Supplementary Materials: Crystallization of Jarosite with Variable Al^{3+} Content: The Transition to Alunite

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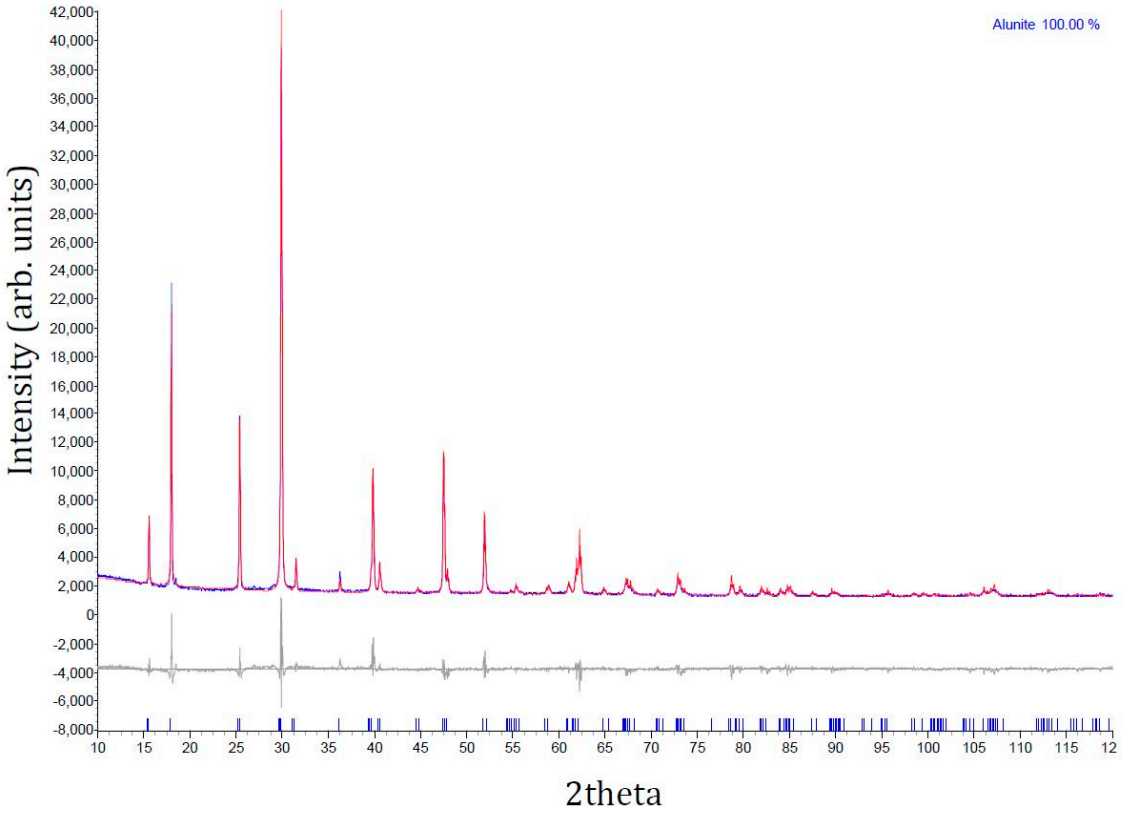


Figure S1. XRD pattern (blue) and Rietveld fit (red) for Jarosite K, showing the residual in grey. GOF was found to be 2.80 for this sample.

