Penetration of amalgam constituents into dentine

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Originally published at:
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Abstract

OBJECTIVES: Amalgam restorations are replaced by adhesively placed composite resin restorations at an increasing rate. After the removal of amalgam dentine often shows marked dark discoloration that is attributed to the penetration of corrosion products from overlying amalgams. It is questioned whether penetration of metals into dentine affects the dentine as a substrate for adhesive procedures. This study has been performed to clarify the origin of dark discoloration of dentine by metals from amalgam with special regards to corrosion products. METHODS: A review of the literature has been performed using Medline database. As keywords dentine and amalgam, subsequently combined with penetration, interface, crevice, interaction, corrosion, were used. This was followed up by extensive hand search using reference lists of relevant articles. RESULTS: Data in the literature have been gathered from extracted amalgam filled teeth and from artificially aged amalgam filled teeth. Corrosion studies have been performed in vivo aged teeth as well as in vitro. Sn is the main element, followed by Zn and Cu, that is consistently found in dentine underneath amalgam, as well as in amalgam corrosion products and in marginal seal deposits. Penetration of elements from amalgam has only been observed in discolored and in demineralised dentine. CONCLUSIONS: Darkly discolored dentine as found underneath amalgam restorations contains amalgam corrosion products and is demineralised. Therefore it must be considered a different substrate for clinical procedures than sound dentine.
Penetration of Amalgam Constituents into Dentin

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Penetration of Amalgam Constituents into Dentin

ABSTRACT

Objective: Amalgam restorations are replaced by adhesively placed composite resin restorations at an increasing rate. After removal of amalgam, dentin often shows marked dark discoloration that is attributed to penetration of corrosion products from overlying amalgams. It is questioned if penetration of metals into dentin effects the dentin as a substrate for adhesive procedures. This study has been performed to clarify the origin of dark discoloration of dentin by metals from amalgam with special regards to corrosion products.

Methods: A review of the literature has been performed using Medline database. As keywords dentin and amalgam, subsequently combined with penetration, interface, crevice, interaction,
corrosion, were used. This was followed up by extensive hand search using reference lists of relevant articles.

**Results:** Data in the literature have been gathered from extracted amalgam filled teeth and from artificially aged amalgam filled teeth. Corrosion studies have been performed in vivo aged teeth as well as in vitro. Sn is the main element, followed by Zn and Cu, that is consistently found in dentin underneath amalgam, as well as in amalgam corrosion products and in marginal seal deposits. Penetration of elements from amalgam has only been observed in discoloured and in demineralised dentin.

**Conclusions:** Darkly discoloured dentin as found underneath amalgam restorations contains amalgam corrosion products and is demineralised. Therefore it must be considered a different substrate for clinical procedures than sound dentin.

1. **Introduction**

Since its introduction in the nineteenth century, generations of patients have profited from amalgam, being applied according to the classic macro-retentive principles of G.V. Black. After a certain lifespan however, many amalgam restorations need to be replaced or repaired as they are exposed to the physico-chemical challenges of intra-oral conditions. In modern dentistry the use of composite resin materials, applied by means of adhesive techniques, is becoming more and more common in case of replacement of amalgam fillings. For the success of such adhesive replacement restorations reliable adhesion to remaining tooth tissue is of major importance. In this respect some problems arise. Firstly the dentin that is exposed by amalgam removal, is in fact the dentin that is left by previous excavation procedures. Hence some of this dentin can
have undergone changes by the caries process (demineralisation, remineralisation, sclerosis of dentinal tubuli). Depending on the extension of the lesion and the extent of excavation procedure this dentin is different from normal dentin. It is known that dark dentin discoloration can be caused by arresting of carious lesions. The origin of this staining is not clear yet, but it has been associated with Maillard reactions.\textsuperscript{2} Several studies have shown lower bond strengths to caries affected and caries infected dentin.\textsuperscript{3-7}

Furthermore, it is a very common observation that dentin underneath previous amalgam restorations shows extensive black discoloration (Fig. 1). Already in the late nineteenth and early twentieth century it has been suggested that dentin staining should be caused by the penetration of silver and mercury ions from the overlying amalgam and deposition of metallic sulfids.\textsuperscript{8} In terms of adhesive properties it is not yet sufficiently known what the effect of this discoloration is. Only very recently Harnirattisai et al. showed that bond strengths to dark dentin after amalgam removal are lower than to normal dentin.\textsuperscript{9}

From a clinical point of view, it is difficult to decide if the staining is caused by the amalgam or by the previous caries process or both. As a consequence, it is hard to determine if and until what degree stained dentin should be removed in order to get a reliable substrate for any kind of adhesive restorative treatment.

