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Review

The Nature of Surface Enamel in Human Teeth

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This review will consider only the developments in the study of surface enamel which have taken place over the past ten years. It has been found necessary to limit the scope to several topics and even then to restrict the discussion of these. Similarly, the bibliography has been kept to a minimum and selected so that the reader can obtain further references on a selected topic from particular papers quoted. The subjects included are the microanatomy of the surface as seen in relief and histological sections; the pros and cons of regarding the acquired pellicle or surface cuticle as an integral part of the enamel, surface remineralization, microhardness and its relationship to variations in density; the chemical composition of the natural enamel surface and some of the modifications to this which have been induced by topical prophylactic treatment.

Key words: Enamel — Surface — Teeth — Composition — Structure.

Introduction

Just over ten years ago I presented a review on "The Nature of Surface Enamel" (Speirs, 1959). Surprisingly, few papers with similar coverage have been written since, though numerous reports have been written on particular aspects (see Brudevold and Söremark, 1967). It would seem timely to collect these reports together and to attempt to summarize the findings. Comprehensive reviews on all aspects of enamel have been published recently (Stack and Fearnhead, 1965; Miles, 1967).

Inherent in the title of this review is a comparison between "surface" and "subsurface" enamel. But "surface" enamel, which usually means enamel *near* the surface, is an ill-defined term. Its properties and composition depend on the amount of enamel included within this arbitrary surface zone. For the present discussion, this surface zone will comprise the outermost 100 μ.

In unerupted teeth, differences between surface and subsurface enamel are attributable to processes associated with the cessation of amelogenesis and longer exposure of the last formed enamel to tissue fluid. In erupted teeth, there are, in addition, acquired differences resulting from the dynamic state at the interface between the enamel surface and the oral fluid environment.

Surface Microanatomy

Since the introduction of the scanning electron microscope the distribution of perikymata, rod-ends and other surface features have attracted renewed atten-

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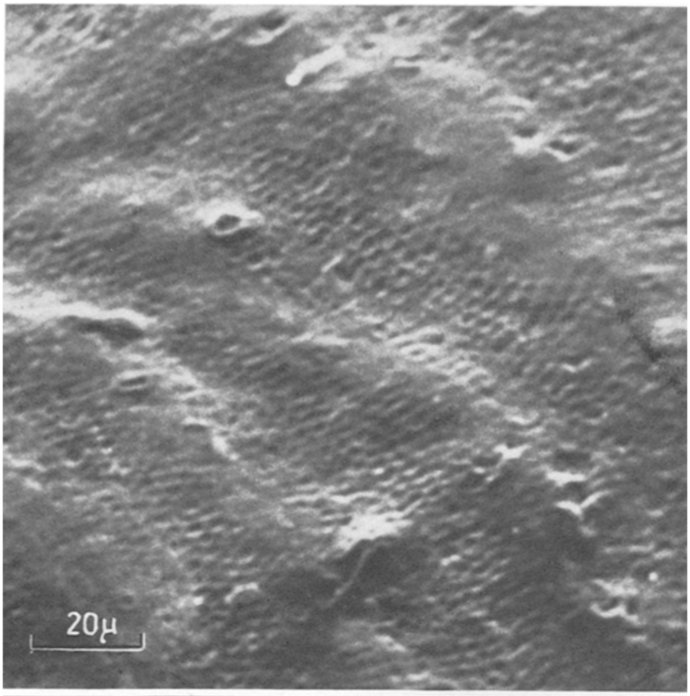
tion (Fig. 1). Small spots which react preferentially to attack by acid were noted by Poole and Tyler (1970, see Fig. 2). These might be coincident with deep pits described by Boyde (1969), and which are now thought to result from the fracturing of surface projections (Boyde, 1971). Other "new" surface features have been described by Boyde (Fig. 3). He considers that various types of pitted and defective surfaces constitute micro-stagnation areas coinciding with certain regions of the surface where caries incidence is greatest. Smooth regions without prisms and perikymata were considered by Innes and Shroff (1966) to be the final product of the ameloblasts rather than an extraneous deposit. However, Mannerberg (1960) suggests that their distribution over the erupted surface is the overall result of uneven wear, erosion and precipitation. In fluorosed teeth, areas of hypoplastic enamel with interrupted perikymata patterns were associated with areas of mottled enamel, in which the typical prism-end pattern was revealed. Contrary to most investigators, Fosse (1968) found less variation in the numbers than in the shape of the rod ends in his small sample of permanent canines. The density of the prisms in the surface was correlated inversely with the degree of curvature of the tooth. Again, this observation seems to contradict the widely held view, that the striae are more prominent, and rod ends deeper and more frequent, where the curvature of the tooth is greatest.

