Hydration of Na-saturated Synthetic Stevensite, a Peculiar Trioctahedral Smectite

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Running title: Hydration of Na-saturated Synthetic Stevensite

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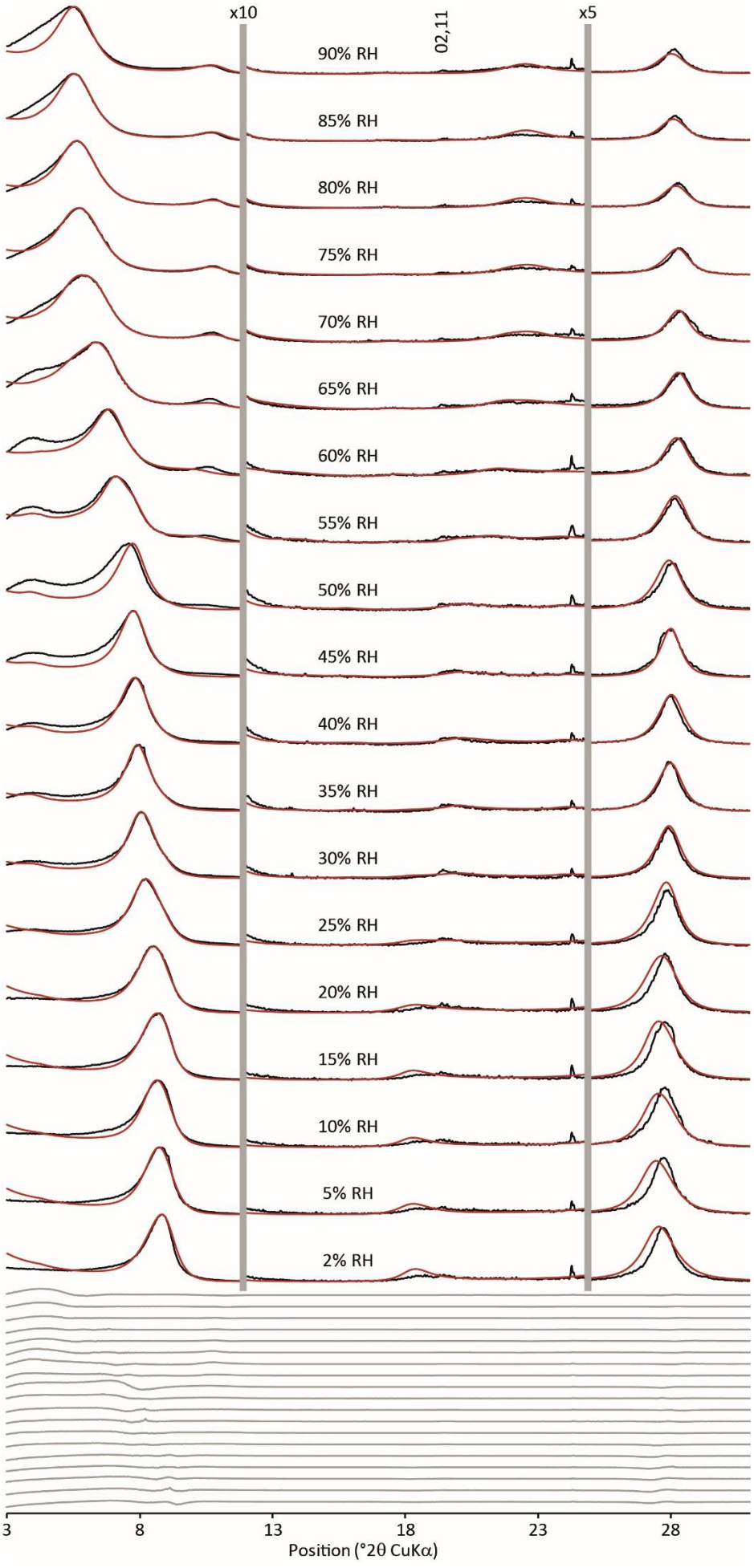
x10
02,11
x5
90% RH
85% RH
80% RH
75% RH
70% RH
65% RH
60% RH
55% RH
50% RH
45% RH
40% RH
35% RH
30% RH
25% RH
20% RH
15% RH
10% RH
5% RH
2% RH
3
8
13
18
23
28
Position (°2θ CuKα)