In an attempt to throw some light on the role of products released from amalgam in the discoloration of dentin a review of the literature has been performed. The main goal of the study was to determine the chemical composition and the rate of penetration of the substances responsible for dentin discoloration as far as they are derived from amalgam restorations.

2. Materials and methods

A literature search has been performed using PubMed search engine. The primary goal was finding articles on the presence of amalgam constituents in dentin. Subsequently the search was directed towards literature on the pathways the amalgam ions might be available for penetration,
i.e. the marginal gap between amalgam and dentin and the corrosion products it contains. As keywords different combinations of the words dentin and amalgam, subsequently combined with penetration, interface, crevice, interaction, corrosion, were used. Initially only articles in English language have been selected based on the titles and the abstracts of the articles. Subsequently, the literature search has been extended by scanning the references and the related links of selected articles on their relevance.

3. Results

3.1. Pathways of transport of metal ions into and along dentin

Theoretically dentin underneath amalgam restorations can be exposed to a variety of ions and molecules originating from amalgam, oral fluids and the pulp. Moreover, caries lesions, such as present before application of amalgam restorations, inevitably have resulted in changes in the dentin in terms of demineralisation, remineralisation and sclerosis of dentinal tubuli.

Amalgam restorations do not chemically adhere to cavity walls. The result is a marginal micro gap or crevice between amalgam and cavity walls, facilitating transport of fluids, ions, molecules, and possibly bacteria and their toxins.\textsuperscript{10} Because of the difference in thermal expansion coefficients of amalgam and tooth structures, intraoral temperature changes result in intermittently opening and closing of the gap thus creating inward and outward transport of fluid (percolation) along the amalgam-tooth interface.\textsuperscript{11-13} This way dentin is easily exposed to the components of saliva, food, drinks, and products from bacterial metabolism.

Exposure of amalgam fillings to the aggressive oral environment results in a complex of physical and chemical challenges that causes alterations of structure and properties e.g. time, temperature changes, mechanical forces, chemical interactions with oral fluids and galvanic phenomena. All these factors act continuously or intermittently and their effect can be complex.\textsuperscript{14} One of the major outcomes of these interactions is release of corrosion products from the amalgam restorations. On one hand, corrosion is regarded as an adverse phenomenon.
Corrosion causes structural changes inside the amalgam and is regarded as the main reason for marginal fractures at the outline of amalgam restorations.\textsuperscript{15} On the other hand, corrosion is regarded as beneficial as it is supposed to be the main factor in reducing marginal leakage over time by deposition of amalgam corrosion products in the marginal gap.\textsuperscript{16}

In the fluid filled marginal gap amalgam constituents in ionic form might be available for deposition of complexes within the gap, as well as for diffusion into dentin and formation of salts within the dentinal structure.

