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# Effects of calcium and phosphate on dissolution of enamel, dentin and hydroxyapatite in citric acid

Calcium, phosphate and erosion

#### KEYWORDS

Enamel  
Dentin  
Hydroxyapatite  
Dental erosion  
Dissolution  
pH-stat  
Calcium  
Phosphate

#### SUMMARY

The aim was to evaluate the effect of dissolved calcium and phosphate on dissolution rate of enamel, dentin and compressed hydroxyapatite (HA) in citric acid solution as a function of pH. At pH 2.5, dissolution rate of enamel increased significantly by 6% in 20 mmol/L added calcium but, otherwise, dissolution rates of neither enamel, dentin nor HA were significantly affected by 10 or 20 mmol/L calcium. However, enamel dissolution rate was reduced by >50 mmol/L calcium. At pH 3.25 and 4.0, 10–20 mmol/L calcium inhibited dissolution of enamel by 29–100% and HA by 65–75% but did not affect dentin dis-

solution. Phosphate (10 or 20 mmol/L) did not inhibit dissolution of enamel, dentin or HA at any pH, but there were increases in dissolution rate of all three substrates at pH 2.5 and, in one test with dentine (at 20 mmol/L phosphate), at pH 3.25. The results suggest that calcium addition to soft drinks and other acidic products such as medications may reduce erosivity against enamel, provided that pH is not too low, that phosphate would not reduce erosivity against enamel and that neither calcium nor phosphate at these concentrations would reduce erosivity against dentin.

## Introduction

Erosive tooth wear has a high prevalence in some populations, particularly among children and young people (JAEGGI & LUSSI 2014; SCHLUETER & LUKA 2018; SHRESTHA & RAJBHANDARI 2018; ENTEZAMI ET AL. 2021; YIP ET AL. 2022). The condition appears to be influenced by several factors associated with socioeconomic status (ENTEZAMI ET AL. 2021), occupation and medical conditions that involve regurgitation (SCHLUETER & LUKA 2018; YIP ET AL. 2022).

Soft drinks, and possibly fruit juices, have been identified as risk factors (LI ET AL. 2012; SALAS ET AL. 2015), and there is interest in investigating the factors that determine their erosive potential and in finding ways to make them less erosive. In vitro tests show that pH, buffering properties and calcium concentration have a statistically significant negative association with erosive potential of a variety of drinks and other products in multiple regression analyses (HARA & ZERO 2008; LUSSI ET AL. 2012, AND REFERENCES THEREIN). In addition, degree of saturation, phosphate concentration and fluoride concentration show significant bivariate correlations with erosive potential.

In principle, the erosive potential can be reduced by adding calcium or phosphate (GRENBY 1996). In this context, “phosphate” signifies orthophosphate. These modifications would reduce the degree of undersaturation with respect to dental mineral, through the common-ion effect. Many experiments have been conducted with complex phosphates, but these are not relevant to the present discussion as any effect they may have will be due to surface effects not to their effect on the degree of saturation. Addition of calcium to acid solutions, soft drinks or candies are known to reduce in vitro dissolution of enamel (ATTIN ET AL. 2003; ATTIN ET AL. 2005; BARBOUR ET AL. 2003; DAVIS ET AL. 2007; JENS DOTIR ET AL. 2007; MAGALHÃES ET AL. 2009) or hydroxyapatite (HA) (ANDON ET AL. 1992; BARBOUR ET AL. 2008; HEMINGWAY ET AL. 2008). Addition of about 10 mmol/L calcium to fruit-based drinks successfully reduced erosion in situ (WEST ET AL. 1999; HOOPER ET AL. 2004).

Information about the effect of phosphate addition on erosion potential is, however, very limited. McDONALD & STOOKEY (1973) reported large reduction in erosion by soft drinks or organic acid solutions supplemented by addition of phosphate. ATTIN ET AL. (2003) reported that supplementation of citric acid solution with low concentrations of phosphate significantly reduced softening and surface loss of enamel.

Dissolution of HA and dental tissues increases with decreasing pH, and dissolution is progressively reduced by increasing calcium concentrations at pH 3.2–3.3 (BARBOUR ET AL. 2003; BARBOUR ET AL. 2008; HEMINGWAY ET AL. 2008). However, there remain lacunae in knowledge of interactions between pH and concentration of calcium or phosphate. Moreover, there is little information in this respect for dentin (SHELLIS ET AL. 2010). The aim of the present study was to examine systematically the effects of adding calcium and phosphate to citric acid solutions on dissolution at defined pH, using not only enamel and dentin but also compressed HA: a useful model for dental hard tissues in erosion studies (BARBOUR ET AL. 2005).

## Materials and methods

Specimens were prepared as described by SHELLIS ET AL. (2010). Slices, about 1.3 mm thick, of which the outer cut surface was composed entirely of enamel, were prepared from the thick enamel lateral to the cusps of human molars by cutting parallel with the surface tangent at depths of 1 and 2.5 mm. Dentin

specimens were prepared by serially sectioning human tooth roots parallel with the long axis and selecting slices that were tangential to the surface and did not include part of the pulp cavity. The outer cut surfaces of both enamel and dentin specimens were polished using 1200 grade silicon carbide powder in water, rinsed in water and dried. The natural surfaces of the specimens, and areas of cementum on the dentin specimens, were coated with nail varnish. The areas of the unvarnished surfaces of the specimens were determined by digitally scanning the specimens alongside a millimeter scale, using a Canoscan 4400F scanner (Canon UK, Reigate, UK) and by image analysis of the scanned images using a Wacom digitizing tablet and ScionImage software (www.scioncorp.com; Scioncorp, Frederick, MD, USA). For each specimen, the mean of three area determinations was calculated. For use in the pH-stat, specimens were attached with wax to the tip of a gas inlet tube (Quickfit) that fitted the reaction vessel lid.

