265 Stability of Tooth Minerals in Plaque Fluid and Saliva.

V.W.-H. LEUNG*, B.W. DARVELL (Dental Materials Science Unit, University of Hong Kong, Hong Kong).

Previous studies have shown that the rate of demineralization of hydroxyapatite would vary significantly with different acids in contact. Since plaque fluid and saliva have different compositions, the aim of the present study is to investigate, numerically, the stability of tooth minerals, *i.e.* hydroxyapatite (HAP) and brushite (DCPD), in them. The composition of plaque fluid and saliva are based on Moreno and Margolis (*J Dent Res* 67:1181-1189, 1988) and Leung and Darvell (*J Chem Soc Faraday Trans* 87:1759-1764, 1991). The plaque and saliva systems with 99 equilibrium equations and 125 ionic species were modelled using the program RAMESES. Speciation diagrams show the distribution and significance of some ion-pairs and complexes. Solubility isotherms have demonstrated the net effects on the stability of tooth minerals due to the interactions of the components of HAP with solution components. The position of the solubility isotherm of tooth minerals in plaque fluid is lower than in saliva, and the gap between the HAP lines are wider at neutral pH, indicating that HAP would be much more stable in plaque fluid than in saliva near neutral. However, preferred stable solid phases could vary due to the difference in typical pHs of plaque fluid and saliva since DCPD would be more stable at lower pH.

266 The Nucleation of Hydroxyapatite and Fluorapatite on Titanium Oxide Surfaces

WENJU WU* and GEORGE H. NANCOLLAS (Dept. of Chemistry, SUNY at Buffalo, Buffalo, NY 14260)

Although titanium has long been used as an implant material, the mechanisms of its subsequent biomineralization are not yet well understood. The nucleation and growth of hydroxyapatite (HAP) and fluorapatite (FAP) on titanium oxide (TiO_2) surfaces have been investigated using constant composition (CC) methods in supersaturated solutions at 37°C and ionic strength 0.15 mol L^{-1} with relative supersaturations 13.4 to 15.0 and 13.5 to 16.5 for HAP and FAP, respectively. The solid phases during the reaction were examined by X-ray diffraction, scanning electron microscopy (SEM) and diffuse reflectance Fourier transform infrared spectroscopy (FTIR). SEM micrographs showed that both crystal phases nucleate at the TiO_2 particle surfaces. The induction periods, τ_{in} preceding the initial crystal growth, varied from 8 to 17 hours for HAP and from 7 to 15 hours for FAP as functions of the relative supersaturations. The interfacial tensions, γ, estimated from initial growth rate data and from the induction times were about 32 mJ m^{-2} and 39 mJ m^{-2} for FAP and HAP, respectively. These values were of the same order of magnitude as those determined by a contact angle method involving thin layer techniques. The results show that titanium oxide surfaces serve as nucleators for both HAP and FAP but only after relatively long induction periods. It is also intersting to note that the X-ray diffraction pattern of HAP on TiO_2 surfaces resembles that of bone and root dentin mineral in the region 2θ from 30° to 35°.

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267 Influence of Polyaspartic Acid and Phosphophoryn on the Crystal Growth of Octacalcium Phosphate.

E.M. BURKE, Y. GUO, L. COLON, A. VEIS, G.H.NANCOLLAS* (Dept. Of Chem., SUNY Buffalo, N.Y. 14260 and Dept. Oral Biol. Northwestern Univ.Chicago, Il.60611)

There is considerable interest in the influence of polyanionic macromolecules on the crystal growth of the calcium phosphates. Constant Composition (CC) studies have been made of the kinetics of crystal growth of octacalcium phosphate (OCP) in the presence of two quite different anionic macromolecules. A homopolymer, polyaspartic acid (PAA), and phosphophoryn (PPn), containing both aspartate and phosphoserine residues in a quite different conformation. Crystal growth reactions were made at 37°C, ionic strength, 0.08 mol L^{-1} with relative supersaturations, 0.80, 5.5, and 0.13 with respect to OCP, HAP, and DCPD, respectively. The measured adsorption of PAA and PPn on OCP surfaces, interpreted by means of a Langmuir isotherm, gave affinity and maximum surface coverage values of 2.5 (± 0.8) x 10^7 L mol^{-1} and 9.7(±1.6) x 10^{-8} mol m^{-2} for PAA and 9.1 (±3.2) x 10^7 L mol^{-1} and 8.4(±2.1) x 10^{-10} mol m^{-2} for PPn. Although the maximum surface coverage for PPn was two orders of magnitude less than for PAA, PPn exhibited a greater extent of inhibition (by more than a factor of six) of the rate of OCP crystal growth. The data support the suggestion that preferential adsorption of PAA occurs on the (100) face and of PPn on the (010) face of the OCP crystals. Measurement of the changes of OCP zeta potential in the presence of additives, normalized for the surface concentrations, and X-ray data, suggest that the difference in inhibitory action may be related to both the size of the molecules and the relative rates of growth of the (010) and (100) OCP crystal faces. Work supported by NIH Grant (DE 03223).