3.2. Penetration of amalgam elements into dentin

Several authors tried to elucidate the origin of the darkly discoloured dentin, by means of different analytical techniques. As early as in 1881 \textit{Dwinelle}\textsuperscript{17} reported black staining in apparently previously soft dentine that seemed to be “fossilized” and he supposed this was caused by uptake of oxides of silver or mercury from the overlying amalgam into dentin. \textit{Applebaum}\textsuperscript{8} attributed the dentine pigmentation to deposition of mercuric sulfides, originating from contact of amalgam with sulphur in dentinal fluid, but he could not prove this. Within dentinal tubuli and in collateral branches black granules could be demonstrated. This is in line with the observation by \textit{Massler and Barber},\textsuperscript{18} who saw black clump-like filamentous projections in dentinal tubuli under high resolution, which could not be removed by acid treatment. In most of the 300 amalgam filled teeth studied by \textit{Massler and Barber},\textsuperscript{18} discoloration was visible. Both black and brown types of discoloration could appear simultaneously in the same teeth. It was stated that brown staining was caused by caries, and could be easily removed by hand instruments. Dark greyish black dentin was attributed to diffusion of amalgam constituents into dentin; it was not necessarily soft and it was radiopaque. Brown discoloration could be bleached by hydrogen peroxide treatment, but the black stain remained. Spectrographic analysis revealed large quantities of Hg and smaller of Ag, Sn, Zn and Cu. In an in-vitro test, it was made plausible that greyish black staining consisted of metal sulfides. Typically Sn was the element that was
found in dentin in all dentin penetration studies.\textsuperscript{9,18-25} Mateer and Reitz\textsuperscript{21} detected low Hg and Ag content in blackened dentin, but the Sn content in dentin adjacent to amalgam was about as high as it is in the amalgam itself. A number of authors also demonstrated high concentrations of Sn and Zn in electron microprobe studies\textsuperscript{18,19,22-25} However, in contrast to the former findings, they did not detect Ag and Hg in dentin.

\textit{Kurosaki and Fusayama}\textsuperscript{22} and \textit{Halse}\textsuperscript{24} concluded that no metal ions had penetrated into non-discoloured dentin. Only in dark discoloured dentin they found penetration of Zn and Sn. Because Sn produces black sulphides and Zn sulphides are white, it was concluded by Kurosaki and Fusayama\textsuperscript{22} that the black staining was caused by tin sulphides. In a very recent study, again Sn was found in various amounts and traces of Zn and Cu in discoloured dentin.\textsuperscript{9}

Table 1 summarizes the studies of dentin discoloration by amalgam ingredients and the chemical elements that are supposed to be responsible for discoloration.

Kurosaki and Fusayama\textsuperscript{22} demonstrated that demineralised dentin is susceptible to uptake of Sn and Zn. Sn and Zn penetrated the softened dentin but never the normal dentin. In an animal study greyish discoloration was exclusively seen in demineralised dentin. No discoloration was found in non-demineralised dentin. Sn seemed to diffuse throughout the outer demineralised layer and accumulated into the inner demineralised layer over time. In extracted human amalgam filled teeth, Sn was present in the dentin layer immediately adjacent to the amalgam restoration, thus in the outer dentin layer. The authors explain this difference by the excavation procedure in human carious teeth by which the outer superficial layer of softened dentin is removed and (part of) the inner layer is left in place. These findings are in agreement with those of other studies\textsuperscript{23-25} that showed large amounts of Sn and Zn in dentin (without Cu, Ag, Hg) which were strictly related to discoloured and apparently demineralised dentin. No Zn was found in dentin without Sn and vica versa.\textsuperscript{23} In vitro residual carious dentin underneath freshly packed amalgam is also susceptible to discoloration by tea and chlorhexidine.\textsuperscript{26}
Underneath amalgam restorations occasionally radiopaque zones are visible on radiographs.\textsuperscript{8,18,23} These radiopaque zones appear to be soft and can easily be removed during excavation.\textsuperscript{23} Because Ca is low, hypermineralisation is not the explanation for the radiopacity. In this demineralised dentin only Sn and Zn have been demonstrated. Apparently Zn and Sn filled the places where Ca was depleted. By means of the use of a caries-disclosing dye during excavation procedures Rudolphy et al.\textsuperscript{27} demonstrated that the radiopaque zone almost entirely consisted of irreversibly demineralised dentin. In another study, it was shown that radiopacities on bite-wing radiographs had not been changed in dimensions over a period of 6 years, therefore it was concluded that these radiopacities correspond with non-progressing caries lesions.\textsuperscript{28}

It should be kept in mind that the studies which are referred to in this paragraph are all performed on teeth restored with conventional amalgam types, except the recent one by Harniratissai et al.\textsuperscript{9} For high-copper amalgams no further studies on the penetration of elements into dentin and only data from studies on marginal seals and corrosion phenomena of high-copper amalgams are available.