Discs of compressed HA (HiMed Inc, Old Bethpage, NY, USA), diameter 12 mm, were conditioned by ultrasonication and pre-treatment in citric acid solution prior to use to ensure consistency of response (SHELLIS ET AL. 2010). After fixation to the specimen holder, the back and edges were coated with nail varnish.

## pH-stat measurements

A Metrohm Combistat system was used in conjunction with a Metrohm 713 digital pH meter (Metrohm UK, Runcorn, UK) as described by SHELLIS ET AL. (2010), using 15 mL citric acid solution, maintained at 36 °C in a 50 mL double-walled reaction vessel and magnetically stirred at a constant rate. The glass combination electrode was calibrated using buffers with an accuracy of 0.01 and nominal pH values of 2.0, 4.0 and 7.0 (Sigma-Aldrich, Poole, Dorset, UK). After equilibration and pH adjustment, the reaction was initiated by introducing the specimen on its holder and addition of titrant (50 mmol/L HCl) was recorded for an appropriate time.

## Experimental details

Dissolution in 14.3 mmol/L citric acid was studied at pH 2.5, 3.25 and 4.0. Dissolution of enamel, HA and dentin was studied at 0, 10 and 20 mmol/L calcium or phosphate. Calcium was added as CaCl<sub>2</sub>·2H<sub>2</sub>O and phosphate as KH<sub>2</sub>PO<sub>4</sub>. Multiple measurements were possible for enamel and HA, since preliminary experiments showed that the effects of calcium or phosphate were not persistent, so four enamel and four HA specimens were used in the experiments with calcium and another four of each in the experiments with phosphate. In these experiments, the order of treatments was determined by a random sequence generator (www.random.org). Exposure of dentin to acid alters the surface by creating a superficial layer of demineralized collagen (SELVIG 1968; KINNEY ET AL. 1995), so four separate dentin specimens were used for each combination of pH and calcium or phosphate concentration.

The pH-stat system used for the bulk of the measurements (Series 1) failed before the experiments on the effect of dentin had been completed: no data had been collected for the experiments on 10 mmol/L phosphate. Therefore, all of the dentin/phosphate experiments were repeated (Series 2) with a different pH-stat system (718 STAT Titrimo, Metrohm UK, Runcorn, UK). However, the same reaction vessel was used, and all variables such as temperature, stirrer and stirring rate were the same.

The results of the experiments with the first pH-stat indicated that dissolution rate sometimes increased following addition of calcium and, to a lesser extent, phosphate. A possible explanation for this result is that the additions, by raising the ionic strength, could reduce ion activity coefficients and hence the degree of saturation. It was calculated that addition of calcium and phosphate salts raised ionic strength by 10.2–59.5 mmol/L (Tab. 1). Therefore, in supplementary experiments the effects of ionic strength on enamel and HA dissolution rate at pH 2.5 (4 specimens of each) were investigated. Rates were measured, in random order, in 14.3 mmol/L citric acid containing 0 (control), 10, 20, 30 or 60 mmol/L KCl.

### Data analysis

After an initial period (typically <60s), the dissolution rate of HA or enamel was constant and the slope of this linear part of the titrant addition recording was the outcome variable. For dentin, the rate decreased with time and the outcome variable was the initial velocity, estimated as the first derivative of a third-degree polynomial fitted to the data ( $r^2 > 0.999$ ). Units were converted to nmol HA/min/mm<sup>2</sup> by multiplying the rate of acid consumption (mL acid/min), as obtained above, by 1000CF/A, where C = the titrant concentration (50 mmol/L); A = exposed surface area of specimen (mm<sup>2</sup>) and F was a factor (= mol HA dissolved per mol H<sup>+</sup> consumed), calculated as described by SHELLIS ET AL. (2010).

At each pH, enamel and HA dissolution rates were compared with the controls (0 Calcium or Phosphate) by paired t-test. Dentin dissolution rates in the presence of calcium or phosphate were compared with that for the controls by unpaired t-test. Enamel and HA dissolution rates at different KCl concentrations were compared by repeated measures ANOVA.

Statistical calculations were performed using XLSTAT v. 7.5 (Addinsoft). Other calculations were performed using ion speciation programs IONPRODUCT (SHELLIS 1988) and CurTiPot (GUTZ 1992–2021).

## Results

### Effect of calcium (Fig. 1)

At pH 2.5, 10 mmol/L calcium had no significant effect on enamel dissolution rate, while 20 mmol/L calcium significantly increased the mean rate compared with the controls by 6.1% ( $p = 0.007$ ). At pH 3.25 and 4.0, 10 and 20 mmol/L calcium sig-

nificantly reduced dissolution rate, by 29% and 46% respectively ( $p < 0.004$ ). At pH 4.0, 10 mmol/L calcium reduced dissolution by 83% ( $p = 0.003$ ). In the presence of 20 mmol/L calcium, dissolution was not detectable.

