Supplementary Material

Octacalcium phosphate - a metastable mineral phase controls the evolution of scaffold forming proteins

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Supplementary Material 1: Oriented adsorption of TC on OCP

As schematically drawn in Figure 4 a, the TC molecule is composed of two $\alpha 1$, and one $\alpha 2$ chain. In Figure S1 (a) a flat schematic mapping of the positions of the amino acids of the major helix is given by their projection on a surface forming a concentric cylinder with a diameter of 1.5 nm. In the Figures S1 (b) and (c) only the sequences of X-Y- amino acids are shown as they could act as adsorption sites for the OCP crystal. Always 20 amino acids are assembled in one group related to three turns with the pitch of 8.58 nm of the major helix. Along this sequence there is a periodic distribution of motifs of positively and negatively charged residues. In the presence of divalent electrolytes (Ca^{2+}), the positively charged groups dominate the overall Coulomb interaction of the major helix, as shown by Freudenberg et al.[1]. Therefore, the post-nucleation complexes in the ribbons arranged at the (100) face and in the 'apatitic layers' of the (010) face (Fig. S 1(b)), as well as the 'non-apatitic' phosphate ions p13, p6 situated in the 'water layer' of OCP (Fig. S1 (c)) are favored adsorption sites for the positively charged motifs of the TC molecule. Here we use the nomenclature for the positions of the phosphate ions introduced by Brown[2]. There is a striking correspondence between the molecular structure of the TC helix and the periodic arrangement of the phosphate ions which enables the TC molecule to perfectly align along the c-axis of OCP. The periodicity of the OCP lattice (equals 0.687 nm along the c-axis) and the repeat length of the TC molecule lead to an ideal fit of positively charged X-Y- motifs of the TC molecule with the 'apatitic' phosphate ions as well as with p13 and p'13 phosphate ions with a repeat of about 3 nm. Furthermore, the graphs show that the periodicity of available binding sites equals c_{OCP} = 0.687 nm if also interaction partners with small deviations (less than 0.3 nm) in the c direction are included.
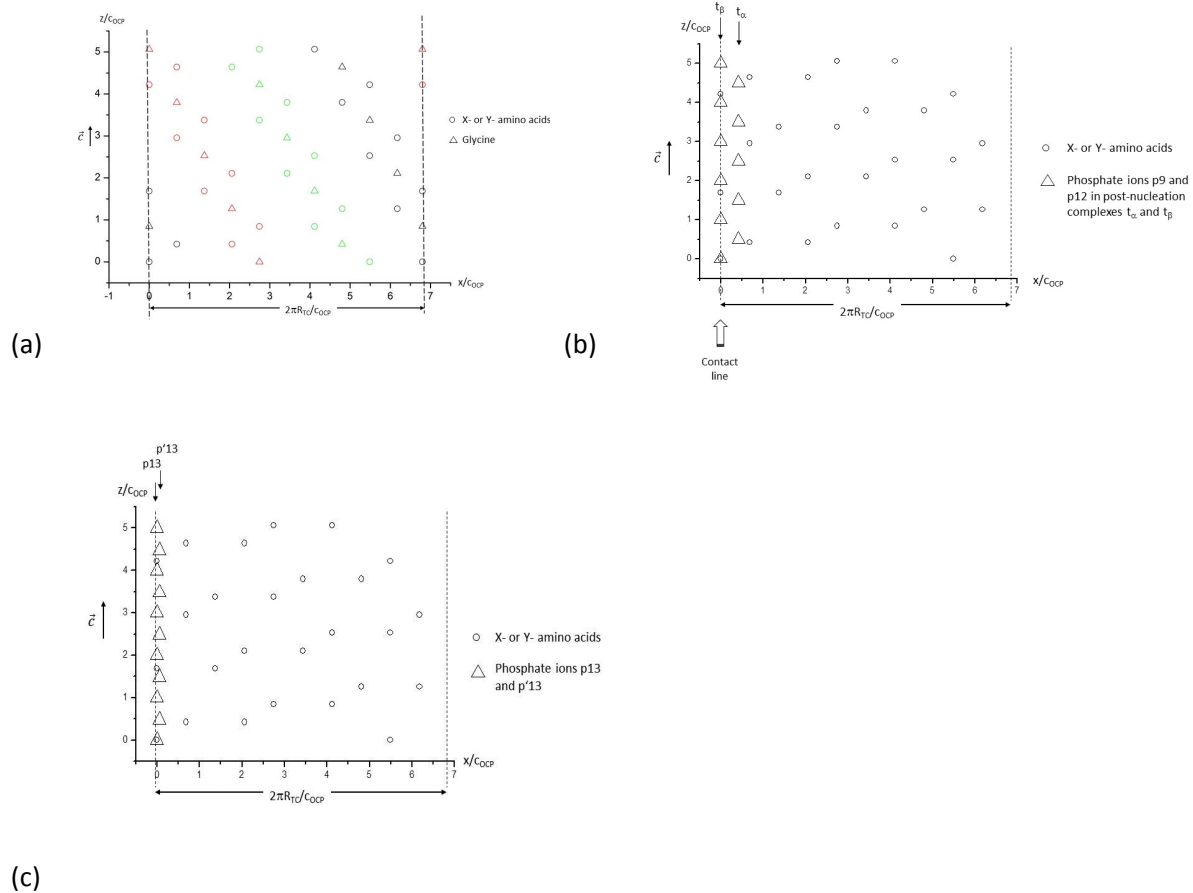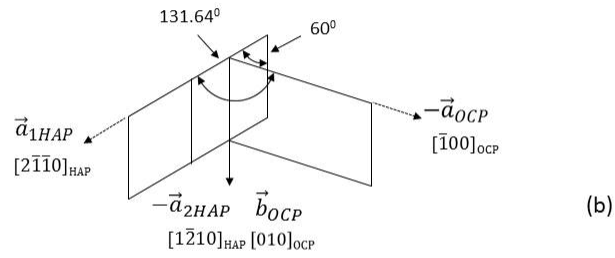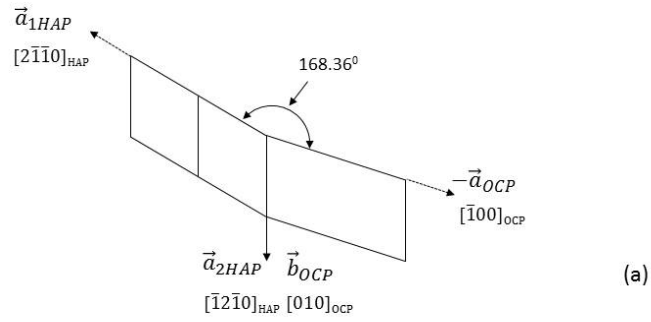
(a)

