

Table S1. Humidity buffers used in this study

RH buffer salt	Reported equilibrium RH (%) at different T					
	0 °C	5 °C	20 °C	25 °C	50 °C	55 °C
LiCl	11.23 ± 0.54	11.26 ± 0.47	11.31 ± 0.31	11.30 ± 0.27	11.10 ± 0.22	11.03 ± 0.23
MgCl <sub>2</sub>	33.66 ± 0.33	33.60 ± 0.28	33.07 ± 0.18	32.78 ± 0.16	30.54 ± 0.14	29.93 ± 0.16
K <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub>	43.13 ± 0.66	43.13 ± 0.50	43.16 ± 0.33	43.16 ± 0.39	n/a	n/a
Mg(NO <sub>3</sub> ) <sub>2</sub>	60.35 ± 0.55	58.86 ± 0.43	54.38 ± 0.28	52.89 ± 0.22	45.44 ± 0.60	n/a
NH <sub>4</sub> NO <sub>3</sub>	n/a	n/a	66.9*	62.7*	48.1*	n/a
NaNO <sub>3</sub>	n/a	78.57 ± 0.52	75.36 ± 0.35	74.25 ± 0.32	69.04 ± 0.42	68.15 ± 0.49
NaCl	75.51 ± 0.34	75.65 ± 0.27	75.47 ± 0.14	75.29 ± 0.12	74.43 ± 0.19	74.41 ± 0.24
KCl	88.61 ± 0.53	87.67 ± 0.45	85.11 ± 0.29	84.34 ± 0.26	81.20 ± 0.31	80.70 ± 0.35
RH measured in this study (±1.5% error)						
LiCl	11.4 at 1.5 °C		11.4 at 23.5 °C		11.3 at 51.0 °C	
MgCl <sub>2</sub>	34.0 at 1.7 °C		33.7 at 22.8 °C		31.1 at 51.5 °C	
K <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub>	43.3 at 1.6 °C		42.9 at 24.3 °C		42.4 at 52.1 °C	
Mg(NO <sub>3</sub> ) <sub>2</sub>	57.4 at 1.7 °C		53.0 at 22.4 °C		45.9 at 51.8 °C	
NH <sub>4</sub> NO <sub>3</sub>	73.0 at 1.9 °C		61.7 at 23.8 °C		46.8 at 51.4 °C	
NaNO <sub>3</sub>	n/a		n/a		69.0 at 51.0 °C	
NaCl	74.9 at 2.0 °C		74.3 at 22.8 °C		73.9 at 51.8 °C	
KCl	n/a		84.0 at 23.0 °C		n/a	
Drierite <sup>§</sup>	0.0 at 1.0 °C		0.0 at 22.1 °C		0.0 at 50.9 °C	

\* data were adapted from (Adams and Merz, 1929); others were from (Greenspan, 1977)

<sup>§</sup> drierite is essentially CaSO<sub>4</sub>, with CoCl<sub>2</sub> as a moisture indicator.

Adams, J.R., and Merz, A.R. (1929) Hygroscopicity of fertilizer materials and mixtures. Industrial and Engineering Chemistry, 21, 305-307.

Greenspan, L. (1977) Humidity Fixed-Points of Binary Saturated Aqueous-Solutions. Journal of Research of the National Bureau of Standards Section a-Physics and Chemistry, 81(1), 89-96.

