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# Understanding the Chemistry of Dental Erosion

*J.D.B. Featherstone<sup>a</sup>, Adrian Lussi<sup>b</sup>*

<sup>a</sup>Department of Preventive and Restorative Dental Sciences, University of California at San Francisco, San Francisco, Calif., USA; <sup>b</sup>Department of Preventive, Restorative and Paediatric Dentistry, School of Dental Medicine, University of Bern, Bern, Switzerland

## Abstract

The mineral in our teeth is composed of a calcium-deficient carbonated hydroxyapatite ( $\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_{6-y}(\text{CO}_3)_z(\text{OH})_{2-u}\text{F}_u$ ). These substitutions in the mineral crystal lattice, especially carbonate, renders tooth mineral more acid soluble than hydroxyapatite. During erosion by acid and/or chelators, these agents interact with the surface of the mineral crystals, but only after they diffuse through the plaque, the pellicle, and the protein/lipid coating of the individual crystals themselves. The effect of direct attack by the hydrogen ion is to combine with the carbonate and/or phosphate releasing all of the ions from that region of the crystal surface leading to direct surface etching. Acids such as citric acid have a more complex interaction. In water they exist as a mixture of hydrogen ions, acid anions (e.g. citrate) and undissociated acid molecules, with the amounts of each determined by the acid dissociation constant ( $\text{pK}_a$ ) and the pH of the solution. Above the effect of the hydrogen ion, the citrate ion can complex with calcium also removing it from the crystal surface and/or from saliva. Values of the strength of acid ( $\text{pK}_a$ ) and for the anion–calcium interaction and the mechanisms of interaction with the tooth mineral on the surface and underneath are described in detail.

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Our objective is to provide a model for the chemical understanding of dental erosion. With a true understanding of the mechanisms involved, it is possible to readily interpret observations both in research and in the clinic, and most importantly as the basis for preventive interventions and therapy for patients. The chemistry behind erosion is the key to embracing the information in this publication and putting it into practice in the real world.

First, we must review the chemical nature of enamel and dentine since this is the substrate upon which erosive agents have their effect.

**Table 1.** Approximate composition of enamel and dentine as volume percent of total tissue [1, 2]

Component	Enamel percent by volume	Dentine percent by volume
Carbonated hydroxyapatite	85	47
Water	12	20
Protein and lipid	3	33

## Enamel and Dentine Composition

Dental enamel and dentine consist of mineral, protein, lipid and water [1–3]. The two tissues are very different in their structure, while at the same time having similar components. Each is comprised of millions of tiny crystals laid down in a water/organic matrix. Dental enamel is approximately 96% by weight mineral, but more importantly if the components are calculated by percent volume instead, it is obvious that the organic and water components play an important role even in enamel compared with dentine. Molecules diffuse through the water/protein/lipid matrix that surrounds the mineral crystals. Table 1 presents approximate composition for enamel and dentine as volume percent of each of the components, as reviewed by Curzon and Featherstone [2].

The mineral in our teeth and bones is composed of a highly substituted hydroxyapatite (HAP), better described as a calcium-deficient carbonated HAP [4]. A simplified formula that helps to illustrate this is  $\text{Ca}_{10-x} \text{Na}_x (\text{PO}_4)_{6-y} (\text{CO}_3)_z (\text{OH})_{2-u} \text{F}_u$  in contrast to HAP which has the perfect formula  $\text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2$ . Tooth mineral is calcium deficient, as indicated by the  $10-x$  after the Ca in the formula. Some calcium ions are replaced by other metal ions, such as sodium, magnesium and potassium totaling approximately 1%, with sodium (Na) being the most abundant. Some of the  $\text{OH}^-$  ions can be replaced by  $\text{F}^-$ . However, the major substitution is carbonate ( $\text{CO}_3$ ) that replaces some of the phosphate ( $\text{PO}_4$ ) but not on a one/one (stoichiometric) basis, hence the phosphate is designated as  $6-y$  and the carbonate as  $z$ . These substitutions in the mineral crystal lattice, especially carbonate, disturb the structure [4, 5]. Because of these substitutions the mineral in enamel and dentine is much more acid soluble than HAP (see fig. 2), which in turn is much more soluble than fluorapatite (FAP) which has the formula  $\text{Ca}_{10} (\text{PO}_4)_6 \text{F}_2$  [1, 4, 6]. Dentine and enamel have similar mineral compositions, although the carbonate content is much higher in dentine. The carbonate content of enamel is approximately 3% while in dentine it is 5–6%, making dentine mineral even more acid soluble. Further,

