

## LETTERS

### A Computer Modeling Study of the Adhesion of Apatite Thin Films on Silicate Surfaces

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Computer simulations of apatite thin films at a range of quartz surfaces have shown how the strength of adhesion between thin films of apatite material and ceramic silica surfaces is crucially dependent upon both the orientation of the film relative to the substrate and the nature of the silica surface—a finding that is important in a wide number of applications, from basic geological research on intergrowth of phosphate and silicate rock minerals to the search for more effective surgical implant materials.

#### Introduction

A major area in the contemporary field of materials science is the study of adhesion of thin films to inorganic surfaces. A topical example is in the field of biomaterials science where deposition and layer growth of synthetic bone materials, such as apatite, onto a ceramic implant may promote integration of the implant with the natural bone;<sup>1</sup> but to date it is unclear how the apatite attaches to the implant material. Apatites  $\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{Cl},\text{OH})_2$  are a complex and diverse class of materials, which are becoming increasingly important as candidates for use as biomaterials. Moreover, they have gained additional prominence due to their biological role as one of the main constituents of mammalian bones and teeth enamel.<sup>2</sup> As such, apatites may be valuable in the manufacture of artificial bones, whereas another possible application is the use of ceramic implants as a support for the crystallization and layer growth of apatite, aiding the acceptance of the implant material by the body. However, the precise nature of the apatite thin film is not known, and there

is a clear need to gain an understanding of the interactions between the apatite layers and the ceramic substrate at the atomic level. In addition, understanding the interface between complex materials is of increasing significance. The present Letter reports detailed atomistic models for the interfaces between apatite and quartz based on computer simulation methods.

#### Theoretical Methods

Computational methods are well placed to calculate at the atomic level the geometries and adhesion energies of solid/solid interfaces. In this first theoretical study of the interfacial structure between apatite and silicates, we have concentrated on  $\alpha$ -quartz as a model for a range of silicate materials and silica-rich bioglasses. Our approach is to employ energy minimization techniques to study the interactions of thin films of fluorapatite, the major apatite phase, with the  $\alpha$ -quartz basal plane, which was calculated to be the most stable quartz surface.<sup>3</sup> We used the METADISE computer simulation code for the calculation of the surface and adsorbate structures and energies,<sup>4</sup> employing an established Born model potential for the silicate substrate<sup>5</sup> and newly developed potentials for apatite.<sup>6</sup> The potential parameters describing the interactions between the apatite film and silicate surface were derived for this

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**TABLE 1: Adhesion Energies ( $\text{J m}^{-2}$ ) for the Interfaces between Single and Double Films of Apatite and the Relaxed and Unrelaxed  $\alpha$ -Quartz Substrate, Calculated with Respect to the Relaxed Quartz Surface and Bulk Apatite**

film rotation (deg)	relaxed $\alpha$ -quartz surface		unrelaxed $\alpha$ -quartz surface	
	single layer	double layer	single layer	double layer
0/360	0.58	0.83	0.74	1.31
60	0.57	1.07	1.23	1.50
120	0.57	0.89	1.07	1.62
180	0.73	0.83	0.64	1.53
240	0.55	0.82	1.65	1.62
300	0.65	1.11	0.72	1.72

work following the approach of Schröder et al.<sup>7</sup> which has been shown to be a reliable method for potential derivation and adjustment where no experimental data are available, e.g., see refs 8 and 9.

## Results and Discussion

Both  $\alpha$ -quartz and apatite have a hexagonal crystal structure, where the basal (0001) planes were calculated to be the dominant surfaces. We therefore decided to use the  $\alpha$ -quartz (0001) surface as the substrate for the layer growth of apatite material, also in the (0001) orientation, although the apatite thin films have to accommodate themselves to the  $\alpha$ -quartz lattice parameters. Quartz has lattice vectors of  $a = b = 4.913 \text{ \AA}$ ,  $c = 5.404 \text{ \AA}$ , whereas the lattice vectors of fluorapatite are  $a = b = 9.360 \text{ \AA}$ ,  $c = 6.880 \text{ \AA}$ . We therefore had to grow the quartz substrate to a  $2 \times 2$  surface supercell,  $a = b = 9.826 \text{ \AA}$ , which could accommodate an overlayer of apatite with a misfit of  $-4.7\%$ . Previous computational studies of solid–solid interfaces, whether grain boundaries in geological systems, e.g., see refs 10 and 11, or thin films of catalytic materials, e.g., see ref 12, have always started their calculations from unrelaxed interfaces, i.e., where the two blocks of material were initially fitted together as bulk-terminated blocks before, only then, allowing the interface to relax in an energy minimization or molecular dynamics simulation. However, in experiment, the quartz substrate relaxes instantaneously upon formation of the surface,<sup>13</sup> well before attachment of the apatite film, and we therefore need to model the interface between substrate and film starting from a relaxed rather than bulk-terminated silica surface to ensure that the correct structures and energies are calculated.