Numerous reports show a distinct "prismless" zone in the outermost part of enamel (Fig. 4 see Gwinnett, 1967a; Gustafson and Gustafson, 1967). Ripa *et al.* (1966) consistently observed this in 28 primary teeth and in 70 out of the 100 permanent teeth examined. Others suggest that the incidence may be lower. This layer, which averages about 30 μ in thickness, seldom extends over the entire surface, being most prominent over the gingival third of the surface of permanent teeth. The scarcity of prisms in this region confirms the distribution described on surface replicas. The finding that prismless zones were "more common in unerupted than erupted teeth" suggested that their uneven distribution might be the result of wear rather than of developmental processes. Within this prismless layer crystallites are orientated approximately perpendicular to the surface (Ripa *et al.*, 1966; Frank and Brendel, 1966; Gwinnett, 1967a), and are probably more closely packed and uniformly arranged than in the subsurface enamel, where, within a prism, a considerable but ordered variation exists in the orientation of the crystallites relative to the prism axis. Differential rates of acid dissolution within a prism have been found by Sharpe (1967). The crystallite was attacked primarily along the c-axis when this was standing perpendicular to the surface. It might seem that prismless zones would be preferentially attacked by acids. However, experimental work by Poole and Johnson (1967) and Poole (1969) does not support Sharpe's observations. Boyde (1965) points out that "the prismless area of the surface is widely held to possess caries-*resistant* charac-

Fig. 1. "Stereoscan" view of untreated, natural surface of an unerupted tooth showing perikymata. In the troughs are the depressions corresponding with the ends of the prisms, whereas the ridges are relatively featureless, × 720. [Reproduced from Arch. oral Biol. **12**, 1621–1634 (1967) through the courtesy of Drs. Poole and Johnson and the Editors of the journal]



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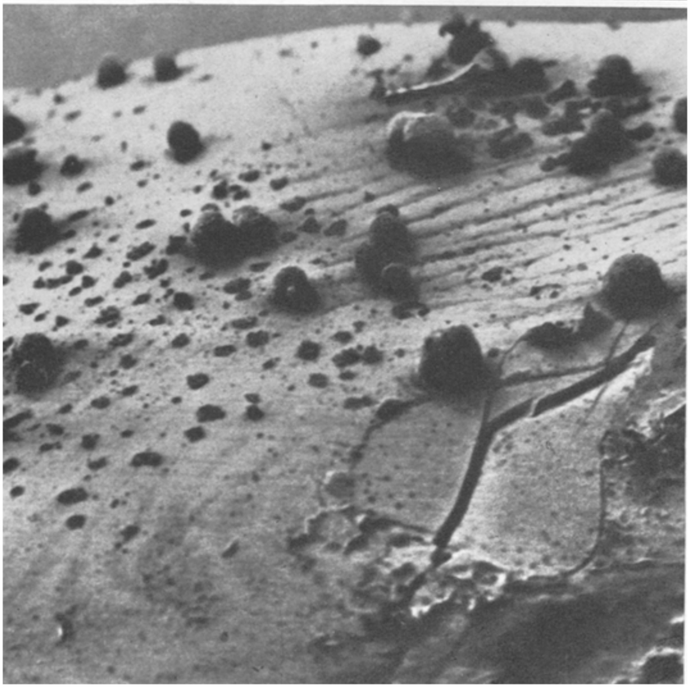

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Fig. 2. Scanning electron micrograph of tooth surface showing preferential attack by oxalic acid. Spheres of calcium oxalate crystals are distributed over the surface, × 45 original magnification. (Reproduced by permission of Drs. Poole and Tyler)

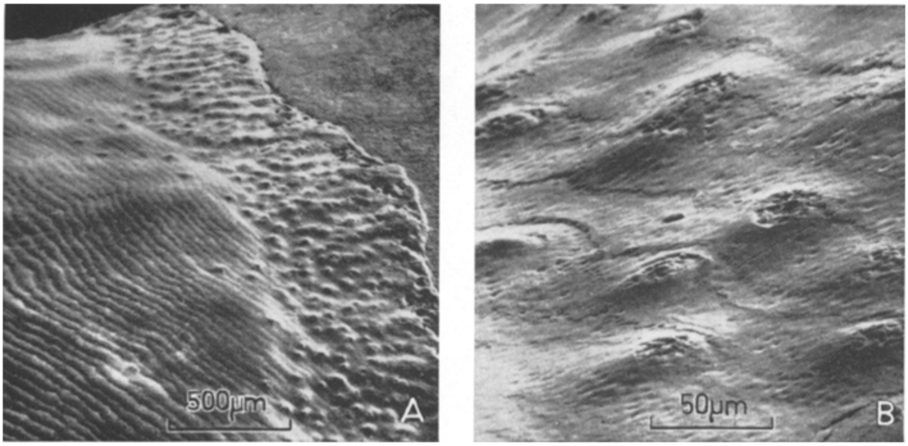

Fig. 3. (A) Surface of premolar, cleaned of organic integuments, showing a band ($^1/_2$–1 mm wide) at the cervical region of the tooth. (B) A series of low mounds about 50 µm in diameter and projecting some 10 µm above the general level of the surface is seen. ["Stereoscan" micrographs reproduced through the courtesy of Dr. Boyde and the Editors of J. Anat., (in Press)]