At pH 2.5, addition of 10 mmol/L calcium resulted in a slight and statistically non-significant increase in HA dissolution rate ( $p = 0.053$ ) but 20 mmol/L calcium had no effect. At pH 3.25, dissolution rate was reduced significantly in 10 mmol/L calcium by 66% at pH 3.25 and 76% in 20 mmol/L calcium ( $p < 0.01$ ). The corresponding reductions at pH 4.0 were 69% and 72% ( $p < 0.013$ ).

The dissolution rate of dentin was not significantly affected by either 10 or 20 mmol/L calcium at any pH ( $p = 0.08–0.89$ ).

### Effect of phosphate (Fig. 2, 3)

Despite efforts to use the same reaction conditions, the results obtained with the replacement pH-stat (Series 2) were consistently higher than those of Series 1. Therefore, the Series 2 data were analyzed separately.

At pH 2.5, enamel dissolution rate increased significantly and substantially: by 14% ( $p = 0.043$ ) and 24% in the presence of 10 or 20 mmol/L phosphate respectively ( $p = 0.007$ ). At pH 3.25 and 4.0, neither phosphate concentration significantly affected dissolution rate ( $p > 0.208$ ).

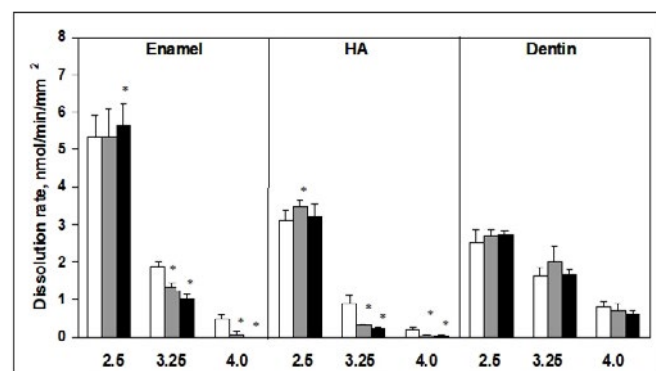
At pH 2.5, addition of 10 mmol/L phosphate significantly increased HA dissolution rate by 25% ( $p = 0.002$ ), but 20 mmol/L had no significant effect ( $p = 0.809$ ). At pH 3.25 and 4.0, phosphate did not affect dissolution rate.

In Series 1 (Fig. 2), at pH 2.5, 20 mmol/L phosphate significantly increased dentin dissolution rate by 25% ( $p = 0.035$ ), but at pH 3.25 and pH 4.0 phosphate had no significant effect.

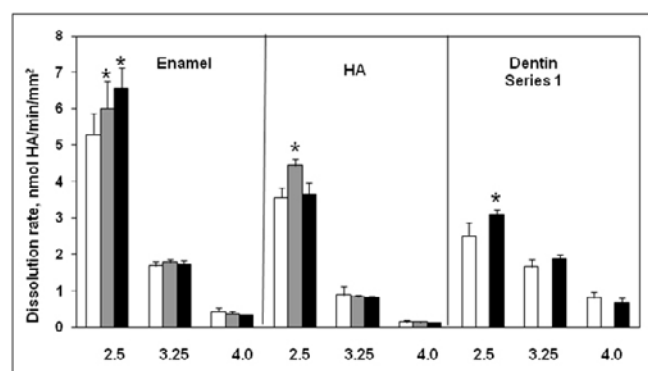
In Series 2 (Fig. 3), at pH 2.5, 10 mmol/L phosphate significantly increased dissolution rate of dentin by 46% ( $p = 0.024$ ), and 20 mmol/L phosphate increased the rate by 51%, but this was not significant. At pH 3.25, dissolution rate was increased by 21% ( $p = 0.08$ ) at 10 mmol/L phosphate and 34% at 20 mmol/L phosphate ( $p = 0.015$ ). At pH 4.0, dissolution rate increased by 9% and 12% in the presence of 10 and 20 mmol/L phosphate ( $p = 0.27$  and 0.06, respectively).

### Effect of ionic strength (Fig. 4)

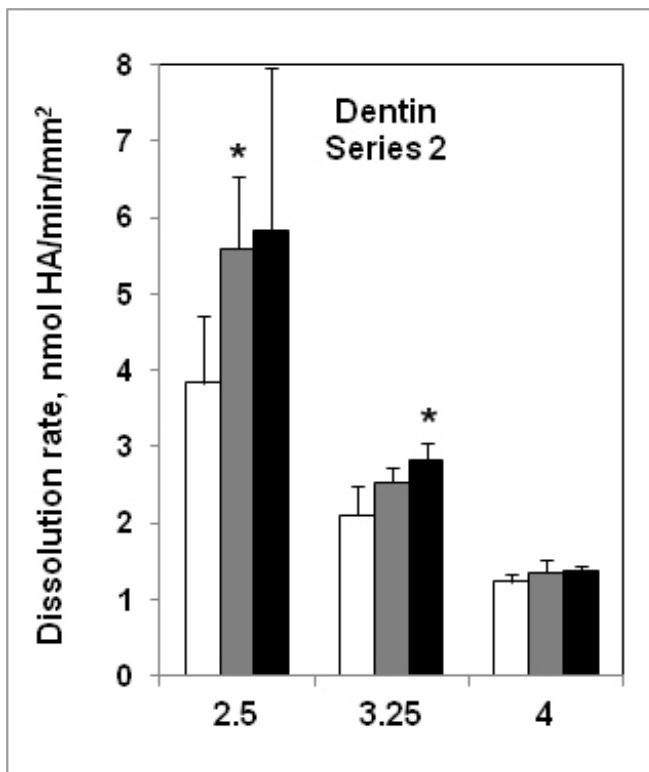
In the presence of 10–60 mM KCl, there was a non-significant increase in dissolution rate of enamel ( $p = 0.077$ ) and no change in that of HA ( $p = 0.79$ ).



