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REVISION 2

Thermodynamic investigation of uranyl vanadate minerals: implications for structural stability

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ABSTRACT

Understanding the crystal chemistry, materials properties, and thermodynamics of uranyl minerals and their synthetic analogues is an essential step for predicting and controlling the long term environmental behavior of uranium. Uranyl vanadate minerals are relatively insoluble and widely disseminated within U ore deposits and mine and mill tailings. Pure uranyl vanadate mineral analogues were synthesized for investigation using high-temperature drop solution calorimetry. Calculated standard-state enthalpies of formation were found to be -4928.52 ± 13.90, -5748.81 ± 13.59, and -6402.88 ± 21.01, kJ/mol for carnotite, curienite, and francevillite respectively. Enthalpies of formation from binary oxides for uranyl vanadate minerals exhibit a positive linear correlation as a function of the acidity of oxides. Normalized charge deficiency per anion (NCDA) is presented to relate bonding requirements of the structural units and interstitial complexes. An exponential correlation was observed between NCDA and energetic stability (enthalpy of formation from binary oxides) for the studied minerals. Additionally, NCDA and oxide acidity exhibit an exponential correlation where decreasing oxide acidity

results in an exponential decrease in NCDA. The number of occurrences of uranyl vanadate mineral species are found to correlate with both enthalpy of formation from oxides, and NCDA.

INTRODUCTION

In 1948, the US Atomic Energy Commission guaranteed a minimum price for uranium ore mined in the United States to decrease dependence on foreign sources (Brugge and Goble, 2002). The resulting expansion of exploration and mining in the southwestern United States led to identification of over 7,000,000 tons of U ore (Brugge and Goble, 2002). Carnotite, ideally $K_2(UO_2)_2V_2O_8 \bullet 3H_2O$, and other uranyl vanadate minerals, are widespread in U deposits of the American Southwest, and were thus especially important during this mining "boom". Uranium and vanadium ore deposits located within the Uravan mineral belt in western Colorado and eastern Utah accounted for nearly 13% of the total U produced by the United States (Chenoweth, 1981). In addition to the American Southwest, uranyl vanadate minerals originating from Africa were an important source of U for the development of both nuclear weapons and nuclear energy during and after World War II (Dumett, 1985). The solid solution series between curienite ($Pb(UO_2)_2V_2O_8 \bullet 5H_2O$) and francevillite ($Ba(UO_2)_2V_2O_8 \bullet 5H_2O$) was first observed in samples from the mines of the Belgian Congo (now the Democratic Republic of the Congo), but has since been observed in other localities (Janeczek, 1999; Mereiter, 1986).

In the American Southwest and Africa, uranyl vanadate minerals are most common in areas where reduced uranium and reduced vanadium species are undergoing oxidation (Finch and Murakami, 1999). Primary U and V minerals that may alter to form uranyl vanadates include uraninite (UO_{2+x}), montroseite (V^{3+},Fe^{2+},V^{4+})O(OH), and davidite ($La(Y,U)Fe_2(Ti,Fe,Cr,V)_{18}(O,OH,F)_{38}$) (Krivovichev and Plášil, 2013; Weeks, 1961). Carnotite and other uranyl vanadates occur in Colorado Plateau-type U-V deposits, located on or near

fossil carbonaceous matter, and as alteration products in close proximity to uraninite (Dahlkamp, 1993; Evans and Garrels, 1958).

Over a range of conditions, uranyl vanadate minerals are amongst the most insoluble alteration products of supergene U oxides, which are also significant ore sources (Barton, 1957; Krivovichev and Plášil, 2013; Plasil, 2014; Weeks, 1961). Owing to their insolubility, they retain uranium in natural systems. Between pH-Eh ranges of 4.5-8, and 1.0-0.0V, respectively, carnotite is stable, and uranyl vanadate minerals precipitate when dilute UO_2^{2+} and VO_4^{3-} are present in aqueous systems (Langmuir, 1978; Schindler et al., 2000). The solubility of carnotite in groundwater is very low, having been noted as being approximately 1ppb U in the pH range of 5.5-7.5 (Barton, 1957). Carnotite precipitation from U-contaminated groundwater has been proposed as a potential method for treatment and remediation of groundwater and legacy wastes from mining operations (Tokunaga et al., 2009). A decrease in U concentrations in water below the drinking water standard of 30 ppb U, as outlined by the United States Environmental Protection Agency, was observed in batch experiments and calculations in which carnotite was precipitated (Tokunaga et al., 2009).