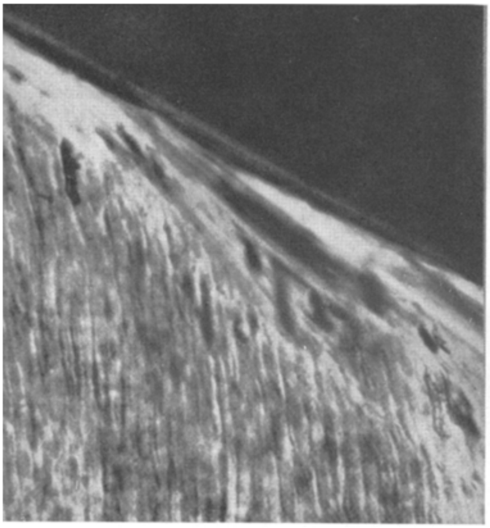

Fig. 4

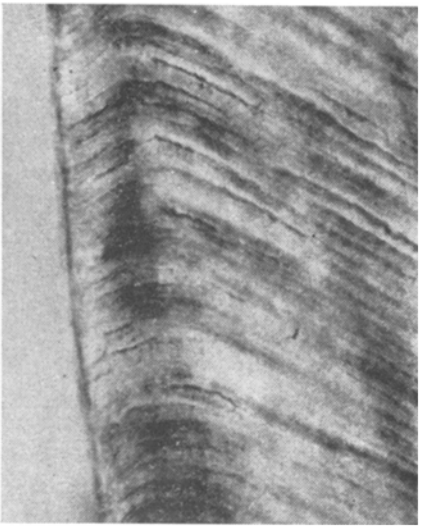

Fig. 5

Fig. 4. Ground section of human enamel in polarized light showing a surface layer of "atypical" prismless structure. The surface zone has a lamellated appearance, × 540. [Reproduced by kind permission of Dr. A.-G. Gustafson from Odont. Tidskr. **67**, 361–472 (1959)]

Fig. 5. Longitudinal ground section through the enamel of the occlusal one third of a tooth viewed by phase-contrast microscopy showing the enamel rods bending apically at the surface. [Reproduced through the courtesy of Prof. Shroff, from N. Z. dent J. **61**, 94 (1965)]

teristics". When visible, prism axes frequently seem to bend as the surface is approached, the direction depending on the contour of the tooth (Fig. 5).

Differences in hardness and rates of dissolution in acid between unerupted and erupted enamel surfaces and between different parts of the erupted surface have been reported. The hardness of the natural enamel surface was greater in old teeth than young and greater towards the occlusal surface than the cervical region, but these differences were not found when the tooth surfaces were abraded, or after these abraded areas had been exposed to the oral environment for several weeks (Von der Fehr, 1967a). Silverstone (1967) concluded from the appearance of subsurface lesions that the rate of acid attack was probably slower in cervical enamel than in incisal or cuspal enamel and fastest in mid-coronal areas. In contrast, when artificial lesions involving cavitation of the surface were produced in cervical and occlusal parts of the tooth under identical conditions, it was found that the cervical lesions were always the more extensive (Stejskalova and Eber, 1969). At present, it is impossible to relate with any degree of confidence these experimental findings to the structural features of surface enamel. There is little doubt that differences in properties exist over the crown of any one tooth, that they are mostly confined to the superficial enamel and that their cause is multifactorial.

Surface Integuments

Are any of the surface integuments, which collectively may only be a few microns in thickness, an integral part of surface enamel, and if so, to what extent are they responsible for some of the characteristic properties of the outer enamel? Armstrong and Hayward (1968) have confirmed the observations of Meckel (1965), who showed the presence of a "subsurface cuticle" extending some 1–3 μ below the enamel surface, the appearance of which varies according to the thickness of the sections examined (Fig. 6). By their methods this seems to be continuous with the acquired surface cuticle and pellicle and might be merely an extension of these into surface defects. Since such defects are probably found extensively in erupted teeth the occurrence of this cuticle *within* the enamel substance is probably universal. McDougall (1963) proposes, in addition, a condensation of the organic matrix at the surface which causes it to stain differently from the deeper parts of the enamel matrix. Similarly, Hoffman *et al.* (1969) suggest that the "surface skin of enamel" may actually be an integral part of the matrix which remains unmineralized at the end of amelogenesis. Perhaps this is the surface organic film which is resistant to mechanical abrasion (Schüle, quoted by Von der Fehr and Steinnes, 1966). Several reports indicate an apparent continuity between the densely-packed apatite crystals and an amorphous (cell-free) covering on interproximal surfaces of sound teeth (Fig. 7). It is difficult, mainly for technical reasons, to differentiate between contributions made by organic and by inorganic components of surface enamel towards the observed increase in acid resistance of the surface. Although several reports suggest that the enamel surface is more resistant to acid *in vitro* when covered by a film of protein (Meckel, 1965) Dawes (1968) concluded from experiments on natural and artificially abraded surfaces that resistance to acid-etching is more attributable to outer enamel proper than to the pellicle covering.

