Micro-PIXE study of metal loss from dental amalgam

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Abstract

Mercury amalgams have been a topic of controversy ever since their introduction over 150 years ago as a dental material. An interesting question is if metals are released from the amalgam into the enamel and dentine tissue. To elucidate this PIXE mapping was used to investigate metal redistribution in an extracted molar tooth with a \textasciitilde30 year old high-Cu content amalgam filling. The tooth was sectioned and polished, and elemental mapping carried out on the amalgam/enamel, bulk amalgam and the wear surface of the amalgam. As expected, the amalgam was multiphase amalgam comprising of Cu-rich and Ag-rich grains with non-uniform distribution of Hg. The amalgam/dentine interface was clearly defined with amalgam elements on one side and C and P from hydroxyapatite on the other side with evidence of only slight interface corrosion. The peaks for Cu Hg and Zn were isolated from interfering signals with concentrations in the enamel tissue, observed to be at, or below the method detection limit. The proximity in energy of the Sn L\alpha and Ca K\alpha, peaks and the background on the Hg M\alpha gave signal overlap which increased the MDL for these elements. Remarkably, a course grain texture in the amalgam was observed just below the biting surface of the amalgam which might be associated with tribochemical processes from mastication. This coupled with the clear absence of the amalgam metals from tooth tissue, even in close proximity to the interface, suggests that for this sample, release of Hg occurred via erosion or dissolution in saliva.

Keywords: PIXE, Mercury amalgam, Teeth, Diffusion,

1. Introduction

Hg-amalgams have been used for over 150 years as a restorative material in treatment of dental cavities. During this time intense controversies have raged. These stem from concerns about introducing toxic mercury into the body e.g. [1, 2, 3, 4] and effects of increased mercury in the environment [5]. The daily Hg uptake from literature values of Hg level in urine is estimated by Ekstrand et al [2] to lie in the range 1-10 \textmu g/day which should be compared to the 2-4 \textmu g/kg body weight/day recommended maximum by various panels [5] and 0.47\textmu g/kg body weight/day by WHO for methyl mercury [6]. The body content of Hg due to amalgams is about 1.5 g according to a report cited by the SCHER [5]

An interesting question, which is investigated in this work, is how mercury and other metals are released from an amalgam filling. Dental amalgam is mixture of 43-50 % Hg with a powder containing up to 70 % Ag, up to 30% Cu and up to 30 % Sn by weight and possibly up to 5 wt. % of other elements (Zn, In, Pd) [1]. After mixing, the amalgam sets in 30 minutes. In the setting of dental amalgam [18, 19]; Ag is dissolved by Hg to form Ag\textsubscript{2}Hg\textsubscript{3} (\gamma\textsubscript{1} phase) [19, 11] where Sn may be incorporated up to \textasciitilde3 wt. % in \gamma\textsubscript{1}. Sn is also incorporated as Cu\textsubscript{6}Sn\textsubscript{5} (\gamma\textsubscript{2} phase) and possibly Cu\textsubscript{3}Sn [18, 19, 15]. Cu is on the other hand, insoluble in Hg at body temperature [10]. The compositional outcome depends on the composition and if the initial solid phase is in the form of an ad-mixed or single phase powder [19].

Both enamel and dentine constitute a potential path between the blood vessels in the pulp and the amalgam for metals released from the latter. Enamel, despite being the hardest calcified tissue of the body, is weakly

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permeable. This is presumably because of the small interstices between the small hydroxyapatite crystals that are packed into 4-8 µm rods which are in turn cemented together to form this tissue. Dentine on the other hand is comprised of calcified tubules extending from the enamel to the pulp and hence can be expected to present a much lesser barrier than enamel against metal perfusion than enamel.