the crystals in dentine are much smaller than those in enamel, therefore the surface area per gram dentine is much higher giving more surface available for acid attack.

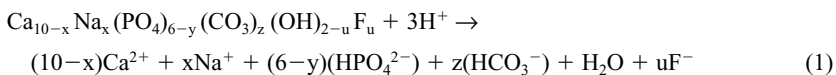
The proteins in enamel (table 1) are primarily present as a very thin covering on the individual crystals and comprise approximately half of the organic material. The other half of the organic material in the enamel is lipid [7]. The water content of enamel is sufficient for diffusion of acids and other components into the tooth and of mineral (calcium and phosphate) out of the tooth during the erosion process [8]. In contrast, dentine has different proteins and a large component of the tissue is collagen type I with about 10% of the protein comprised of a range of noncollagenous proteins, such as phosphoproteins, proteoglycans and Gla proteins [9]. There is also about 1% by weight of lipid in dentine [7]. As can be seen from table 1, the water content of dentine is substantial.

During erosion by acid and/or chelators these agents interact with the surface of the mineral crystals but only after they diffuse through the plaque (if there is plaque present), through the pellicle (see below), and through the protein/lipid coating on the individual crystals themselves.

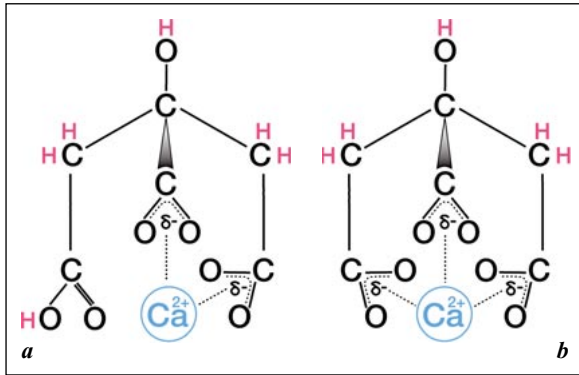
### Acids and Chelating Agents

Chemical erosion of the teeth occurs either by the hydrogen ion derived from strong/weak acids, or by anions which can bind or complex calcium. The latter are known as chelating agents. It is rare that a simple inorganic acid, such as hydrochloric acid, is present in the mouth. Mostly, we are concerned with so-called weak acids, such as citric and acetic acid.

The hydrogen ions,  $H^+$ , are derived from acids as they dissociate in water. For example, citric acid (fig. 1) has the possibility of producing three hydrogen ions from each molecule. The  $H^+$  ion itself can attack the tooth mineral crystals and directly dissolve by combining with either the carbonate ion or the phosphate ion, as shown in equation (1).



The effect of direct attack by the hydrogen ion is to combine with the carbonate and/or phosphate releasing all of the ions from that region of the crystal surface leading to direct surface etching. For example, hydrochloric acid, which dissociates completely in water to hydrogen ions and chloride ions, rapidly and directly dissolves and removes the mineral surface. The chloride ion plays no role in the mineral dissolution process.



**Fig. 1.** Schematic representation of citrate ion chelating a calcium ion. The diagram represent the situation where two of the COOH groups have lost the hydrogen and are negatively charged, thereby attracting the positively charged calcium ion (**a**). In the basic pH range even three COOH groups may have lost the hydrogen (**b**).