From the referred studies only qualitative and semi-quantitative data are generated as they generally are based on electron microprobe analysis and characteristic x-ray image analysis. The amalgam constituents that penetrate into the dentin can theoretically only be derived directly from the amalgam restoration or from the corrosion products that are present in the marginal gap between amalgam and cavity walls. Therefore in the next section the data on marginal seal composition are described.

### 3.3 Composition of marginal seal

Frequently upon removal of old amalgam a black granular layer can be seen, which is rather loosely attached to the underlying dentin (Fig. 2) and can rather easily be removed by
excavation burs under gentle pressure. Remaining hard dentin still shows considerable black speckled pigmentation.

In Table 2 the results of studies on marginal seal products and on tooth-amalgam interface are listed. In these studies, Sn was consistently found in marginal gaps. In a number of these studies Zn was also identified. It was supposed that the Zn was released from Zn containing amalgams as well as from liners and bases.

Cu was detected in marginal seals of high and medium copper amalgams, but also in some seals of low-copper amalgams. Sutow et al. identified SnO, Sn₄(OH)₆Cl and Cu₂O in conventional amalgam interfaces, and in high-Cu amalgams they found CuCl and Cu₂O. Also Ca and P have been detected as a component of marginal seals in some studies. The origin of Ca and P was supposed to be the saliva (penetrating the marginal gap), cement bases and the dentin underlying the amalgam as a result of low pH in the marginal gap.

In order to prevent interaction of underlying or adjacent structures with the measurements, Grossman et al. and Witcomb et al. used a replica extraction technique on marginal seal products. Except the already mentioned elements, they also measured smaller amounts of Cu, Ag, P, Cl, S and traces of Fe, K, Al. Another in vitro study indicated that after 3 months and 1 year tin is the essential element in marginal seals around both low- and high copper amalgams.

From the above mentioned studies it is evident that in marginal seal products underneath conventional amalgams Sn is present in most copious amounts, followed by Zn. Cu is found in marginal seals of high copper amalgams. The reason why these elements were found and only sporadically Ag and Hg might be explained by corrosion phenomena of respective amalgam alloys.

3.3 Corrosion products of dental amalgam
Corrosion of amalgam is a destructive phenomenon which is not limited to the external surfaces or amalgam-tooth interfaces, where it is evident, but also affects the bulk of the restoration. Over a period of time corrosion progresses from interfaces toward the center of the restoration, reducing hardness and embrittling the matrix structure by molecular disintegration of the $\gamma_2$ phase. Chloride ions in saliva, food and drinks play an essential role in the corrosion process and the deposition of metallic salts.

In conventional amalgams the result of trituration of alloy and mercury and subsequent setting is essentially a matrix structure of $\text{Ag}_2\text{Hg}_3$ ($\gamma_1$ phase) and $\text{Sn}_8\text{Hg}$ ($\gamma_2$ phase) surrounding the original alloy particles containing $\text{Ag}_3\text{Sn}$ ($\gamma$ phase). The $\gamma_2$ phase forms an interconnecting network throughout the bulk of the amalgam. It is the most easily corroded phase in conventional amalgams and it is also the weakest phase in mechanical aspect. The $\text{Ag}_3\text{Sn}$ ($\gamma$) and $\text{Ag}_2\text{Hg}_3$ ($\gamma_1$) phase are electrolytically stable and do not dissociate. In the complex interactions the $\gamma_2$ phase is selectively attacked by the corrosion process, resulting in oxidation of Sn. The protons that are released by this process are responsible for decreasing the pH in the corrosion crevices, as a result corrosion will promote in an acid milieu. Sn migrates from amalgam to the interface to form poorly soluble deposits.

In conventional amalgam restorations retrieved from patients, corrosion products have been identified as a variety of Sn salts: tin-oxides, tin sulfide, tin chloride, tin oxychloride, tin hydroxide, tin hydroxychloride. Also Ca was found in corrosion products. The mercury that is released from the $\gamma_2$ phase stays in its molecular form. This metallic mercury is not dissolved in the surrounding electrolyte, but diffuses into the $\text{Ag}_3\text{Sn}$ phase and will further react to $\gamma_1$ and $\gamma_2$. This phenomenon causes mercuroscopic expansion and plays an important role in the origin of marginal defects.

