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Interfacial Properties of Hydroxyapatite, Fluoroapatite and Octacalcium Phosphate

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The surface properties of calcium phosphate salts, such as hydroxyapatite (OHAp), fluoroapatite (FAP) and octacalcium phosphate (OCP), determine their overall interfacial behavior, which includes processes such as adsorption, chemical uptake and exchange, dissolution, nucleation, crystal growth, wettability, and adhesion. These properties are essential to understanding the use of these salts as catalysts, chromatographic columns in protein chemistry, and biomaterials for dental and bone applications, as well as to understanding many of the properties and functions of calcified tissues such as bone and tooth. They also control factors in mineral beneficiation such as flotation and flocculation, in soil science, in sugar purification, and in waste treatment processes. In this chapter, these important properties are reviewed, especially surface composition, surface charge, adsorption behavior, as is the role these properties play in dissolution, crystallization and biological processes.

Surface Composition

In aqueous solutions, the liquid double layer adjacent to the surfaces of ionic solids is different from the bulk of the liquid. The surfaces of the ionic solids are likewise different from the bulk solid and, on a molecular level, are largely disordered. The transition layer between bulk OHAp and the aqueous phase is assumed to be similar to that of OCP [Brown et al., 1981 a, b, 1984; Brown and Chow, 1983]; hence, both salts have similar surface structure and properties (fig. 1). The transition layer between bulk FAP and the

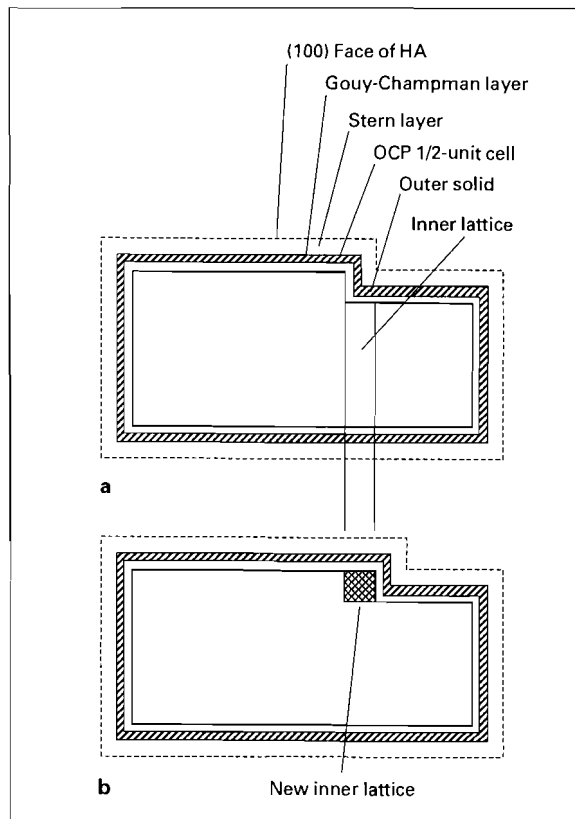


Fig. 1. A hydroxyapatite crystal in a calcium phosphate solution (*a*) before and (*b*) after an incremental growth of the new lattice at the kink site [Brown and Chow, 1983].

aqueous phase is apparently also similar to that of OCP and OHAp in the presence of F. On the other hand, OHAp is stable in the presence of F and has the solubility of FAp [Wier et al., 1972], whereas OCP is transient and will convert to FAp because the underlying OCP structure is not stable with respect to the surface structure of FAp.