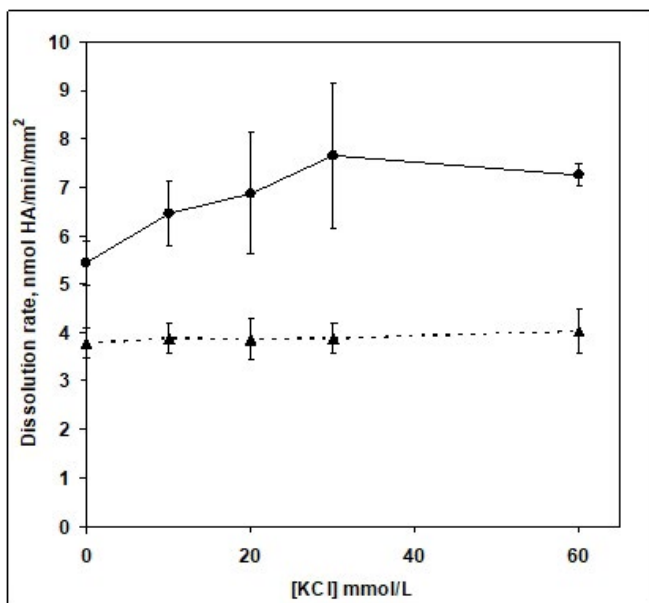
**Fig. 1** Effect of calcium on dissolution of enamel, compressed hydroxyapatite and dentin. White bars = control (no calcium); grey bars = 10 mmol/L calcium; black bars = 20 mmol/L calcium. Error bars = 1 SD. Asterisks indicate significant difference from control.



**Fig. 2** Effect of phosphate on dissolution of enamel, compressed hydroxyapatite and dentin (Series 1). White bars = control (no phosphate); grey bars = 10 mmol/L phosphate; black bars = 20 mmol/L phosphate. Error bars = 1 SD. Asterisks indicate significant difference from control.



**Fig. 3** Effect of phosphate on dissolution of dentin (Series 2). White bars = control (no phosphate); grey bars = 10 mmol/L phosphate; black bars = 20 mmol/L phosphate. Error bars = 1 SD. Asterisks indicate significant difference from control.



**Fig. 4** Effect of KCl concentration on dissolution rate of enamel (solid line) and compressed hydroxyapatite (broken line). Error bars =  $\pm 1$  SD.

## Discussion

The pH range was chosen as representative of soft drinks (LUSSI ET AL. 2012). In agreement with previous studies (DAVIS & WINTER 1980; BARBOUR ET AL. 2003; BARBOUR ET AL. 2008; HEMINGWAY ET AL. 2008), dissolution rate fell rapidly from pH 2.5 to pH 3.25 and then more slowly to pH 4.0. The concentrations of added calcium and phosphate were based on the fact that addition of

10 mmol/L calcium successfully reduced the erosivity of a fruit-based drink in situ (WEST ET AL. 1999). Addition of calcium or phosphate carries with it increased risk of calcium-phosphate precipitation and of taste alteration. If added as basic salts, there can also be a rise in pH that both affects taste adversely and reduces stability against bacterial contamination and proliferation. Thus, high calcium or phosphate concentrations are not practical. We therefore confined our experiments to two relatively low concentrations.

At pH 3.25 and 4.0, the enamel dissolution rate responded to calcium as predicted by the common-ion effect. This agrees with previous studies that had been conducted at pH 3.0–3.7 (BARBOUR ET AL. 2003; ATTIN 2005; JENSDOTTIR ET AL. 2007; MAGALHÃES ET AL. 2009). We found that at pH 2.5 enamel dissolution rate was not reduced by 10 or 20 mmol/L calcium and even increased. This effect was also observed in preliminary experiments that showed that, at this pH, the rate was only reduced by 3% at 50 mmol/L then continued to fall up to 200 mmol/L calcium (data not shown).

However, our results do not agree with the study by ATTIN ET AL. (2003), who reported that addition of only 0.5–1.5 mmol/L calcium reduced softening of enamel and surface loss by 52 mmol/L citric acid, pH 2.21.

Despite the marked structural differences between the two materials (SHELLIS ET AL. 2010), the dissolution rate of compressed HA responded to calcium and phosphate in a very similar fashion to that of enamel. Although compressed HA is less influenced by acid concentration (SHELLIS ET AL. 2010), the evidence supports the utility of this material as a convenient substitute for enamel.