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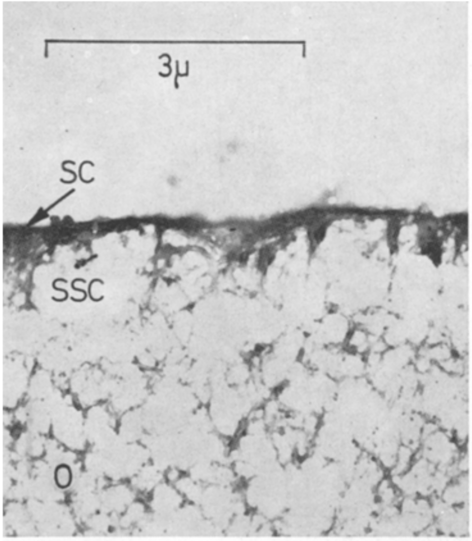

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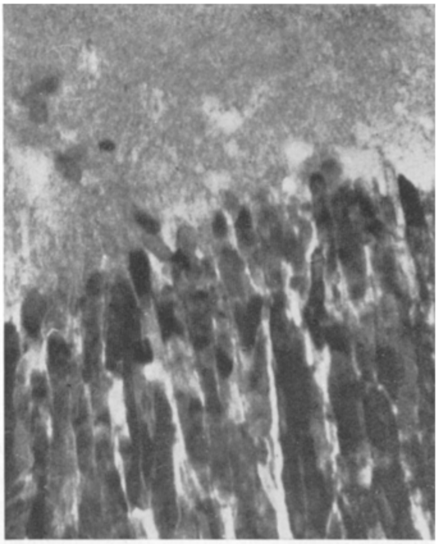

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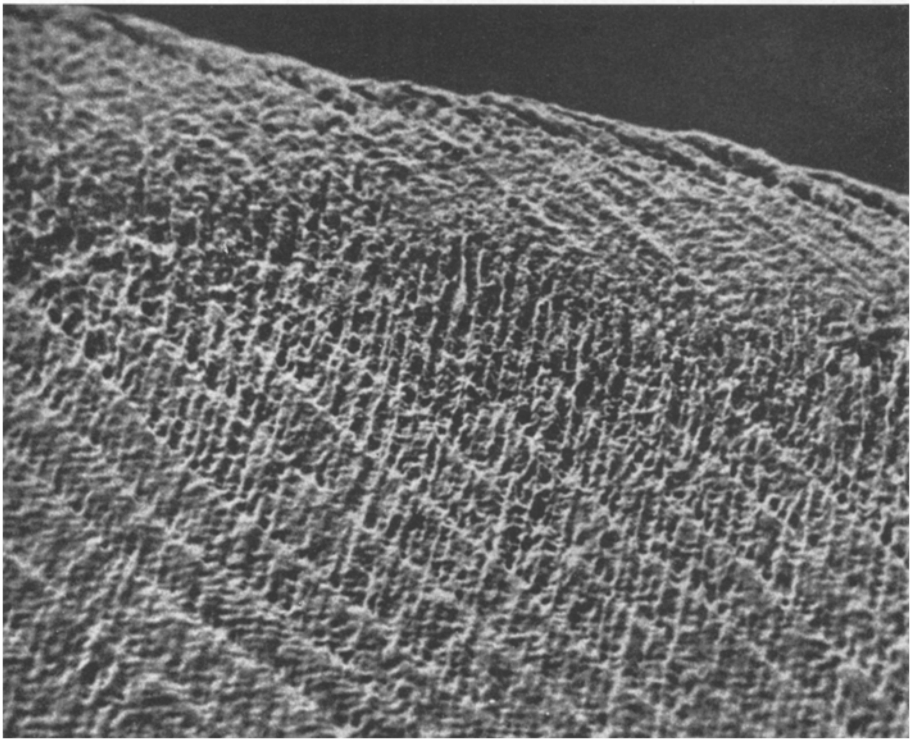

Fig. 6. Electron micrograph of the organic deposit on the labial surface of a freshly extracted upper central incisor. Demineralized cross section. *SC* surface cuticle, *SSC* subsurface cuticle and *O* organic residue of enamel. [Reproduced from Arch. oral Biol. **10**, 585–597 (1965) through the courtesy of Dr. Meckel and the Editors of the journal]

Surface Remineralization

In fissures, contact and interproximal regions a dynamic process might operate so that the first few microns in depth of the enamel is "remineralized" enamel (Brudevold *et al.*, 1964). This concept is supported by the experimental studies of Koulourides, Pigman and their associates (see Koulourides, 1966) and by those showing that *in situ*, surface defects become obliterated by acquiring a deposit of salivary origin, probably inorganic in nature, though Lenz and Mühlemann (1963) disagree about this. It is perhaps unfortunate that Von der Fehr (1965 and 1967a) has introduced the term "maturation" to describe this reparative process, the nature of which has not been extensively studied. It would be better to use this term to describe the progressive reactions involved when developmentally, immature enamel becomes fully formed. Backer-Dirks has also used the expression "post-eruptive maturation" to describe the somewhat obscure mechanism involved in the arrest or repair of early carious lesions and also the acquisition of some resistance to caries shortly after eruption. Although the phenomenon has received some attention in rats there is a dearth of information about this important issue in human teeth. It has been recently shown, however, that enamel surfaces, particularly those of unerupted teeth, will react with metastable, fluoride-free, calcifying solutions *in vitro* and become more resistant to penetration by weak acids and to the development of subsurface lesions (Silverstone, 1970).