The composition of the surface layer of calcium phosphates and of chemical species adsorbed thereon has been studied by x-ray photoelectron spectroscopy (XPS) [Lu et al., 1998, 2000], secondary ion mass spectroscopy (SIMS) [Leadley et al., 1997; Chusuei et al., 1999], nuclear magnetic resonance (NMR) spectroscopy [Yesinowski, 1998] and exoemission [Davies, 1984]. XPS consists of radiating a sample with a monochromatic x-ray beam and measuring the kinetic energies of the ejected electrons. The XPS spectrum of a given element is like a fingerprint, consisting of several discrete,

energy-specific peaks whose intensities correspond to the amount of the element present. With this method, Lebugle and Sallek [1994], and Leadley et al. [1997] determined the Ca, P, HPO_4 and CO_3 contents at the apatite surface and found that the Ca/P ratio of this surface is lower than that of the bulk phase, and is consistent with the model (fig. 1) proposed by Brown et al. [1981 a, b, 1984] for OCP-like surfaces. The adsorption mechanism of organic molecules adsorbed onto calcium phosphate surfaces and new calcium phosphate growth on these surfaces have also been determined by XPS [Lebugle and Sallek, 1994].

High-resolution solid-state NMR spectra of H, F, and phosphate were obtained on OHAp surfaces reacted with F [Yesinowski et al., 1984], fluoridated apatite surfaces [Yesinowski, 1998], and surfaces after adsorption of diphosphonates and polypeptides [Yesinowski, 1981]. The studies indicated that the fluoride at the surface of OHAp after exposure to fluoride solutions was coordinated by three Ca ions, as in the bulk structure, and occupied the OH site in the apatite lattice.

Surface Charge

The net charge of ionic calcium phosphate solids in aqueous solution is mainly due to the preferential dissolution or adsorption of lattice ions. Species that form complexes with the surface may also contribute to the surface charge. The surface charge of OHAp and FAp have been studied by measuring electrokinetic potentials such as zeta and membrane potentials. The former is obtained by the streaming technique [Somasundaran and Wang, 1984] and the latter is obtained in a concentration cell in which an apatite disk serves as a membrane to separate the two electrolyte compartments. The ionic permselectivity of the apatite disk depends on its surface charge [Tung, 1976]. Compared to oxides such as alumina, silica and titania, the surface charge properties of calcium phosphate salts are affected by more variables and charge generation mechanisms. The surface charge, for example, is a complex function of the solution conditions; H^+ , Ca^{2+} , OH^- , phosphate and fluoride ions are potential-determining either directly or by shifting the chemical equilibrium in solution and altering the concentration of other potential-determining ions [Chander and Fürstenau, 1984; Somasundaran and Wang, 1984; Somasundaran and Markovic, 1998]. The apatite surface at lower pH is more positive (or less negative) than that at higher pH. At lower pH, the potential-determining ions are H^+ and Ca^{2+} while H_2PO_4^- species is not effective; at higher pH, the potential-determining ions are OH^- , HPO_4^{2-} , and PO_4^{3-} in addition to Ca^{2+} . The OHAp surface becomes more negatively

charged when fluoride is adsorbed and/or forms FAp, but becomes more positively charged when CaF_2 forms [Tung, 1983; Somasundaran and Markovic, 1998]. This is because the fluoride is potential-determining, and the point of zero charge of FAp is lower than that of OHAp while that of CaF_2 is higher. Adsorption of charged compounds, such as surfactants and biological and synthetic macromolecules, depends upon the surface charge of the apatite. Their adsorption, in turn, can change the surface charge [Tung, 1976].

The point of zero charge (PZC) or the isoelectric point is the pH at which the net charge of the surface is zero. For OCP, OHAp and FAp which all contain three lattice ions, the PZC may be obtained by changing the concentration of two of the ions independently. This leads to a line of zero charge on the solubility surface [Chander and Fürstenau, 1984]. The PZC can be measured by titration, electrophoresis, and streaming or membrane potential. The PZC values for OHAp and FAp prepared by different methods, when measured in the absence of added calcium or phosphate ions, vary from pH 6.4 to 8.5 and 4.5 to 6.9, respectively [Tung, 1976; Chander and Fürstenau, 1984]. These variations reflect the effects that different bulk properties of apatite, such as impurities, Ca/P ratio and lattice defects, have on their surface properties.