Because the net effect of corrosion process is decrease or depletion of gamma 2 phase in old amalgam restorations, little or no remaining $\gamma_2$ phase might be found. For this reason it
is not surprising that Sn has been found as the main metal that is released by corrosion processes in conventional amalgams.

Modern high-copper amalgams contain little or no Sn₈Hg phase, as a consequence these amalgams are also called non-gamma-2 amalgams. Instead of γ₂ phase, a copper-tin product is formed as a result of the high copper content: Cu₆Sn₅, also called η' phase.⁴₆,⁴₇ In these amalgams, introduced by Innes and Youdelis in 1963, the η' phase is the most corrosion prone phase.⁴₈ Because no mercury is released by the corrosion process in high copper amalgams, mercuroscopic expansion is prevented, thus reducing marginal fracture potential.

Corrosion of Cu₆Sn₅ involves oxidation of Sn followed by oxidation of Cu. Like in conventional amalgams oxidation of Sn results in rather insoluble corrosion products but in smaller amounts than in conventional amalgams.⁴⁴ Subsequent oxidation of Cu may lead to disintegration of η' phase and relatively soluble Cu complexes, which may leach out in the liquid environment.⁴⁷,⁴⁹,⁵⁰ On Cu-rich amalgams in extracted and exfoliated teeth as well as in in-vitro corrosion experiments complexes of Ca-Sn-P-Cl and crystalline products containing Sn or SnCl have been found on external surface, at amalgam-tooth interface and within the restoration. No Cu was shown as Cu complexes were assumed to be leached out into the liquid environment.⁵¹ However, in contrast to the in vivo observations, Cu containing corrosion products are detected and classified as Cu₂O and CuCl₂·3Cu(OH)₂ in-vitro. The latter compound has a typical green color. It was also present on retrieved amalgam restorations that had been kept in storing solutions over time.⁴⁹,⁵⁰

From zinc containing amalgams (conventional as well as high copper amalgams) Zn is the most easily corroded element. Corrosion of Zn is supposed to delay corrosion of Sn₈Hg (γ₂ phase) and Cu₆Sn₅ (η' phase).⁵²,⁵³ Zn has been identified as the major corrosion product released in saliva and ZnSn(OH)₆ has been detected on Zn-containing amalgams.⁴⁹,⁵₀,⁵₁,⁵₄ On both Zn-free conventional and Zn-free Cu-rich amalgams, CuSn(OH)₆ was found.⁵₄ The
ZnSn(OH)$_6$ appeared after a few days, whilst CuSn(OH)$_6$ appeared later, probably due to the initial high dissolution rate of Zn compared to Cu. The small amounts of Zn in the zinc-containing amalgams play a sacrificing role in corrosion processes in dental amalgam, thereby protecting the $\gamma_2$ phase as well as the $\eta'$ phase from early attack. Quick dissolution of Zn ions has been found from conventional and high-Cu amalgam specimens in lactic acid solutions, but no Zn was detected in adherent corrosion products. Main corrosion products in all tested amalgams were based on Sn and Cu.

From above mentioned studies it is evident that Sn, Zn and Cu are the main elements that are involved in amalgam corrosion processes and might be available for penetration into dentin. The Sn containing products are rather insoluble, and might be integrated in the marginal seal and precipitates. Zn is easily dissolved and tends to migrate into the environment. Cu is found in soluble complexes (chlorides, sulphides). Still Sn, Zn and Cu might be available in ionized forms in the liquid surroundings of the amalgam restorations, depending on the composition of the amalgam. No Ag and Hg could be demonstrated in corrosion products.

4. Discussion

Different aspects of corrosion of dental amalgams and its consequences have been studied. The results of these studies cannot readily be compared because of differences in analytical methods, objectives, duration of observation periods and number of specimens studied. In some studies elements have been searched for selectively thereby excluding other elements. Due to the analytical methods used by the authors, data in the literature on elements in dentin and marginal seals were either qualitative or semi-quantitative (Tables 1 and 2).

