

Like bones, archaeological teeth may fracture as a result of taphonomic causes. This may expose the inner enamel without the need for sawing. Therefore, in an effort to reduce damage to human archaeological remains and to increase the applicability of LA-ICP-MS to museum specimens that may not be available for destructive analysis, the present study aims to investigate whether the results obtained from an artificially sectioned tooth differ significantly from those obtained from the inner surface of a tooth that was broken naturally in a post-depositional context. The results might differ because an uneven surface may induce variation in the interaction between the laser beam and the surface, with a consequent change in the process of vaporization and transportation of sample material to the ICP-MS.

2. Materials and methods

The instrument set-up used in this study consisted of a New Wave UP213 laser ablation system coupled to a GBC Optimass 8000 time-of-flight (TOF) ICP-MS. The TOF-ICP-MS separates analytes according to mass/charge ratio on the basis of elapsed time to reach the detector (heavier ions arriving after lighter ions). This approach to mass spectrometry dramatically reduces the time needed for data acquisition and provides analytical precision that is independent of the number of analytes being monitored.

In order to simulate a naturally broken enamel surface, 12 archaeological teeth from various sites in Yucatan (México) were initially broken mechanically with pliers, positioning the two blades along the vector that crossed one or two adjacent cusps, so that the fracture would expose the enamel below them. This was a simple and fast process that required only a few seconds and very little power. The teeth used in this study are part of a long term project that aims to use LA-ICP-MS to detect variability in trace elements from dental enamel as determinants of individuals of foreign origin (Cucina, 2005a,b; Cucina et al., 2005).

In most cases, the broken surface appeared fairly regular and flat, in particular when the tooth was solid and sturdy. At this point, one half of each tooth was mounted on an Isomet low speed chuck with the broken inside facing parallel to the diamond blade in order to remove the thinnest possible section and obtain a flat surface, which would resemble that of an artificially cut tooth. The sectioned half of the tooth was then cleaned with distilled water to remove possible contamination from the saw. This process yielded two homologous surfaces of the same tooth, one broken and one cut separated by a distance of less than 1 mm (the equivalent of the portion cut out by the blade). Such closely spaced portions of the same tooth can be expected to have very similar chemical signatures.

The two halves of each sample were placed in the laser chamber, one next to the other with the inner surface as horizontal as possible. The laser chamber was large enough to hold four pieces (two teeth) at the same time, along with SRM614 and SRM612 glass standards used for calibration. A raster drawn on every surface was pre-ablated to remove potential contaminants on the surfaces. The raster was drawn in the very same location on the crown of each half of each tooth in order to limit error introduced by analyzing different parts of the crown that may potentially reflect different moments in life (Budd et al., 1998; Lochner et al., 1999; Kang et al., 2004; Dolphin et al., 2005). After the pre-ablation pass, data collection was initiated on the ICP-MS. Data from the two glass standards were recorded before and after each set of samples in the laser chamber, in order to provide precise calibrations that compensate for instrumental drift. Each raster provided three sets of five readings for each element, which were then averaged to get the final signal intensities. Data were calibrated to parts per million using the NIST glasses, with ^{43}Ca as an internal standard (see Dolphin et al., 2005). In most cases, the SRM614, with concentrations of most elements less than 1 ppm, was used for calibration. As mentioned previously, a further improvement to our method would be to fabricate a series of hydroxyapatite standards with graded concentrations of trace and minor elements found in teeth. Normalized data for the elements from the broken and cut surfaces of each tooth are presented in Table 1.

3. Results

Table 1 lists the normalized element concentration from the two halves of each tooth.

The mean and standard deviation of the 13 elements from the 12 teeth are listed at the bottom of each column. Elements whose concentration was below 1 ppm were not considered for further elaborations. In the case of Ba and Hg, one or two individuals (teeth 1 and 2) were below detection level. Table 2 lists the results obtained from the two-tailed *t*-test for dependent samples performed using SPSS 11.5 software.