**Table 2.** Acid dissociation constants ( $\text{pK}_a = -\log K_a$ , where  $K_a$  is the acid dissociation constant) and calcium association constants (where  $\log K^*$  is the stability constant with calcium ion) for selected acids and chelating agents (thermodynamic values for 25°C except where indicated) [in part from 18]

Acid	$\text{pK}_{a1}$	$\text{pK}_{a2}$	$\text{pK}_{a3}$	$\log K_{Ca}(1)$	$\log K_{Ca}(2)$	$\log K_{Ca}(3)$
Acetic	4.76			1.18		
Lactic	3.86			1.45		
Citric	3.13	4.76	6.40	1.10	3.09	4.68
Phosphoric	2.15	7.20	12.35	1.40	2.74	6.46
Tartaric	3.04	4.37		0.92**	2.80	
Carbonic	6.35	10.33		1.00	3.15	
Oxalic	1.25	4.27		1.84	3.00***	
EDTA				10.7		

\*Higher numbers indicate stronger binding.

\*\*Temperature not stated, ionic strength 0.2.

\*\*\*18°C, zero ionic strength.

Acids such as citric acid (fig. 1) have a more complex interaction. In water they exist as a mixture of hydrogen ions, acid anions (e.g. citrate) and undissociated acid molecules, with the amounts of each determined by the acid dissociation constant and the pH of the solution. The hydrogen ion behaves exactly as described above and directly attacks the crystal surface. Over and above the effect of the hydrogen ion the citrate anion may complex with calcium also removing it from the crystal surface. Each acid anion has a different strength of calcium complexation dependent on the structure of the molecule and how easily it can attract the calcium ion (fig. 1). Consequently, acids such as citric have double actions and are very damaging to the tooth surface.

The strength of acids are given by their acid dissociation constant ( $K_a$ ) values. The most useful way of describing the strength of acids is the  $pK_a$  value (table 2) which is the negative logarithm of the  $K_a$  value. When the pH value (acidity) of a solution equals the  $pK_a$  of a weak acid the acid exists as 50% anion and 50% undissociated acid molecule, providing hydrogen ions to the solution. In the case of erosion as the hydrogen ions interact with the apatite mineral the acid equilibrium shifts providing more hydrogen ions to continue the erosion. Equation (2) illustrates the equilibrium for such acids using acetic acid as an example:



The stability constant (K) for the anion–calcium interaction is a measure of the strength of this interaction. Increasing values of  $\log K$  (table 2) indicate a stronger bond. Citric acid is much more damaging to the mineral than acetic acid from the perspective of calcium binding. The stronger the bond, the more likely the anion is to pull calcium from the apatite mineral surface and into solution, i.e. to erode the crystal surface. Dental erosion is a combination of the mineral being dissolved by attack from the hydrogen ion and mineral dissolving by calcium being complexed by anions, especially those with strong chelating action such as citric acid and EDTA (table 2). EDTA is a well known chelating agent that is used to demineralize bone and teeth samples for histological evaluation. EDTA can demineralize at neutral pH because of the strength of the binding with calcium ions (table 2).

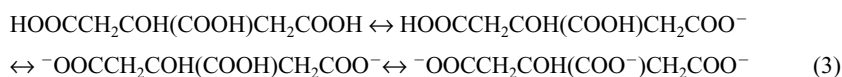
For weak acids, such as acetic acid, as the hydrogen ions are used up in their interaction with the apatite the equilibrium shifts to the right (eq. (2)) continually providing hydrogen ions until all the acid is used up. This describes chemically how acetic acid erosion in the form of vinegar works to dissolve the teeth as reported by Lussi et al. [10] for salad dressing erosion. In the case of acetic acid, the calcium/acetate formation is very weak and plays little part in erosion. On the other hand, lactic acid binds stronger to calcium because of the added OH side group on the molecule. Lactic acid ( $pK_a = 3.86$ ) is also stronger than acetic