It is obvious that corrosion of amalgam plays a major role in the efflux of metal ions. It is agreed that the $\gamma_2$ phase (Sn$_8$Hg) in conventional amalgams and the $\eta'$ phase (Cu$_6$Sn$_5$) in high-copper amalgams are the phases that are most easily corroded. Corrosive attack of Sn$_8$Hg renders Sn that is oxidized to form oxides and hydroxides. In contrast to Sn, the Hg is released.
in metallic form and it is supposed to react further with remaining $\gamma$ phase ($\text{Ag}_3\text{Sn}$) to new reaction products inside the amalgam. This might explain that Hg is not found in corrosion products of amalgam or in dentin.

From the $\text{Cu}_6\text{Sn}_5$ in high-copper amalgams again Sn is released, but at a smaller rate because of the higher corrosion resistance compared to the $\gamma_2$ phase. As a result, it is not surprising that the same Sn oxides and hydroxides are found as on conventional amalgams in smaller quantities. Cu is available to form relatively soluble complexes of chlorides and sulfides on the amalgam. Zn however is the most easily corroded element from Zn-containing amalgams. The Zn forms soluble complexes on amalgam and it is easily dissolved in the liquid environment. Zn has also been shown to be released from bases and liners.

Most authors studied the characteristics of corrosion products on retrieved amalgam restorations from extracted teeth. In many of these studies it was not known how long the fillings had survived intra-orally. In other studies fresh amalgam restorations were subjected to artificial corrosive attacks in-vitro. In both types of studies the same corrosion products were found, essentially products based on tin (Sn), thus confirming that $\gamma_2$ and $\eta^*$ phases are prone to selective chemical attack.

It is evident that Sn, Zn and Cu are the essential elements that are related to corrosion processes in dental amalgam. After insertion in cavities, amalgam is surrounded by irregular micro crevices or marginal gaps that are filled with fluid, originating from saliva and dentinal liquor from dentinal tubuli. In this liquid environment corrosion products are formed resulting in obturation of marginal gaps.

Deposits in marginal gaps contain considerable amounts of products formed by Sn, Zn and Cu, in accordance with what might be expected from corrosion studies. In some earlier studies also Hg and Ag have been detected, but these findings might be attributed to methodological imperfections producing interferences by the composition of structures adjacent or underlying
the products in the shallow gap. Grossman et al.\textsuperscript{32} and Witcomb et al.\textsuperscript{33} tried to overcome this problem by the use of a replica extraction technique for studying the composition of the marginal seal. Also Ca and P have been detected in considerable amounts in marginal gap deposits. It is suggested that these elements are released from tooth structure by the acidity in the marginal gap. Low pH might have been caused by oxidation of Sn and/or by acids from metabolism of micro organisms in gaps or secondary carious lesions.

The dentin along the amalgam-tooth interface is exposed to corrosion products in several ways, the fluid in the marginal gap being a transport medium released by corrosion of amalgam at the interface can form complexes but might diffuse also into the fluid filled marginal gaps and subsequently into the underlying hydrophilic dentin.\textsuperscript{39} Additionally, marginal seal products might dissolve depending on the pH changes in the marginal gap. Within dentinal tubuli new complexes can be formed. Applebaum\textsuperscript{8} and Massler and Barber\textsuperscript{18} found clumplike black structures within tubuli visible with light microscopy.