Solubility, Dissolution and Surface

In their treatise on the surface equilibria of calcium phosphates, Brown and Chow [1983] demonstrated that the thermodynamic properties of growth and solubility involve only 'stoichiometric' reactions related to the bulk properties, although the reactions involving the disordered impingement and ejection of the reactant ions at the crystal surfaces can be 'non-stoichiometric'. This is illustrated by a crystal of hydroxyapatite in a calcium phosphate solution in figure 1 a. Between the bulk solution and the crystal surface lies an outer Gouy-Chapman liquid layer and a similarly disordered inner Stern layer. The surface region of the crystal immediately under the Stern layer is structurally and stoichiometrically different from the interior of the crystal (for example, a layer similar to a half unit cell of OCP in the case of the 100 face of OHAp) [Brown et al., 1981 a]. This disordered surface layer results from liquid interfacial forces disrupting the underlying order of the crystal lattice. The step on the upper edge of the crystal outlined in figure 1 a represents a kink site where crystal growth and dissolution can take place. An increment of growth at this kink site is indicated by cross-hatching in figure 1 b. As depicted, there is an incremental increase in lattice volume but no significant net change in surface area or in surface energy.

Therefore, the stoichiometry and change in Gibbs energy associated with this incremental process are for the inner lattice and not the outer layer. This also applies to dissolution; the removal of the cross-hatched area of a crystal in figure 1 b results in the new crystal in figure 1 a. A study of surface and lattice effects on the solubility of OHAp [Chuong, 1973] showed that the dissolved Ca/P ratio can deviate significantly from the Ca/P ratio of the bulk: the deviations were greater at higher solid to solution ratios and a lower degree of dissolution, yet the solubility product remained constant.

On the other hand, the solution affects the interior of the crystal by way of rearrangements in the surface layers. Therefore, the kinetics of nucleation, crystal growth and dissolution depend on surface energy, as shown by Wu and Nancollas [1996 a, b, 1998 a, 1999; Nancollas and Wu, 2000]. For apatite dissolution in acidic solutions, surface reactions have been proposed and studied [Christoffersen, 1980, Christoffersen et al., 1996 a, b; Dorozhkin, 1997] that involve sequential ionic detachment from the surface in a non-stoichiometric (incongruent) manner. Other factors that have been suggested as controlling dissolution kinetics include metastable equilibrium solubility, surface complexes, and site geometry (two-site model) [Higuchi et al., 1965, 1968; Fox et al., 1995; Chhetry et al., 1999]. The solubility of OHAp in the presence of F also demonstrates the importance of surface complexes and the surface layer of FAp [Wier, 1972]. In studies of the OCP dissolution mechanism [Veerbeck and Devenyns, 1990, 1992], surface phenomena associated with the dissolving crystals and characteristics of the double layer about the OCP crystallites are believed to contribute to the abrupt changeover of the rate-controlling mechanism from transport into nucleation-controlled dissolution.

The above results and discussions on the dissolution of apatite [Pearce, 1988; Chow, 1988] demonstrate the importance in making the distinction between solubility as an equilibrium property related to crystal bulk and rate of dissolution as a kinetic property related, at least in part, to the crystal surface. Also pertinent, although there are some exceptions, is that the smaller the solubility of a solid electrolyte, the larger is the interfacial tension between the crystal and solution, [Nielsen and Christoffersen, 1982; Nielsen, 1983]. This implies that the interfacial tension may be related more to bulk than to surface properties.

Crystallization and the Interfacial Energy

The morphology of a crystal is controlled by the relative rates at which the different faces grow, and in turn is controlled in part by interfacial ener-

gies. Therefore, the interfacial energies are related to crystallization and the morphologies of crystals. This relation between the crystallization and interfacial energy is illustrated below with homogeneous nucleation.