(b)

(c)

Figure S1: Relation between possible adsorption sites of the right-handed major helix of tropocollagen and the positions of phosphate ions at various faces of an OCP crystal: (a) Projection of the complete TC molecule on a face cylindrically arranged around the molecule (diameter 1.5 nm). The three α chains are distinguished by different colors. (b) Overlapping of the positions of the 'apatitic' phosphate ions p9 (t_α: relative positions $x/c_{OCP}=0$, $y/c_{OCP}=0.626$) and p12 (t_β: relative positions $x/c_{OCP}=0.42$, $y/c_{OCP}=0.099$) at the (100) face of OCP with positions of X- or Y- amino acids. (c) Overlapping of the positions of the 'non-apatitic' phosphate ions p13 (relative positions $x/c_{OCP}=0$, $y/c_{OCP}=1.210$), and p'13 (relative positions $x/c_{OCP}=0.058$, $y/c_{OCP}=0.190$) at the (010) in the 'water layer' of OCP with positions of X- or Y- amino acids.

Supplementary Material 2: Model assumptions for simulation of the OCP/HAP transition in thin layered structures.

- There are two competitive modes of OCP/HAP solid-state transformations as shown in Figure S2:

  - the direction $[\bar{1}2\bar{1}0]_{HAP}$ of the unit cell of HAP is 'glued' with one unit cell of OCP along the direction $[010]_{OCP}$, and $[0001]_{HAP}$ is parallel to $[001]_{OCP}$[2];

  - the direction $[1\bar{2}10]_{HAP}$ is 'glued' with $[010]_{OCP}$, and the *c*-axes of HAP and OCP are antiparallel[3].

- Individual OCP unit cell transforms into two HAP unit cells.

- The phase transition of a polycrystalline OCP structure is connected with the formation of transient residual stresses caused by the symmetry and size of the unit cells. Stress driven microtwinning is the dominating stress relaxation mechanism in carbonate HAP crystals.

- The formed HAP-TC composites are densified by surface diffusion driven by minimization of their total interface free energy.

- Usually the microtwinning and surface diffusion are connected with shape instability of the total structure.

$\vec{a}_{1HAP}$

$[2\bar{1}\bar{1}0]_{HAP}$

168.36⁰ → 168.36^0

$-\vec{a}_{OCP}$

$[\bar{1}00]_{OCP}$

$\vec{a}_{2HAP}$ $\vec{b}_{OCP}$

$[\bar{1}2\bar{1}0]_{HAP}$ $[010]_{OCP}$

(a)

131.64^0 60^0

$\vec{a}_{1HAP}$

$[2\bar{1}\bar{1}0]_{HAP}$

$-\vec{a}_{OCP}$

$[\bar{1}00]_{OCP}$

$-\vec{a}_{2HAP}$ $\vec{b}_{OCP}$

$[1\bar{2}10]_{HAP}$ $[010]_{OCP}$

(b)

$$|\vec{a}_{1HAP}| = |\vec{a}_{2HAP}| = a_{HAP} \quad |\vec{a}_{OCP}| = a_{OCp} \quad |\vec{b}_{OCP}| = b_{OCp}$$

Figure S2: The two alternative growth modes of the solid-transformation of OCP phase into HAP phase: The *c*-axes of HAP and OCP are parallel [2] (a), and antiparallel [3] (b), respectively. Note that $\beta_{OCP} > 90^0$ and a_{HAP} differs slightly from b_{OCP}.

In the following the basic processes governing the phase transition of individual mineralized MFs are considered. The transitions in the overlap region (Figures S3-S5) and in the gap region (Figures S6-S8) are studied.
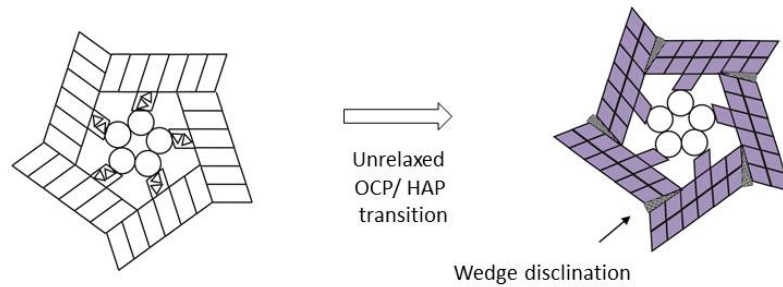
Overlap region:

Figure S3: Initial stage of the OCP/HAP transition at an overlap region of a mineralized MF. The lattice misfit causes elastic strains in the unrelaxed HAP structure. These elastic strains can be modeled by incorporation of five wedge disclinations[4].
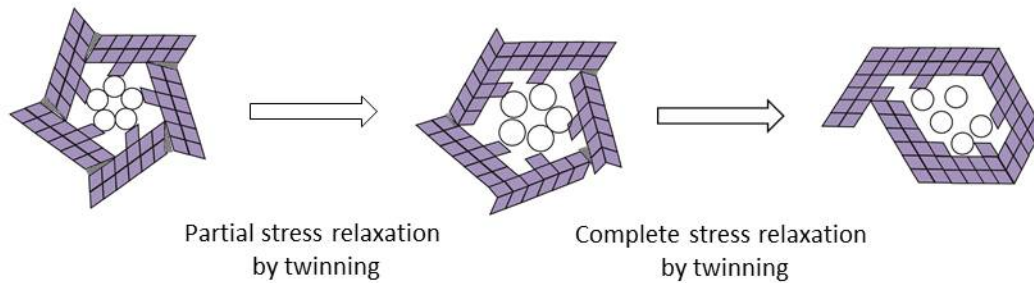