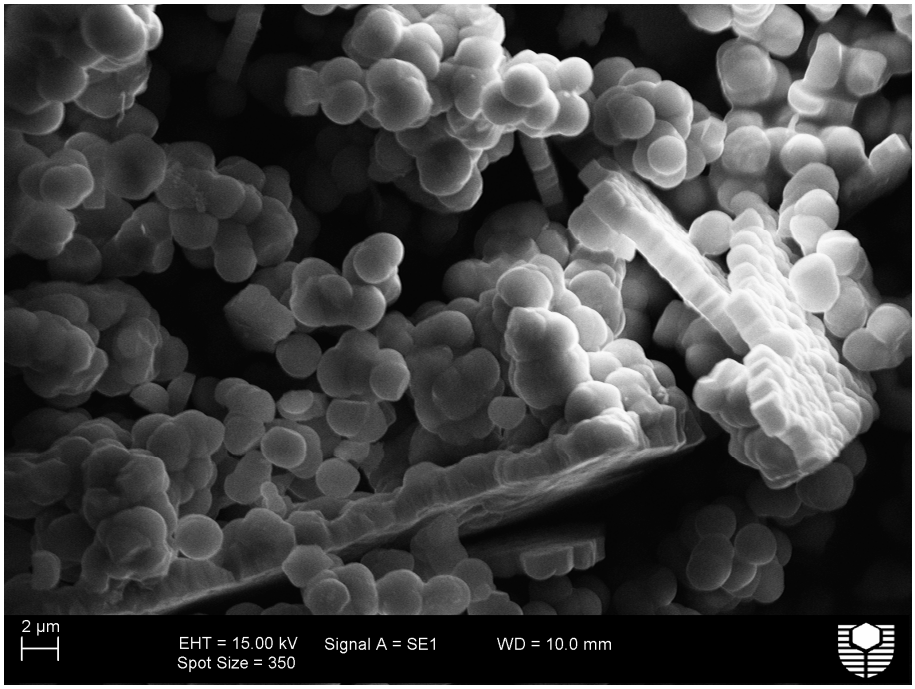


Figure S2. SEM image of particles formed in the synthesis of the Jarosite J sample

Table S1. Fitting statistics for Rietveld refinement of samples.

Sample name	A	B	C	D	F (as Jar)
GOF	2.07	1.87	1.90	1.81	2.20
Rexp	1.55	1.40	1.37	1.46	1.49
Rwp	3.21	2.62	2.60	2.64	3.27
Rp	2.03	1.66	1.67	1.74	2.02
Weighted Durbin Watson	0.53	0.74	0.76	0.81	0.48
Sample name	H (as Alu)*	I	J	K	Alunite
GOF	1.85	2.26	2.96	2.80	1.64
Rexp	1.89	2.52	2.52	2.36	5.22
Rwp	3.50	7.09	7.44	6.60	8.53
Rp	2.46	4.69	5.33	4.72	6.86
Weighted Durbin Watson	0.63	0.40	0.37	0.45	0.80

* fitted either as an Al-containing jarosite or an Fe-containing alunite and structure with lowest GOF chosen.

