Supplementary Information: Water Structure, Dynamics and Ion Adsorption at the Aqueous {010} Brushite Surface

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1 Radial Distribution Functions

The water distribution was further analysed by computing the radial distribution functions (RDFs) for oxygen atoms of water around the calcium sites (See Figure S3). For each site a single peak at ∼2.6 Å corresponds to the first coordination shell, and the inset integral of the RDF at short distances reaches an initial plateau corresponding to the coordination number for this first shell. The RDF of the bulk Ca atoms within brushite confirms the bonding patterns seen experimentally, with each water O coordinated to alternating Ca atoms. The exposed atoms of the upper row (U1 and U'1) were the only sites with coordination numbers for water greater than one. These sites had two waters coordinated, as seen qualitatively in the 3D density maps. The RDFs at positions L2 and U2 already closely resemble the RDF of a surface Ca.

In the first coordination shell, there was no difference between the step with hydrogens exposed and without. Small differences occur past 4 Å which includes the second water layer, but also potentially includes oxygens coordinated to neighbouring calcium atoms.

2 Supplementary Figures and Tables

Table S1: Modified force field parameters for C2. All other parameters were taken unmodified from Demichelis et al. [?].

Interaction	A_{buck} (eV)	ρ_{buck} (Å)	C_{buck} (eVÅ^6)	A_{LJ} (eVÅ^{12})
O2-O8	8592.3854	0.255024	0.0	
O2-O9	12304.5870	0.242223	0.0	
O8-H8				63.291605
H8-O9				14.975024
Ca-P1	2132.9786	0.342800	0.0	

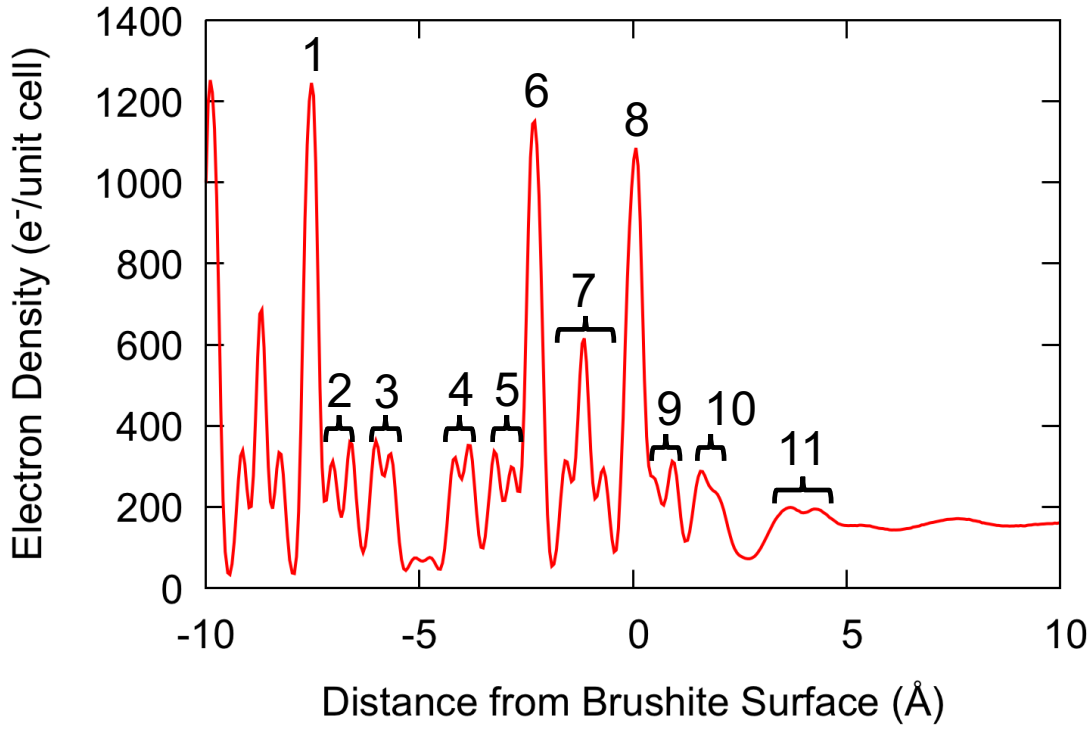

Figure S1: Electron density normal to the brushite-water interface calculated using MD-C2 with labelled peak positions corresponding to Table S2.

