Interaction of stable aggregates drives the precipitation of calcium phosphate in supersaturated solutions

Supplementary information

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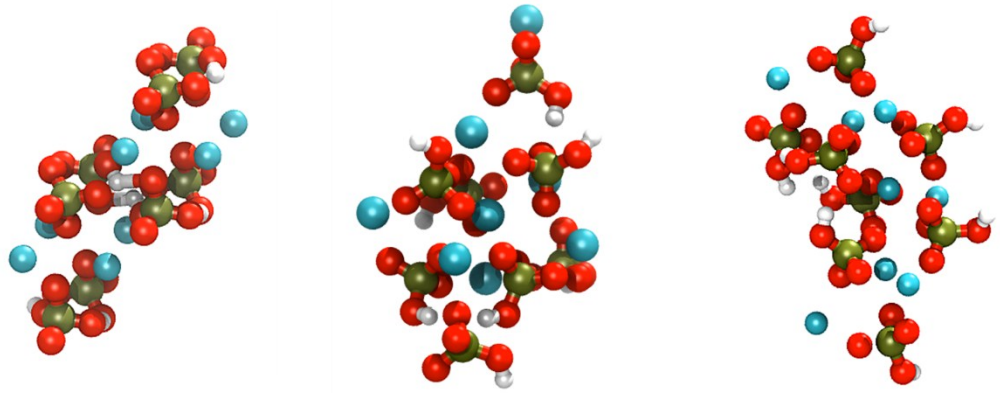

a) Monetite based nanoparticle

b) Monetite based nanoparticle after 20 ns of simulation

c) Nanoparticle extracted from large scale simulation and simulated for additional 30 ns at infinite dilution

Figure S1. Snapshots of nanoparticles from different simulations. a, b and c are described in the figure. In the image, the Ca^{2+} is coloured in cyan, phosphorous in green, oxygen in red and hydrogen in white.

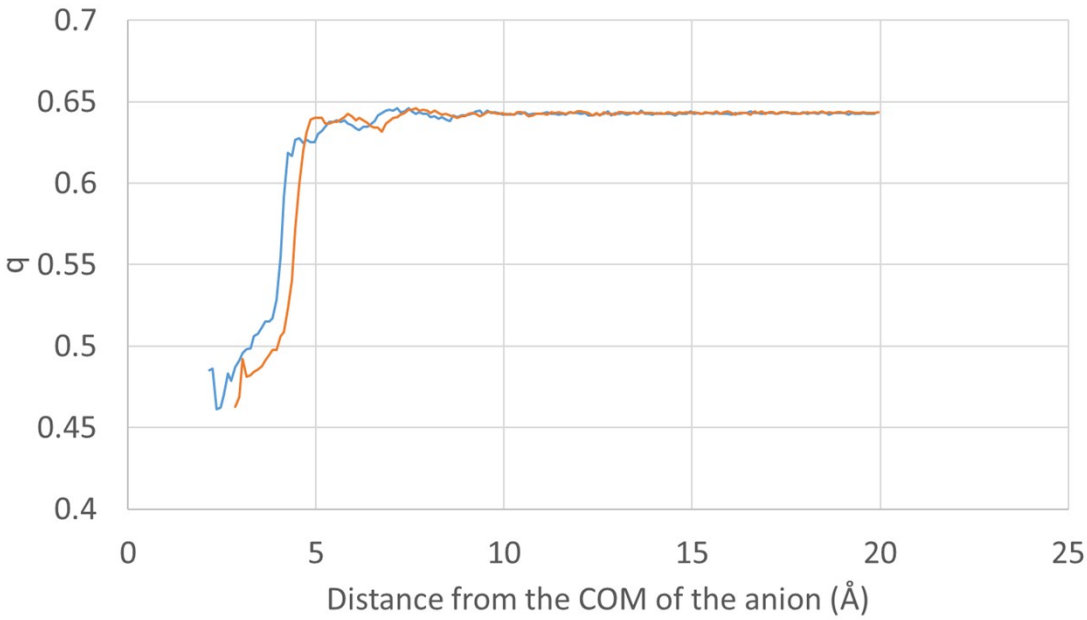

Figure S2. Tetrahedral order parameter of water, *q,* as a function of the distance from the centre of mass of CO_3^{2-} (blue) and HPO_4^{2-} (orange). The tetrahedral order parameter is defined as:

$$q = 1 - \frac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}\left(cos\varphi_{jk} + \frac{1}{3}\right)^2$$

where φ_{jk} is the angle between the vectors from an oxygen atom of a water molecule to the oxygen atoms of its two nearest neighbours.