The isothermal formation of a new particle in a supersaturated liquid solution depends theoretically on macroscopic parameters such as particle volume (V), chemical potential ($\Delta\mu$), surface area (A), and interfacial or surface tension (σ). The corresponding change in Gibbs free energy is defined [Nielsen, 1983] as

$$\Delta G = \Delta G_{\text{volume}} + \Delta G_{\text{surface}} = V \cdot \Delta\mu_v + A \cdot \sigma. \quad (1)$$

The formation rate, J , is defined by the Arrhenius expression:

$$J = B \exp(-\Delta G/RT). \quad (2)$$

Relating the rate (J) to the number of particles in a unit volume (N) and the induction time (t_i) gives the equation:

$$J = B \exp(-(V \cdot \Delta\mu_v + A \cdot \sigma)/RT) \sim N/t_i. \quad (3)$$

While the nucleation and growth rates are controlled, in part, by the interfacial energies, the energy terms cannot be determined unambiguously by direct experiments. Yet, the surface tension (σ) can be calculated in principle from eq. 3 [Nelson et al., 1986; Sohnle and Mullin, 1988]. The value of σ , derived from classical nucleation models, ranged from 100 mJ/m² to 331 mJ/m², based on the rates or induction times for OHAp growth on proteins and amino acids. These approaches and results, however, are considered inadequate [Wu and Nancollas, 1996 a]. New approaches [Van Oss, 1994; Wu and Nancollas, 1996 a, b, 1999] used interfacial energy measurements, such as thin-layer wicking techniques, to calculate the rates of nucleation and growth, and used these rates to calculate the surface tensions. The interfacial energies (IFEs) of OCP, OHAp, and FAp were 4.3, 9.0 and 18.5 mJ/m², respectively, and these energies compared favorably with those calculated from nucleation and growth data [Liu et al., 1997 b]. The calculated low IFE of 0.93 mJ/m² between OCP and OHAp provides support for the hypothesis that OCP forms first as a precursor and then induces OHAp formation on its surface [Brown et al., 1981 a, b; Liu et al., 1997 a]. Wu and Nancollas [1997 a, b, 1998 a] and Wu et al. [1997] have extended the surface-energy approach to foreign substrata. The IFEs of OCP are 11.4 and 13.8 mJ/m² respectively, as estimated from initial growth rates and induction times when OCP is grown on a titanium oxide surface. The IFEs for FAp and OHAp, estimated in the same way, are 32 and 39 mJ/m², respectively. Growth on polymer surfaces demonstrated the importance of Lewis acid-base surface: high values of Lewis base surface favor the formation of calcium phosphates [Wu and Nancollas, 1998 a, b]. The importance of interfacial tension in con-

trolling the formation of the accreted phase has also been revealed in seeded crystal growth studies [DeRoosj et al., 1984; Heughebaert et al., 1984; Ebrahimpour et al., 1991]. During the hydrolysis of the less hydrated form of amorphous calcium phosphate to apatite, the amorphous calcium phosphate surface appeared likewise to be directly involved in the conversion process by initiating the nucleation of the apatite phase [Eanes, 1975].

The specificity of molecular interactions at inorganic/organic surfaces was investigated by crystallization of CaPs [Lu et al., 1995]; OCP precursors formed initially in the presence of organized, negatively charged stearic acid monolayers. Modifications of surface structures and properties of OHAp by use of alkyl phosphates created a new surface function for OHAp [Tanaka et al., 1997].

Oriented growth of OCP on cation-selective membranes and in the collagenous matrix under physiological conditions suggested that surface interactions are important in the growth of biological apatite [Iijima and Moriwaki, 1991, 1999; Iijima et al., 1994 a, b; 1995; 1996]. These studies also indicate that a low F-substituted OHAp can grow on a F-containing OCP or on a surface-reaction layer of OCP.

Extensive studies on the dissolution kinetics and surface properties of both human enamel powder and synthetic OHAp [Voegel et al., 1987; Gramain et al., 1987, 1989; Thomann et al., 1989, 1990, 1991] indicated that fluoride, stannous cations, organic acids or polymers interacted strongly with calcium phosphate ions at surfaces and formed precipitated layers. These surface layers promoted the remineralization processes and/or reduced the dissolution rates. Interfacial calcium accumulation occurred in parallel with the progressive slowing of the demineralization. OHAp surfaces also acted as a buffer over a rather large pH range.

