Supporting information

Kinetics of Calcium Phosphate Nucleation and Growth on Calcite: Implications for Predicting the Fate of Dissolved Phosphate Species in Alkaline Soils

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1. Experimental details.

(1) AFM and related analysis. Cleavage rhombs were cut to *ca.* 3 × 3 × 1 mm dimensions and mounted in the fluid cell holder. Reaction solutions were passed through the fluid cell. All experiments were performed under ambient conditions (22 ± 1°C and partial pressure CO_2 ~ $10^{-3,5}$ atm.). Solutions were prepared from high-purity solids, $(NH_4)_2HPO_4$, NaCl, and monosodium citrate dissolved in doubly-deionized water (resistivity > 18 mΩcm^{-1}). Each of the solutions was gradually passed over the calcite surface at a constant flow rate *ca.* 50 mL h^{-1} using a syringe pump connected with vinyl tubes. Experiments were repeated at least twice to ensure reproducibility of the results. At least four etch pits in sequential images were measured for each given solution concentration. The AFM images were analyzed using the NanoScope software (Version 5.12b48). The scanning frequency was *ca.* 3 Hz with an average scan time 1.5 min per scan and areas scanned were mostly 10 × 10 µm.

The evolution of solution and surface speciation during calcite dissolution was simulated via the addition of a small increment of calcite to each of the experimental solutions. Moreover, the SI (Saturation Indices) for given solutions were calculated at the last step (500 steps) of each dissolution reaction.

Inductively coupled plasma optical emission spectrometry ICP-OES (Atom Scan Thermo Jarrell Ash) was used for determining the calcium concentration from aliquots of 5 mL collected after flowing each concentration of $(NH_4)_2HPO_4$ solution over a calcite surface.

The scattered Raman light was collected in 180° backscattering geometry, and after having passed a 100 µm entrance slit, it was dispersed by a grating of 1800 grooves/mm. A 100 times objective, with a numerical aperture of 0.9, was used for all measurements. The resulting spectral resolution in the range of 200 cm^{-1} to 1400 cm^{-1} is 0.9 cm^{-1}. All spectra were fitted using the software Fytik.[1] Taking the spectral resolution into account, all obtained full widths at half maximum (FWHM) were corrected using the equation of Dijkman and van der Maas.[2]

(2) Calcite dissolution reactions

Overall calcite dissolution rate (r) can be described:

$$r = r_+[1 - S^n] = k_{Ca}\{> CaOH_2^+\}^n[1 - S^n] \tag{1}$$

in which r_+ is the forward reaction rate, k_{Ca} is the rate constant, n is the reaction order (n=1 for calcite dissolution),[3] $\{i\}$ is the concentration of the ith surface species, and S is the saturation state of the aqueous solution with respect to calcite. The presence of organic ligands such as citrate can influence calcite dissolution rates by changing its surface composition. At conditions where >$CaOH_2^+$, >$CaCO_3^-$, and >CaL^{1-m} dominate Ca speciation at the calcite surface (other potential surface species are negligible), mass conservation on surface sites requires:[4]

$$\{Ca_{TOTAL}\} => CaOH_2^+ + > CaCO_3^- + > CaL^{1-m} \tag{2}$$

Ligand promoted dissolution rates are proportional to the >CaL^{1-m} surface complex concentration[4] such that at pH>6:

$$r_+ = [k_{Ca}\{> CaOH_2^+\} + k_L\{> CaL^{1-m}\}] \tag{3}$$

2. Results

Table S1. Surface complexation reactions in the presence of phosphate and their stability constants at the calcite-solution interface (modified from Pokrovsky et al., 2000 and SØ et al., 2011)[5,6]

Reaction on the surface	Log K (25 °C)
$> CO_3H^0 = >CO_3^- + H^+$	-5.1
$> CO_3H^0 + Ca^{2+} = >CO_3Ca^+ + H^+$	-1.7
$> CaOH^0 = >CaO^- + H^+$	-12.0
$> CaOH^0 + H^+ = >CaOH_2^+$	11.5
$> CaOH^0 + CO_3^{2-} + 2H^+ = >CaHCO_3^0 + H_2O$	23.5
$> CaOH^0 + CO_3^{2-} + H^+ = >CaCO_3^- + H_2O$	17.1
$> CaCO_3^- + CaHPO_4^0 = >CaHPO_4Ca^+ + CO_3^{2-}$	-1.75
$> CaCO_3^- + CaHPO_4^- = >CaPO_4Ca^0 + CO_3^{2-}$	-0.79
$> sCaCO_3^- + CaHPO_4^0 =>sCaHPO_4Ca^+ + CO_3^{2-}$	0.90
$> sCaCO_3^- + CaHPO_4^- = >sCaPO_4Ca^0 + CO_3^{2-}$	2.21
$> CaCO_3^- + HPO_4^{2-} = >CaHPO_4^- + CO_3^{2-}$	-2.0

