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Structure of the fluorapatite (100)-water interface by high-resolution X-ray reflectivity

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ABSTRACT

A complete understanding of the surface chemistry of the apatite-water system requires direct observation of the interfacial structure at the molecular scale. We report results for the structure of the apatite (100)-water interface obtained with high-resolution specular X-ray reflectivity from a natural growth surface of Durango fluorapatite. A uniform termination at the crystallographic unit-cell boundary was determined. An atomistic model of the interfacial structure is compared to the experimental results and optimized through non-linear least-squares fitting in which the structural parameters were selected to be both physically and chemically plausible. The best-fit structure includes a Ca- and/or F-deficient outermost surface, minimal structural relaxations of the near-surface apatite crystal, and the presence of a layered interfacial water structure exhibiting two distinct water layers. The height of the first water layer is 2.64(9) Å relative to the relaxed surface with 3.5(1.3) water molecules per surface unit-cell area (64.9 Å^2). A second layer of adsorbed water is found 1.53(5) Å above the first layer, followed by a nearly featureless profile of the bulk liquid water. The layered structure of water is interpreted as being due to hydrogen bonding at the solid-water interface. The interfacial structure shows a strong similarity with the octacalcium phosphate structure projected along a surface normal direction.