All but one study was on penetration of elements in dentin concern conventional amalgams. Contrary to what Dwinelle\textsuperscript{17} and Applebaum\textsuperscript{8} suggested, consistently Sn and Zn were found in dentin adjacent to amalgam. No Ag and Hg were detected in in-vivo studies on retrieved amalgam filled teeth. Surprisingly Söremark\textsuperscript{19} found considerable amounts of Hg in dentin tubuli, besides Sn and Zn, within short evaluation periods in artificially corroded amalgam restorations. In animal studies Hörsted-Bindslev et al.\textsuperscript{56} and Akyüz and Çaglar\textsuperscript{57} demonstrated penetration of Hg from amalgam into dentin and pulp tissue. The former authors suggested that base material can prevent mercury uptake into dentin, the latter showed significant reduction of mercury uptake but bases could not prevent this. Ferracane et al.\textsuperscript{58} and Okabe et al.\textsuperscript{59} demonstrated Hg release from fresh amalgam into solutions. Release was influenced by pH of the fluids. Maybe these phenomena can be explained by free mercury that is released from amalgam while hardening reactions have not been completed.
It is still unclear then why no mercury could be demonstrated in dentin in other studies. Application of cavity varnishes has been a regular treatment over time. The rationale was to reduce the initial microleakage and to prevent discoloration of tooth structures by prevention of ion penetration. Tveit and Halse\textsuperscript{60} demonstrated that copal varnish is no barrier for Zn ions. Liners do not seem to be able to block electric currents and prevent transport of Sn ions.\textsuperscript{39} Dentin cavity walls underneath amalgam restorations must have undergone structural histological and chemical changes by past caries attacks. Subsequent operative treatment is aimed at excavating soft caries infected dentin, obturation of the cavity and remineralisation of the remaining hard caries affected dentin. If the cavity preparation principles of Black are applied, some parts of the dentine are prepared until apparently sound dentine, resulting in trauma of tubuli and their content. In central parts of the prepared cavity discoloured caries affected dentin is left if it feels hard when touched with an explorer tip. In very deep carious lesions even soft dentin can be left in place locally if properly capped by restorative material.\textsuperscript{61}

From different studies it is apparent that demineralised dentin is susceptible to penetration of Sn and Zn. No metal ions were detected in non-demineralised dentin.\textsuperscript{22,23,27} Moreover Sn and Zn ions only could be shown in black discoloured dentin. So it is suggested that there is a relationship between ion penetration, demineralisation and discoloration. This susceptibility of demineralised dentin to Sn is supported by a study by Wei et al.\textsuperscript{62} They reported uptake of Sn from stannous fluoride solutions in such quantities that radiopacity was highly increased and it was suggested that tin ions had replaced missing calcium ions in the demineralised layers.

Caution is needed in interpretation of the findings of Zn in dentin underneath amalgam fillings because Zn in dentin does not necessarily originate from the amalgam as indicated by Takuma et al.\textsuperscript{63} In primary carious lesions in dentine they demonstrated an increase of Zn, especially in remineralised surface layers. Except amalgam components external pigments can also cause discoloration of dentin. Under freshly-packed amalgam restorations residual carious dentin can
be stained if exposed to tea and chlorhexidine in-vitro.\textsuperscript{26} This demonstrates that external pigments can penetrate via marginal gaps into demineralised (caries-affected) dentin.

Interpretation of darkly discoloured dentin is complicated by the physiological feature of dark discoloration of carious dentin in slowly progressing and arrested caries lesions.\textsuperscript{64} The exact origin of this darkening has not been elucidated, but it has been associated with chemical changes in dentine comparable to Maillard reactions.\textsuperscript{2} Underneath amalgam fillings both types of dentin discoloration can be found, either from the changes caused by the caries process or from penetration of amalgam constituents.

5. Conclusions

On the basis of the literature, it is concluded that discoloration of dentin underneath amalgam is an indicator for the presence of amalgam constituents. As demineralised dentin appears susceptible to uptake of metals from amalgam, this discoloration can be regarded as an indicator for demineralised dentin. It is likely that this demineralised dentin in fact is the layer of affected (i.e. reversibly demineralised) dentin that remained after cavity preparation before application of the amalgam restoration. It is not known which are the effects of elements from amalgam in dentin in relation to adhesive restorative procedures. As several authors have shown that caries affected dentin renders lower bond strengths to adhesive restorations,\textsuperscript{3-7} caution should be exercised in applying adhesive techniques on darkened dentin after amalgam removal. Indeed Harnirattisai et al.\textsuperscript{9} found lower bond strengths to dark discoloured dentin after amalgam removal. Further studies will be required for developing clinical guidelines for adhesive restorative procedures on discoloured dentin after amalgam removal.
References


Legends

Fig. 1. Darkly discoloured dentin just after removal of an old amalgam restoration.