At pH 3.25 and 4.0, neither calcium nor phosphate reduced the rate of dentin dissolution. Because the surface of eroding dentin is covered by demineralized collagenous matrix, the advancing front of demineralization becomes isolated from the bulk solution and exchange between the two will be slow and diffusion-controlled. The demineralization process might then be relatively less responsive to changes in the driving force in the bulk solution. Constant-composition dissolution of dentin is insensitive to the degree of undersaturation (PASCHALIS ET AL. 1996). Thus, modification of drinks that have a pH in the range 3.25–4.0 by addition of low concentrations of calcium or phosphate is unlikely to reduce erosion of exposed root surfaces in adults. The reason for the lack of effect of added phosphate seems to be the very low concentration of  $\text{PO}_4^{3-}$  ions at these pH values (Tab. 1).

At pH 2.5, addition of phosphate tended to increase the rate of dissolution of both enamel and dentin. There are two possible explanations for this phenomenon. First, the increased ionic strength (Tab. 1), by reducing ion activities, could lower the degree of saturation and hence increase dissolution rate. However, our experiments with enamel and HA suggest that the rate, at least of these materials, is not increased by the observed increase in ionic strength (BARBOUR ET AL. 2008). The second possibility is that the increased buffer capacity in the calcium- and phosphate-containing solutions (Tab. 1) is likely to cause an increase in the dissolution rate. Buffering is an important factor in erosion in vitro (SHELLIS ET AL. 2010; SHELLIS ET AL. 2013) and has been identified as important in the erosive potential of soft drinks (LUSSI ET AL. 2012).

At first sight, the data of McDONALD & STOOKEY (1973) suggest that phosphate could reduce erosion potential if added at high enough concentration, since they observed large reductions in

Tab.1 Properties of test solutions

pH	Added Ca mmol/L	Increase in ionic strength mmol/L	Buffer capacity $\beta$ mmol/(L.pH)	Added P mmol/L	Increase in ionic strength mmol/L	Buffer capacity $\beta$ mmol/(L.pH)	[PO <sub>4</sub> <sup>3-</sup> ] mmol/L
2.5	0		13.5	0		13.5	
	10	29.7	14.8	10	10.2	19.0	7.24.10 <sup>-12</sup>
	20	59.5	15.4	20	20.3	24.1	1.81.10 <sup>-13</sup>
3.25	0		10.6	0		10.6	
	10	28.1	10.8	10	9.5	12.3	4.04.10 <sup>-12</sup>
	20	56.8	11.0	20	19.0	13.9	9.84.10 <sup>-12</sup>
4.0	0		9.0	0		9.0	
	10	28.2	9.0	10	17.4	9.6	1.67.10 <sup>-10</sup>
	20	53.6	9.4	20	27.6	10.1	3.92.10 <sup>-10</sup>

P = total phosphate

calcium release from enamel when 83 mmol/L phosphate was added to soft drinks or to three organic acid solutions. However, addition of NaH<sub>2</sub>PO<sub>4</sub> will also raise the pH of the solution. Using CurTiPot software (GUTZ 1992–2021), we calculate that pH of the acid solutions used by McDONALD & STOOKEY (1973) would have increased from initial values of 2.53, 2.68 and 2.58 by 0.54, 0.63 and 0.56, respectively. Figures 1–3 suggest that such increases in pH would produce significant reductions in dissolution rate of either enamel or dentin.

The effect on pH of adding calcium or phosphate salts to acid solutions may have influenced results of previous studies. Alterations of solution pH after supplementation with calcium are seen in MAGALHÃES ET AL. (2009) and in JENS DOTTIR ET AL. (2007). In the latter, pH fell after addition of calcium citrate. In the study of calcium-containing soft drinks by DAVIS ET AL. (2007), an increase of calcium concentration by 8.4–36.9 mmol/L<sup>1</sup> reduced erosion depth in enamel by 60–100% and in dentin by 7–36% after 25 h exposure. However, in <sup>3</sup>/<sub>4</sub> comparisons, the pH of the high-calcium drink was 0.33–0.4 units higher than that of the low-calcium drink. In the remaining comparison (equal pH), the difference in dissolution rates of both enamel and dentin was much lower than in the other comparisons, and it appears that the erosive potential of the drinks was determined in part by pH. The reduction of in situ erosion by a drink with an original pH of about 2.9 was not achieved solely by addition of calcium since it was added as CaCO<sub>3</sub>, which raised the pH by nearly 1 unit (WEST ET AL. 1999). For each modification of a drink by calcium addition, the reduced erosive potential has to be balanced against possible changes in pH and hence palatability and shelf life.

In conclusion, the effects of calcium and phosphate on dissolution rate in the pH-stat are highly pH- and tissue-dependent. The results suggest that, with respect to enamel, calcium at the concentrations used here would not usefully reduce erosivity of highly acidic drinks, that phosphate would not reduce erosivity at any pH < 4.0 and that neither would reduce erosivity against dentin, but that calcium would reduce erosion by

moderately acidic drinks (pH > 3.25). Compressed HA responded to changes in calcium and phosphate concentration in a very similar manner to enamel highlighting its utility as a convenient and consistent alternative to enamel without the constraints of human tissue legislation and the biological variability that enamel inevitably exhibits.