Fig. SI1. Comparison between experimental and calculated XRD patterns along the H_2O vapor desorption isotherm for Zn-stev. Experimental and calculated XRD patterns are shown as solid red and black lines, respectively. Difference plots are shown at the bottom of the figure as gray lines. The vertical gray bar indicates a modified scale factor for the angle region higher to 12° 2θ compared to the 3-12 °2θ angular range. Diffraction lines from halite (NaCl) impurity are indicated as Hal.

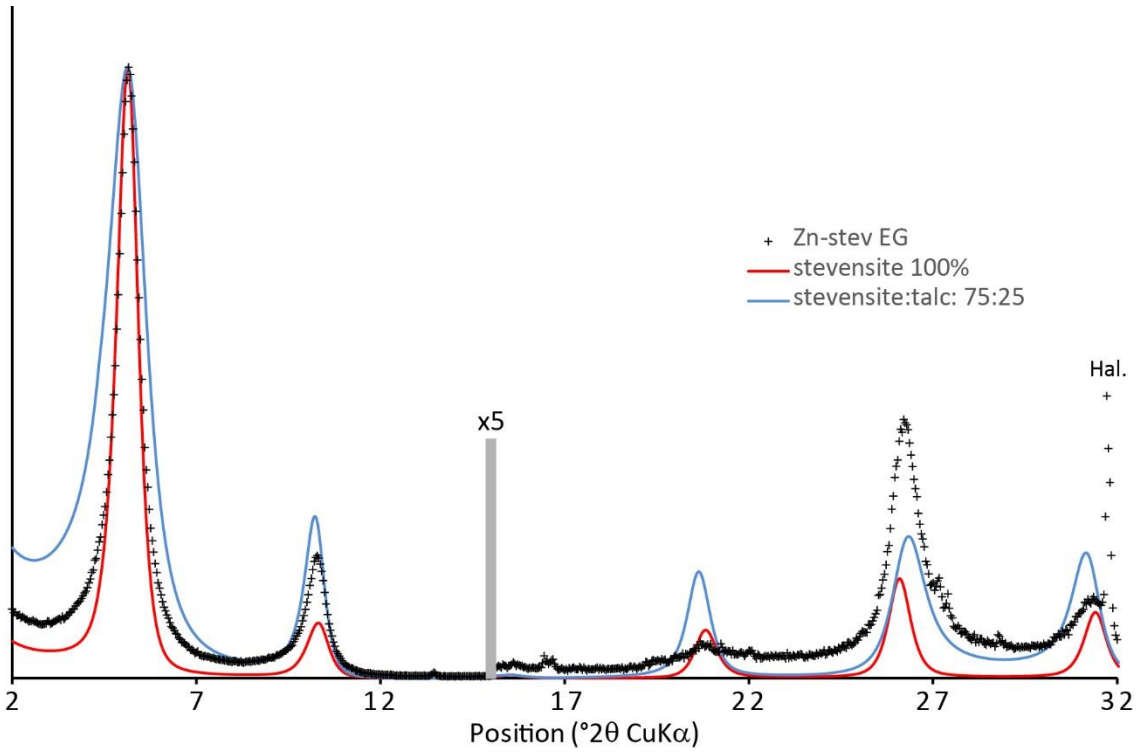

Fig. SI2. Comparison between experimental and calculated XRD patterns for Zn-stev after EG solvation. Experimental data are shown as crosses. Solid red line and blue dashed line correspond to Zn-stev models containing 0 and 25% talc-like layers randomly interstratified with swelling layers. The latter value corresponds to the content of dehydrated (0W) layers in Zn-stev equilibrated at 90% RH (Table SI1). Interlayer model for EG-solvated steventsite layers was not refined from that reported by Moore and Reynolds (1997). The vertical gray bar indicates a modified scale factor for the angle region higher to 15° 2θ compared to the 2-15 °2θ angular range. Diffraction line from halite (NaCl) impurity is indicated as Hal.