Table S2: Electron density peak positions and intensities. Peak positions are given as a function of height in Å above the brushite {010} surface top layer calcium ion, with peak intensity in electrons per unit cell (where one unit cell corresponds to lattice parameters a=5.812Å, b=15.18Å, c=6.239Å, and β=114.13°). See Figure S1 for the corresponding image in the case of MD-C2.

	SXRD-1		SXRD-2		MD-A		MD-C1		MD-C2	
Peak	Height (Å)	Density (e^-/UC)	Height (Å)	Density (e^-/UC)	Height (Å)	Density (e^-/UC)	Height (Å)	Density (e^-/UC)	Height (Å)	Density (e^-/UC)
1	-7.62	1413.22					-7.60	1245.39	-7.40	1209.56
2	-6.98	320.52					-7.10	312.26	-7.05	339.92
	-6.56	318.62					-6.70	359.93	-6.44	381.36
3	-6.05	354.73	-5.99	413.79			-6.09	362.36	-5.89	380.22
	-5.75	328.13					-5.74	330.73	-5.73	360.34
4	-4.16	328.13			-4.22	345.98	-4.23	321.38	-4.03	349.35
	-3.84	354.73	-3.90	413.49	-3.87	394.92	-3.93	351.58	-3.87	374.18
5	-3.32	316.72	-3.30	341.20	-3.47	307.60	-3.32	336.99	-3.27	346.92
	-2.93	320.52	-2.96	334.50	-2.98	312.85	-2.92	298.28	-2.71	330.46
6	-2.28	1392.31	-2.29	1402.50	-2.32	1493.80	-2.37	1150.58	-2.31	1122.36
7	-1.60	309.12	-1.64	324.45	-1.69	302.90	-1.66	313.47	-1.66	286.23
	-1.11	569.47	-1.16	608.69	-1.23	549.74	-1.21	615.50	-1.16	630.89
	-0.61	307.22	-0.67	324.24	-0.58	281.46	-0.76	294.05	-0.70	278.25
8	0.00	1396.11	0.00	1401.50	0.00	1457.19	0.00	1085.17	0.00	1101.40
9	0.64	318.62	0.67	343.76	0.90	342.96	0.44	312.37	0.41	291.21
	1.03	371.83	1.08	471.87	1.41	261.19	0.85	269.91	0.96	333.71
10	1.37	571.37	1.56	507.77	2.13	237.13	1.51	287.74	1.27	246.17
	1.69	550.47					1.89	235.33	2.07	231.84
11	3.79	590.37	4.02	520.38	3.41	335.98	3.62	198.65	3.31	267.01
	4.11	639.78					4.17	194.72		