Over one century of research concerning uranyl vanadate minerals has yielded limited insight into the thermodynamic properties of these materials (Karyakin et al., 2003). Quantitative thermodynamic data are needed to define the relations between structural and energetic characteristics of these environmentally important phases (Karyakin et al., 2003). All uranyl vanadate minerals contain topologically identical uranyl vanadate sheets and substitution of interlayer cations is common. It has been suggested that the geometric arrangement of the interlayer cations is similar for all uranyl vanadate minerals, and thus does not substantially alter the stability of members of this group (Schindler et al., 2004b). Thermodynamic studies

71 presented here clarify the effect of structural arrangement and interlayer occupancy on the
72 stabilities of mineral species that are chemically similar and occur in comparable geologic
73 environments. Furthermore, investigating the thermodynamic properties of these minerals will
74 aid in understanding the environmental behavior of U.

75 Previous studies have investigated the thermochemistry of some synthetic alkaline-earth
76 uranyl vanadate mineral analogues (Karyakin et al., 2003). An adiabatic vacuum calorimeter was
77 used to determine the heat capacities of synthetic crystalline alkaline-earth (Mg, Ca, Sr, and Ba)
78 uranyl vanadates in the temperature range of 80-300K (Karyakin et al., 2003). High temperature
79 calorimetry is necessary for rapid and reproducible data acquisition for refractory materials
80 (Navrotsky, 1997). This technique is particularly applicable for enthalpy measurements of uranyl
81 minerals as it ensures complete dissolution of materials regardless of chemical composition or
82 structure (Shvareva et al., 2012).

83 ## STRUCTURES OF URANYL VANADATE MINERALS

84 Uranium is removed from primary minerals largely by oxidative dissolution, which forms
85 the relatively soluble and environmentally mobile uranyl ion, UO_2^{2+} (Finch and Murakami,
86 1999). Aqueous U(VI) chemistry is dominated by this near-linear uranyl ion. The uranyl moiety
87 is ubiquitous in secondary uranium minerals and synthetic hexavalent uranium phases (Burns,
88 2005). The formal charge of +2 on the uranyl ion requires further coordination by four, five, or
89 six ligands in the equatorial planes of bipyramids about the uranyl. The coordination geometries
90 include square, pentagonal, and hexagonal bipyramidal units (Burns, 2005). Owing to the uneven
91 distribution of bond strengths in uranyl polyhedra, linkages through the equatorial ligands favor
92 an abundance of sheet structures (Burns, 2005; Burns, 1997).

93 The sheets in the crystal structures of all uranyl vanadate minerals are topologically
94 identical. In 2013, Krivovichev & Plasil (Krivovichev and Plášil, 2013) listed 13 naturally
95 occurring uranyl vanadates (Table 1), all of which contain the $[(UO_2)_2(V_2O_8)]^{2-}$ sheet that is
96 based on the francevillite anion topology, and either mono, di, or tri-valent interstitial cations
97 (Abraham et al., 1993; Cesbron and Morin, 1968; Mereiter, 1986). The anionic sheet possesses
98 V_2O_8 dimers consisting of edge-sharing $V^{5+}O_5$ square pyramidal units that are linked by uranyl
99 ions in pentagonal bipyramidal coordination (Burns, 2005) (Figure 1). Neutrality is achieved by
100 incorporation of interlayer cations between successive sheets. Hydration ranges from anhydrous
101 to 11 water molecules per formula unit (Krivovichev and Plášil, 2013).