Reference cited

Moore D.M. & Reynolds R.C., Jr. (1997) *X-ray diffraction and the identification and analysis of clay minerals*. Pp. 378. Oxford University Press, Oxford.

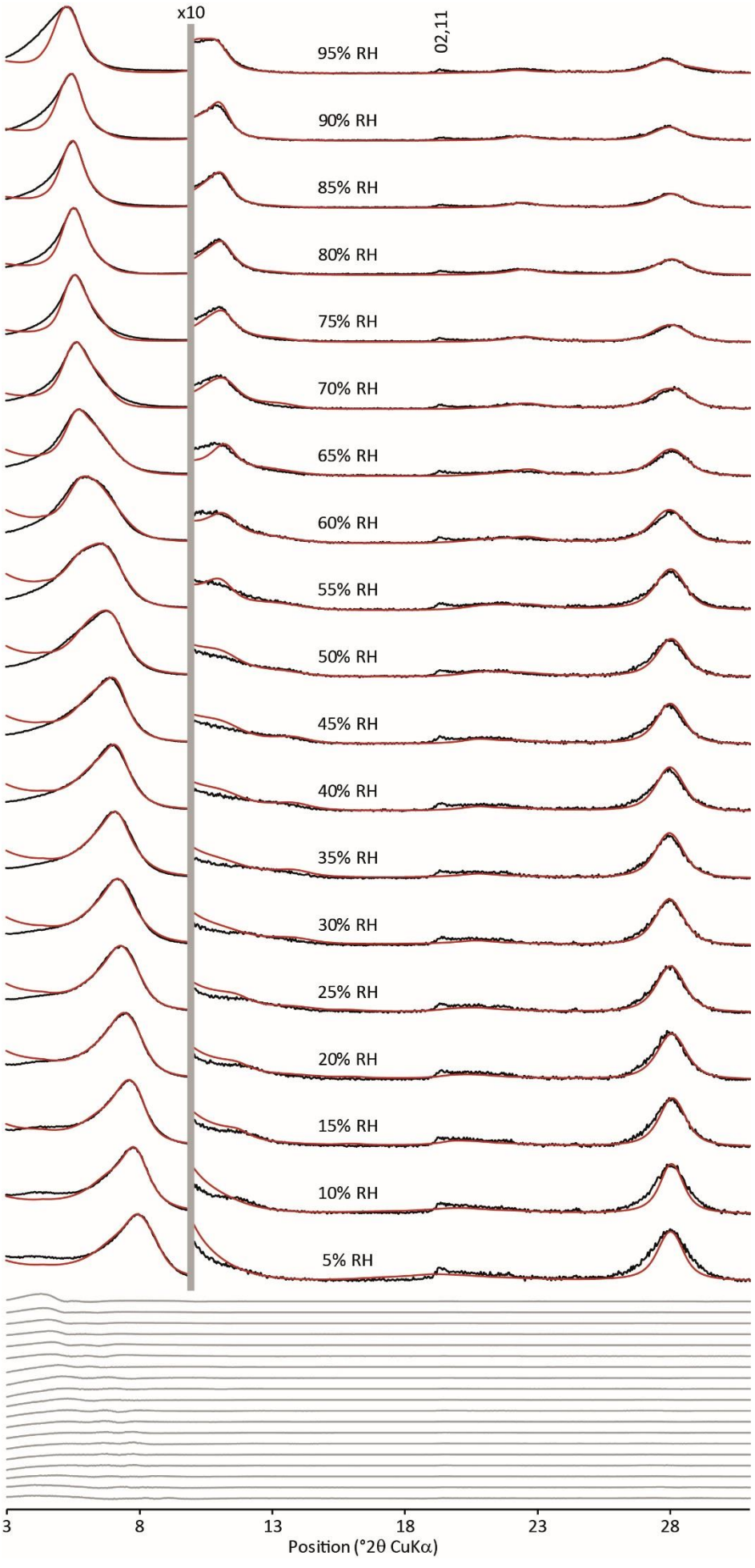
x10
02,11
95% RH
90% RH
85% RH
80% RH
75% RH
70% RH
65% RH
60% RH
55% RH
50% RH
45% RH
40% RH
35% RH
30% RH
25% RH
20% RH
15% RH
10% RH
5% RH
3
8
13
18
23
28
Position (°2θ CuKα)