268 Mechanisms of Inhibition of Dissolution of Carbonated Apatites.

Z. WANG, J. HSU, K. WARNER, K. SEARS, J.L. FOX* and W. I. HIGUCHI, (Department of Pharmaceutics, University of Utah, Salt Lake City, Utah).

Two mechanisms are well established by which solution species can suppress the rate of dissolution of inorganic substances: 1) kink site poisoning (affecting dissolution kinetics, but not solubility), and 2) the common ion effect in which lattice ions in solution diminish the amount of solid that can ultimately dissolve and hence reduce the dissolution driving force. Foreign ions that could potentially be adsorbed onto or incorporated into the crystal lattice have been treated either as kink site poisons or as participants in a solubility determining surface complex. In most cases, only initial dissolution rates are measured and the two possible mechanisms are not readily distinguished. In this study, the approach of CAP to its metastable equilibrium solubility (MES) was followed in the presence of a putative kink site poison (etidronate, or HEDP) and a foreign ion (strontium). At micromolar levels, HEDP was shown to affect the kinetics, but not the MES ultimately attained. Strontium concentrations up to about 0.1 mol/l, on the other hand, had no affect on the kinetics, but did reduce the MES, as would be the case for a lattice ion in solution. Both these findings were in accord with expectations. In summary, two distinct mechanisms for the suppression of CAP dissolution were observed. Moreover, these mechanisms could only be distinguished by following the kinetics of dissolution until the MES was reached. Supported by NIDR grant DE 06569.

269 Solubility Behavior of Bone Mineral in Solutions of Various pH's.

A. BAIG*, Z. WANG, J. HSU, J.L. FOX, A. CHHETTRY, M. OTSUKA, W.I. HIGUCHI, and S.C. MILLER (University of Utah, Salt Lake City, UT).

It has been shown that the solubility behavior of carbonated apatites (CAP's) and human dental enamel is best described by the MES (metastable equilibrium solubility) distribution phenomenon and that the magnitude of the MES is determined by the crystallinity of CAP's. Recently, the role of solution variables on the MES behavior of CAP was assessed and a surface complex with the stoichiometry of hydroxyapatite (HAP) was found to control the MES. In this study the solubility behavior of bone apatite was investigated by applying the MES distribution concept. By varying the pH of the equilibrating solution, the stoichiometry of the surface complex function controlling the MES of bone and a synthetic CAP prototype was deduced. The bone sample, obtained from the femur and tibia of an 8 month old rat was prepared by hydrazine deproteination followed by sequential washing with ethanol and then water. The sample was air dried and then manually ground into fine powder. CAP was synthesized by the hydrolysis of DCPD in a bicarbonate containing medium for 48 hours at 50°C, washed with water and then dried at 60°C. The MES's of the bone and CAP samples were determined at three pH's by a previously described method. From the composition of a series of 0.1M acetate buffer solutions at pH's 5.0, 5.7 and 6.5 the corresponding ion activity products based on the stoichiometries of DCPD, OCP, HAP, TCP, CAP, and TeCP were calculated and used as potential candidates for the MES controlling surface complex function. The following conclusions were drawn from the results of this study. 1) Both the CAP and bone samples exhibited the MES distribution phenomenon. 2) The surface complex based on the stoichiometry of HAP was found to best describe the MES behavior of bone and CAP. 3) The CAP used in this study was found to be an excellent model system for studying the physicochemical properties of bone mineral with regards to the similarity in the chemical and crystalline properties, and the superposition of MES distributions. Supported by NIDR grant DE 06569.

270 The Possible Role of Calcium Phosphonates in Inhibition of Calcium Phosphate Formation.

N. EIDELMAN*[1], M. MATHEW[1], B.O. FOWLER[2], E. BREUER[3], G. GOLOMB[3] and D. SKRTIC[2] ([1]ADAHF, PRC, NIST, Gaithersburg, MD; [2]NIDR, NIH, Bethesda, MD; [3]The Hebrew University, Jerusalem, Israel).