We calculated the adhesion energies for the interface as a function of rotation of the apatite layer with respect to the underlying quartz substrate. The adhesion energy  $\gamma_{\text{adh}}$  is a measure of the stability of the interface with respect to the free quartz (0001) surface, which is calculated as shown in eq 1,

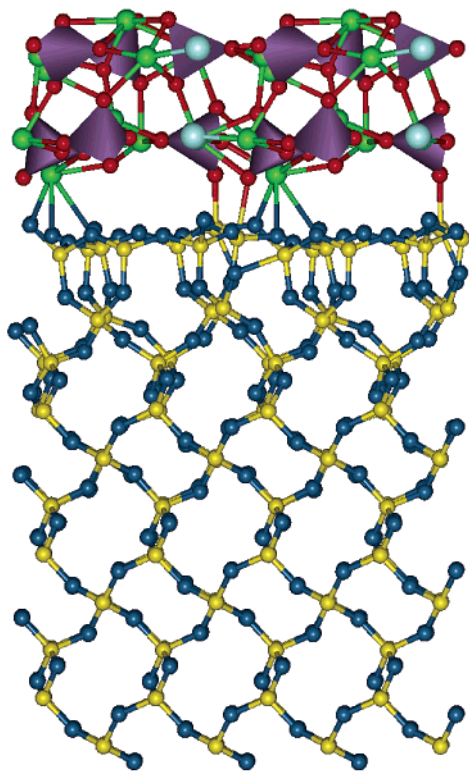
$$\gamma_{\text{adh}} = \frac{E_{\text{int}} - (E_{\text{surf,quartz}} + E_{\text{apatite}})}{A} \quad (1)$$

where  $E_{\text{int}}$  is the energy of the interfacial system,  $E_{\text{surf,quartz}}$  is the energy of the free quartz surface,  $E_{\text{apatite}}$  is the energy of the relevant number of bulk apatite units in the film, and  $A$  is the area of the interfacial region. Calculations were performed for both single and double layers of apatite on the quartz support. The resulting adhesion energies are displayed in Table 1, where the most stable interface has the lowest value of  $\gamma_{\text{adh}}$ . Before energy minimization of the interfacial system, the apatite film was kept at a constant height above the surface, but moved laterally with respect to the quartz surface to find the lowest energy position. When the lowest energy position had been

established, a full geometry optimization was performed to obtain the energy of the relaxed interfacial system, in which the initial height above the surface was varied in a series of calculations to check that this parameter did not affect the final energy and to ensure that a global rather than a local energy minimum had been obtained. During geometry optimization, not only was the apatite film free to move in any direction with respect to the underlying quartz surface but all atoms in the apatite film and in a quartz surface region of about  $22 \text{ \AA}$  into the bulk were also completely unconstrained so as not to prejudice the geometry of the interface. The complete process was then repeated for a series of rotations of the apatite film with respect to the quartz substrate, and the adhesion energies, shown in Table 1, were calculated. For the sake of completeness and comparison, we have also included the adhesion energies of the interfaces formed at an unrelaxed quartz surface. The main difference between the relaxed and unrelaxed quartz surface is the presence of dangling bonds on the unrelaxed surface where the surface silicon and oxygen atoms have a lower coordination than in the bulk material. Upon relaxation the surface Si and O atoms form bonds parallel to the surface and regain their bulk coordination numbers of 4 and 2, respectively. As a result, the unrelaxed quartz surface is much more reactive toward the apatite film, but this enhanced reactivity of the substrate leads to irregular and distorted structures of the apatite films, and to a lesser extent the quartz surface, resulting in higher interfacial energies.