2. Method

An archive specimen of an extracted adult molar tooth (31, universal tooth number) with a high-Cu amalgam filling after 30 years in vivo was investigated. The filling had remained rigidly adhered to the enamel since its original placement and the subject had no Au-basted prosthetic that might enhance corrosion[20]. The dry tooth was externally cleaned in deionised water using a new toothbrush to remove external residue. Subsequently it was embedded in Agar resin without plasticiser and sectioned with a diamond saw vertically through the filling along the root canal to the root canal opening. The sectioned surface was polished so that debris was swept away and not reincorporated in the tooth. This exposed an enamel/amalgam interface with no evidence of caries attack. Three areas were analysed using PIXE with 2 MeV protons using the MeV ion microscope at the 1.7 MV Tandetron Accelerator at Haute Ecole Arc Ingénierie in La Chaux-de-Fonds, Switzerland. Area "A" was taken from within the bulk amalgam and enamel. Area "C" was the upper surface of the amalgam that was exposed to wear during mastication (Fig. 1).

The data from Areas A and C was analysed using ImageJ [8] by compressing the original 1024×1024 pixel images to 256×256 pixel 8-bit grey-scale images. Subsequently, the contrast was expanded, ignoring outliers, so ~ 97% of the intensity histogram data was covered by the intensity scale. To identify the regions with different phases the ImageJ colocalization plugin was used with default parameters [7, 8, 9]. To quantify the elemental contents from the PIXE spectra the GUPIX code [23] was used.

3. Results

From Area "A", only X-ray signals that could be attributed to Ag, Cu, Hg and Sn were observed. Since there was no apatite (enamel) in this area, the interfering signals from (Ca kα) are absent and it follows that the amalgam sample represents a quaternary system made up of Ag, Cu, Hg and Sn. The maps for the Ag Lα, Cu Kα, Hg Lα, Sn Lα signals (not shown) revealed significant spatial inhomogeneity on a scale of 20-100 µm. The Hg signal being the most homogeneous.

To identify the distribution of the different phases co-localisation [7] of the elemental maps was employed. Fig 2 presents the Hg–Ag and Cu–Sn co-localised elemental images. For the binary mixture A-B in this representation; intermetallic phase ABn regions will appear as white areas because both element A and B are present. Areas rich in A or B, but not both, will appear as red and green, respectively. It should be noted that white pixels are not only consistent with the presence of ABn phases because grains with different composition may be superposed within the same pixel.

Fig 2 (a) presents the colocalised elemental image of Hg–Ag from Area A. This shows there is a fairly uniform distribution of Ag and Hg with some hotspots (green regions) i.e. particles, that are Ag-rich with little, or no, Hg content. The fairly uniform distribution of Ag + Hg is consistent with the dissolution of Ag in Hg to form the expected γ1 phase during setting [19]. In the corresponding elemental co-localised images for Cu–Sn, (Fig 2 (b)) it can be clearly seen that the Cu distribution is inhomogeneous. Close inspection of this image shows that Sn is co-localised with Cu consistent with formation of Cu₆Sn₅ (γ2 phase) and possibly Cu₃Sn [18, 19, 15]. The Hg–Sn co-localised elemental images (not shown) were unremarkable while the Ag-Cu (not shown) showed regions of co-localised Ag and Cu with regions with non-co-localised Cu and Ag. The composition of the amalgam determined using the GUPIX code[23] from the PIXE spectra was Cu 12.6 ±1.5 wt. %, Ag 30.9 ±1.4 wt. %, Sn 35.6 ±2.8 wt. %, Hg (Lα)35.6 ±1.3 wt. %. The uncertainty corresponds to 2σ. This corresponds to a high copper amalgam. No evidence was observed for the presence of other elements. The levels in Area A corresponding to Ca and P, which correspond to hydroxyapatite were below the detection limits of 1700 and 600 wt. ppm, respectively. Since these levels also include possible contamination during sample preparation they can be considered to be the Method Detection Levels (MDL) for these elements in an amalgam matrix.