"Caries-Resistant Layer"

Microradiography, polarized-light microscopy and electron-probe analysis have confirmed that the early carious lesion, both naturally and artifically produced, lies beneath a surface zone of enamel which appears to retain much of the integrity of the natural surface, and can be from 10–200 μ (usually about 30 μ) in thickness (Bergman and Lind, 1966; Frazier, 1967). Since this zone is observed overlying an induced subsurface lesion in *unerupted* teeth (Silverstone, 1968) and in artificially abraded enamel of erupted teeth it cannot be a posteruptive surface deposit. The evidence suggests that the two principal explanations for this "caries-resistant layer" need not be mutually exclusive. One of these attributes the surface layer to known differences in chemical and possibly physical composition between surface and subsurface enamel. In support of this explanation is the finding that the application of acid to a *section* of enamel produced a distinct intact surface layer (Fig. 8). The alternative proposal is that the

Fig. 7. Electron micrograph of non-decalcified section of molar tooth. The surface crystallites with their c-axes almost perpendicular to the enamel surface are embedded in a bacterial-free, acquired cuticle, × 76000. [Reproduced from Arch. oral Biol. **12**, 1209–1210 (1967) through the courtesy of Dr. Frank and the Editors of the journal]

Fig. 8. Scanning electron micrograph of a longitudinal mesio-distal section of a molar tooth which was polished and then etched with HCl. In the superficial layer of the enamel the striae of Retzius converge towards the natural surface of the tooth. The subsurface enamel shows more severe damage than either the superficial layer or the deeper enamel. [Reproduced by permission of Dr. N. W. Johnson and Archives of Oral Biology; Poole and Johnson, Arch. oral Biol., **12**, 1621 (1967)]

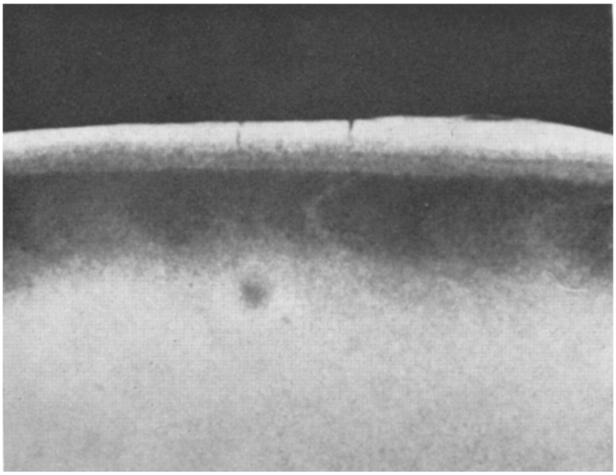

Fig. 9. Microradiograph of a section through dentine showing the appearance of a subsurface lesion. The ground surface of dentine was exposed to acidified gelatine prior to sectioning. (Reproduced by permission of Dr. L. M. Silverstone)

apparently intact zone represents remineralization or precipitation of material behind the advancing subsurface lesion and occurs by virtue of the physicochemical conditions at the surface interface. In support of this explanation are the findings that subsurface lesions can develop even in dentine exposed to oral fluids (Mjör, 1967) or *in vitro* to acidified gelatine (Fig. 9), and in teeth from which the original enamel surface was first abraded thus removing the "chemical contributor to caries resistance" (Sperber and Buonocore, 1963; Von der Fehr, 1967b; and Silverstone, 1968). Von der Fehr observed that lesions produced under fluoride-treated tooth surfaces have a broad, more X-ray dense, surface layer; evidence which could support the first of these two proposed mechanisms. However, since fluoride also encourages mineralization, such as could proceed at the enamel surface behind the advancing lesion, this evidence could also support the second explanation.