Previous studies (Eidelman et al., IADR Abs. No. 1683, 1995) have shown that the main product formed in calcium phosphate spontaneous precipitation (SP) between 11 days and 3 months in the presence of 100μM of Etidronate (EHBP) or tetrasodium tetrahydrogen 1,12-dihydroxydodecane-1,1,12,12-tetrakis-phosphonate (DHDTP) was amorphous calcium phosphate (ACP) and associated organic components that were attributed to phosphonates, whereas apatite was formed almost instantly in the control. The identification of the organic components was not done at that time. In the present study, calcium phosphonate salts (Ca-Phs) of Pamidronate (Pam), Suberoylbisphosphonate (SuBP), tetrasodium tetrahydrogen 1, 8-dihydroxyoctane-1,1,8,8-tetrakis-phosphonate (DOTP), DHDTP and EHBP were prepared by mixing 2:1 molar ratio solutions of $Ca(NO_3)_2$ and the related Phs at various pHs (7-10) and temperatures (22°C to 55°C). The solid products were characterized by FTIR and X-ray diffraction (XRD). FTIR spectra and XRD patterns of the Ca-Phs were compared to SP products collected at various times from supersaturated solutions (Tris, pH=7.4, Ca=3.12 mM, P=1.88 mM and 100μM of the above Phs) at 37°C. Minute amounts of ACP and Ca-Phs were formed instantly and simultaneously in the experiments with Pam, EHBP, DOTP and DHDTP. The amounts of ACP increased slowly with time relative to the original amounts of the Ca-Phs, as shown by FTIR. In SP experiments with SuBP, Ca-SuBP ($Ca_4[O_3PCO(CH_2)_6COPO_3].2H_2O$, Mathew et al., IADR, 1997) was the only phase detected by both FTIR and XRD in products collected at 3 and 7 days. The identification of the organic components in the SP products as Ca-Phs suggests that Ca-Phs have an active role in the inhibition of calcium phosphate formation. Supported in part by NIH grants HL30035, DE05030, NIST, ADAHF and the GIF for R&D.

271 Formation and Stability of Magnesium-substituted Whitlockites (β-TCMP).

R.Z. LeGEROS*, R. KIJKOWSKA, C. BAUTISTA, D. MIJARES, M. RETINO, J.P. LeGEROS. (New York University College of Dentistry, New York)

Magnesium-substituted whitlockites (β-TCMP) is a principal inorganic component in human dental calculus and has been reported in other pathological calcification and in arrested human dentin caries. Like unsubstituted β-tricalcium phosphate, β-TCP, it has been proposed as possible bone-graft materials. This study aimed to continue studies on the formation and stability of β-TCMP to gain insights into its biological occurrence and stability. β-TCMP was prepared by direct precipitation or by hydrolysis of dicalcium phosphate dihydrate (DCPD) or anhydrous dicalcium phosphate dihydrate (DCPA); and characterized by x-ray diffraction, infrared spectroscopy (IR), scanning and transmission electron microscopy (SEM, TEM), atomic absorption and thermo-gravimetric analyses (TGA). Dissolution properties were determined in acidic buffer (0.1M KAc, pH 6, 37°C) by monitoring the Ca^{2+} ions released to the buffer with time using Ca-ion selective electrode. Results: (1) β-TCMP forms in both acid and basic conditions; (2) Mg incorporation in β-TCMP is higher at higher pH; (3) formation is suppressed by either F or CO_3; which promote the in stead the formation of (F,OH)- or (CO_3,PO_4)-apatite (CHA); (4) β-TCMP contains HPO_4; (5) extent of dissolution (EOD) of β-TCMP is proportional to Mg incorporation; (6) comparative EOD: β-TCP > > β-TCMP; DCPD > OCP > CHA > β-TCMP. The in vivo stability of β-TCMP maybe due to its ability to form in both acid or basic conditions and on its lower extent of dissolution compared to the other calcium phosphates. As a bone-graft material, bioresorbability of β-TCMP may be adjusted by regulating Mg incorporation. [Supported by research grant No. DE 07223 from the National Institute for

272 Rationale for Laser-Induced Inhibition of Enamel Demineralization.

J.D.B. FEATHERSTONE *, D. FRIED, E. BITTEN and D. MACHULE (University of California San Francisco, San Francisco, CA).

Carbon dioxide (CO_2) laser treatment of dental enamel can inhibit subsequent subsurface caries-like lesion progression by up to 65% (Featherstone et al. 1995). The present study tested the hypothesis that specific wavelength irradiation is absorbed by the mineral, converted efficiently to heat at the surface, causing thermal decomposition of the carbonated apatite enamel crystals to a less soluble form. Samples of enamel 5x5 mm were prepared with polished surfaces and examined before and after laser irradiation by x-ray diffraction and by specular reflectance FTIR. Sample surfaces were irradiated by pulsed CO_2 laser at 9.3, 9.6, 10.3 or 10.6 μm, 100 μs pulse duration. 25 pulses per spot, with fluences of 0-8 J/cm^2. In separate experiments surface temperatures were measured by radiometry, and surface dissolution rates in acetic acid at pH 4.5 were measured. Loss of carbonate (CO_3), estimated from FTIR, was laser wavelength dependent, and fluence dependent. For example, for 9.6 μm irradiation at 0,2,3,4, J/cm^2 CO_3 loss was 0, 36(±13)%, 61(±18)%, and 100% respectively. Optimum inhibition of subsurface caries was achieved in previous studies at 5 J/cm^2 for 9.6 μm, and reduction in enamel surface dissolution rate (55.1±3.7%) occurred at 4 J/cm^2. We conclude that irradiation of dental enamel by specific wavelengths and fluences of CO_2 laser light alters the chemical composition of the crystals, decomposing the CO_3 component, thereby markedly reducing the reactivity, without necessarily melting the surface. This study was supported by NIH/NIDR grant DE 09958.