

**Appendix 2. Percent of initial band area (2700-3600 cm<sup>-1</sup>) as a function of temperature for *in situ* heating experiments.**

H-birnessite pH=2		Li-birnessite		Na-birnessite starting material		K-birnessite		Cs-birnessite	
T (°C)	% initial IR area	T (°C)	% initial IR area	T (°C)	% initial IR area	T (°C)	% initial IR area	T (°C)	% initial IR area
22.2	nd†	22.6	100.0	22.1	100.0	21.9	100.0	22.6	100.0
30	100.0	30	98.9	32.1	97.3	30.5	94.8	30	90.9
40	96.3	40	96.7	40	95.2	40	90.7	40	82.9
50	90.8	50	94.2	50	89.1	50.8	86.4	50	74.7
60	83.9	60	92.9	60	64.0	60.3	81.4	60	67.0
70	76.4	70	91.7	70	45.1	70	74.0	70	59.5
80	66.5	80	89.6	80	33.2	80	55.2	80	51.1
90	57.9	90	38.4	92.4	24.6	90	43.7	90	40.7
100	50.1	100	27.1	100	22.1	100	27.2	100	28.6
110	43.8	110	22.9	110	19.5	110	20.6	110	13.8
120	37.8	120	18.3	120	16.5	120	17.7	120	0.2
130	32.9	130	15.0	130	13.8	130	14.6	130	0.0
140	28.7	140	12.1	140	10.5	140	12.1	140	0.0
150	24.3	150	9.0	150	8.2	150	9.8	150	0.0
160	21.2	160	5.9	160	6.4	160	7.2		
170	18.9	170	2.8	170	3.8	170	6.2		
180	16.0	180	0.0	180	2.7	180	4.0		
190	11.3	22.9*	1.3	190	1.0	190	3.7		
200	10.4			200	0.0	200	2.2		
210	9.2			210	0.0	22.5*	50.0		
220	8.7			220.1	0.0				
230	7.9								
240	7.6								
250	7.9								

\*Spectrum obtained *in situ* 30 minutes to 2 hours after heating run.

†Not determined at this temperature.

<b>Mg-birnessite</b>		<b>Mg-buserite</b>		<b>Ca-birnessite</b>		<b>Ni-birnessite</b>	
<b>T (°C)</b>	<b>% initial IR area</b>	<b>T (°C)</b>	<b>% initial IR area</b>	<b>T (°C)</b>	<b>% initial IR area</b>	<b>T (°C)</b>	<b>% initial IR area</b>
21.9	100.0	22.1	100.0	21.7	100.0	22.8	100.0
30	99.2	30	99.0	30	98.2	30	97.8
40	96.9	40	99.7	40	93.5	40	93.4
50	94.6	50	100.6	50	90.4	50	87.2
60	92.3	60	100.9	60	88.0	60	79.4
70.1	89.2	70	99.6	70	84.2	70	71.1
80	85.7	80	96.3	80	82.1	80	62.5
90	81.8	90	91.3	90	79.4	90	55.5
100	77.5	102.4	81.0	100	75.7	100	50.5
110	70.7	110	51.3	110	72.7	110	45.7
120	63.5	120	72.5	120	65.3	120	41.8
130	58.0	130	67.6	123	59.1	130	38.1
141.2	51.8	141	62.1	130	53.4	140	34.5
150	46.2	150	57.9	140	45.4	150	30.8
160	40.9	160	52.5	150	40.3	160	28.0
170	36.6	170	48.1	160	34.6	170	23.9
180	33.0	180	44.7	170	28.9	180	20.9
190	29.7	190.2	38.4	180	22.7	190	18.1
200	26.6	200	35.0	190	18.1	200	15.8
210	22.8	210	31.0	200	16.0	210	14.0
220	20.2	220.5	26.7	210	11.4	220	12.3
230	18.3	230	23.9	30*	28.3	230	10.4
240	15.9	240	20.9			240	9.3
250	14.4	250	19.1			250	7.8
260	12.6	260	17.5			24.1*	12.9
270	11.9	270	14.2				
280	11.1	280	11.6				
290	8.7	290	10.5				
300	7.6	300	8.8				
23.2*	17.0	310	7.4				
		320	5.6				
		330	5.7				
		340	3.9				
		350	3.5				
		22.4*	7.5				

**Chalcophanite**

T (°C)	% initial IR area
22.3	100.0
30	99.5
40	99.3
50	97.7
60	90.0
70	51.5
80	40.5
90	35.8
100	33.1
110	31.1
120	29.0
130	28.2
140	26.5
150	25.4
160	24.1
170	23.0
180	21.7
190.1	20.4
200	19.0
210	18.5
220	17.4
232.8	17.3
261	16.6
270	15.6
280	14.8
290	14.1
300	14.0
310	14.0
320	12.2
330	9.0
341.4	8.1
350.1	6.3
360	4.5
370	4.3
380.1	3.4
28*	8.4

**Pb-birnessite**

T (°C)	% initial IR area
22.5	100.0
30	93.5
40	85.0
50	76.7
60	66.5
70	51.5
80	43.0
90	36.8
100	25.0
110	26.2
120	23.4
130	20.2
140	18.1
150	15.9
160	13.1
170	11.5
180.7	9.7
190	8.3
200	6.8