**Table 3.** Acid composition of different beverages (g/l)

Beverage	pH	Phosphoric acid	Citric acid	D-isocitric acid	Malic acid	Miscellaneous acids
Pineapple juice	3.4–3.5		5.9		1.3	Salicylic: 0.16
Apple juice, fresh	3.0–3.4		0.05–2	0.01	7.4	Lactic: 0.17 Formic: 0.02
Cola beverage	2.2–2.6	3.3	9			Carbonic: 4–6
Grapefruit juice, fresh	3.2–3.4		13.9	194	0.44	
Orange juice, fresh	3.4–3.7		7.6–11.9	0.1	1.1–2.9	
Red wine	3.4–3.7				0.3–5.1	Lactic: 2.4 Tartaric: 1.5
White wine	3.4–3.7		0.14		3.5	Lactic: 1.7 Tartaric: 0.3

acid ( $pK_a = 4.76$ ) therefore providing hydrogen ions more readily, producing a lower pH in solution and behaving similarly to equation (2) for acetic acid. However, lactate also binds calcium. Interestingly, because of this, lactic acid can erode dental enamel even at pH 6–7, where there is almost no hydrogen ion present and the etching is due to binding of calcium with the lactate ion [11].

Citric acid is even more complicated. It has three  $pK_a$  values, one for each of the hydrogen ions reversibly bound to the citrate ion (table 2), as illustrated in figure 1 and equation (3):



The citrate ion can exist in each of the forms shown in equation (3), and when two or even all of the three H's have been removed from the molecule it forms a complex with calcium by a three-dimensional electrostatic interaction from each of the  $\text{COO}^-$  groups to the calcium ion (fig. 1; eq. (3)), thereby acting as a so-called chelator. This form will only occur in basic pH values. This means that citric acid at lower pH, such as 2, provides hydrogen ions to directly attack the mineral surface and at higher pH, such as 7, the citrate ion draws the calcium out of the crystal surface. At intermediate pH values both mechanisms are in place. In the case of fruits and fruit juices (table 3) which are high in citric acid many reports of erosion are in the literature (see chapter 7.1.1 by Lussi et al., this vol, pp 77–87).

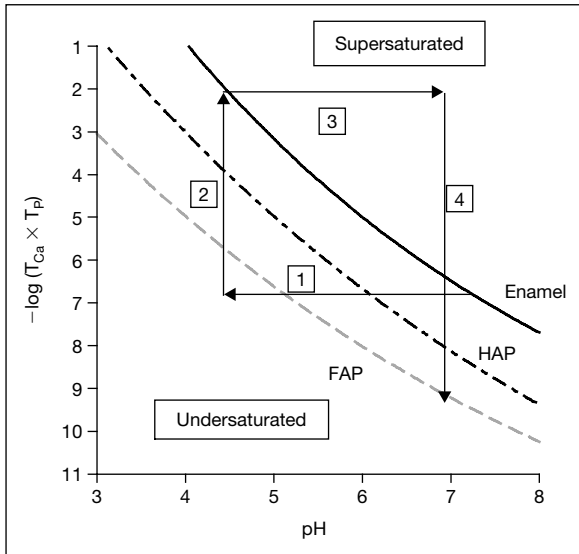
Phosphoric acid has three  $pK_a$  values and further binds to calcium in solution (table 2). Phosphoric acid provides hydrogen ions at low pH, such as 2,

and binds calcium at higher pH, such as 7. In between, both mechanisms are in effect, just as with citric acid. Citrate, however, forms a complex with calcium because of the relative sizes and three-dimensional shapes of the molecules.

### **Acid Interactions with the Mineral**

Figure 2 shows the solubility lines (so-called isotherms) for enamel mineral, HAP and FAP versus the pH, taking into consideration the concentrations of calcium and phosphate in the solution. The vertical axis is the negative logarithm of the combined total concentrations of calcium and phosphate, in any solution, which could be in saliva, in plaque fluid, in the aqueous film on the surface of the tooth, or inside the enamel or dentine. The enamel line is above the HAP line, which in turn is above the FAP line, indicating orders of magnitude differences in solubility between each of these. Dentine (not shown for clarity) is even higher in solubility than enamel. Calcium and phosphate combinations above any line are so-called ‘supersaturated’ with respect to that mineral and cannot dissolve. Below the line they are ‘undersaturated’ and dissolves. This means that if we start at a point on the enamel surface step 1 (fig. 2) indicates changing to a lower the pH, and because the solution is undersaturated with respect to enamel mineral must dissolve until the concentration increases back to the enamel solubility line (step 2). As the pH is raised by buffering from saliva (step 3; fig. 2) the solution becomes supersaturated and new mineral can form on the crystal surface (step 4; fig. 2). If fluoride is present FAP can form, which has a much lower solubility than the original enamel as described in more detail below. The additional importance of this diagram is that if the concentrations of calcium and/or phosphate are increased at any pH it is possible to be above the solubility line and to stop dissolution of the crystals. With respect to erosion it is therefore possible to add calcium and or phosphate to food and beverages, such as orange juice or black currant juice, and to protect against the erosion caused by the citric acid content. Further, the added calcium can complex with the citrate also inhibiting the chelation effect described above.

