

Supplement 1. FTIR spectra of HA (top) and CHA (bottom). Two absorbance bands in CHA at 1500-1400 cm-1 and 870-880 cm-1 correspond to v_3 and v_2 of CO₃²⁻ respectively.



Supplemet 2. FTIR spectrum of CHA with CO_3^{2-} v₂ band in the insert, this peak is composed of 2 peaks at 879 and 873 cm⁻¹, corresponding to type A and type B carbonate substitution in hydroxypatite, respectively. These data imply that the mineral used in the study is AB type carbonated apatite. Note that the intensity of the peak at 873 cm⁻¹ is much higher, suggesting higher percentage of B type substitution in the CHA.



Supplement 3. Adsorption isotherm of PRP1 on to HA (\blacktriangle) and CHA (\bullet). Binding experiments were carried out by incubating the apatite samples (1.2 mg) with protein solutions (50 to 1000 μ g/ml). The mixture was then rotated at a constant speed for 4 hours at 37°C, until equilibrium was attained. Following the incubation of the proteinapatite mixtures, the suspensions were centrifuged (Eppendorf Scientific, Westbury, NY) at ~12,000 x g for 15 minutes at 4° C. The protein concentration in the resulting supernatants was determined using the BCA assay (Pierce, Rockford, IL). Using these analytical data, the amount of protein adsorbed per unit surface area (Q) and the concentration of protein remaining in solution (C) were determined. Experimental points are indicated by the noted symbols. The curves shown represents those derived from the adsorption parameters (K and N) obtained from the least square fitting $(r^2 =$ (0.99) of the linearized form of the Langmuir adsorption isotherm model, C/O =1/NK + C/N, where Q is the amount of protein adsorbed per unit surface area, C is the amount of protein in solution at equilibrium, N is the maximum number of binding sites, and K is the affinity constant. The binding curves of PRP1 with both HA and CHA showed saturation and the Langmuir model fit the data very well. The binding curves show that PRP1 exhibits a significantly (p <0.05) lower number of binding sites (N = 899 μ g/m²) on CHA, in comparison to HA (N = 2810 µg/m^2). Although not significantly different (p >0.05), due in part to a relatively large standard error in this measurement, PRP1 exhibits a higher affinity constant for CHA (K = $0.068 \text{ ml/}\mu\text{g}$) compared to HA (K = $0.04 \text{ ml/}\mu\text{g}$).



Supplement 4. FTIR spectrum of PRP1 in 6M CaCl₂ solution of CaCl₂ in binding buffer. Note that there is no peak around 1620 cm⁻¹. At the same time a prominent peak appears around 1642 cm⁻¹ characteristic of anhydrous PPII. Similar peak shift has been previously described for poly-L-proline PPII structures in aqueous solution upon addition of CaCl₂ ¹. It has been attributed to a substitution of hydrogen bonds between the peptide backbone and water with Ca²⁻ complexes. The strongest peak in the Amide I region had a maximum at 1612 cm⁻¹. Such low frequency FTIR absorbance is attributed to extended β -strands with intra molecular hydrogen bonds. Such structures have been previously reported in amyloid fibrils and thermally denatureted proteins ²⁻⁴. It is very possible that a portion of PPII structure is transformed into extended β -strands upon addition of Ca²⁺ since PP II has also been shown to be a precursor conformation in amyloid formation⁵. However additional studies are needed to clarify this issue.

| Peak Maxima (cm ⁻¹) | Area under peak (%) |
|---------------------------------|---------------------|
| 1612 | 40 |
| 1630 | 4 |
| 1642 | 12 |
| 1650 | 2 |
| 1658 | 19 |
| 1674 | 22 |

Table. Peak positions and their corresponding area percentages based on the peak fitting analysis of the FTIR spectrum of PRP1 in 6 M CaCl₂.

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