We recognize that our experiments were conducted under “clean” conditions, so the results may well not be transferable directly to clinical conditions. A particularly important factor is the presence in vivo of salivary pellicle, which is well known to reduce the rate of dissolution of dental enamel in acid (HANNIG & HANNIG 2014). However, in vitro measurements of erosion of enamel specimens coated with a salivary pellicle (LUSSI ET AL. 2023) support the results of the present study. The quantitative response of dental hard tissues to modification of erosive conditions is likely to differ in vivo. However, we suggest that addition of calcium or phosphate to erosive products should not be assumed to simply reduce dissolution of dental minerals. The overall effect, influenced by interactions between calcium and phosphate ion concentrations, pH and buffering, may be difficult to predict.

## Acknowledgement

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## Zusammenfassung

Einfluss von Kalzium und Phosphat auf die Auflösung von Zahnschmelz, Dentin und Hydroxylapatit in Zitronensäure

## Einleitung

Die Zugabe von Kalzium oder Phosphat wurde als mögliche Methode zur Verringerung der erosiven Wirkung von Erfrischungsgetränken und anderen Produkten vorgeschlagen. Wir untersuchten in Abhängigkeit des pH-Wertes und des Kalzium- und Phosphatgehaltes von Zitronensäure die Auflösung der Zahnhartsubstanz und von komprimiertem Hydroxylapatit (HA).

<sup>1</sup> Our calculations, assuming a serving size of 236.6 mL (8 ounces) and a daily value for calcium of 1000 mg.

## Material und Methoden

Die Testlösungen enthielten 14,3 mmol/l Zitronensäure mit pH-Werten von pH 2,5, 3,25 oder 4,0. Bei jedem pH-Wert wurde die Auflösung von Schmelz, Dentin und HA bei Zugabe von 0, 10 oder 20 mmol/l Kalzium oder Phosphat festgehalten. Die Auflösungsrate wurde mit einem pH-stat-System gemessen.

## Resultate

In Übereinstimmung mit früheren Studien sank die Auflösungsrate von Schmelz, Dentin und HA mit der Erhöhung des pH-Wertes von pH 2,5 auf pH 4,0. Der Rückgang war bei Zahnschmelz und HA ausgeprägter als bei Dentin.

Bei pH 2,5 stieg die Auflösungsrate des Zahnschmelzes um 6%, sofern 20 mmol/l Kalzium zugesetzt wurden. Die Auflösungsraten weder von Zahnschmelz, noch Dentin oder HA wurden bei diesem pH-Wert signifikant durch Zugabe von 10 oder 20 mmol/l Kalzium beeinflusst. Zusätzliche Experimente zeigten jedoch, dass die Schmelzauflösungsrate bei Zugabe von mehr als 50 mmol/l Kalzium reduziert wurde. Bei pH 3,25 und 4,0 hemmten 10–20 mmol/l Kalzium die Auflösung des Zahnschmelzes um 29–100% und von HA um 65–75%, beeinflussten aber nicht die Dentinauflösung.

Phosphat (10 oder 20 mmol/l) hemmte unabhängig vom pH-Wert die Auflösung von Zahnschmelz, Dentin oder HA nicht. Wir beobachteten hingegen eine Erhöhung der Auflösungsgeschwindigkeit aller drei Substrate bei pH 2,5 und in einem Test mit Dentin (bei 20 mmol/l Phosphat) bei pH 3,25. Es wird vermutet, dass eine Erhöhung der Auflösungsrate auf eine erhöhte Pufferkapazität zurückzuführen ist.

## Diskussion

Die Ergebnisse zeigen, dass die Zugabe von Kalzium zu sauren Lösungen die Erosivität für Zahnschmelz verringern kann, vorausgesetzt der pH-Wert ist nicht zu niedrig. Die Zugabe von Phosphat hingegen kann die Erosivität für Zahnschmelz nicht verringern. Weder Kalzium noch Phosphat hat bei diesen Konzentrationen einen protektiven Effekt bei Dentin. In vivo wird die Erosion noch durch andere Faktoren beeinflusst, die in dieser Studie nicht berücksichtigt wurden. Zum Beispiel kann die Beimischung von Speichel zu einem sauren Produkt die Erosivität beeinflussen. Die Pellikel und organische Bestandteile, die an der Zahnoberflächen adsorbieren, können die Interaktion von Zähnen mit erosiven Produkten beeinflussen. Die Ergebnisse zeigen ferner, dass der Einfluss von Kalzium und Phosphat auf die Auflösungs geschwindigkeit pH- und gewebeabhängig ist. Diese Faktoren sollten bei der Formulierung von Produkten mit kleinem erosivem Potenzial berücksichtigt werden. Eine praktische Schwierigkeit besteht ferner darin, dass einige Kalziumsalze wie Kalziumchlorid den Geschmack beeinträchtigen und alternative Substanzen den pH-Wert beeinflussen können. So erhöht die Modifikation eines erosiven Produkts durch Zugabe von Kalziumkarbonat den pH-Wert, was sich nachteilig auf Geschmack und Haltbarkeit auswirken könnte.