Fig. SI3. Comparison between experimental and calculated XRD patterns along the H_2O vapor desorption isotherm for Zn-hect. Experimental and calculated XRD patterns are shown as solid red and black lines, respectively. Difference plots are shown at the bottom of the figure as gray lines. The vertical gray bar indicates a modified scale factor for the angle region higher to 10° 2θ compared to the 3-10 °2θ angular range.

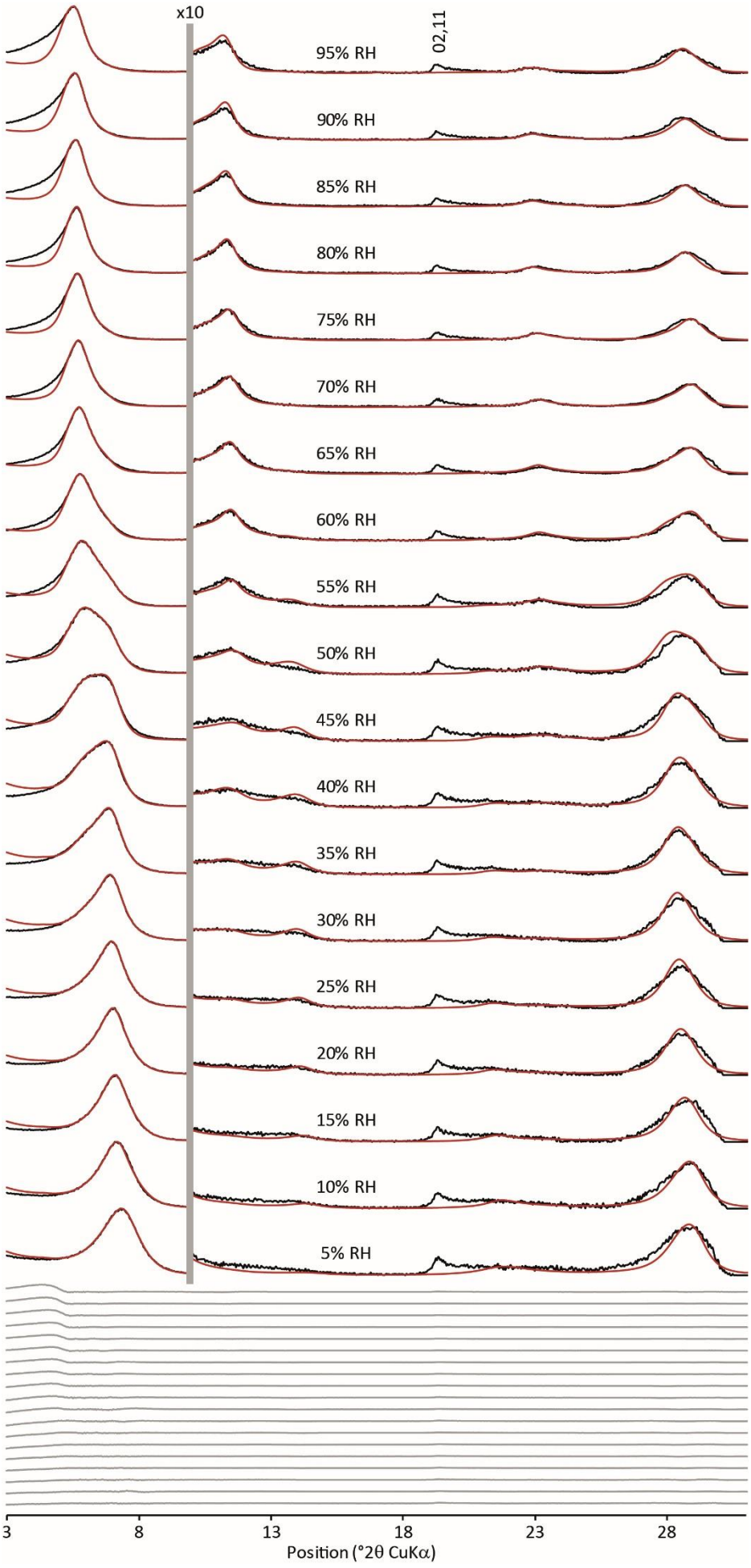
x10
02,11
95% RH
90% RH
85% RH
80% RH
75% RH
70% RH
65% RH
60% RH
55% RH
50% RH
45% RH
40% RH
35% RH
30% RH
25% RH
20% RH
15% RH
10% RH
5% RH
3
8
13
18
23
28
Position (°2θ CuKα)