Adsorption and Exchange

Due to their small sizes and platy and needle-like morphologies, OHAp and OCP have high specific surface areas that are very reactive to specific ions and/or molecules [Brown et al., 1981 b; Blumental and Posner, 1987; Tung et al., 1992]. The presence of different foreign ions and/or molecules in aqueous solutions, in turn, affects the complex interfacial interactions during dissolution/growth of OHAp, FAp, and OCP. Equilibrium with the solution is reached only under very carefully controlled conditions with low supersaturations and long time periods. At short time intervals, surface adsorption is one of the main parameters that control the stability and behavior of the solid phase(s) in aqueous systems.

Theoretically, adsorption is functionally dependent on the amount of material adsorbed on a solid substrate (adsorbent) and on the concentration of the adsorbate in solution as expressed by the classical Langmuir isotherm equation [Kresak et al., 1977]:

$$C/Q = (1/KN) + (C/N), \quad (4)$$

where C is the solution concentration of adsorbate in equilibrium with the adsorbent, and Q and N are the amount adsorbed and the maximum number of adsorption sites per gram of adsorbent, respectively. K reflects the affinity of adsorbate molecules for the adsorption sites. From a linear plot of (C/Q) versus C , one can calculate the adsorption parameters K and N from the slope and the intercept, respectively. The majority of the adsorption data reviewed in this chapter has been quantitatively interpreted in terms of eq. 4. Reported data, however, should be evaluated with caution and used for comparison purposes only, because the Langmuir model does not include interactions between adsorbate molecules, and assumes a monolayer coverage of energetically equal adsorption sites. The Freundlich isotherm (eq. 5), on the other hand, may be more suitable for fitting experimental adsorption data obtained from aqueous suspensions, since it assumes that the adsorption sites are not energetically equivalent [Koutsoukos, 1998]:

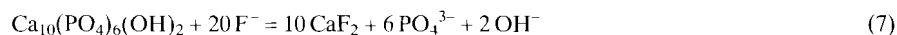
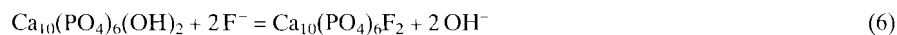
$$\Gamma = K_e C^{1/n}, \quad (5)$$

where Γ is the surface concentration of adsorbate, while K_e and n represent empirical constants.

Adsorption of and Exchange with Inorganic Ions

Fluoride substitutes for OH^- in OHAp and promotes the formation of more highly crystalline mineral. The uptake of F^- by OHAp and the formation of FAp and CaF_2 have been extensively studied. The relative stabilities of FAp and CaF_2 have also been reviewed [Chow and Markovic, 1998]. Several approaches have been used in these studies of F/OHAp interactions:

Specific Adsorption and Ion Exchange [Chander and Fürstenau, 1982]. OH/F exchange in the OHAp lattice structure at low F^- concentrations (eq. 6) takes place mainly at the crystal surface. It is accompanied by partial disintegration of the crystal lattice and CaF_2 formation for F^- concentration > 5 mmol/l (eq. 7).



pH-Dependent F⁻ Uptake [Ramsey et al., 1973]. OHAp partially dissolves and CaF₂ forms at low pH (4.0) while OHAp converts into FAp at higher pH values.

Interfacial Layer-Mediated F⁻ Uptake [Chander and Fürstenau, 1984]. An interfacial layer consisting of Ca²⁺, phosphate and F⁻ ions is postulated with bonds weaker than those inside the lattice. The layer forms through dissolution of OHAp and reprecipitation in F-containing solutions and then transforms into FAp or CaF₂ depending on F⁻ concentration in solution.

Diffusion and Chemical Reaction Model [Nelson and Higuchi, 1970]. CaF₂ formation at the OHAp/solution interface was followed by the progression of this solid inward.