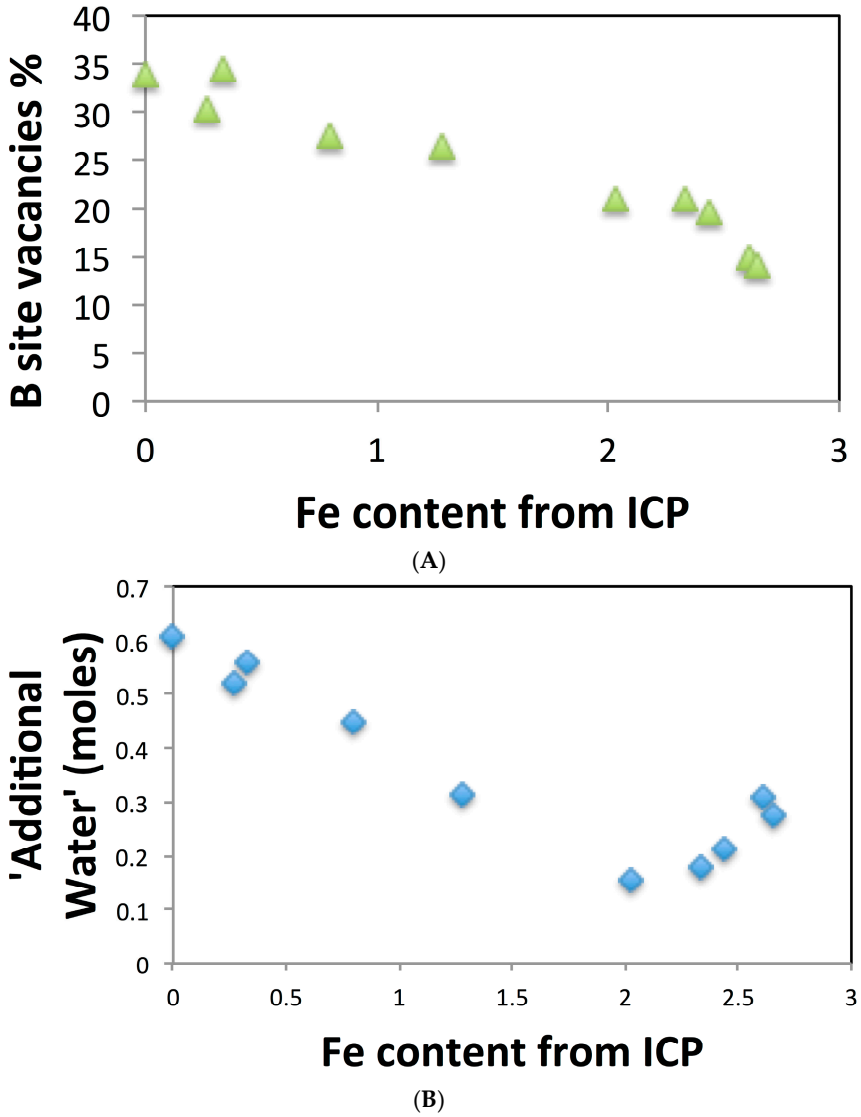
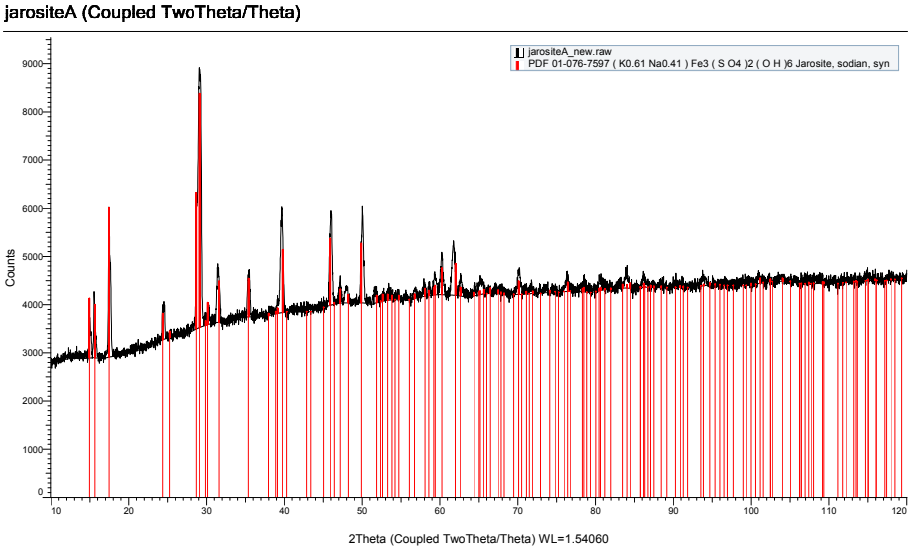
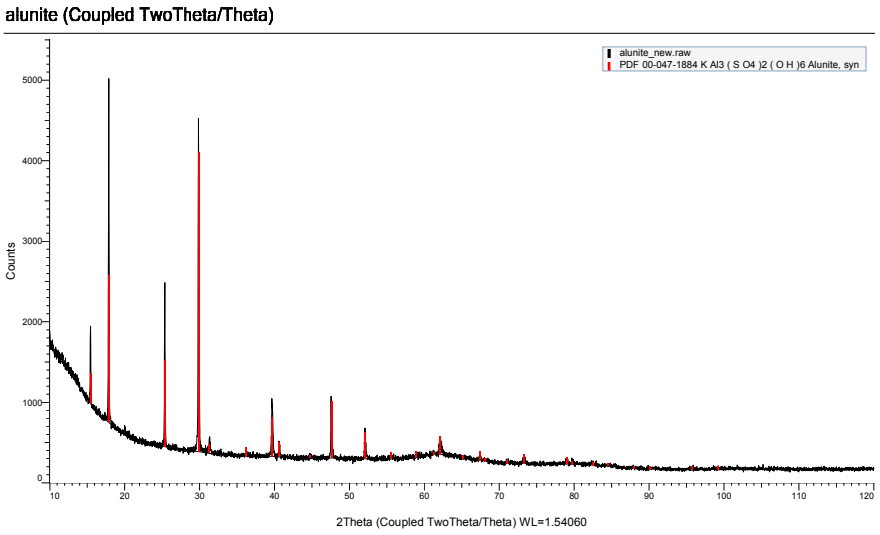


Figure S3. Fe content (in moles) as calculated from the ICP data versus (A) % vacancies in the B site and (B) the 'Additional water' content as measured from the TGA mass loss up to 285°C.