Fig. SI4. Comparison between experimental and calculated XRD patterns along the H_2O vapor desorption isotherm for Zn-sap. Experimental and calculated XRD patterns are shown as solid red and black lines, respectively. Difference plots are shown at the bottom of the figure as gray lines. The vertical gray bar indicates a modified scale factor for the angle region higher to 10° 2θ compared to the 3-10 °2θ angular range.

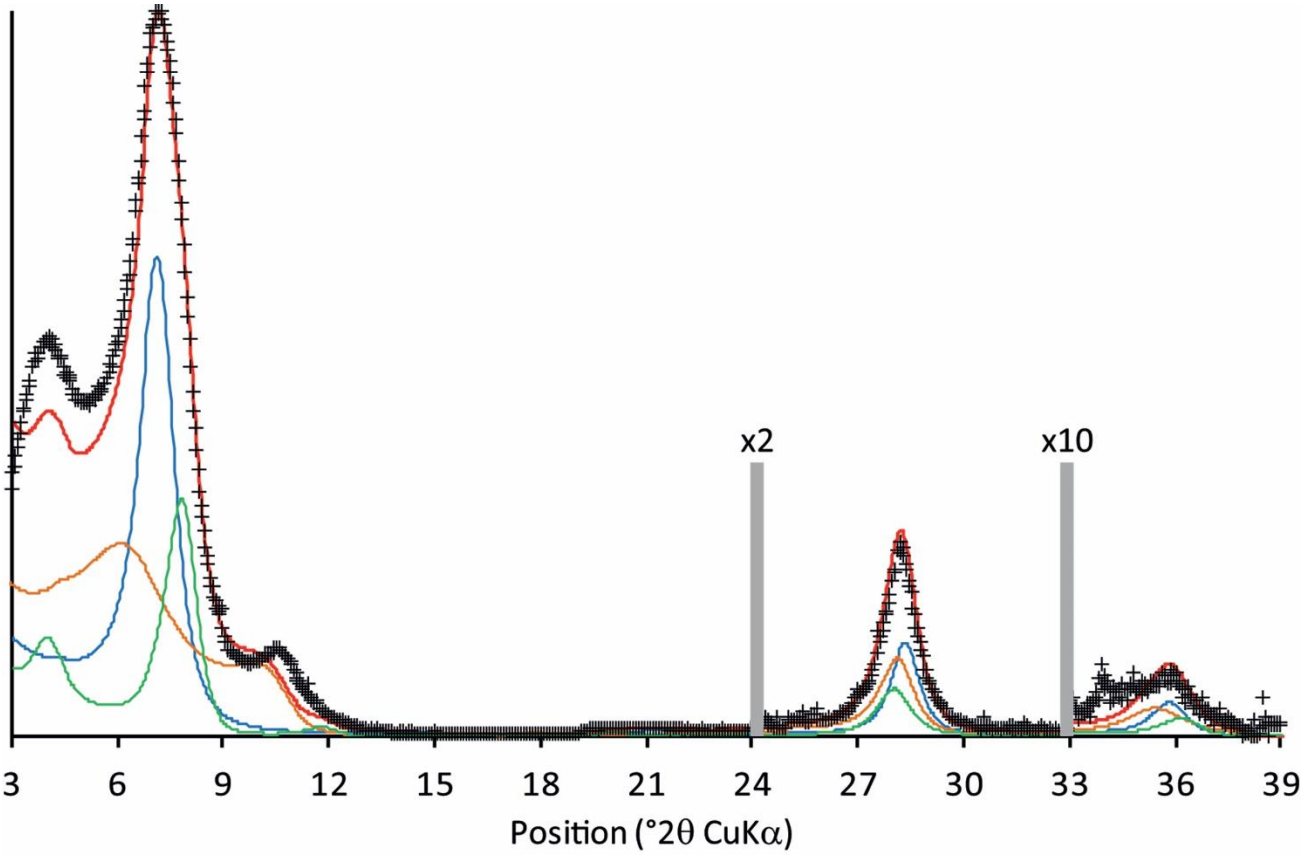

Fig. SI5. Respective contributions of the various mixed layers to the diffraction profile calculated for Zn-stev at 55% RH. Mixed layers #1, #2, and #4 (Table SI1) are shown as solid orange, blue, and green lines, respectively. Optimum fit and diffraction data are shown as solid red line and black crosses, respectively. The vertical gray bars indicate a modified scale factor for the high-angle regions compared to the 2-24 °2θ range.

Table SI1. Structural parameters used to fit experimental XRD patterns of Zn-stev as a function of relative humidity.

	%RH	90	85	80	75	70	65	60	55	50	45	40	35	30	25	20	15	10	5	2
Layer-to-layer distance (in Å)	2W	15.80	15.77	15.73	15.69	15.66	15.63	15.58	15.55											
	1W	12.80	12.70	12.60	12.58	12.57	12.57	12.53	12.53	12.50	12.50	12.45	12.43	12.40	12.40	12.25	12.20	12.10	11.90	11.80
	0W	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.70
Number of H_2O molecules [per $O_{20}(OH)_4$]	2W layers	10.6	10.4	10.0	10.0	9.8	9.6	9.4	9.0	8.8										