Table S2. In situ RH-T experiment --- paracoquimbite -1

T(°C)	RH and time	Phase change
40	50%, 2 hrs; 40%, 2 hrs; 30%, 2 hrs; 20%, 2 hrs; 10%, 2 hrs; 4%, 7 hrs	Starting: Paracoquimbite No change
60	50%, 2 hrs; 40%, 2 hrs; 30%, 2 hrs; 20%, 2 hrs; 10%, 2 hrs; 4%, 2 hrs	No change
80	50%, 2 hrs; 40%, 2 hrs; 30%, 2 hrs; 20%, 2 hrs; 10%, 2 hrs; 3%, 2 hrs	Paracoquimbite decreased slightly $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ formed at 30% RH (Fig. 3.3)
80	3%, 2 hrs; 10%, 2 hrs;	Paracoquimbite decreased slightly $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ growth halted
80	20%, 2 hrs	$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ decreased slightly $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ continued to increase (Fig. 3.4)
80	30%, 2 hrs; 40%, 2 hrs; 50%, 2 hrs; 60%, 2 hrs	Paracoquimbite decreased $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ increased
80	70%, 2 hrs; 80%, 2 hrs; 70%, 3 hrs; 80%, 5 hrs	Paracoquimbite decreased slowly $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ increased slowly
80	70%, 6 hrs	Paracoquimbite diminished $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ remained (Fig. 3.4)
60	80% → 10%, 10% RH change per step, 3 hrs stay at each step	No change
60	4%, 3 hrs	No change
60	70%, 4 hrs; 75%, 7 hrs; 80%, 3 hrs	No change

Table S3. In situ RH-T experiment --- paracoquimbite -2

<b>T(°C)</b>	<b>RH and time</b>	<b>Phase transformation</b>
50	80% → 10%, 10% RH change per step, 2 hrs stay at each step	Starting: Paracoquimbite No change
50	5%, 2 hrs	No change
60	4%, 3 hrs	No change
70	3%, 3 hrs	No change
80	3%, 3 hrs	Paracoquimbite decreased (amorphization; Fig. 3.5)
80	10%, 3 hrs; 20%, 3 hrs	Paracoquimbite decreased
80	30%, 3 hrs; 40%, 3 hrs; 30%, 3 hrs	Paracoquimbite decreased $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ formed at 30% RH
80	20%, 3 hrs; 10%, 3 hrs; 1%, 3 hrs	Paracoquimbite decrease slightly $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ increase halted
60	10% → 80%, 10% RH change per step, 3 hrs stay at each step	No change
60	70%, 3 hrs; 60%, 3 hrs	No change
80	70%, 3 hrs; 80%, 3 hrs; 70%, 3 hrs	No change
80	60%, 3 hrs; 50%, 3 hrs; 40%, 7 hrs	Paracoquimbite decreased $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ increased

Table S4. In situ RH-T experiment --- paracoquimbite and rhomboclase

<b>T(°C)</b>	<b>RH and time</b>	<b>Phase change</b>
50	30%, 2 hrs; 20%, 2 hrs; 10%, 2 hrs; 1%, 4 hrs; 20%, 2 hrs; 30%, 2 hrs	Paracoquimbite and rhomboclase No change
50	40%, 2 hrs; 50%, 2 hrs; 60%, 2 hrs; 70%, 3 hrs	Paracoquimbite remained no change Rhomboclase diminished at 60% (deliquescence)

Table S5. In situ RH-T experiment --- paracoquimbite and kornelite

<b>T(°C)</b>	<b>RH and time</b>	<b>Phase change</b>
30	10%, 2 hrs; 20%, 2 hrs; 30%, 2 hrs; 40%, 2 hrs; 50%, 2 hrs; 60%, 2 hrs	Paracoquimbite and kornelite No change
29	68%, 2 hrs; 70%, 4 hrs	Paracoquimbite remained no change Kornelite diminished at 70% (deliquescence)

