Thermodynamic investigation of uranyl vanadate minerals: implications for structural stability

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Supporting Information

Powder X-ray diffraction

Powder X-ray diffraction data were collected using a Bruker D8 Advance Davinci powder diffractometer in Bragg-Brentano configuration. Cu-Kα radiation was produced with an accelerating voltage of 40 kV and 40 mA current. An incident-beam slit of 1.0 mm was reduced by a 0.6 mm slit in combination with 0.02 mm absorber and diffraction (0.6 mm) slits. Data were collected using a step scan with a step velocity of 0.8° min^{-1} in the range of 5-55 degrees 2θ using a LynxEye solid-state detector. Diffraction patterns all exhibited sharp profiles consistent with simulated powder diffraction patterns for carnotite, curienite, and francevillite, without additional peaks attributable to impurities.

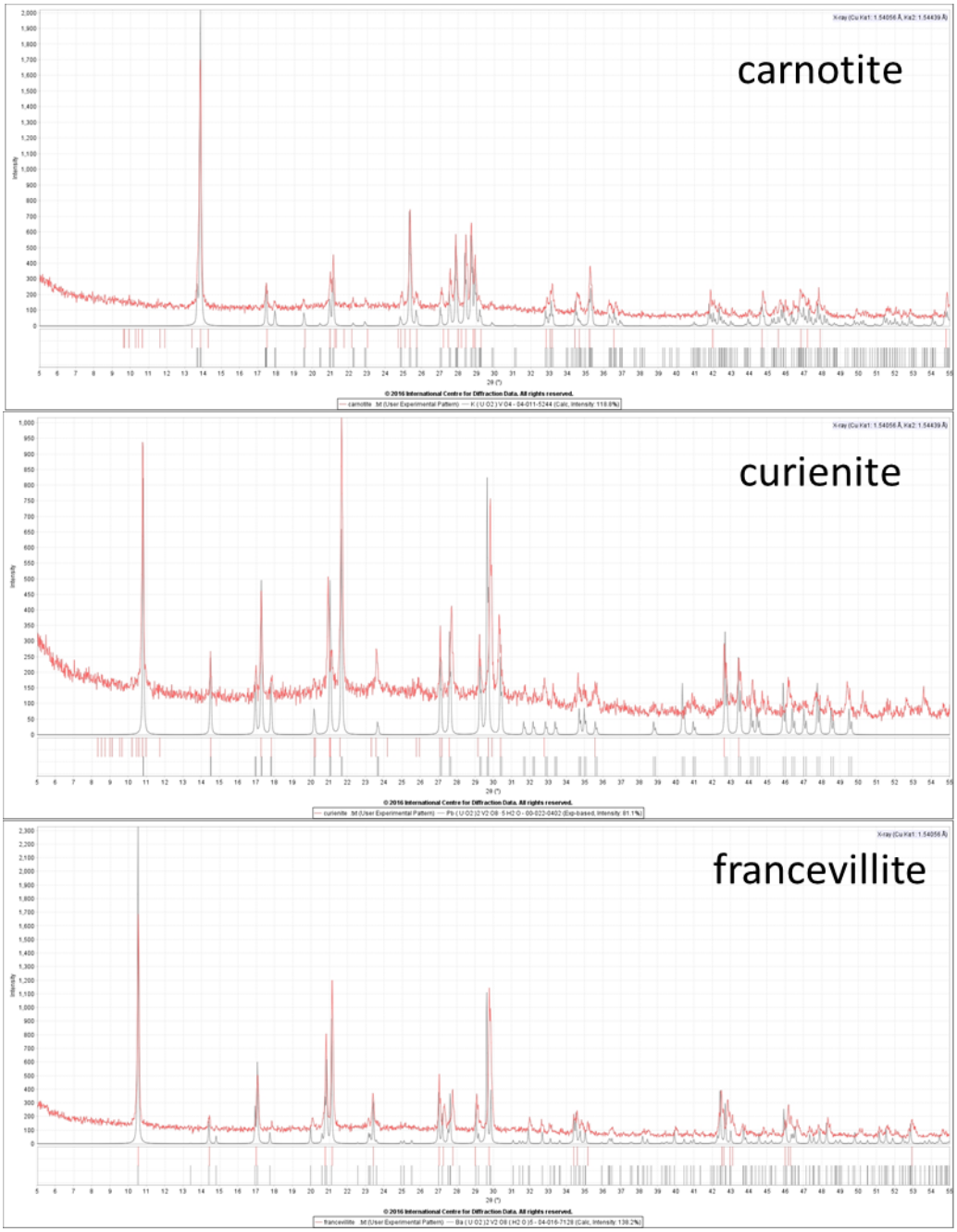
Chemical Analysis

Chemical analyses were done using a Perkin Elmer Optima 8000 inductively coupled plasma-optical emission spectrometer (ICP-OES) with an analytical uncertainty of 3.5%. Analysis parameters were: 1400W torch power; nebulizer flow rate of 0.6 L/min; sample flow rate of 1.8 mL/min and a 45 second read delay. Approximately 25 mg of synthetic mineral powders were dissolved in 15 mL aqueous HNO_3 (5%) in triplicate. U, V, K, Ba, and Pb concentrations were determined using linear regression of seven standard solutions after background subtraction. Calculated calibration coefficients were 0.99 or better for all elements of interest.

Thermogravimetric analysis

Thermogravimetric analyses were completed on a Netzsch TG209 F1 Iris thermal analyzer for ~25 mg aliquots of synthetic carnotite, curienite, and francevillite. Synthetic minerals were heated at 5°C/min from room temperature to 900°C under a stream of Ar gas at a rate of 50mL/min. Mass loss in the range of 30-105°C was assigned to the water present in each compound. No mass loss was observed for carnotite, indicating an anhydrous material as is typical of synthetic carnotite (Appleman and Evans, 1965). Observed mass loss for curienite and francevillite was in agreement with the chemical formulae $Pb(UO_2)_2V_2O_8 \cdot 4.5H_2O$ and $Ba(UO_2)_2V_2O_8 \cdot 5H_2O$, respectively. Limited quantities of analyzed material precluded analysis of final products after heating, although mixed U and V oxides are the likely result.