Monovalent Na⁺ and Li⁺ can substitute for Ca²⁺ [Neuman et al., 1962; Brown et al., 1981 b; LeGeros and Tung, 1983; Koutsoukos and Nancollas, 1986] while other ions such as K⁺, Cs⁺ and NH₄⁺ only affect the kinetics of precipitation and/or the morphology of the crystals by surface adsorption [Koutsoukos, 1980]. If the solution in contact with OHAp contains divalent metal ions, heteroionic substitution may occur. One of the critical steps involved in this process is proposed to be surface adsorption of the ions onto the OHAp surface [Lundager Madsen, 1983; Dalphi et al., 1993]. Biologically important divalent Mg²⁺ ion has a high affinity for OHAp surfaces at pH = 8.0, when the apatite surface is predominantly negative. A shift of the isoelectric point of OHAp towards lower pH values observed in the presence of Mg²⁺ is evidence of the cation's adsorption on the crystal surface [Van der Mel et al., 1988]. A significant difference has been found in the adsorption behavior of Zn²⁺ and Mg²⁺. At only 0.011 mmol/l of Zn²⁺ a surface layer of Zn-phosphate formed over the OHAp surface, while Mg²⁺ at pH 7.0 exhibited only a Langmuir-type adsorption isotherm at concentrations up to 1.5 mmol/l [Fuierer et al., 1994]. A surface mechanism with no structural modification has been proposed for the interaction of oxovanadium (IV) with crystalline calcium hydroxyapatite [Vega et al., 1999]. Adsorption of trivalent ions such as Ga³⁺ and Al³⁺ has also been reported [Christoffersen and Christoffersen, 1985; Blumental and Posner, 1987; Donnelly and Boskey, 1989]. Both ions are postulated to block crystal growth and proliferation of OHAp by strongly adsorbing to surface growth sites.

Adsorption of Amino Acids, Proteins and Macromolecules

Amino acids, small molecules with a limited number of functional groups, were evaluated for their adsorption affinity toward apatitic surfaces as a simplified model for protein adsorption [Kresak et al., 1977; Chander

and Fürstenau, 1984]. Parameters derived from the adsorption isotherms were then used to advance a mechanistic view of the adsorption of more complex molecules on apatitic mineral surfaces, i. e., the amino acid terminal carboxyl group is attached to Ca^{2+} ions on the surface of the adsorbent [Kresak et al., 1977]. A geometric model has been proposed to explain the differences in the maximum number of adsorption sites for the various amino acid adsorbate molecules. These differences were attributed to the size of the amino acid molecules and the distances between Ca^{2+} ions on the surface based on the crystallographic structure of OHAp.

The adsorption of proteins is a subject of considerable interest because of: the use of OHAp as separating material for proteins in column chromatography, the involvement of salivary proteins in the formation of 'acquired enamel pellicle', and interactions of proteins and apatite in bone. Only a few of the studies that have examined the interactions between organic surfactants and macromolecules with apatitic substrates determined the adsorption parameters as shown in table 1 [Attia and Fürstenau, 1980; Mishra et al., 1980; Juriaanse et al., 1980 a, b; 1981; Pearce, 1981]. The elucidation of adsorption mechanisms for macromolecules is hindered by the complexity of the molecular structures and the diversity of the functional groups found in these compounds. However, the following interaction mechanisms have been proposed: physical adsorption that takes place in the electrical double layer [Mishra et al., 1980], chemisorption that involves direct bond formation between the adsorbing species and apatite [Chander and Fürstenau, 1984], specific adsorption of Ca^{2+} ions that may act as a bridge to bind anionic species to PO_4 sites of the OHAp lattice [Chander and Fürstenau, 1984], H-bonding that enables interactions with phosphate, OH^- and/or F^- groups of OHAp [Chander and Fürstenau, 1984], displacement of phosphate on the surface with anionic groups [Pearce, 1981], and formation of multilayers on the surface [Tung and Brown, 1985].