Table S6. In situ RH-T experiment --- Ferricopiapite and rhomboclase -1

<b>T(°C)</b>	<b>RH and time</b>	<b>Phase change</b>
26	60%, 2 hrs	Ferricopiapite and rhomboclase No change
26	65%, 2 hrs	Ferricopiapite remained no change Rhomboclase diminished (deliquescence) (Fig. 3.6)
26	70%, 2 hrs; 65%, 3 hrs; 60%, 3 hrs	Ferricopiapite remained no change
26	55%, 3 hrs	Ferricopiapite diminished Paracoquimbite formed (Fig. 3.7)
26	50%, 3 hrs; 45%, 3 hrs; 40%, 2 hrs; 30%, 3 hrs	No change, only paracoquimbite
26	60%, 1 hrs; 65%, 3 hrs; 70%, 3 hrs	No change
26	75%, 4 hrs; 80%, 3 hrs; 75%, 2 hrs; 70%, 2 hrs; 65%, 2 hrs	No change
28	80%, 2 hrs; 81%, 2 hrs	Paracoquimbite decreased slowly (deliquescence)
28	81%, 3 hrs; 84%, 2 hrs	Paracoquimbite decreased
26	75%, 3 hrs; 70%, 3 hrs	No change
26	65%, 3 hrs	Paracoquimbite increased
26	60%, 3 hrs; 55%, 3 hrs; 50%, 3 hrs	Paracoquimbite increased
50	30%, 2 hrs; 40%, 2 hrs; 50%, 2 hrs; 60%, 2 hrs, 63%, 2 hrs	No change, still paracoquimbite
50	70%, 6 hrs	Paracoquimbite decreased slowly (deliquescence)
50	75%, 6 hrs	Paracoquimbite diminished
50	70%, 2 hrs; 65%, 3 hrs	No change
50	60%, 4 hrs; 55%, 4 hrs; 50%, 4 hrs; 45%, 4 hrs; 40%, 20 hrs	Ferricopiapite formed at 60% RH Rhomboclase formed at 45% RH