It is possible after an erosion challenge to remineralize a softened subsurface provided it has not been directly etched away. Saliva buffers the acid returning the pH to neutral, as illustrated by step 3 in figure 2. In this case calcium and phosphate from saliva or other sources can now cause remineralization, and in the presence of sufficient fluoride a new mineral surface forms which is much less soluble in acid (step 4; fig. 2). However if a severe erosion challenge follows it can still overcome the protection and directly erode the surface, especially if a chelator, such as citric acid is present.

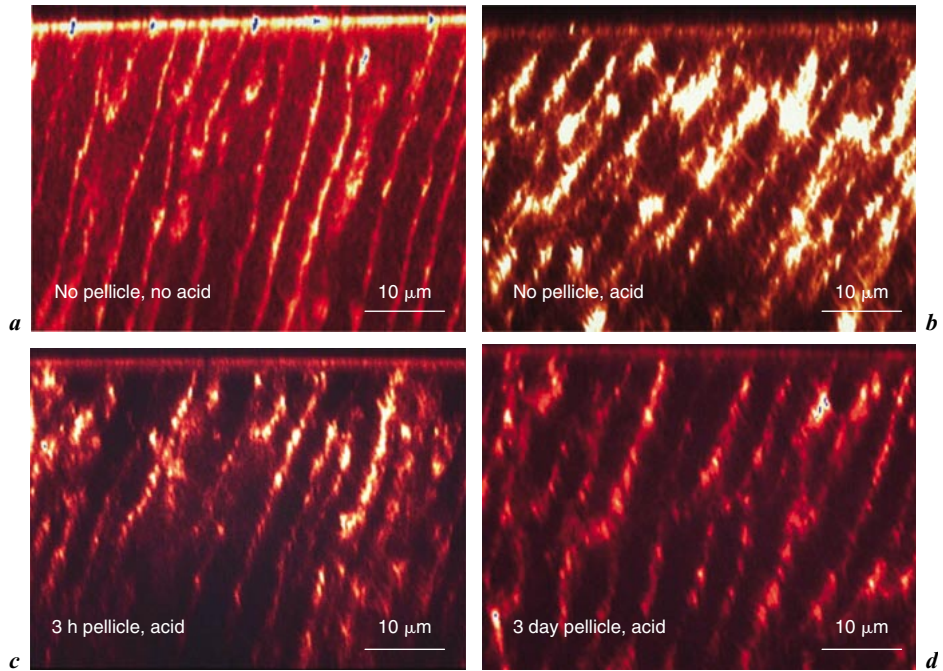


**Fig. 2.** Solubility lines for enamel, HAP and FAP.  $T_{Ca}$  and  $T_P$  are the total concentrations of calcium and phosphate in solution, respectively. The numbered steps represent stages in mineral loss by acid attack, namely lowering the pH from say 7.3 to 4.5 at the enamel surface as the acid beverage attacks the tooth surface (step 1), and dissolving calcium and phosphate (step 2). Step 3 is when saliva flows over the affected area and the pH rises to say 7.0. If fluoride is present, together with saliva the softened surface is repaired (step 4), at least partially, forming a mineral surface closer to FAP which then requires a larger pH drop to be dissolved. If fluoride is not present then the step 4 line stops at the enamel line, and the cycle simply repeats itself and the tooth mineral continues to dissolve.