Fig. 3 shows the Cu-P and Hg-P co-localised elemental images of the amalgam/enamel interface in Area "B". The interface is evidently sharp and there is no broad co-localisation of P (characteristic of apatite in enamel) with either Cu or Hg. A narrow band of co-localised Ca and Cu is of the order of 10 µm wide which may either indicate slight Cu interdiffusion, or an inter-
face that is rough on a few \( \mu m \) scale. Inspection of the X-ray spectra revealed the presence of P co-localised with Cu and Hg deep in the amalgam which can be attributed to the low energy tail from the Ag and Sn La peaks. The sensitivity of the co-localisation is of the order of a few at. %. Then to study if lower concentrations of the amalgam elements had migrated into the PIXE spectra from the enamel and amalgam at greater that 50 \( \mu m \) from the amalgam/enamel interface compared using GUPIX. From this area the relative contents of Ca and P were Ca 72.5 \( \pm 0.46 \) wt. %, P 27.5 \( \pm 1.4 \) wt. %. The uncertainties are again 2\( \sigma \). The atomic Ca/P ratio of 2.04 is close to the stoichiometric value of 2.5 however, Ca deficient phases are known. Furthermore, the detector geometry dependant overlap of the P peak with the Ca escape peak implies this is difficult to characterise using GUPIX. It should be born in mind that our PIXE set-up is blind to O and H and hence these contents cannot be measured. The content of the amalgam elements were at, or below the limits of detection of: Cu 212 wt. ppm, Ag 4220 wt. ppm, Sn 9988 wt. ppm and Hg 17930 wt. ppm. These again correspond to MDL for these elements in dental enamel. The high MDL for Ag, Sn and Hg can be attributed to the background in the X-ray spectrum that originates from the strong Ca K\( \alpha \) X-rays. Comparing with the composition from the amalgam spectrum and the X-ray maps for amalgam in the enamel shows there is no observable leaching of amalgam elements into the enamel.

It was observed that within 20-50 \( \mu m \) of the wear surface of the amalgam (Area “C” in Fig. 1) the Sn signal (not shown) was enhanced in grains at the wear surface. This can be seen in Fig. 3 which shows the Cu-Sn and Ag-Sn colocalised elemental images. These show some Sn rich grains are depleted in Cu and others in Hg. This, with the colocalised elemental images for the other elements (not shown) revealed that some Sn rich grains were depleted of Cu, or Ag or Hg, suggesting they are a mixture of phases, e.g. Sn + Ag\(_2\)Hg\(_3\)+Cu\(_6\)Sn\(_5\). The enhancement of Sn, and or Sn rich phases was only observed at the wear surface and not at the amalgam/enamel interface (Area “B” discussed above.) This Sn rich enhancement suggests erosion of the wear surface by abrasive friction and/or chemical effects. Roberts et al [21] report plan-view electron microprobe studies of amalgam wear traces which exhibited regions of enhanced Sn and conclude the wear is by loss of the Sn-Hg phase. Unfortunately, the elemental composition of the alloys studied was not specified, which prevents direct comparison with our results. Pitting corrosion during abrasive wear in artificial saliva has been reported for various amalgam compositions [22]. Taken together the lack of observed amalgam elements in the enamel and enhancement of Sn-rich phases at the surface suggests the main transport route of these elements into the body is ingestion of wear debris during mastication.

4. Conclusions

This study was an in-depth investigation of a single tooth. The wide range of amalgam formulations and the different oral and diet environments rule-out generalisation. The amalgam studied was constituted of Ag, Cu, Hg and Sn. The co-localised elemental maps were consistent with Ag\(_2\)Hg\(_3\) and Cu\(_6\)Sn\(_5\) phases. The amalgam exhibited a sharp interface with enamel that was \( \sim 10 \mu m \) wide. The content of amalgam metals in enamel 20\( \mu m \) from the interface was of the order of the MDL. This implies that no metal transport via amalgam had taken place. An enhancement of the Sn content in grains within 100 \( \mu m \) of the amalgam surface exposed to mastication wear and corrosion was observed which suggest the main route for Hg ingestion was erosion through the wearing surface and not by diffusion through the enamel.

Ethical considerations

The study has been approved by the Ethical Review Board of Kasetsart University ref. COE 59/001.

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Figure 3: Co-localised elemental images of Area B. (Fig. 1) (a) Cu-P. (b) Hg-P. The colour key is described in the text. The field size is 1000 × 1000 µm.

Figure 4: Co-localised elemental images of Area C. (Fig. 1) (a) Cu-Sn. (b) Ag-Sn. The colour key is described in the text. The field size is 1000 × 1000 µm.