The acquired pellicle of teeth is an organic film that covers the enamel surface and underlies the dental plaque. It is formed by selective adsorption of salivary proteins onto tooth surfaces [Juriaanse et al., 1981]. Since the pellicle may protect the enamel against acid dissolution, it is important to determine the conditions that inhibit or promote its formation. The interdependence between the adsorption of salivary proteins on synthetic OHAp and the effects of H^+ , Ca^{2+} and phosphate ions on this interdependence has been extensively studied and the relevance of these *in vitro* experimental systems to physiological conditions has been evaluated [McGaughey and Stowell, 1971 a, b, 1974]. It has been found that: Ca-precipitable salivary glycoproteins are involved in exogenous pellicle formation, phosphate ions at physiological concentrations inhibited protein adsorption on apatite surfaces, and that there is a mutual dependence of promotive H^+ and inhibitory phosphate effects, mediated through

$\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$ interconversion. The possibility that adsorbed protein-Ca- PO_4 complexes form on OHAp surfaces has also been indicated. Salivary proteins with pronounced affinities for OHAp surfaces include phosphorylated acidic proline-rich proteins (PRPs), statherin, histatins, cystatins, and glycosylated proline-rich proteins [Lamkin et al., 1996]. These proteins also inhibit crystal growth in solutions supersaturated with respect to CaPs. Single-component physicochemical studies have further shown that of these proteins statherin, cystatin and PRPs have the highest affinity for various apatites and the highest binding density per unit area of surface [Moreno et al., 1984; Johnsson et al., 1991]. Lamkin et al. [1996] report three different adsorption patterns for salivary proteins that are controlled either by direct adsorption onto OHAp substrates or through the interactions of the adsorbing protein with the proteins already bound to OHAp. Embery et al. [1979] found that the negative charge on glycosaminoglycan molecules is the major determinant in their binding to apatitic substrates, and pointed out the role of electrostatic interactions of polyanions with Ca sites in the OHAp lattice. Geometric considerations appear to be crucial in determining the promotional or inhibitory nature of various phosphorylated amino acids [Wong and Czernuska, 1995].

Differences between synthetic OHAp and whole enamel may affect protein adsorption. These differences include the presence or absence of inorganic impurities and/or organic matrix, point-of-zero charge, Ca/P ratio, surface/liquid ratio, and the crystalline structure of the different substrates. For this reason, numerous adsorption studies have been carried out on intact or purified enamel as a substrate [Pruitt et al., 1970; Juriaanse et al., 1980 a, b, 1981]. The results suggested that the surface interactions were mainly ionic. On the basis of chromatographic experiments with phosphoproteins, polyaspartic acid, and polylysine, the following adsorption-controlling mechanisms were proposed (listed in order of effectiveness): adsorption of protein phosphate through exchange reactions > interactions of protein amino groups with enamel > interactions of protein carboxyl groups with enamel \geq additional interactions involving Ca^{2+} bridges. Interactions of cationic side chains of macromolecules with apatite and enamel are also involved [Tung, 1976; Tung and Brown, 1983].

Typical adsorption parameters, adsorption affinity constants (K) and the maximum number of adsorption sites (N) (calculated according eq. 4), for different substrates and adsorbents are compiled in table 1.

Adsorption of Microorganisms

Adhesion of oral microorganisms is a prerequisite for plaque formation. Bacterial colonization of tooth surfaces depends on factors that change the