Chemical Composition

a) Water and Degree of Mineralization

Weidmann *et al.* (1967) found that the specific gravity of small particles dissected out from enamel sections, gradually increased from about 2.86 near the amelodentinal junction to 3.01 at the surface of unabraded cusps, a difference which agrees reasonably well with that obtained indirectly from quantitative microradiography and retardation measurements of birefringence by Angmar *et al.* (1963). Coklica and Brudevold (1966) found the mean density of layered samples to gradually decrease towards the amelodentinal junction. According to Weatherell (1970) the gradient of density values is by no means regular or comparable over the tooth surface. Variations exist between cervical, cuspal

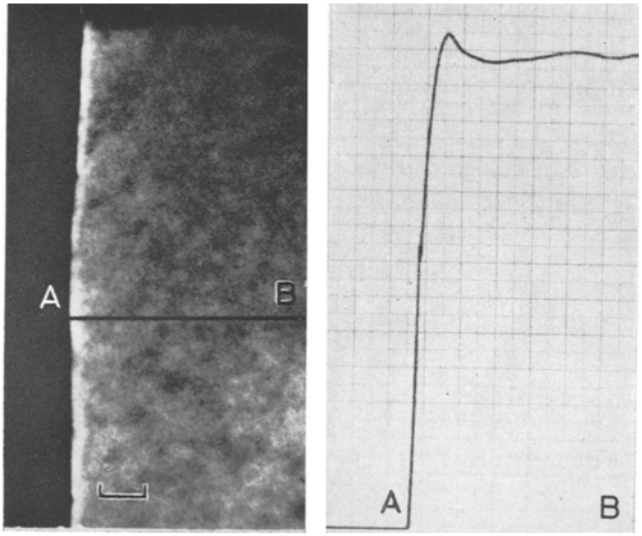

Fig. 10. Microdensitometric trace taken across the radiograph in the region of line A–B. The increased radiopacity of the outer enamel is shown as a discrete crest in the trace. In the microradiograph the increased radiodensity of the "prismless" surface enamel can be compared with the subsurface enamel. Line A–B traverses just over half the enamel thickness. That the surface opacity is not an artifact is shown by its absence along the edge of a crack in the enamel at the top of the picture. Bar represents 50 μ. Titanium target. [Reproduced through the courtesy of the author, Dr. Gwinnett and the editors, from Arch. oral Biol. **12**, 381–387 (1967)]

and mid-coronal enamel. This emphasizes the heterogeneity of this tissue and the dangers in generalizing about enamel composition.

There now seems less reason to suggest an *abrupt* fall in the degree of mineralization on penetrating the subsurface enamel as was inferred from some of the earlier radiographic studies. Recently, microradiographic densitometric measurements have been correlated with the calcium Kα X-radiation as recorded with an electron-probe microanalyzer. Studies with one or other of these methods have confirmed that there is a very gradual increase in mineralization towards the surface with no evidence for a discrete hypermineralized surface layer (Baud and Lobjoie, 1966; Frank *et al.*, 1966; Frazier, 1967; Besic *et al.*, 1969). However, other workers (e.g. Gwinnett, 1967a, b), on the evidence from microradiographs, maintain that the superficial layer is distinctly denser than subsurface enamel (Fig. 10) though this demarcation may sometimes be seen only in old teeth. Great care has been taken in some studies to evaluate the contribution of section thickness variations towards the radiopacity values.

The increase in negative birefringence towards the enamel surface may be gradual (Angmar *et al.*, 1963; Ripa *et al.*, 1966) or marked as reported by others (Houwink, 1970). It has been ascribed to an increase in the degree of mineralization or to a more regular arrangement of the crystallites near the surface.

The finding by Koulourides (1966) that a surface zone, about 100 μ in thickness, was harder than the rest of the enamel must find an additional or alternative explanation to that of variations in density, if, in fact, these are gradual and small in magnitude. Baud and Lobjoie (1966) consider that the arrangement of the surface crystallites could be responsible. However, even the concept of a discrete layer which is harder than subsurface enamel, is not proven. Since density (and to a greater extent hardness) are composite parameters, it is probable that several factors contribute to the variations which are found. Brudevold *et al.* (1960) deduced that there was less water in surface enamel since both radiodensity and organic content were found to be higher in surface than subsurface enamel and Carlström *et al.* (1963) have confirmed experimentally that there was less "loosely bound water" in surface enamel. The results on diffusion rates of ^{18}F and ^{24}Na into fragments taken from various depths of the enamel thickness are compatible with this hypothesis. Weatherell *et al.* (1969) were unable to find a high degree of correlation between the density patterns in enamel and the percentage of calcium or phosphorus. They have noted large variations in the calcium and phosphorus concentrations but a constancy in the Ca/P ratios in particles of enamel.

b) Protein

There is remarkably little new information about the quantitative distribution of protein in mature enamel. Low surface values reported by Weidmann and Eyre (1969) seem at variance with those reported earlier by Brudevold, but it must be noted that only protein released by acid dissolution was determined by Weidmann and Eyre in the outer enamel. If the *type* of protein in the outermost enamel differs from that in the deeper parts (see Speirs, 1959 for some earlier references and McDougall, 1963) then this might explain the apparent discrepancy between these different workers. Alternatively, Weidmann and Eyre might have removed more of the organic surface integuments prior to their enamel demineralization than Brudevold *et al.* (1960) or different areas of the tooth crowns could have been sampled in the two laboratories.