102 ## EXPERIMENTAL METHODS

103 ### Synthesis

104 Carnotite, francevillite, and curienite used in this study were synthesized through mild
105 hydrothermal reactions of uranyl pyrovanadate (UPV) (Karyakin et al., 2000) and KOH,
106 $Ba(OH)_2$, or $Pb(NO_3)_2$. UPV was synthesized by the high temperature solid-state reaction of
107 NH_4VO_3 (MV Laboratories, 99.99%) and γ-UO_3 (previously synthesized) (Appleman and Evans,
108 1965; Requena Yáñez et al., 2012). To synthesize UPV, stoichiometric quantities of NH_4VO_3
109 and UO_3 were weighed and ground together with acetone to promote homogeneity. The resulting
110 powder was dried for 6 hours at 150° C and was then slowly heated in a Thermolyne 47900 box
111 furnace to 760° over 12 hours, held at temperature for 72 hours, and then cooled to room
112 temperature over another 72 hours (Karyakin et al., 2000). The resulting powder was identified
113 as UPV by powder X-ray diffraction (Karyakin et al., 2000; Requena Yáñez et al., 2012).

To synthesize carnotite, 1.57g of UPV and 0.25g of KOH (Fisher, ACS grade) were weighed and ground together to ensure homogeneity. Approximately 450 mg of the mixture was placed in each of four Teflon-lined 23 mL Parr reaction vessels with 8 mL of 18 MΩ H_2O in each. The pH of the mixture was initially between 12.3 and 12.4, and was adjusted to 2.3 by adding 0.4M HCl. Prior to all pH measurements, BDH Buffer Reference Standards were used for calibration. Similar methods were used to synthesize francevillite. For this, 1.57 g of UPV and 0.76g $Ba(OH)_2$ (Fisher, ACS grade) were weighed, ground, and divided evenly amongst 4 reaction vessels. Upon addition of 8 mL of 18 MΩ H_2O the pH of the mixtures ranged from 11.9 to 12.5, and each was adjusted to 2.2 by adding 0.4M HCl. Curienite was synthesized by the reaction of 1.74g of UPV with 0.80g of $Pb(NO_3)_2$ (Alfa Aesar, 99.99%). Reagents were weighed, ground, and placed in 4 reaction vessels with 8 mL 18 MΩ H_2O in each. Initial pH values for these mixtures ranged from 2.9-3.5 and were adjusted to 2.3 by adding 0.4M HCl. For all hydrothermal reactions, limited initial solubility of reagents was observed.

The increase of temperature and pressure in the hydrothermal reactions promoted solubility of reagents and enabled formation of uranyl vanadate mineral analogues. After determining appropriate parameters from preliminary experiments, reaction vessels for all syntheses were sealed and placed in a Fisher Scientific Isotemp oven at 170°C for 5 days. Subsequent to cooling to room temperature, the products were recovered via vacuum filtration and rinsed with several aliquots of 18 MΩ H_2O. No significant change in pH was observed following hydrothermal reactions.

Whereas uranyl vanadates are stable and form over a broad pH range, preliminary experiments had demonstrated that high purity material, as required for thermochemical studies, was obtained when the initial pH was adjusted to 2.2-2.3 (Barton, 1957; Karyakin et al., 2003;

Murata et al., 1949). As is commonly the case in hydrothermal synthesis, the exact speciation of U and V during the 5 day reaction time is not known. However, the aqueous speciation of both uranyl and vanadyl is strongly dependent on pH (Barton, 1957; Hostetler and Garrels, 1962). Under acidic conditions such as used here, U(VI) speciation is dominated by the uranyl ion, whereas vanadyl hydrolyzes significantly to form complex polyatomic species. (Gorman-Lewis et al., 2008; Hostetler and Garrels, 1962; Plasil, 2014; Weeks, 1961).

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

159 background subtraction. Calculated calibration coefficients were 0.99 or better for all elements of
160 interest.

161 **Thermogravimetric analysis**

162 Thermogravimetric analyses were completed on a Netzsch TG209 F1 Iris thermal
163 analyzer for ~25 mg aliquots of synthetic carnotite, curienite, and francevillite. Synthetic
164 minerals were heated at 5°C/min from room temperature to 900°C under a stream of Ar gas at a
165 rate of 50mL/min. Mass loss in the range of 30-105°C was assigned to the water present in each
166 compound. No mass loss was observed for carnotite, indicating an anhydrous material as is
167 typical of synthetic carnotite (Appleman and Evans, 1965). Observed mass loss for curienite and
168 francevillite was in agreement with the chemical formulae $Pb(UO_2)_2V_2O_8 \bullet 4.5H_2O$ and
169 $Ba(UO_2)_2V_2O_8 \bullet 5H_2O$, respectively. Limited quantities of analyzed material precluded analysis of
170 final products after heating, although mixed U and V oxides are the likely result.