Table 1. Adsorption of different species to various calcium phosphate substrates

| Substrate | Adsorbate | Affinity constant K ml/ μ mol | Maximum number of adsorption sites, N μ mol/g | Reference |
|---------------------|---|-----------------------------------|---|---------------------------|
| OCP | Mg ²⁺ | 0.74 | 31.2 | Tung et al. [1992] |
| FAP | Zn ²⁺ | 250 | – | Chin and Nancollas [1991] |
| OHAp | Zn ²⁺ | 150 | 7.7 ^a | Fuierer et al. [1994] |
| OHAp | Sr ²⁺ | 0.22 | – | Raicevic et al. [1996] |
| | | – | 15.0 | Lazic and Vukovic [1991] |
| OHAp | <i>L</i> -aspartic acid | 0.203 | 53.5 | Kresak et al. [1977] |
| | <i>L</i> -glutamic acid | 0.206 | 24.4 | |
| | <i>D,L</i> -amino adipic acid | 0.218 | 11.9 | |
| | <i>D,L</i> -amino pimelic acid | 0.275 | 7.9 | |
| | Succinic acid | 0.558 | 35.5 | |
| | Adipic acid | 0.425 | 11.1 | |
| OHAp | <i>o</i> -phospho-serine | 6.5 | 1.18 ^a | Misra [1997] |
| OHAp | phosphatidyl serine | 3.33 | 4.87 ^a | Boskey and Dick [1991] |
| OHAp | PMDM ^b | 0.034 | 77.3 | Misra and Bowen [1987] |
| (EtOH solvent) | N-phenylglycine | 0.090 | 106.1 | |
| | phenoxyacetic acid | 0.064 | 95.2 | |
| OHAp | polyelectrolytes containing quarternary F salts | 0.31–0.48 | 6.4–18.2 | Rawls et al. [1987] |
| OHAp | statherin | 1,130 | 0.44 ^a | Johnsson et al. [1991] |
| | cystatin | 420–455 | 0.15–0.22 ^a | |
| OHAp | salivary + 0 ppm F | 940 ^c | 1,290 ^d | Voegel et al. [1981] |
| | proteins + 5 ppm F | 1,900 ^c | 540 ^d | |
| | + 10 ppm F | 9,320 ^c | 143 ^d | |
| whole bovine enamel | poly- <i>L</i> -lysine | 0.03 ^c | 1.84 ^a | Juriaanse et al. [1981] |
| | poly- <i>L</i> -ornithine | 0.12 ^c | 0.54 ^a | |
| | poly- <i>L</i> -aspartic acid | 0.25 ^c | 2.37 ^a | |

^a N expressed in μ mol/m².

^b Adduct of pyromellitic dianhydride and 2-hydroxyethyl methacrylate.

^c K expressed in mL/ μ g.

^d N expressed in μ g/m².

chemical potential in the tooth/saliva interfacial region and influence the adhesion of bacteria to salivary components adsorbed on the tooth [Ericson et al., 1975; Magnusson et al., 1976]. In vitro experimental modeling of bacterial adhesion to the teeth that utilized saliva-coated OHAp surfaces revealed the proline-rich proteins, secretory immunoglobulin A, lysozyme, parotid agglutinin and salivary α -amylase as potential receptors for streptococcal adhesion to OHAp [Scannapieco et al., 1951].

Interfaces in Biological Processes and Diseases

The surface interactions of calcium phosphates with proteins and cells play important roles in the formation of surface complexes on the bone mineral, in their biorecognition, osteoinductance and osteoconductance. The surface properties of OHAp implants, such as geometrical configuration, influence bone ingrowth and osteogenesis in connection with the activity of bone morphogenetic proteins adsorbed at the interfaces [Magan and Ripamonti, 1996; Ripamonti et al., 1992]. The surface charges of apatite in bone also induce the electrokinetic phenomenon of streaming potentials observed in wet bone and may be involved in the generation, repair and remodeling of bone tissues [Walsh and Guzelsu, 1993].

Bone can be considered as a biological composite of inorganic apatite embedded in an organic matrix of collagen and noncollagenous proteins, where the anionic and cationic side chains of the latter bind readily to the calcium and phosphate on the surface of apatite mineral. The higher level of structural organization created by the interlocking of mineral and matrix gives bone the strength and rigidity not possessed by these two components separately. Spatial geometries and interfacing are key factors in establishing these properties. As the filler/resin interfaces in composites play an important role in their transverse, interlaminar, compressive and tensile strength, and stress-transfer properties, so do the surface properties of apatite contribute in a similar manner to the mechanical strength of the bone. Walsh and Guzelsu [1993, 1994] and Walsh et al. [1994] have demonstrated that interfacial bonding of bone components affects the tensile and compressive strength, stiffness and ultrasonic properties of cortical bone. Modifications of mechanical properties can be achieved by fluoride or phosphate treatment and are attributed, at least in part, to their effects on the bonding interface between mineral and matrix [Walsh et al., 1994; Hall et al., 1995]. Hall et al. [1995] also show that F^- can dramatically alter both the collagenous and the noncollagenous components of mineralized tissues, thereby affecting the interfacial bonding with mineral.

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