	1W layers	4.1	4.1	4.1	4.0	4.0	3.9	3.9	3.9	3.8	3.8	3.7	3.5	3.4	3.0	2.8	2.8	2.5	2.3	1.8
σ_z (in Å)		0.22	0.20	0.22	0.20	0.20	0.20	0.22	0.18	0.18	0.18	0.18	0.18	0.20	0.18	0.15	0.15	0.15	0.15	0.15
σ^* (in °)		4.0	3.8	4.0	3.8	3.5	3.6	3.6	3.0	2.0	3.0	2.4	2.5	2.5	2.0	2.0	2.0	2.0	2.0	2.0
Mixed layer 1	Ab (%)	93	92	79	77	64	48	41	38	3	3	2	2	5	14	20	39	41	53	58
	2W	75	75	75	72	72	65	40	40											
	1W									15	10	10	2	2	2	2	2			
	0W	25	25	25	28	28	35	60	60	85	90	90	98	98	98	98	98	100	100	100
	CSD size (in layers)	4.0	4.0	4.0	4.0	4.0	4.0	8.0	6.0	6.0	7.0	6.0	9.0	9.0	6.0	5.0	6.0	5.5	5.0	5.5
Mixed layer 2	Ab (%)	7	8	12	15	27	43	56	42	80	82	80	81	83	81	75	61	59	47	42
	2W	40	30	25	25	25	20	15	5											
	1W	50	60	60	60	60	60	65	75	48	48	44	38	34	30	20	20	20	15	15
	0W	10	10	15	15	15	20	20	20	52	52	56	62	66	70	80	80	80	85	85
	CSD size (in layers)	5.0	5.0	5.0	5.3	6.0	6.0	6.5	6.0	6.0	9.0	7.0	7.0	9.0	8.0	6.0	6.0	7.0	6.0	5.0
Mixed layer 3	Ab (%)	9	8	9	9	3														
	2W	50	45	40	35	15														
	1W	50	55	60	65	35														
	0W					50														
	CSD size (in layers)	4.2	6.0	7.0	7.0	4.0														
Mixed layer 4 R=1 with maximum possible degree of ordering (MPDO)	Ab (%)									21	16	15	18	17	13	5				
	2W																			
	1W									50	50	50	50	48	48	40				
	0W									50	50	50	50	52	52	60				
	CSD size (in layers)									5.0	5.0	5.0	5.0	7.0	9.0	6.0				