Fig. 2. Black discoloured dentin after removal of an old amalgam restoration in tooth 17 before and after excavation procedure.

Table 1. Chronological list of publications on amalgam ingredients found in discoloured dentin underneath amalgam restorations.

Table 2. Chronological list of publications on amalgam elements detected in marginal gaps or amalgam-tooth interfaces and the respective chemical elements detected in-vivo and in-vitro.
<table>
<thead>
<tr>
<th>Authors</th>
<th>Year of publication</th>
<th>Metals in dentin substantial</th>
<th>Analytical methods</th>
</tr>
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<tbody>
<tr>
<td>Massler and Barber</td>
<td>1953</td>
<td>Sn, Zn, Cu, Ag, Hg</td>
<td>spectrographic analysis</td>
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<td>Söremark et al</td>
<td>1968</td>
<td>Sn, Zn, Hg</td>
<td>thermal neutron activation + γ-ray spectrometric analysis</td>
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<td>Wei and Ingram</td>
<td>1969</td>
<td>Sn</td>
<td>electron microprobe</td>
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<tr>
<td>Mateer and Reitz</td>
<td>1972</td>
<td>Sn</td>
<td>x-ray microprobe</td>
</tr>
<tr>
<td>Kurosaki and Fusayama</td>
<td>1973</td>
<td>Sn, Zn</td>
<td>electron microprobe analysis (characteristic x-ray analysis)</td>
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<td>Van der Linden and Van Aken</td>
<td>1973</td>
<td>Sn, Zn</td>
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<td>Halse</td>
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<td>Harnirattisai et al.</td>
<td>2007</td>
<td>Sn</td>
<td>energy dispersive spectroscopy</td>
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*Table 1.* Chronological list of publications on amalgam ingredients found in discoloured dentin underneath amalgam restorations.
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<tr>
<th>Authors</th>
<th>Year of publication</th>
<th>Metals in marginal gap</th>
<th>Other elements in marginal gap</th>
<th>Analytical methods</th>
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<tr>
<td>Wei and Ingram</td>
<td>1969</td>
<td>Sn</td>
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<td>electron microprobe</td>
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<td>Holland and Asgar</td>
<td>1974</td>
<td>Sn</td>
<td>P, Cl, S</td>
<td>electron dispersive spectroscopy</td>
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<tr>
<td>Halse</td>
<td>1975</td>
<td>Sn, Zn</td>
<td></td>
<td>electron microprobe</td>
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<td>Sarkar et al.</td>
<td>1981</td>
<td>Sn, Zn (low-copper amalgams), Sn, Zn, Cu, Hg (high-copper amalgams)</td>
<td>Ca, P</td>
<td>electron dispersive spectroscopy</td>
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<td>Port and Marshall</td>
<td>1985</td>
<td>Sn</td>
<td>Ca</td>
<td>electron dispersive spectroscopy – in vitro</td>
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<tr>
<td>Grossman et al.</td>
<td>1986</td>
<td>Sn, Zn</td>
<td>Cu, Ca, Fe</td>
<td>electron dispersive spectroscopy</td>
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<td>Witcomb et al.</td>
<td>1987</td>
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<td>Cu, Ag, Fe, K, Al, Ca</td>
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<tr>
<td>Weiland et al.</td>
<td>1990</td>
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<td>Ca, Mg, Na</td>
<td>electron dispersive spectroscopy</td>
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<tr>
<td>Sutow et al.</td>
<td>1991</td>
<td>Sn, Cu (low copper amalgams) Cu (high copper amalgams)</td>
<td>P, O</td>
<td>electron dispersive spectroscopy</td>
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<tr>
<td>Grossman et al.</td>
<td>1995</td>
<td>Sn, Zn</td>
<td>Ca</td>
<td>electron dispersive spectroscopy</td>
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</table>

**Table 2.** Chronological list of publications on amalgam elements detected in marginal gaps or amalgam-tooth interfaces and the respective chemical elements detected in-vivo and in-vitro.