## Résumé

### Introduction

L'ajout de calcium ou de phosphate a été proposé comme méthode possible pour réduire l'effet érosif de boissons rafraîchissantes et d'autres produits. Nous avons investigué la dissolution

de la substance dentaire dure et de l'hydroxyapatite (HA) comprimée en fonction de la valeur du pH et de la teneur en calcium et en phosphate de l'acide citrique.

### Matériel et méthodes

Les solutions testées contenaient 14,3 mmol/l d'acide citrique, et leur pH était de 2,5, 3,25 ou 4,0. Pour chacune de ces valeurs de pH, la dissolution de l'émail, de la dentine et de l'HA a été déterminée après ajout de 0, 10 ou 20 mmol/l de calcium ou de phosphate. Les taux de dissolution ont été déterminés à l'aide d'un système pH-stat.

### Résultats

Conformément à des études précédentes, le taux de dissolution de l'émail, de la dentine et de l'HA a diminué avec l'augmentation de la valeur du pH de pH 2,5 à pH 4,0. Cette diminution a été plus importante pour l'émail et l'HA comparativement à la dentine.

À pH 2,5, le taux de dissolution de l'émail a augmenté de 6% lorsque 20 mmol/l de calcium avaient été ajoutées. Le taux de dissolution de l'émail, de la dentine et de l'HA n'a pas été modifié significativement, à ce pH, par l'ajout de 10 ou 20 mmol/l de calcium. Des expériences supplémentaires ont cependant montré que le taux de dissolution de l'émail était réduit après ajout de plus de 50 mmol/l de calcium. À pH 3,25 et 4,0, l'ajout de 10–20 mmol/l de calcium a inhibé la dissolution de l'émail de 29–100% et de l'HA de 65–75%, mais n'a pas influencé la dissolution de la dentine.

Le phosphate (10 ou 20 mmol/l) n'a pas inhibé la dissolution de l'émail, de la dentine et de l'HA aux différentes valeurs de pH testées. En revanche, nous avons observé une augmentation de la vitesse de dissolution de ces trois substrats à pH 2,5 et, lors d'un test avec la dentine (avec 20 mmol/l de phosphate), à pH 3,25. Il semble bien que l'augmentation du taux de dissolution résulte d'une augmentation du pouvoir tampon.

### Discussion

Les résultats montrent que l'ajout de calcium à des solutions acides peut en diminuer l'érosivité sur l'émail dentaire, à condition que le pH ne soit pas trop bas. En revanche, l'ajout de phosphate ne permet pas de réduire l'érosivité sur l'émail dentaire. Aux concentrations testées, un effet protecteur du calcium et du phosphate sur la dentine n'a pas été mis en évidence. In vivo, l'érosion est également influencée par d'autres facteurs qui n'ont pas été pris en compte dans cette étude. Par exemple, l'ajout de salive à un produit acide peut influencer son érosivité. La pellicule et les composants organiques adsorbés à la surface dentaire peuvent influencer l'interaction entre les dents et les produits érosifs. Les résultats montrent également que l'influence du calcium et du phosphate sur la vitesse de dissolution dépend du pH et du substrat tissulaire considéré. Ces facteurs devraient être pris en compte afin d'élaborer des produits à faible potentiel érosif. Une autre difficulté pratique réside dans le fait que certains sels de calcium, comme le chlorure de calcium, peuvent altérer le goût des boissons et autres produits, et que certaines substances alternatives peuvent en modifier le pH. Ainsi, la modification d'un produit érosif par adjonction de carbonate de calcium en augmente le pH, ce qui pourrait avoir un effet négatif sur son goût et sa durée de conservation.