Note: Ab.: Relative abundance; CSD: coherent scattering domain; σ_z: fluctuation of the layer-to-layer distance (in Å); σ^*: orientation parameter(in °)

Table SI2. Structural parameters used to fit experimental XRD patterns of Zn-hect as a function of relative humidity.

	%RH	95	90	85	80	75	70	65	60	55	50	45	40	35	30	25	20	15	10	5
Layer-to-layer distance (in Å)	3W	18.0	18.0	18.0	18.0	18.0	18.0													
	2W	15.88	15.80	15.74	15.70	15.67	15.62	15.60	15.56	15.55	15.52	15.50	15.48	15.47	15.46	15.45	15.43	15.42	15.40	15.38
	1W	13.00	12.98	12.96	12.95	12.95	12.90	12.85	12.75	12.68	12.66	12.65	12.64	12.63	12.61	12.57	12.54	12.49	12.48	12.45
	0W												9.70	9.70	9.70	9.70	9.70	9.70	9.70	9.70
Number of H_2O molecules [per $O_{20}(OH)_4$]	2W layers	11.4	11.2	10.2	9.8	9.6	9.4	9.4	9.2	9.0	8.8	8.0	7.8	7.8	7.8	7.6	7.6	7.2	6.6	6.0
	1W layers	5.6	5.6	5.5	6.0	6.0	5.9	5.8	5.7	5.6	5.4	5.3	5.2	5.1	5.0	4.6	4.2	3.6	2.8	2.3
σ_z (in Å)		0.22	0.24	0.22	0.22	0.22	0.22	0.24	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.24	0.24
σ^* (in °)		7.0	9.0	9.0	8.0	9.0	7.0	9.0	9.0	9.0	9.0	9.0	8.0	8.0	7.8	7.8	7.5	6.5	7.5	8.0
CSD size (in layers		4.0	4.6	4.8	5.0	5.2	4.5	4.0	4.2	4.5	4.7	5.0	5.0	5.0	5.0	5.0	5.0	6.0	9.0	9.0
Mixed layer 1	Ab (%)	44	57	48	35	30	42	29	27	24	33	41	32	25	20	21	18	23	33	34
	3W	7	6	6	6	6	6													
	2W	90	90	90	90	88	80	95	80	75	55	48	48	45	45	42	40	38	30	25
	1W	3	4	4	4	6	14	5	10	5	23	28	28	31	31	31	33	34	35	35
	0W								10	20	22	24	24	24	24	27	27	28	35	40
Mixed layer 2	Ab (%)	38	24	23	21	20	13	20	36	32	12	3	8	19	20	14	14	15	3	14
	3W	60	60	45	40	37	35													
	2W	40	40	55	60	63	65	5	5	5	10									
	1W							65	65	65	70	75	50	53	45	45	45	45	30	20
	0W							30	30	30	20	25	50	47	55	55	55	55	70	80
Mixed layer 3	Ab (%)	18	16	14	15	21	27	51	37	44	54	56	60	55	60	66	68	62	64	52
	3W																			
	2W	40	30	25	20	20	15	30	30	20	10									
	1W	60	70	75	80	80	85	65	65	70	68	80	80	80	75	70	65	60	50	45
	0W							5	5	10	22	20	20	20	25	30	35	40	50	55
Mixed layer 4	Ab (%)		3	15	28	29	17													
	3W																			
	2W		68	65	65	60	45													
	1W		32	35	35	40	55													
	0W																			

Note: Ab.: Relative abundance; CSD: coherent scattering domain; σ_z: fluctuation of the layer-to-layer distance (in Å); σ^*: orientation parameter(in °)

Table SI3. Structural parameters used to fit experimental XRD patterns of Zn-sap as a function of relative humidity.