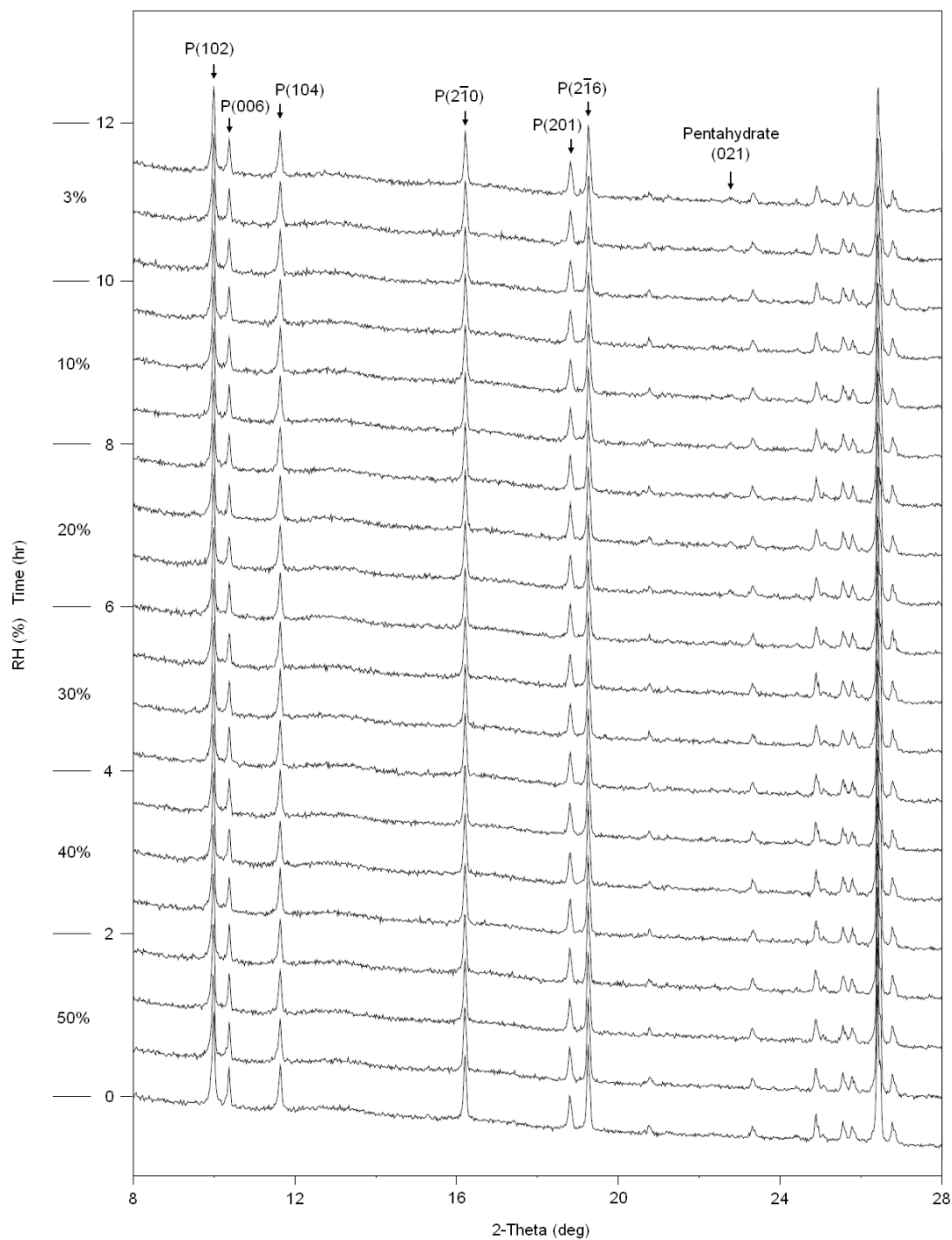


Figure S1. XRD patterns showing transformation of paracoquimbite-1 to  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  at 80 °C and RH 50% down to 3%.  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  (021) peak is observed at 30% RH (not easy to see here due to the plot scale). Several paracoquimbite peaks are marked with letter P and their Miller indices.