Powder X-ray Diffraction

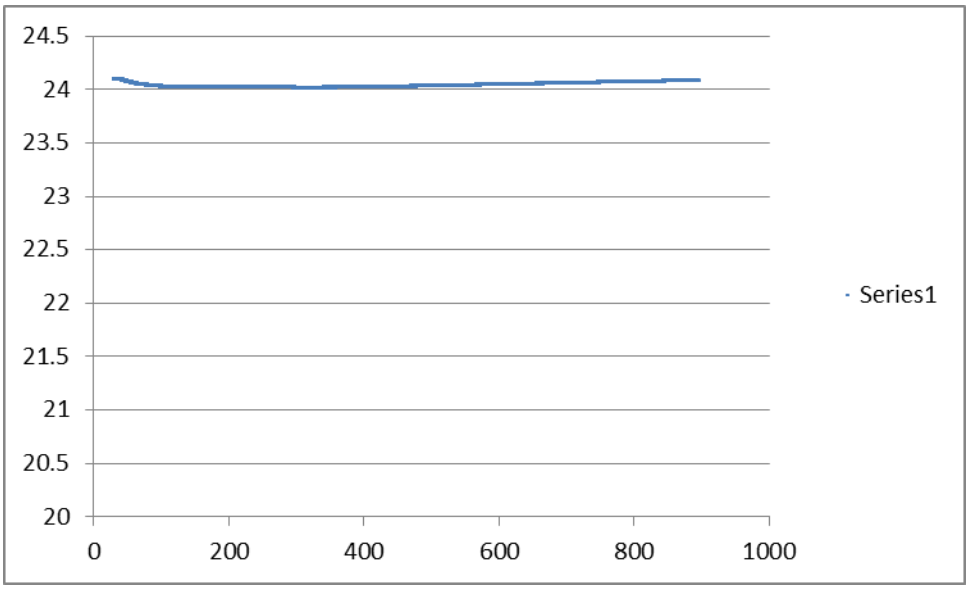


ICP-OES

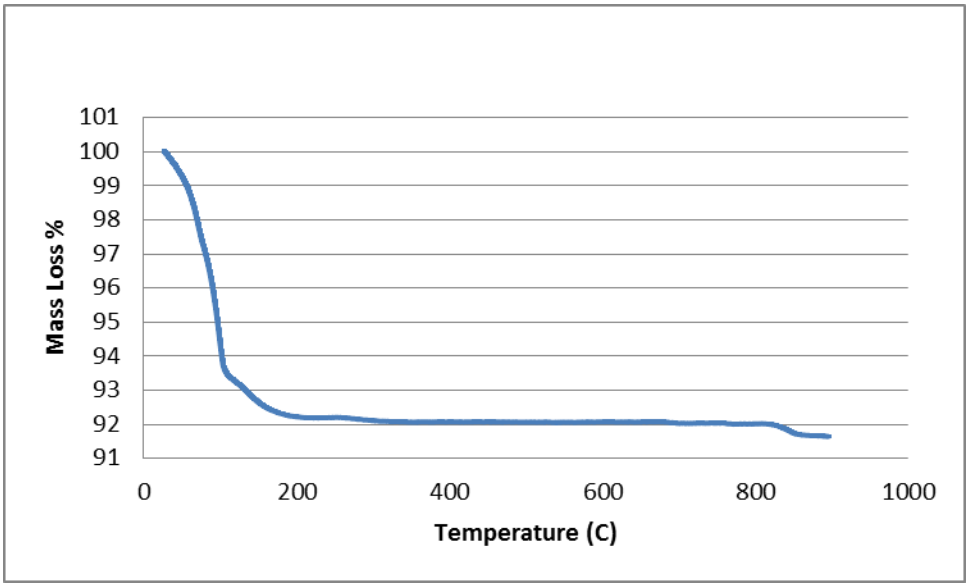
Mineral	Weight % Cation (by ICP)	Weight % Cation (calc.)	Weight % U (by ICP)	Weight % U (calc.)	Weight % V (by ICP)	Weight % V (calc.)
Carnotite (K)	8.1	9.2	55.4	56.13	13.5	12.01
Francevillite (Ba)	13.1	15.13	48.2	52.47	12.1	11.23
Curienite (Pb)	18.4	19.42	43.4	44.61	12.1	9.55

TGA

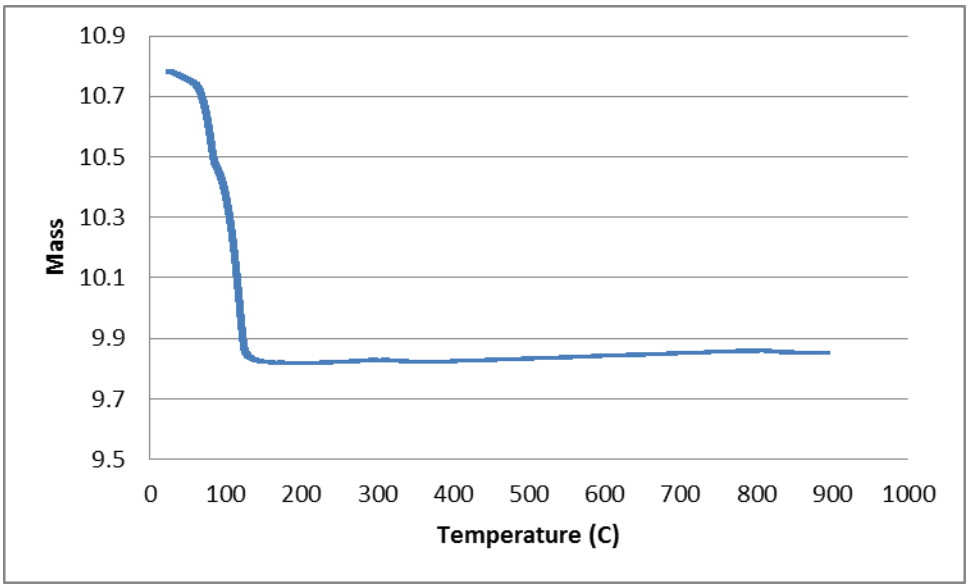
Carnotite



Curienite



Francevillite



Measured Heat Content

Carnotite		Curienite		Francevillite	
Pellet Mass (mg)	ΔH_{ds} (kJ/mol)	Pellet Mass (mg)	ΔH_{ds} (kJ/mol)	Pellet Mass (mg)	ΔH_{ds} (kJ/mol)
6.47	435.11	6.69	705.90	5.99	732.44
7.22	412.02	5.77	704.23	5.25	736.37
5.14	401.66	6.19	714.67	5.16	776.10
5.83	432.85	4.97	656.32	6.30	765.26
5.38	457.63	5.65	691.54	6.36	791.37
4.76	433.34	4.69	710.83	4.56	690.80
5.39	451.88	6.25	719.82	5.83	745.90
5.16	431.43	6.26	697.27	5.40	783.53
5.52	407.38	5.62	689.98	5.25	691.53
5.14	452.99	5.37	697.48	5.63	774.52
5	452.99			5.23	745.01
				4.05	726.10
Average	433.57	**Average**	698.80	**Average**	746.58
Error	11.82	**Error**	11.27	**Error**	19.26
Error (%)	2.73	**Error (%)**	1.61	**Error (%)**	2.58