	%RH	95	90	85	80	75	70	65	60	55	50	45	40	35	30	25	20	15	10	5
Layer-to-layer distance (in Å)	3W	18.0	18.0	18.0	18.0	18.0	18.0	18.0												
	2W	15.58	15.53	15.52	15.50	15.40	15.38	15.37	15.34	15.32	15.27	15.24	15.23	15.22	15.21	15.16	15.16	15.15	15.15	15.15
	1W	12.82	12.81	12.80	12.80	12.80	12.80	12.79	12.78	12.74	12.70	12.60	12.55	12.55	12.55	12.50	12.46	12.38	12.29	12.24
	0W												9.70	9.70	9.70	9.70	9.70	9.70	9.70	9.70
Number of H_2O molecules [per $O_{20}(OH)_4$]	2W layers	11.0	10.4	10.0	9.4	8.8	8.6	8.4	8.2	8.0	8.0	7.8	7.6	7.4	7.0	6.8	6.6	6.0	4.4	4.0
	1W layers	5.7	5.6	5.5	5.5	5.3	5.7	5.7	5.7	5.6	5.5	5.4	5.3	5.2	5.0	4.5	4.1	3.5	3.1	2.5
σ_z (in Å)		0.22	0.22	0.22	0.22	0.22	0.21	0.18	0.18	0.17	0.17	0.19	0.21	0.24	0.22	0.22	0.22	0.22	0.22	0.20
σ^* (in °)		4.0	5.0	5.0	4.8	4.5	4.2	3.6	3.4	3.2	3.0	4.0	4.0	4.6	4.6	4.3	4.6	4.6	3.8	3.8
CSD size (in layers		4.5	4.8	5.2	5.5	5.5	5.5	5.5	5.0	5.0	4.5	4.5	4.2	4.7	4.7	5.0	5.1	5.0	5.0	5.0
Mixed layer 1	Ab (%)	48	49	38	39	34	33	28	28	19	21	14	28	21	17	14	10	9	7	5
	3W	3	2	2	2	2	2	2												
	2W	97	97	97	96	96	96	96	97	96	88	85	74	74	68	68	65	60	60	58
	1W		1	1	2	2	2	2	3	4	12	15	11	11	15	15	18	20	20	20
	0W												15	15	17	17	17	20	20	22
Mixed layer 2	Ab (%)	30	32	32	28	29	25	22	19	15	11	9	7	22	32	30	38	38	40	37
	3W	50	45	40	40	40	40	40	40	40	40	35								
	2W	50	55	60	60	60	60	60	60	60	60	65	10	10	8					
	1W												60	60	62	65	65	60	55	50
	0W												30	30	30	35	35	40	45	50
Mixed layer 3	Ab (%)	17	13	10	10	12	14	18	17	32	45	46	49	45	48	42	37	42	41	47
	3W	10																		
	2W	20	30	25	20	18	18	18	10	3	3	3	3	3	3	1				
	1W	70	70	75	80	82	82	82	90	97	97	97	97	97	97	98	99	96	94	80
	0W															1	1	4	6	20
Mixed layer 4	Ab (%)	5	7	20	23	25	28	32	36	35	23	30	16	12	3	15	15	12	12	11
	3W	5																		
	2W	70	72	72	70	70	65	65	55	55	45	42	25	25	25	25	25	25	25	25
	1W	25	28	28	30	30	35	35	45	45	55	58	73	73	73	73	73	73	73	73
	0W												2	2	2	2	2	2	2	2

Note: Ab.: Relative abundance; CSD: coherent scattering domain; σ_z: fluctuation of the layer-to-layer distance (in Å); σ^*: orientation parameter(in °)