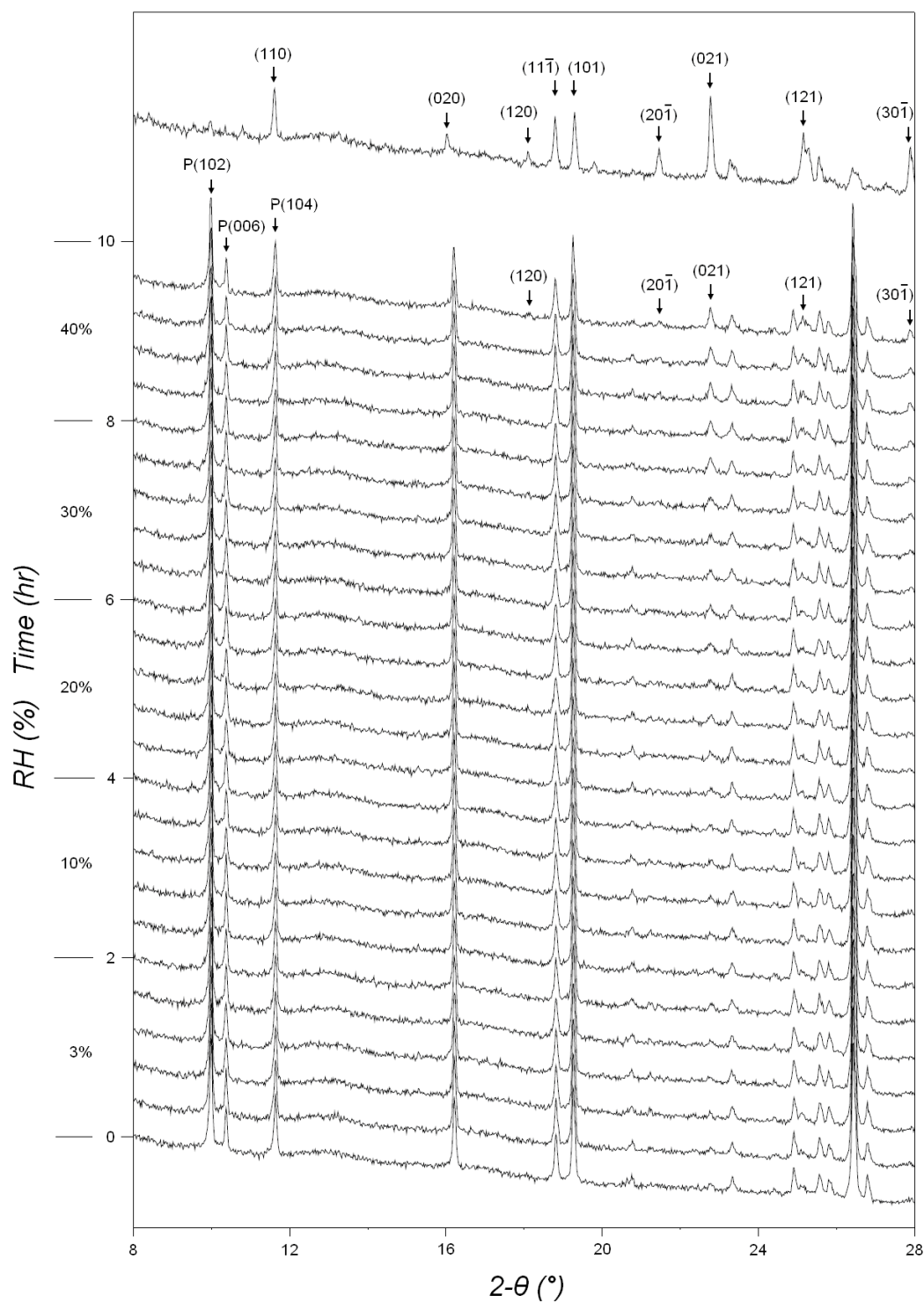


Figure S2. XRD patterns showing paracoquimbite transforming to  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  at 80 °C with increasing RH.  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  peaks are marked with their Miller indices. Paracoquimbite peaks are marked with letter P and the Miller indices. The pattern at the top was collected at 70% RH showing a complete transformation to  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ .



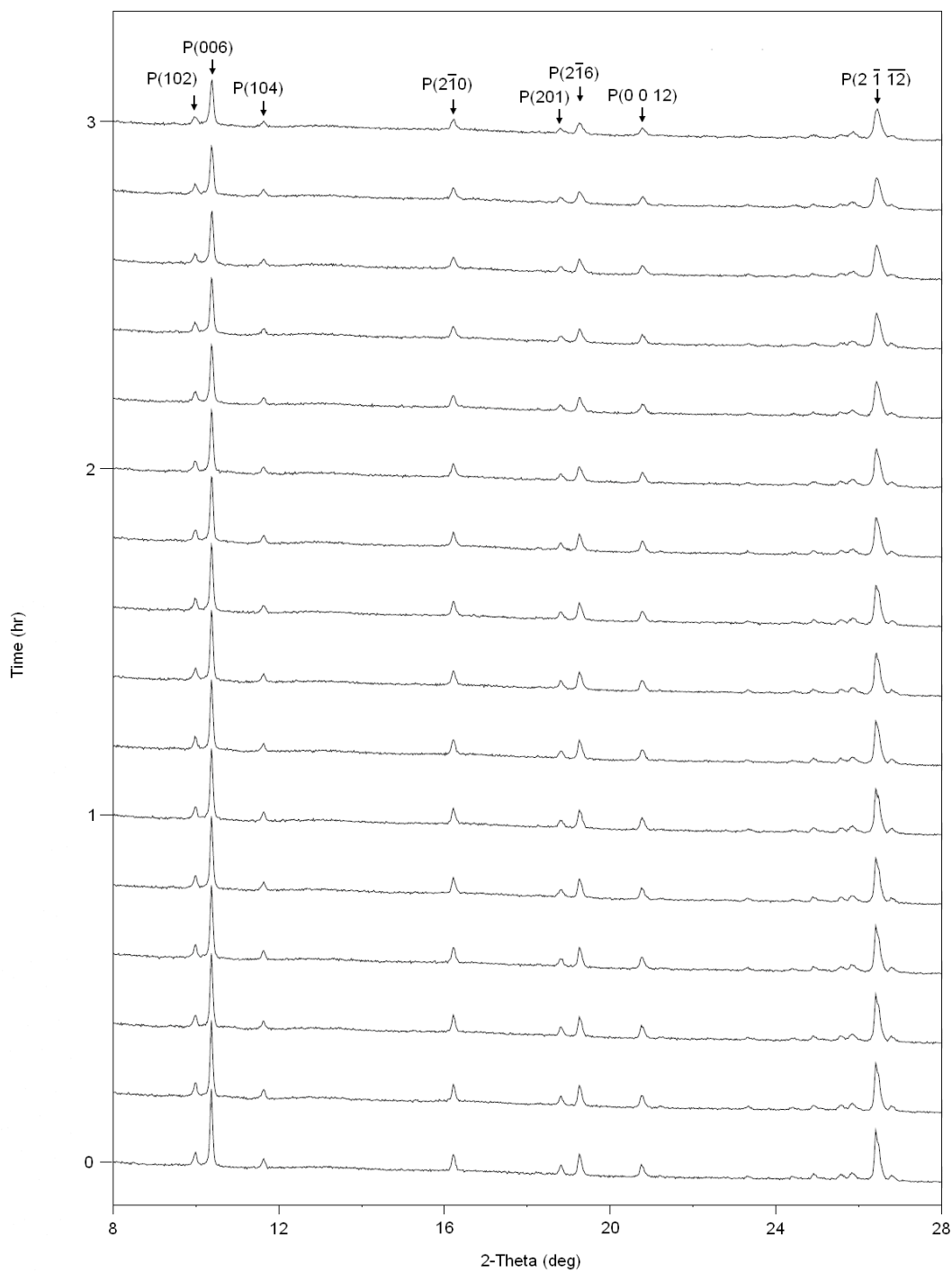


Figure S3. XRD patterns showing the paracoquimbite-2 destabilized at 80 °C and 3% RH over 3 hours. Paracoquimbite peaks, marked with letter P and the indices, decrease in intensity from bottom to top. Due to preferred orientation effect induced by the sample preparation, reflections perpendicular to *c* axis is stronger than normal, e.g. P(006).

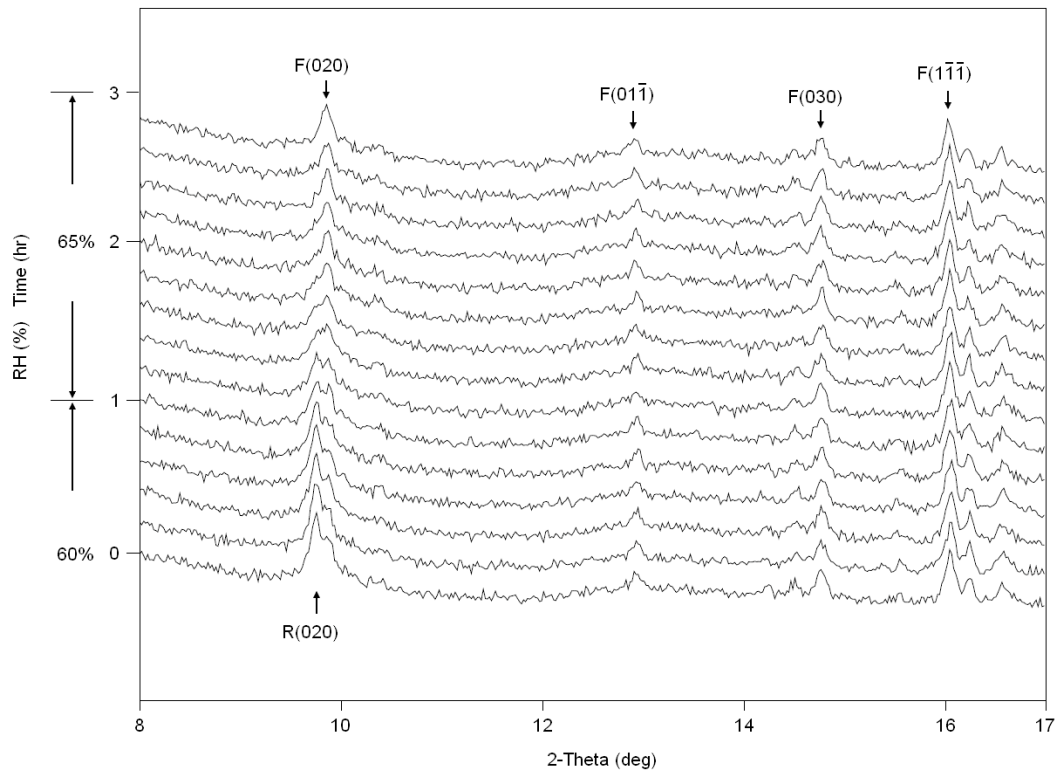


Figure S4. XRD patterns showing the deliquescence of rhomboclase and the retaining of ferricopiapite at 26 °C and 65% RH. Several peaks are marked with their Miller indices and the mineral name initial: R for rhomboclase; F for ferricopiapite.