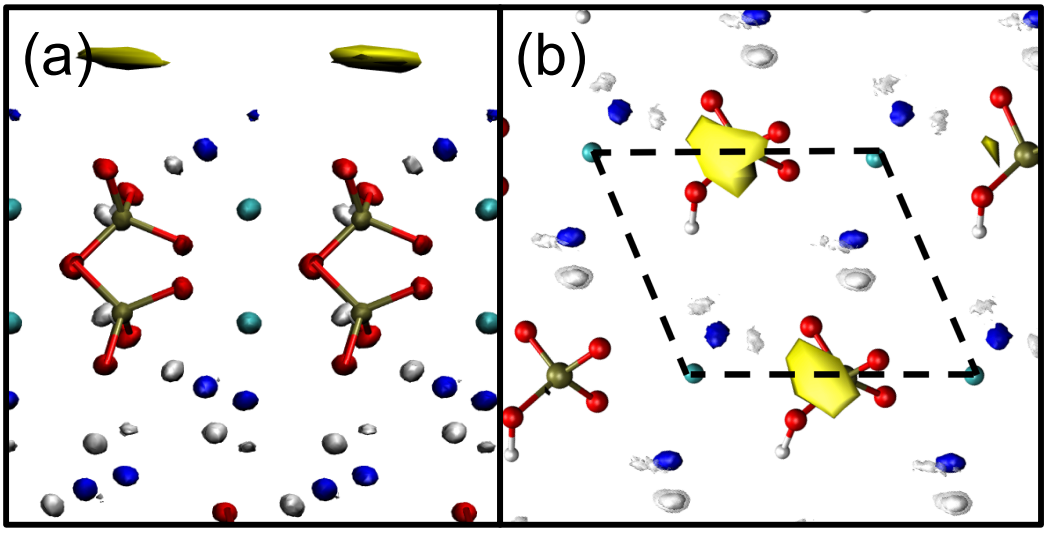

Figure S2: The atom density isosurfaces for brushite and water averaged over the molecular dynamics simulation (MD-C2). (a) The {010} surface of $CaHPO_4{\cdot}2H_2O$ is shown through the [201] plane. For the calcium and phosphate ions, H is white, O is red, P is tan, and Ca is cyan, while for the water density isosurfaces the bulk water is blue and H is white (all isosurfaces at 2 atoms/Å^3). Oxygens of water from beyond the first layer are shown with yellow isosurfaces (0.02 atoms/Å^3). (b) Top view of the 3D atomic structure of the flat brushite-water interface for the {010} plane. Average positions of the crystal are represented with a ball-and-stick model with only the top layer of the phosphate bilayer shown and calculated density isosurfaces for the first two water layers. For average positions, H is white, O is red, P is tan, and Ca is cyan. In the water density isosurfaces the first layer H is white and the first layer O is blue (both isosurfaces set to 2 atoms/Å^3), the second layer O is yellow (0.02 atoms/Å^3) The surface unit cell is indicated with a dashed black line.

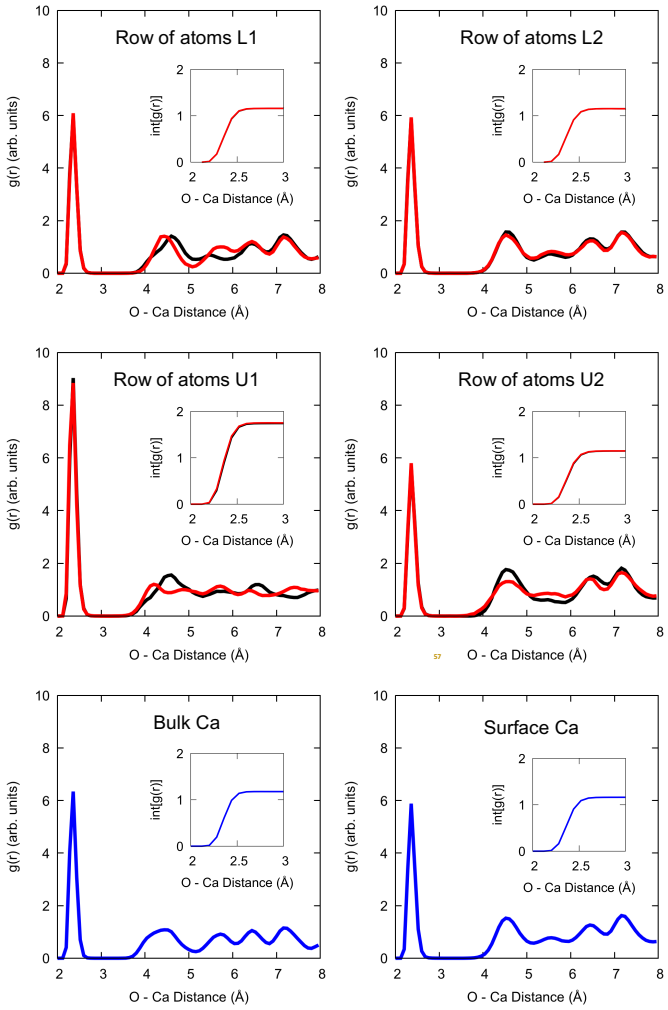

Figure S3: Radial distribution functions for the oxygen atoms of water around selected surface calcium sites near the step, where labels are indicated as per Figure 6 in the main manuscript. The integral of the radial distribution function at shorter distances is shown in the inset graphs. Black curves refer to a step with hydrogens pointing outward towards the bulk water and red curves indicate hydrogen pointing inward towards the bulk brushite. Blue indicates a flat surface where "surface" refers to a calcium at the {010} brushite-water interface and "bulk" refers to a calcium within the brushite solid.