$> CaCO_3^- + CaPO_4^- => CaPO_4Ca^0 + CO_3^{2-}$	-0.72
$> sCaCO_3^- + HPO_4^{2-} => sCaHPO_4^- + CO_3^{2-}$	0.17
$> sCaCO_3^- + CaPO_4^- => sCaPO_4Ca^0 + CO_3^{2-}$	2.30

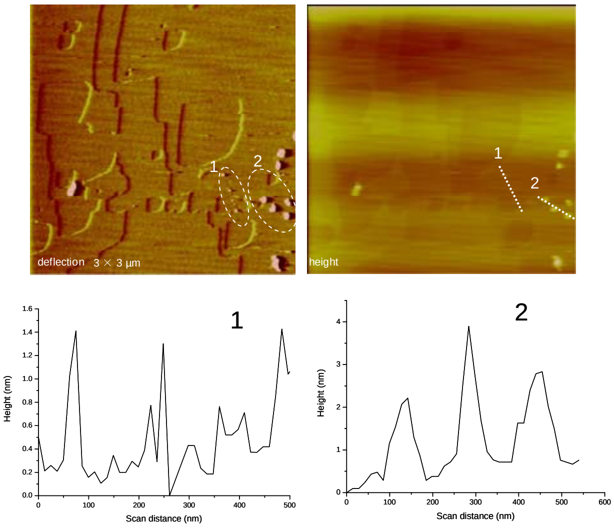

Figure S1. Initially forming nuclei ranging from 0.9 to 1.4 nm in size, and the growing clusters ranging from 2.4 to 3.9 nm in height.

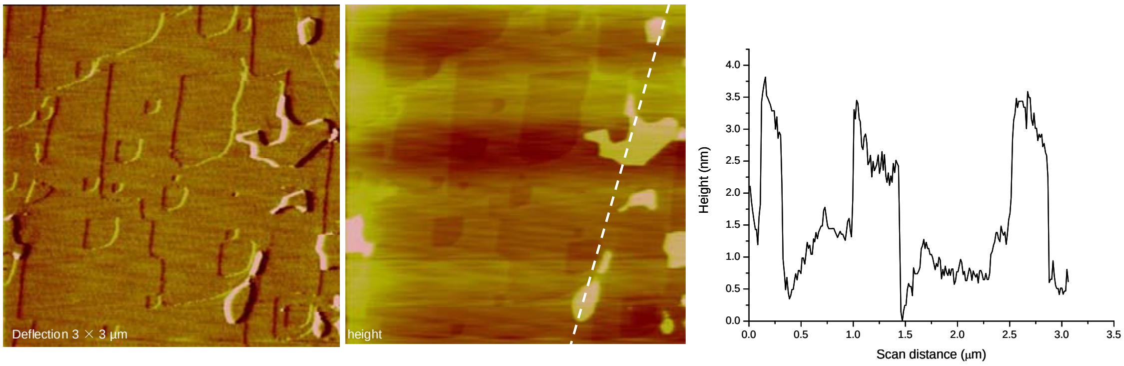

Figure S2. AFM images of initially forming Ca-P plates. AFM height image showing the layers with about 2.3 nm in height.

Supporting References:

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(5) Pokrovsky, O. S.; Mielczarski, J. A.; Barres, O.; Schott, J. Surface speciation models of calcite and dolomite/aqueous solution interfaces and their spectroscopic evaluation. *Langmuir* **2000**, *16*, 2677-2688.

(6) SØ, H. U.; Postma, D.; Jakobsen, R.; Larsen, F. Sorption of phosphate onto calcite; results from batch experiments and surface complexation modelling. *Geochim. Cosmochim Acta* **2011**, *75*, 2911-2923.