Calcium, Phosphate, and Fluoride Deposition on Enamel Surfaces

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Concurrent calcium, phosphate and fluoride depositions, and the rate of hydrogen ion production, during formation on acid etched enamel surfaces were kinetically measured in a closed system. The deposition rate of calcium and phosphate from solution was dependent on the fluoride concentrations and pH. The proportions of calcium to phosphate and calcium to fluoride indicated fluorapatite or fluorhydroxyapatite formation on the enamel. The hydroxyl ion additions to maintain constant pH, concurrent with mineral deposition, exceeded the total phosphate ions deposited from solution. This indicates the possibility that acid phosphate hydrolysis occurs during mineral deposition.

Key words: Calcium — Phosphate — Fluoride — Calcification — Tooth Enamel.

Introduction

The exact mechanism of apatite formation is presently unknown and the subject of much current research and controversy. However, hydroxyapatite is the only solid phase of the calcium-phosphate-water system which is stable at neutral pH (Neuman and Neuman, 1958). It is assumed, on the basis of solubility and the ratios of calcium/phosphate and calcium/fluoride in the solid phase,
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that fluorapatite is formed when apatitic calcium phosphates are precipitated from, or immersed in, solutions containing less than 5 mM/l fluoride (Neuman et al., 1950; Rathje, 1952; McCann, 1953; McCann and Bullock, 1955; Leach, 1959; Brudevold et al., 1961; Kuyper and Kutterian, 1962). Definitive evidence of fluorapatite formation has not been demonstrated by crystallographic methods (Elliot, 1969).

Calcium phosphate minerals deposit within, and on, partially demineralized surfaces of enamel from saliva and solutions (Johansson, 1965; McDougall, 1967; Lenz, 1967; Frank, 1967; Silverstone and Poole, 1969). Additions of 0.05 mM/l fluoride to metastable calcium phosphate solutions increase the rehardening rates of partially demineralized enamel (Koulourides et al., 1961). The minerals that deposit during enamel rehardening from solutions with added fluoride are slightly less soluble than minerals that deposit on the enamel from the same solutions without fluoride (Feagin et al., 1969). It is not known if fluoride is deposited along with calcium phosphate during mineral deposition on etched enamel. However, significant accumulations of fluoride may occur in enamel during its mineralization (Volker, 1940; Saunders and Weidmann, 1969), and within hypomineralized or altered areas of the enamel surface in situ (Dowse and Jenkins, 1957; Little and Steadman, 1966).

The mechanism of fluoride action in preventing dental caries is still not clear (Hodge and Smith, 1968). Koulourides et al. (1961) implied that topically applied fluoride may prevent caries by enhancing mineralization of hypomineralized or pre-curious enamel. The use of fluoride in the treatment of resorptive bone disease (Shambaugh, 1969) is based on observations such as a relative increase of crystal size in bone apatite formed during fluoride ingestion (Schraer et al., 1962).

The purpose of this study was kinetically to measure the concurrent rates of calcium, phosphate, and fluoride deposition on enamel surfaces that were etched to a known depth. It was anticipated that knowledge of the relationships of calcium, phosphate, and fluoride incorporation in a preformed mineral phase would afford a better insight into the clinical use of fluorides.

Material and Methods

Enamel slabs were cut from the labial surface of bovine incisor teeth with a dental diamond separating disk (Fig. 1, A and B). The dentin side of the slabs was ground with abrasive paper to a flat surface (Fig. 1, C). A Gillings-Hameco sectioning machine was used to cut the sides of the tooth slabs to provide 0.2 cm² surfaces of labial enamel (Fig. 1, D). Except for the labial surface, the tooth slabs were coated with nail varnish and attached to plexiglass strips. The spaces around and between the slabs were filled with dental inlay wax (Fig. 1, E), leaving only the labial enamel exposed. Either 12 or 15 tooth slabs were attached to a plexiglass strip, providing either 2.4 cm² or 3 cm² area of total enamel surface. The enamel surfaces were successively polished by hand with grades 600 (wet) and 4/0 (dry) silicon carbide abrasive paper. The polished surfaces were etched by immersion of 2.4 cm² or 3 cm² surface area in 500 ml of 1-2 mM sodium acetate buffer at pH 5.0-5.1 for 6 to 12 h, with a stirring rate of 150 rpm, at 37°C.

The following stock solutions were prepared from reagent grade chemicals: 0.1 M calcium (CaCl₂); 0.06 M phosphate (NaH₂PO₄·H₂O); 0.0125 M fluoride (NaF); 0.05 M NaOH; and 1.0 M NaCl. Each experimental solution contained 150 mM/l NaCl to provide a relatively constant ionic background and was adjusted to pH 7.0. The calcium/phosphate ratio of the solutions was 1.67 at the beginning of each experiment. The composition and pH of the