Comparing the structures of the interfaces due to the different rotations of the single apatite layer, we observed that the stability of the interface as given by its adhesion energy depends on a number of factors. The number of bonds that can form between the calcium and oxygen ions of the apatite film to oxygen and silicon ions respectively in the quartz substrate plays a role, but more so the lengths of the bonds, especially between calcium ions and substrate oxygen atoms. For example, the least stable  $180^\circ$  rotational interface forms only two bonds per apatite unit cell to the underlying quartz structure, one O–Si bond of  $2.03 \text{ \AA}$ , and one rather long Ca–O interaction of  $2.97 \text{ \AA}$ , whereas the more stable  $0^\circ$  rotation forms one shorter Ca–O bond at  $2.55 \text{ \AA}$  and several O–Si interactions between  $2.09$  and  $2.56 \text{ \AA}$ . The most stable interface at a rotation of  $240^\circ$ , shown in Figure 1, contains both a large number of bonds between the film and substrate, which are also short (O–Si  $2.02$ – $2.78 \text{ \AA}$ , Ca–O  $2.52$ – $2.81 \text{ \AA}$ ) and often the oxygen or calcium ions form multiple bonds across the interface. The other factor, which determines the stability of the interface is the size of the empty region between substrate and film. In the  $0^\circ$ ,  $120^\circ$ , and  $240^\circ$  rotations, which have very similar interfacial energies, the film fits closely to the substrate (the gaps are  $2.11$ – $2.20 \text{ \AA}$  wide) and the interfacial region is relatively dense, whereas in the less stable interfaces, larger interfacial cavities and channels are formed ( $\sim 2.50 \text{ \AA}$  gap width), which destabilize these interfacial regions. The same effect is seen to occur in rock grain boundaries, where large cavities lead to unstable grain boundary regions, which only become stable when the cavities collapse or are filled with interstitial species such as water molecules.<sup>7</sup>

Following our simulations of single apatite layers on the quartz substrate, we also studied the interfacial structures and energies of a series of thicker apatite films of two unit cells deep ( $\sim 14 \text{ \AA}$ ). From the adhesion energies in Table 1, it is clear that the effect of the increased thickness is to destabilize the interfaces in all cases, although the  $240^\circ$  rotation remains the preferable configuration. The  $60^\circ$  and  $300^\circ$  rotations are clearly less energetically favorable and the spread in adhesion energies



**Figure 1.** Geometry optimized structure of a single layer of apatite film grown onto the relaxed quartz (0001) surface at a rotation of  $240^\circ$ , showing Ca–O<sub>quartz</sub> bonds up to 2.5 Å and O<sub>apatite</sub>–Si bonds up to 3.0 Å (Si = yellow, O<sub>quartz</sub> = dark blue, O<sub>apatite</sub> = red, F = pale blue, P = purple, Ca = green, PO<sub>4</sub> groups shown as tetrahedral).

is somewhat larger than for the single apatite layer, varying over  $0.29 \text{ J m}^{-2}$  rather than  $0.18 \text{ J m}^{-2}$  for the single layer. The higher adhesion energies and their greater variance with rotation are due to a lesser flexibility of the double apatite layer. The ions in the thicker film are more constrained to remain in an environment, which is approximating the apatite crystal structure, although stretched to accommodate the underlying quartz lattice. For example, whereas in the single layers the PO<sub>4</sub> groups had rotated freely and the columns of fluoride ions had often become severely distorted in the *a* and *b* directions, in the double layer film the basic structure of the apatite lattice remains intact. The PO<sub>4</sub> groups are no longer rotated with respect to the apatite lattice and the fluoride ions remain in regular columns, one above the other in the *c* direction.

In this computer modeling study of a range of interfaces between two complex oxide materials, we have shown how the stability and orientation of the apatite thin film is determined by the nature of the bonding between the materials across the interface. On the basis of our calculated adhesion energies, we predict that the apatite thin film will form local domains of both  $(2 \times 2)$  as well as clockwise and anticlockwise  $(2 \times 2)R120^\circ$  adsorbate layers. Apatite films formed at unrelaxed quartz surfaces lead to significantly more distorted and less stable interfaces, in addition to giving different lowest energy rotations. Hence, if we are to interpret experimental findings correctly and predict growth behavior and energies for use in film deposition onto inorganic surfaces, the nature of the substrate surface needs to be included in the computer simulations.

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**Supporting Information Available:** Table of potential parameters derived for this work (short-range cutoff 20 Å). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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