### Pellicle and Diffusion Barriers

As soon as the tooth erupts into the mouth a salivary pellicle begins to form on the surface. The pellicle is derived from specific salivary proteins and lipids that bind to the surface of the tooth [12, 13]. The salivary proteins such as statherin, proline rich proteins, some histatins, and phospholipids comprise the initial pellicle [14]. The pellicle is continually regenerated throughout the life of the tooth in the mouth. The net effect with respect to erosion is that the pellicle forms a diffusion barrier, similar to a lipid/protein membrane, and protects the very outer surface against direct acid attack. The plaque bacteria build upon the pellicle, forming a further diffusion barrier, wherever plaque is present (see chapter 7.1.2 by Hara et al., this vol, pp 88–99). On smooth accessible surfaces there is often little or no plaque leaving only the pellicle as the first barrier to





**Fig. 3.** *a* Optical section perpendicular to the surface of sound enamel made with the confocal laser scanning microscope. Light-yellowish area represent interprismatic enamel, red areas represent prismatic area. From Duschner et al. [15], with permission. *b* After 15 min immersion in a Cola-like beverage the enamel was removed and dissolved underneath the surface (in the subsurface region). Further, hardness measurement showed distinct softening of the surface. *c* Image of enamel after a pellicle was formed for 3 h and 15 min immersion in a Cola-like beverage. The band-like structure of enamel can be identified indicating partial protection against subsurface dissolution. Hardness measurement showed still softening of the surface. *d* Image of enamel after a pellicle was formed for 3 days. The band-like structure of enamel can be clearly identified with only small differences to the control. Hardness measurement showed no significant softening of the surface.

acid erosion. At the gingival margin there is almost always plaque and crevicular fluid access thereby protecting a narrow band from erosion.

To investigate these aspects experiments were done with and without pellicle present [15]. Figure 3 illustrates, using confocal microscopy, the partial protective effect of pellicle against erosion. In these experiments enamel samples, with or without pellicle, were immersed for 15 min in a Cola type beverage, pH 2.6, which included phosphoric acid. The control panel shows no erosion. Without pellicle, removal and surface softening of enamel was observed together with dissolution underneath the surface (in the subsurface region) (fig. 3b).

When pellicle was formed over 3 h, the surface was still softened, but there was partial protection against subsurface dissolution (fig. 3c). The samples with 3-day pellicle markedly reduced surface softening and essentially eliminated subsurface attack. These observations can be interpreted using the information set out above for phosphoric acid. At pH 2.6 the hydrogen ion concentration is such that direct etching occurs by the hydrogen ion in the absence of pellicle since there is nothing to protect the surface. In the case of the 3-h pellicle it is not sufficient to protect the outer surface but it does form a partial diffusion barrier to the subsurface. In this case, the phosphoric acid molecule is able to diffuse in its undissociated state into the subsurface region [8, 16], dissociating as it goes providing hydrogen ions and phosphate ions to attack the mineral. In the case of the 3-day mature pellicle there was considerable surface protection as expected from earlier studies that showed protection increased after 18 h and took 7 days to be essentially complete [17]. Importantly, the 3-day pellicle markedly reduced the ability of even the phosphoric acid molecule to diffuse into the subsurface regions.

The conclusions from the pellicle experiments described above are clinically significant because they illustrate how important the type of acid is and whether there is a pellicle present from the saliva. Further, if the dental erosion lesion has a subsurface softening component rather than direct etching alone there is a chance for repair and reversal, since the saliva can provide calcium and phosphate to remineralize these regions, aided by fluoride. Salivary pellicle can partially protect against erosion challenges providing they are not too severe and/or frequent. Saliva also clears the erosion-inducing acids from the surface, but again the eventual outcome depends on the balance between the frequency and severity of the erosion challenge versus the protective effects of saliva.

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Prof. Dr. J.D.B. Featherstone  
Department of Preventive and Restorative Dental Sciences  
University of California at San Francisco  
Room 0603, Box 0758  
707 Parnassus Avenue  
San Francisco, CA 94143 (USA)