Force field input file used in LAMMPS

```
variable P    equal    1
variable O9   equal    2
variable O8   equal    3
variable H8   equal    4
variable OW   equal    5
variable HW   equal    6
variable CA   equal    7

mass  ${P}     30.974
mass  ${O9}    16.000
mass  ${O8}    16.000
mass  ${H8}     1.000
mass  ${OW}    15.999
mass  ${HW}     1.001
mass  ${CA}    40.078

bond_style hybrid harmonic
#@ P   - O9
bond_coeff    1   harmonic   21.570600     1.52000
#@ P   - O8
bond_coeff    2   harmonic   12.117050     1.60000
#@ O8  - H8
bond_coeff    3   harmonic   21.576300     0.98000
#@ OW  - HW
bond_coeff    4   harmonic   22.965000     1.01200


angle_style hybrid harmonic class2
#@ O9  - P  - O9
angle_coeff  1   class2      109.50000      5.9375000      0.0000000
0.0000000
angle_coeff  1   class2 bb     1.61990      1.5200000      1.5200000
angle_coeff  1   class2 ba     0.00000      0.0000000      1.5200000
1.5200000
#@ O8  - P  - O9
angle_coeff  2   class2      109.50000      2.2033000      0.0000000
0.0000000
angle_coeff  2   class2 bb     2.91010      1.5200000      1.6000000
angle_coeff  2   class2 ba     0.00000      0.0000000      1.5200000
1.6000000
#@ H8  - O8 - P
angle_coeff    3   harmonic  1.45275     111.40000
#@ HW  - OW - HW
angle_coeff   4    harmonic  1.645680     113.24000

dihedral_style hybrid charmm
#@ H8  - O8 - P   -O9
dihedral_coeff     1     charmm   0.042272    3     180  0.0


pair_style hybrid/overlay coul/long 9. lj/cut 9. buck/mdf 6. 9. lennard/mdf
6. 9.  lj/mdf 6 9
```

```
pair_coeff   ${OW}   ${OW}   lj/cut     0.006738     3.165572

pair_modify tail yes


pair_coeff     ${O8}   ${O8}    buck/mdf    12534.455000  0.202    0.
pair_coeff     ${O9}   ${O8}    buck/mdf    12534.455000  0.202    0.
pair_coeff     ${O9}   ${O9}    buck/mdf    12534.455000  0.202    0.
pair_coeff     ${O8}   ${H8}    lennard/mdf    54.        0.
pair_coeff     ${O9}   ${H8}    lennard/mdf    54.        0.

pair_coeff     ${O8}   ${OW}    buck/mdf    19534.455133  0.2151     0.
pair_coeff     ${O9}   ${OW}    buck/mdf    19534.455133  0.2426     0.
pair_coeff     ${O8}   ${HW}    lennard/mdf    28.0       0.0

pair_coeff     ${OW}   ${CA}    lj/mdf          0.00095   3.35


pair_coeff     ${P}   ${CA}     buck/mdf     2132.9786    0.3428     0.
pair_coeff     ${P}   ${O8}     lennard/mdf  1000.0       0.
pair_coeff     ${P}   ${O9}     lennard/mdf  1000.0       0.
pair_coeff     ${O8}  ${CA}     buck/mdf     2010.878     0.276289   0.
pair_coeff     ${O9}  ${CA}     buck/mdf     2590.878     0.276289   0.



pair_coeff   ${P}    ${P}                        coul/long
pair_coeff   ${P}    ${O9}                       coul/long
pair_coeff   ${P}    ${O8}                       coul/long
pair_coeff   ${P}    ${H8}                       coul/long
pair_coeff   ${P}    ${OW}                       coul/long
pair_coeff   ${P}    ${HW}                       coul/long

pair_coeff   ${O9}   ${O9}                       coul/long
pair_coeff   ${O9}   ${O8}                       coul/long
pair_coeff   ${O9}   ${H8}                       coul/long
pair_coeff   ${O9}   ${OW}                       coul/long
pair_coeff   ${O9}   ${HW}                       coul/long
pair_coeff   ${O8}   ${O8}                       coul/long
pair_coeff   ${O8}   ${H8}                       coul/long
pair_coeff   ${O8}   ${OW}                       coul/long
pair_coeff   ${O8}   ${HW}                       coul/long
pair_coeff   ${H8}   ${H8}                       coul/long
pair_coeff   ${H8}   ${OW}                       coul/long
pair_coeff   ${H8}   ${HW}                       coul/long

pair_coeff   ${OW}   ${OW}                       coul/long
pair_coeff   ${OW}   ${HW}                       coul/long
pair_coeff   ${HW}   ${HW}                       coul/long

pair_coeff   ${P}    ${CA}                       coul/long
pair_coeff   ${O9}   ${CA}                       coul/long
pair_coeff   ${O8}   ${CA}                       coul/long
```

```
pair_coeff   ${H8}   ${CA}                        coul/long
pair_coeff   ${CA}   ${CA}                        coul/long

pair_coeff   ${OW}   ${CA}                        coul/long
pair_coeff   ${HW}   ${CA}                        coul/long
```