c) Chloride and Sodium

It is generally agreed that there is a steady decline in the chloride content from the surface to the inner enamel (Besic *et al.*, 1969) and that this distribution obtains in unerupted teeth. Söremark and Grøn (1966) discussed the lack of correlation between the chloride distribution pattern and that for sodium, which is evenly distributed at least throughout the outer half of the enamel thickness. Recent work supports their suggestion that chloride might be firmly bound to, or incorporated in, apatite thus precluding a stoichiometric relationship between chloride and sodium.

d) Fluoride

In the last ten years it has been repeatedly confirmed that the fluoride concentration in enamel falls exponentially from the surface inwards towards a plateau in the middle third of the enamel. A few points of controversy have emerged, however. It was considered by Little *et al.* (1967) that high surface fluoride levels, found particularly in old teeth, are due to accumulation in visually intact but discoloured areas. When teeth were carefully selected before analysis to exclude as far as is practical such regions, less steep gradients were obtained. It is debatable if this selection procedure is meaningful. As Weatherell *et al.* (1969) state, "opaque and pigmented areas are indeed so common that their composition and properties must be considered if the behaviour of the tissue as in integrated whole is to be understood".

The second issue relates to analytical methods. Little *et al.* (1969) claimed that the fluoride which does accumulate in surface enamel is organically bound, stable and requires drastic methods for its release. The *total* fluoride levels greatly exceed those reported in the literature. Again, the implications of these results must be questioned. It seems that the fluoride released by relatively mild acid etching is probably the more physiologically significant. If the results of Little *et al.* (1967) are substantiated, it may be that fluoride figures in the dental literature will require the prefix "inorganic" attached to them.

The other point of apparent disagreement has been resolved. It concerns the increase in surface fluoride in permanent teeth with age reported by Brudevold and Söremark (1967) and others, but not observed by Weatherell. Later work by Hallsworth and Weatherell (1969) has shown that labial surfaces of incisors, upon which their earlier studies were made, are often abraded, particularly in older teeth, and that these consequently have lower fluoride values. Any post-eruptive uptake of fluoride does not compensate for the loss due to attrition. Since fluoride concentrations fall markedly, even within 20 μ of the surface, the radio-opaque "intact" surface layer seen above early carious lesions is probably in the high fluoride zone, whereas the subsurface lesion proper lies within a region with lower fluoride levels.

More fluoride has been reported in incisors than molars and in buccal and lingual surfaces than in proximal surfaces. Since this regional variation was absent in fully formed unerupted teeth (Gedalia *et al.*, 1967) the suggestion was made, without much supporting evidence, that preferential loss from proximal surfaces was responsible. It seems more likely that these sheltered areas acquire less surface fluoride post-eruptively. Preferential uptake of ions on particular surfaces can occur (Brudevold and Söremark, 1967). Candeli *et al.* (1970) claim that in teeth from residents in a high-fluoride area the fluoride concentration in the enamel of different surfaces can be related inversely to the caries frequency in these surfaces. Many factors must contribute to these findings including the known effect of attrition. The relatively low surface fluoride values reported suggest that the mean thickness of the enamel sampled was probably 500 μ (0.5 mm) and not 500 mμ as stated.

In this discussion no attempt has been made to quote actual fluoride concentrations because useful comparisons can only be made when the thickness of the enamel being sampled is taken into consideration. An enamel biopsy method devised by Brudevold *et al.* (1968) removes less than 2 μ and so, as anticipated from the fluoride distribution pattern, values are considerably higher in consequence.

e) Carbonate

By means of an ingenious microanalytical method Weatherell *et al.* (1968) have confirmed the results of Brudevold which show that carbonate increases in concentration from the enamel surface towards the middle region and then more gradually towards the amelodentinal junction in primary, and in unerupted and erupted permanent teeth. There is a decrease in surface carbonate with age (Brudevold and Söremark, 1967) and surfaces worn down by attrition have higher carbonate levels than unabraded surfaces. The fact that unerupted teeth also have less carbonate in surface enamel suggested to Weatherell *et al.* (1969) that this reflects the reduced metabolic activity of the ameloblasts, "towards the end of their amelogenic path". The possibility that phosphate (particularly when present in high concentrations as in topically-applied, acidulated phosphate-fluoride solutions) might displace surface carbonate has been proposed.

f) Citrate

Gedalia *et al.* (1969) found that citrate levels varied on different surfaces of erupted teeth and increased with age in erupted molar teeth. They concluded, without analysing the subsurface, that there must be less citrate at the surface though Brudevold *et al.* (1960) and Nikiforuk and Grainger (1965) had shown more citrate in the outer third of the enamel thickness than in the middle zone. The latter authors have related fluoride, citrate and carbonate in analyses performed on pooled, layered enamel samples. Only in primary teeth (and only in one of their studies) was there a significant inverse relationship between fluoride and carbonate concentrations in surface enamel. Brudevold *et al.* (1965) found no evidence for this in permanent teeth, including some with high fluoride contents. In permanent teeth studied by Nikiforuk and Grainger (1965) there was a trend towards less surface citrate in those teeth with the high fluoride levels, but the degree of correlation was apparently not statistically significant; a result which agrees with that found by Gedalia *et al.* (1969).

g) Other Trace Elements

Zinc is concentrated in surface enamel some 10 times to reach levels of 1000 to 2000 ppm (Brudevold *et al.*, 1963), but unlike fluoride, there appears to be no appreciable post-eruptive deposition. Variations were attributed to the variable intake of zinc during tooth development. Although the authors do not comment on any relationship between zinc levels in teeth and fluoride in the water supplies it would appear that none exists. This tends to disagree with the findings of others showing decreased zinc in fluorosed teeth.

