

Detection of Posner's clusters during calcium phosphate nucleation: a molecular dynamics study

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Amorphous calcium phosphate (ACP) has been proposed as the first phase nucleating from aqueous solution. [1] ACP presents short-range order in the form of small domains with size of 0.9 nm and chemical formula $\text{Ca}_9(\text{PO}_4)_6$, known as Posner's clusters.

We studied the aggregation and clustering of calcium and phosphate ions in water using shell-model molecular dynamics simulations. We employed a force field originally developed in our group for phosphate based bioglasses, [2] that we tested against ab initio molecular dynamics simulations of a calcium triphosphate complex [3] and a Posner's cluster.

Our simulations show that calcium phosphate aggregates form in solution with composition and calcium coordination similar to those found in Posner's cluster, but the stoichiometry of these species is dependent on the ionic composition of the solution: calcium deficient clusters originate in solutions with low Ca:P ratio; cluster containing protonated phosphate groups form in neutral solutions; sodium ions partially substituting calcium appear in solutions containing a mixture of sodium and calcium ions. These Posner-like clusters can be connected by phosphate groups, which act as a bridge between their central calcium ions.

The simulations of the aggregation in solution of calcium phosphate represent an unequivocal validation of the Posner's model, and reveal for the first time the structure and composition of the species that form during the early stages of ACP nucleation at a scale still inaccessible to the experiment.

[1] M. J. J. M. van Kemenade & P. L. de Bruyn (1987) *J. Colloid Interface Sci.*, **118**, 564. [2] R. I. Ainsworth *et al.* (2012) *J. Chem. Phys.*, **137**, 234502. [3] G. Mancardi *et al.* (2016) *Cryst. Growth Des.*, **16**, 3353.