Figure S4: Relaxation of residual stresses in the HAP structure at an overlap region of a mineralized MF.
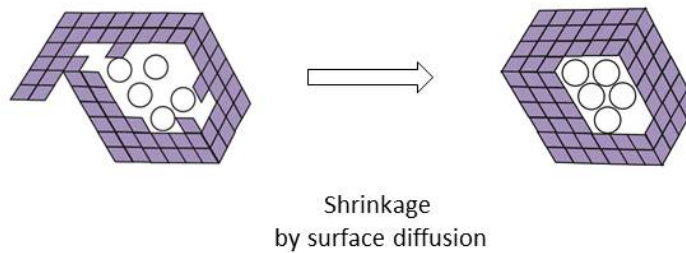

Figure S5: Densification of the HAP structure by surface diffusion at an overlap region of a mineralized MF.
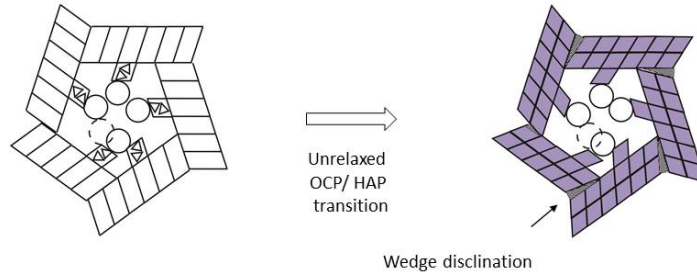
Figure S6: Initial stage of the OCP/HAP transition at a gap region of a mineralized MF. The lattice misfit causes elastic strains in the unrelaxed HAP structure which can be modeled by incorporation of five wedge disclinations.
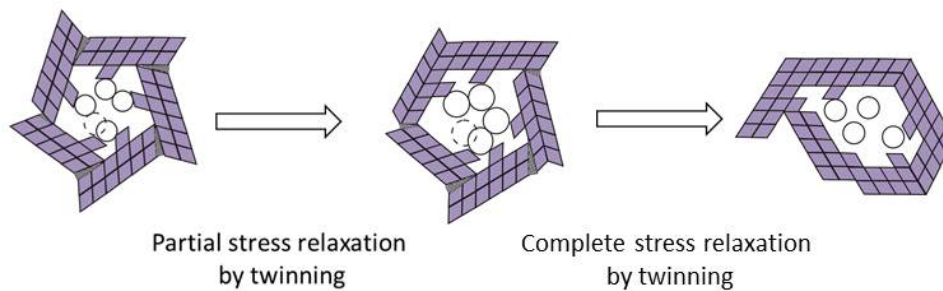

Figure S7: Relaxation of residual stresses in the HAP structure at a gap region of a mineralized MF.
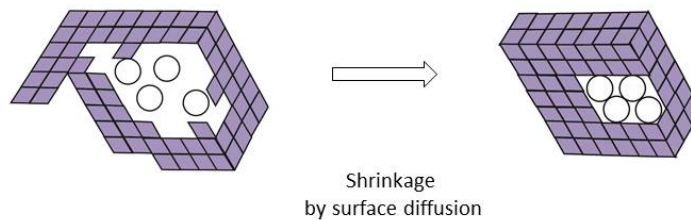

Figure S8: Densification of the HAP structure by surface diffusion at a gap region of a mineralized MF.

A possible reaction path of a OCP/HAP transition can be modeled by a combination of these basic processes.

References

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3.   M. E. Fernandez, C. Zorrilla-Cangas, R. Garcia-Garcia, J. A. Ascencio and J. Reyes-Gasga, *Acta crystallographica. Section B, Structural science*, 2003, 59, 175-181.
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