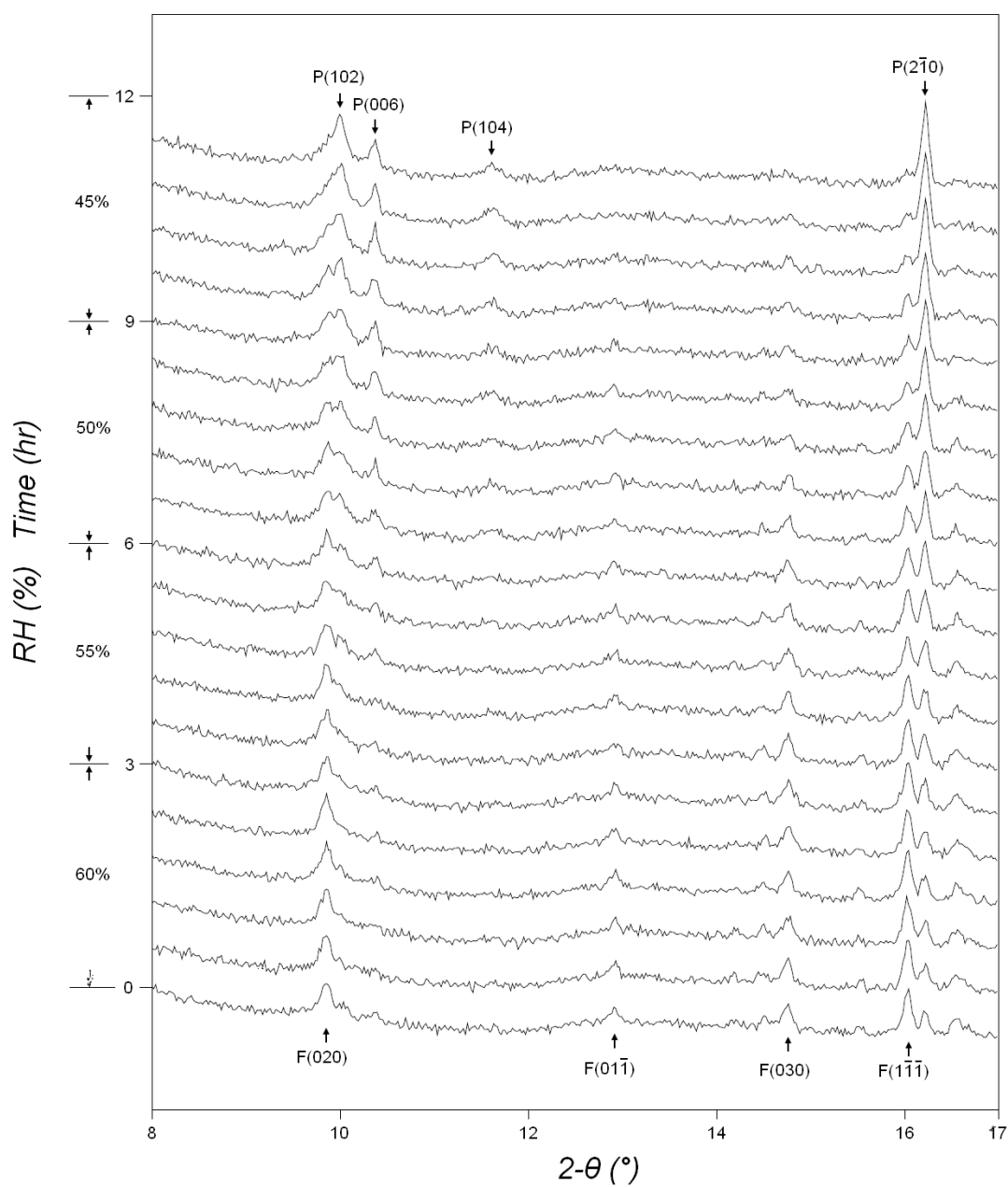


Figure S5. XRD patterns showing the formation of paracoquimbite out of the wet ferricopiapite at 26 °C with decreasing RH. Some peaks are marked with their Miller indices and the mineral name initial: P for paracoquimbite; F for ferricopiapite.