171 **Calorimetry**

172 Calorimetric data were collected using a Setaram AlexSys Calvet-type high-temperature
173 calorimeter. Pellets of pressed synthetic carnotite, curienite, and francevillite weighing ~5mg
174 were dropped from room temperature into the molten $3Na_2O\text{-}4MoO_3$ solvent at 700°C under a
175 stream of O_2. Complete dissolution of sample pellets in solvent was confirmed by visual
176 inspection. The well-established heat content of $\alpha\text{-}Al_2O_3$ was used as a calibrant (Shvareva et al.,
177 2012). The measured enthalpies of drop solution, ΔH_{ds}, were used to calculate enthalpies of
178 formation using thermochemical cycles. Table 2 contains the thermochemical cycles for
179 carnotite, curienite, and francevillite. The measured heat effect is the sum of heat capacity and

enthalpy of solution in the $3Na_2O$-$4MoO_3$ solvent (Navrotsky, 1977; Navrotsky, 1997; Shvareva et al., 2012).

RESULTS

Enthalpies of reaction

The standard-state enthalpies of formation from the elements are -4928.52 ± 13.90 kJ/mol for carnotite, -5748.81± 13.59 kJ/mol for curienite, and -6402.88 ± 21.01 kJ/mol for francevillite. Calculated enthalpies of formation from binary oxides can be compared to reveal energetic trends of synthetic uranyl vanadate mineral analogues and are -566.62 ± 12.11, -244.70 ± 11.90, and -427.18 ± 19.86 kJ/mol for carnotite, curienite, and francevillite, respectively. Carnotite is thus more energetically favorable than curienite or francevillite when compared with the mechanical mixture of their constituent oxides.

Experimentally determined enthalpies of formation from binary oxides indicate that all uranyl vanadate minerals examined here are more energetically favorable than uranyl oxide hydrates, peroxides, phosphates, and silicates (Shvareva et al., 2012). The only uranyl minerals that are more energetically favorable with respect to calculated enthalpies of formation from binary oxides are the uranyl carbonates andersonite ($Na_2Ca[(UO_2)(CO_3)_3]•5H_2O$) and grimselite ($K_3NaUO_2(CO_3)_3•3H_2O$), with enthalpies of formation from binary oxides of -710.4±9.1, and -989.3±14.0 $kJ•mol^{-1}$, respectively (Navrotsky et al., 2013). The strongly negative formation enthalpies from oxides for uranyl carbonates has been attributed to robust acid-base interactions between acidic zero-dimensional uranyl tricarbonate clusters and basic interstitial cations Na, Ca, and K (Shvareva et al., 2012).

As carnotite, curienite, and francevillite contain identical uranyl vanadate sheets, it is possible to compare the contribution of acid-base interactions with counter cations to formation energetics. The interactions between charge-balancing cations and the $[(UO_2)_2(V_2O_8)]^{2-}$ sheet are probed by plotting the measured formation enthalpies of oxides as a function of the acidity of the oxide as indexed on the Smith scale in which binary oxides have been assigned a numerical value based on stoichiometry (Smith, 1987). The observed linear relationship in Figure 2 confirms the correlation between formation enthalpies from oxides and oxide acidity. Similar experimentally determined linear trends have been reported for uranyl silicates and uranyl hydroxide oxides (Navrotsky et al., 2013; Shvareva et al., 2012).

DISCUSSION

Structural stability, in addition to being quantified through thermodynamic measurements, can be inferred by comparing the balance of bond strengths between the structural unit and interstitial complexes (Hawthorne, 2012; Hawthorne, 2015; Hawthorne and Schindler, 2008; Schindler and Hawthorne, 2004; Schindler and Hawthorne, 2008). The structural unit of a crystalline solid is usually an anionic moiety of strongly bonded coordination polyhedra (Hawthorne, 2012). Interstitial complexes consist of lower-valence cations and water (Hawthorne, 2012). The number of bonds required by a structural unit can be estimated and related to its formal charge and number of O atoms (Hawthorne, 2012). The total number of bonds (NB_T) in a structure is the sum of cation coordination numbers modified by the number of each cation in the chemical formula (Hawthorne, 2012). The number of bonds within the structural unit (NB_{SU}) can be calculated in the same way, and the number of bonds required by the structural unit (NB_R) is the difference between (NB_{SU}) and (NB_T) (Hawthorne, 2012). Using this method, NB_T and NB_R have been calculated for carnotite, curienite, and francevillite.