A similar distribution pattern has been described for lead and little further information has been added in recent years. Strontium and copper are fairly uniform in their distribution in enamel. Tin accumulates to only a small extent in the surface layers. The high levels of tin and copper occasionally found in surface enamel are probably due to corrosion of various neighbouring restorations (Speirs, 1959; Söremark *et al.*, 1962).

Attention has recently been drawn to the concentrations of aluminium and titanium in surface enamel (McCann, 1969). These might be directly related to those of fluoride. Increased titanium has been reported in fluorosed teeth.

Acquisition of Trace Elements by Surface Enamel after Topical Treatment

The clinical effectiveness of topically-applied fluorides is generally accepted and is usually ascribed to elevated fluoride levels in surface enamel, which in some way, still controversial, increase resistance to carious attack. Even though the optimal fluoride concentration in enamel is not known, efforts to raise surface fluoride further have been made in recent years and a variety of techniques and formulations have been tried.

Several workers have shown that surfaces of young teeth take up more fluoride than old; unerupted more than erupted, and primary more than permanent. The inverse relationship between mean fluoride increments and mean initial levels would account for some of these results although additional factors must influence the uptake. Fluoride is acquired at depths of up to 80 μ from the surface in unerupted teeth but is restricted to about 15 μ in erupted teeth. The question of the number of treatments and the interval between treatments for maximum incorporation of fluoride into enamel has received some attention as has the loss of surface fluoride which occurs *in vivo* after topical treatment (Brudevold *et al.*, 1967). Despite a rapid and variable loss of fluoride there is some evidence of fluoride retention several months or even years after treatment.

Hoerman *et al.* (1966) concluded from their study with the electron-probe that the penetration of tin from topically applied stannous fluoride into the enamel surface was confined to a depth of 5–20 μ and was variable over the tooth surface. This irregular uptake has been confirmed by histochemical localization. Tin readily accumulated in defects and early carious lesions and was greater in young than in old teeth.

Surface Solubility

My view (Speirs, 1959) that the link between surface solubility and chemical composition or resistance to caries is weak was shared by Brudevold and McCann (1968) in their useful review on enamel solubility. Reports still appear in which attempts are made to relate surface fluoride levels, hardness values and caries incidence to solubility measurements. Considering the "sledge-hammer" methods sometimes used in estimating dissolution rates it is not surprising that better correlations have not been produced. Gray and Francis (1963) argue that the composition of surface enamel should not alter the initial rate of dissolution (the parameter frequently studied) but could alter the solubility rate as equilibrium is attained. Conditions approaching equilibrium are, however, rarely used in estimating "solubility". Two measurements of solubility in common use, namely "rate of dissolution in acid" and "rate of penetration by acid" (as judged microscopically) probably depend on different structural features and properties. It is possible to induce decreased penetration of subsurface demineralization in treated tooth surfaces without an accompanying decrease in "solubility" of these surfaces. In contrast to results obtained on dissolution rates of "windowed" surfaces, it has been found that resistance of enamel *sections* to acid-etching was greater in older teeth. The zone of resistant enamel at the surface was wider in older teeth.

Conclusion

Probably the most important finding to emerge concerns the heterogeneity of enamel, which, even within a single tooth, now seems to be a characteristic of this tissue. With each refinement of the chemical and physical analytical methods used in studying enamel, the degree of heterogeneity becomes more pronounced. The ingenious microanalytical work of Weidmann, Weatherell and their colleagues and the pioneering studies by Brudevold and his associates have contributed greatly to this concept. Thus, the variations observed clinically in the susceptibility to caries of different parts of one tooth and different sites in the complete dentition, which have hitherto been explained in terms of the gross morphological features of contact areas, widths of fissures etc. may now have to take into account the possible influence of physical, structural and chemical differences. The acceptance of a dynamic state at the interface between enamel and the oral fluids and the reactivity of surface enamel has resulted in many attempts to induce modifications of the surface in the hope of imparting increased resistance to caries. All too often, however, laboratory findings and figures showing alterations in enamel composition and properties, when taken in isolation, permit us only to guess as to their significance as far as caries resistance is concerned. The introduction of ultramicroanalytical methods for use on biopsied samples of enamel, to mention one of the current lines of study, offers a way of eliminating some of the speculation.

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