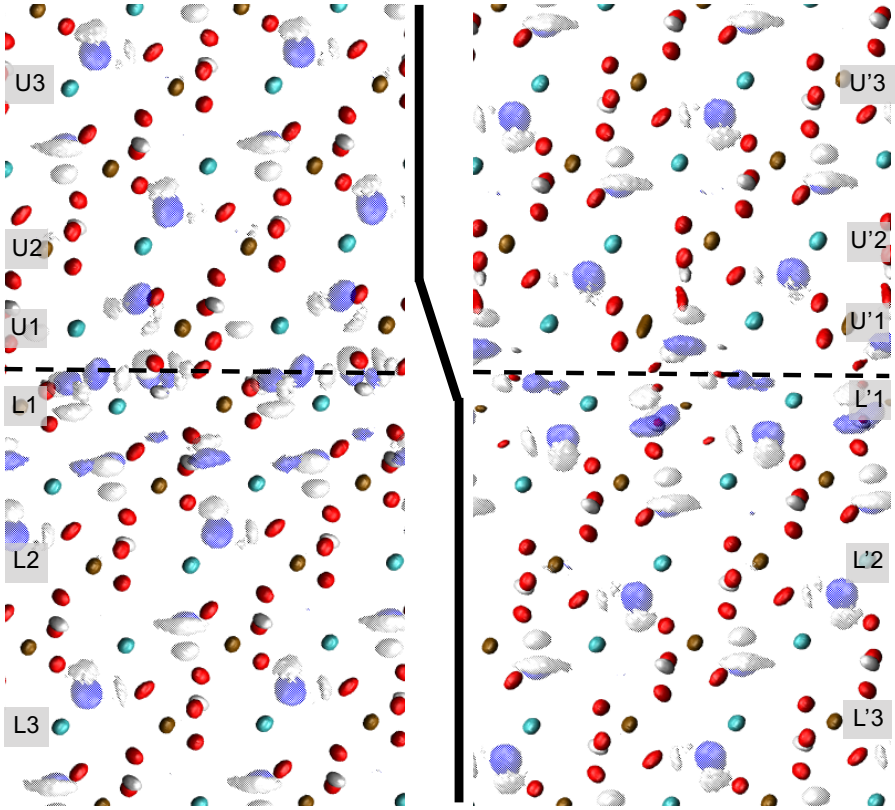

Figure S4: Top view of the density isosurfaces for the [101] steps with (left) hydrogens facing outward towards water and (right) hydrogens facing inward towards the bulk. Average positions of the crystal are represented with a ball-and-stick representation where H is white, O is red, P is tan, and Ca is cyan. The first water layer is shown via isosurfaces where O is blue and H is white. The step edge lies horizontally at the centre of the figure.

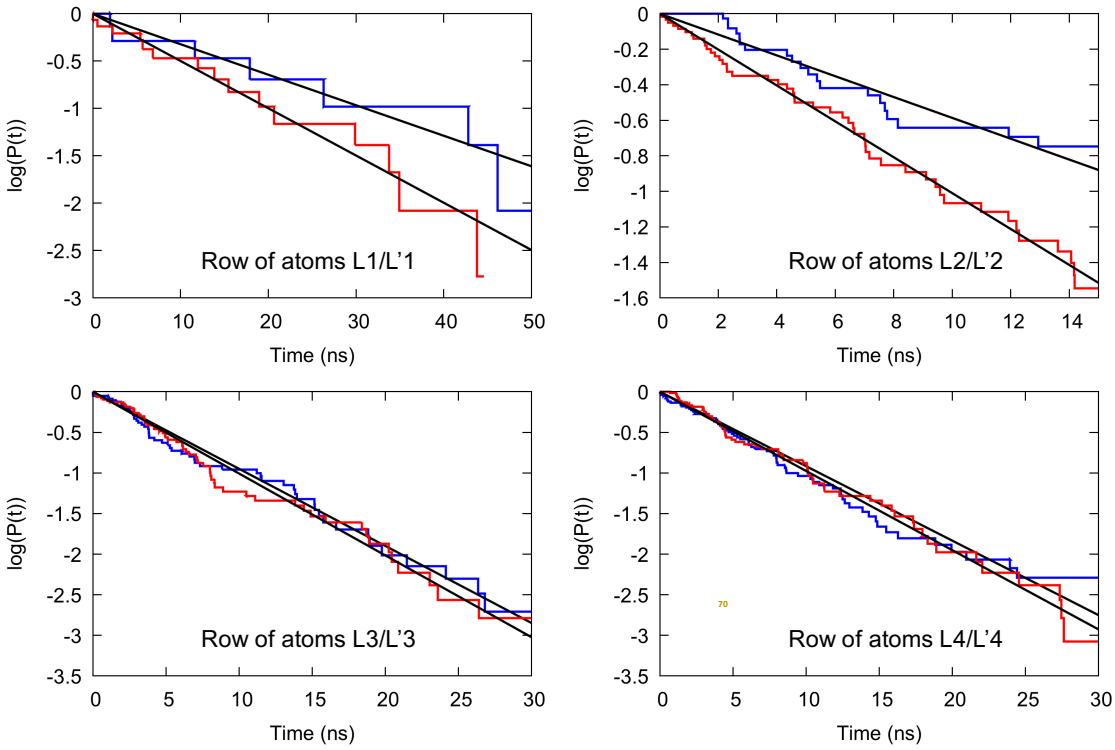

Figure S5: Survival functions (logarithmic scale) for water molecules around a set of calciums on the lower row of the step with hydrogen facing outward towards the bulk water (red) and hydrogen facing inward away from the bulk water (blue). Lines of best fit are shown in black.