## References

- ANDON M B, KANERVAS R L, ROTRUCK J T, SMITH K T: Method of preventing tooth enamel erosion utilizing an acidic beverage containing calcium. US Patent 5,108,761 (1992)
- ATTIN T, MEYER K, HELLWIG E, BUCHALLA W, LENNON Á M: Effect of mineral supplements to citric acid on enamel erosion. *Arch Oral Biol* 48: 753–759 (2003)
- ATTIN T, WEISS K, BECKER K, BUCHALLA W, WIEGAND A: Impact of modified acidic soft drinks on enamel erosion. *Oral Dis* 11: 7–12 (2005)
- BARBOUR M E, PARKER D M, ALLEN G C, JANDT K D: Enamel dissolution in citric acid as a function of calcium and phosphate concentrations and degree of saturation with respect to hydroxyapatite. *Eur J Oral Sci* 111: 428–433 (2003)
- BARBOUR M E, SHELLIS R P, PARKER D M, ALLEN G C, ADDY M: Inhibition of hydroxyapatite dissolution by whole casein: the effects of pH, protein concentration, calcium, and ionic strength. *Eur J Oral Sci* 116: 473–478 (2008)
- DAVIS R E, MARSHALL T A, QIAN F, WARREN J J, WEFEL J S: In vitro protection against dental erosion afforded by commercially available, calcium-fortified 100 percent juices. *J Am Dent Ass* 138: 1593–1598 (2007)
- DAVIS W B, WINTER P J: The effect of abrasion on enamel and dentin after exposure to dietary acid. *Br Dent J* 148: 253–256 (1980)
- ENTEZAMI S, PERES K G, LI H, ALBARKI Z, HIJAZI M, AHMED K E: Tooth wear and socioeconomic status in childhood and adulthood: Findings from a systematic review and meta-analysis of observational studies. *J Dent* 115: 103827 (2021)
- GRENBY T H: Lessening dental erosive potential by product modification. *Eur J Oral Sci* 104: 221–228 (1996)
- GUTZ I G R: CurTIPot software. [http://www2.iq.usp.br/docente/gutz/Curtipot\\_.html](http://www2.iq.usp.br/docente/gutz/Curtipot_.html) (1992–2021)
- HANNIG M, HANNIG C: The pellicle and erosion. In: Lussi A, Ganss C, (editors): *Erosive Tooth Wear. From Diagnosis to Therapy*. Monogr Oral Sci 25, Karger, Basel, pp 206–214 (2014)
- HARA A T, ZERO D T: Analysis of the erosive potential of calcium-containing acidic beverages. *Eur J Oral Sci* 116: 60–65 (2008)
- HEMINGWAY C A, SHELLIS R P, PARKER D M, ADDY M, BARBOUR M E: Inhibition of hydroxyapatite dissolution by ovalbumin as a function of pH, calcium concentration, protein concentration and acid type. *Caries Res* 42: 348–353 (2008)
- HOOPER S, WEST N X, SHARID N, SMITH S, NORTH M, DE'ATH J, PARKER D M, ROEDIG-PENMAN A, ADDY M: A comparison of enamel erosion by a new sports drink compared to two proprietary products: a controlled cross-over study in situ. *J Dent* 32: 541–545 (2004)
- JAEGGI T, LUSSI A: Prevalence, incidence and distribution of erosion. In: Lussi A, Ganss C, (editors): *Erosive Tooth Wear. From Diagnosis to Therapy*. Monogr Oral Sci 25, Karger, Basel, pp 55–73 (2014)
- JENSODOTTIR T, NAUNTOFTE B, BUCHWALD C, BARDOW A: Effects of calcium on the erosive potential of acidic candies in saliva. *Caries Res* 41: 68–73 (2007)
- KINNEY J H, BALOOCH M, HAUPT D L, MARSHALL S J, MARSHALL G W: Mineral distribution and dimensional changes in human dentin during demineralization. *J Dent Res* 74: 1179–1184 (1995)
- LI H, ZOU Y, DING G: Dietary factors associated with dental erosion: A meta-analysis. *PLoS ONE* 7: e42626 (2012)
- LUSSI A, MEGERT B, SHELLIS R P: The erosive effect of various drinks, foods, stimulants, medications and mouthwashes on human tooth enamel. *Swiss Dent J* 133: 457–471 (2023).
- LUSSI A, MEGERT B, SHELLIS R P, WANG X A: Analysis of the erosive effect of different dietary substances and medications. *Br J Nutr* 107: 252–262 (2012)
- MAGALHÃES C A, MORAES C M, RIOS D, BUZALAF M A R: Effect of ion supplementation of a commercial soft drink on tooth enamel erosion. *Food Additives Contam* 26: 152–156 (2009)
- MCDONALD J L, STOOKEY G K: Laboratory studies concerning the effect of acid-containing beverages on enamel dissolution and experimental dental caries. *J Dent Res* 52: 211–216 (1973)
- PASCHALIS E P, TAN J, NANCOLLAS G H: Constant composition dissolution kinetics studies of human dentin. *J Dent Res* 75: 1019–1026 (1996)
- SALAS M M, NASCIMENTO G G, VARGAS-FERREIRA F, TARQUINIO S B, HUYSMANS M C, DEMARCO F F: Diet influenced tooth erosion prevalence in children and adolescents: Results of a meta-analysis and meta-regression. *J Dent* 43: 865–875 (2015)
- SCHLUETER N, LUKA B: Erosive tooth wear—a review on global prevalence and on its prevalence in risk groups. *Br Dent J* 224: 364–370 (2018)
- SELVIG K A: Ultrastructural changes in human dentin exposed to a weak acid. *Arch Oral Biol* 13: 719–734 (1968)
- SHELLIS R P: A microcomputer program to evaluate the saturation of complex solutions with respect to biominerals. *Computer Appl Biosci* 4: 373–379 (1988)
- SHELLIS R P, BARBOUR M E, JONES S B, HUGHES J A, HEMINGWAY C A, ADDY M: Effects of pH and acid concentration on dissolution of enamel, dentin, and compressed hydroxyapatite. *Eur J Oral Sci* 118: 475–482 (2010)
- SHELLIS R P, BARBOUR M E, JESANI A, LUSSI A: Effects of buffering properties and undissociated acid concentration on dissolution of dental enamel in relation to pH and acid type. *Caries Res* 47: 601–611 (2013)
- SHRESTHA D, RAJBHANDARI P: Prevalence and associated risk factors of tooth wear. *J Nepal Med Assoc* 56: 719–723 (2018)
- WEST N X, HUGHES J A, PARKER D M, NEWCOMBE R G, ADDY M: Development and evaluation of a low erosive blackcurrant juice drink. 2. Comparison with a conventional blackcurrant juice drink and orange juice. *J Dent* 27: 341–344 (1999)
- YIP K, LAM P P Y, YIU C K: Prevalence and associated factors of erosive tooth wear among preschool children – A systematic review and meta-analysis. *Healthcare* 10: 491 (2022)