(**A**)



(**B**)

Figure S4.XRD plots of pure (A) alunite and (B) jarosite and the powder diffraction pattern it matched to.

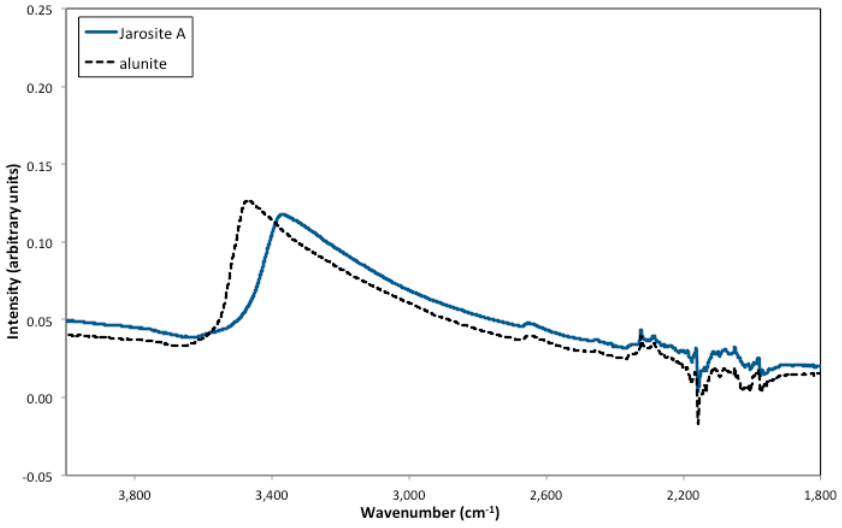


Figure S5. Infrared spectra of pure jarosite (jarosite A) and pure alunite for wavenumbers 4000–1800 cm^{-1}. The bands at 1900–2400 cm^{-1} are due to the diamond ATR.

Table S2. Empirical Potentials used in the modeling.

Buckingham Potentials			
Interaction	A (eV)	ϱ (Å)	C(eVÅ^6)
K – O1	1080.992	0.30	0.0
K – O2	1250.666	0.30	0.0
Fe – O1	1008.478	0.29912	0.0
Fe – O2	1652.266	0.29912	0.0
Al – O1	429.74758	0.29912	0.0
Al – O2	1070.52479	0.29912	0.0
H – O1	102.2763	0.25	0.0
H – O2	161.8440	0.25	0.0
O1 – O1	103585.02	0.2	25.98
O1 – O2	103585.02	0.2	25.98
O2 – O2	103585.02	0.2	25.98
Morse			
Interaction	D (eV)	a (Å^{-1})	r_0 (Å)
S – O1	5.0	1.2	1.515
H – O2	7.0525	2.1986	0.9685
Three-body			
Interaction	k (eV.rad^{-2})	θ_0 (^{o})	
O1 – S – O1	7.1524	109.47	

Table S3. Comparison between simulated (from supercell simulations) and experimental values (from references given).

	Simulated		**Experimental**		**Ref**
	Jarosite (%difference)	Alunite (%difference)	Jarosite	Alunite	
a	7.58 (3.7%)	7.26 (0.68%)	7.311	6.974	Becker & Gasharova [19] and Majzlan et al. [41]
b	7.58 (3.7%)	7.26 (0.68%)	7.311	6.974	
c	17.35 (1.0%)	16.90 (1.7%)	17.175	17.19	
Vol	863.0	771.8	795.0	715.4	
C11	186.3	207.9	189.0	181.9	Majzlan et al. [41]
C33	64.1	71.0	50.8	66.8	
C44	33.1	42.3	36.0	42.8	
C12	55.5	42.9	55.5	48.2	
C13	27.5	35.1	27.2	27.1	
C14	1.11	7.0	6.8	5.4	

References

1. Becker, U;, Gasharova, B. AFM observations and simulations of jarosite growth at the molecular scale: probing the basis for the incorporation of foreign ions into jarosite as a storage material. *Phys. Chem. Minerals* **2001**, *28*, 545–556.
2. Majzlan, J.; Speziale, S.; Duffy, T.S.; Burns, P.C. Single-crystal elastic properties of alunite, $KAl_3(SO_4)_2(OH)_6$. *Phys. Chem. Minerals* **2006**, *33*, 567–573.