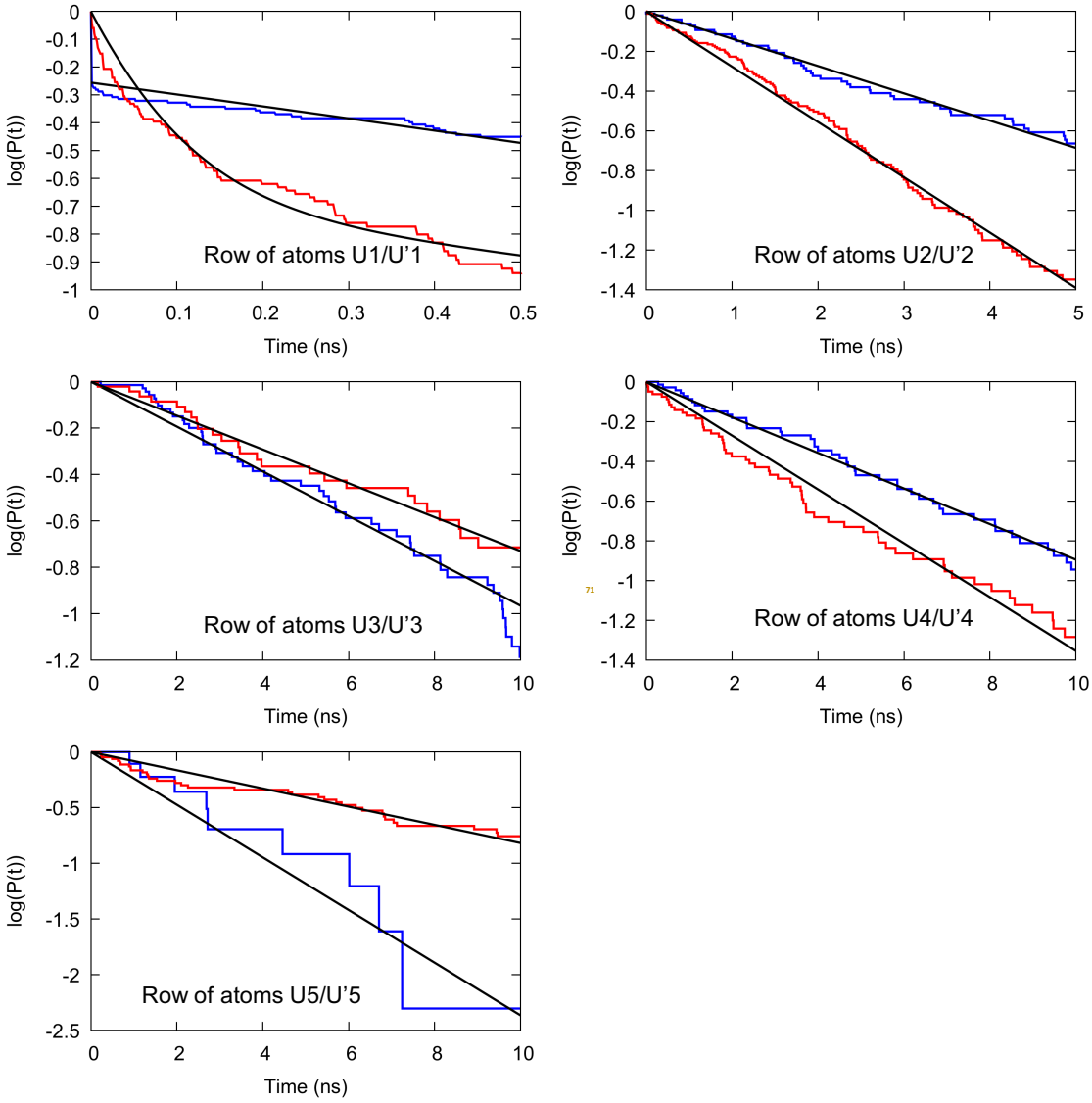

Figure S6: Survival functions (logarithmic scale) for water molecules around a set of calciums on the upper row of the step with hydrogen facing outward towards the bulk water (red) and hydrogen facing inward away from the bulk water (blue). Lines of best fit are shown in black.