The number of bonds required (NB_R) by the structural unit can be further modified by calculating the charge deficiency per anion (CDA). CDA is calculated by dividing the formal charge (FC) of the structural unit by the number of oxygen atoms (N_o) within the structural unit (Schindler and Hawthorne, 2008). In all uranyl vanadate minerals, FC = -2 and N_o = 12, therefore the CDA for all uranyl vanadate minerals is 0.166 valence units (v.u.) (Schindler et al., 2004a; Schindler et al., 2004b). The charge deficiency per anion may be normalized, for the purpose of comparison across different structures, by dividing by NB_R, yielding the normalized charge deficiency per anion (NCDA). Calculated NCDA values for carnotite, curienite, and francevillite are 0.0093, 0.0208, and 0.0185 v.u. respectively. Experimentally determined enthalpies of formation plotted as a function of NCDA in Figure 3, reveals an exponential decrease in stability (less-negative $\Delta H_{f\text{-}ox}$) as NCDA increases. NCDA is a measure of the degree of unsatisfied bonding of the structural unit and structure stability depends on the degree to which this can be accounted for by linkages to the interstitial complex. This model confirms that a higher degree of unsatisfied bonding requirements correlates exponentially to a decrease in energetic favorability.

Oxide acidity of the interstitial complex is exponentially related to calculated NCDA values. Decreasing oxide acidity results in an exponential decrease in normalized charge deficiency per anion. This observation, coupled with the relationship between oxide acidity and enthalpy of formation from oxides clarifies the relation between structure and thermodynamics. Correlations between NCDA and energetics have yet to be investigated in other mineral systems that have identical structural units.

IMPLICATIONS

Observed enthalpies of formation for carnotite, curienite, and francevillite indicate that uranyl vanadate phases are energetically stable relative to the oxides at 298 K. Each of these minerals contain identical uranyl vanadate sheets, and differences in stabilities therefore relate to the identity and bonding behavior of interstitial complexes. There is an exponential relationship between the enthalpies of formation of these minerals from the oxides and the normalized charge deficiency of the anions in the structural unit. This confirms the importance of charge density matching between the structural unit and interstitial complex in determining the thermodynamic properties of these minerals. In addition to element availability in a given set of geochemical conditions, these energetic considerations impact mineral occurrences.

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Figures and Tables

TABLE 1. Recognized Uranyl Vanadate Mineral Species

Modified from Krivovichev and Plášil (Krivovichev and Plášil, 2013)

Chemical Formula	Mineral Name	Space Group	*a*[Å]/α[°]	*b*[Å]/β[°]	*c*[Å]/γ[°]
$Cu[(UO_2)_2(V_2O_8)](OH)(H_2O)_3$	sengierite	*$P2_1/a$*	10.60/ 90	8.09/ 103.4	10.09/ 90
$K_2[(UO_2)_2(V_2O_8)]$	carnotite	*$P2_1/a$*	10.47/ 90	8.42/ 103.8	6.59/ 90
$Cs_2[(UO_2)_2(V_2O_8)]$	margaritasite	*$P2_1/a$*	10.51/ 90	8.45/ 106.1	7.32/ 90
$Pb[(UO_2)_2(V_2O_8)](H_2O)_5$	curienite	*Pcan*	10.42/ 90	8.49/ 90	16.41/ 90
$Ba[(UO_2)_2(V_2O_8)](H_2O)_5$	francevillite	*Pcan*	10.48/ 90	8.45/ 90	16.65/ 90
$Ca[(UO_2)_2(V_2O_8)](H_2O)_8$	tyuyamunite	*Pnna*	10.63/ 90	8.36/ 90	20.40/ 90
$Ca[(UO_2)_2(V_2O_8)](H_2O)_5$	metatyuyamunite	*O**	10.63/ 90	8.36/ 90	16.96/ 90
$Al[(UO_2)_2(V_2O_8)](OH)(H_2O)_{11}$	vanuralite	*M**	10.33/ 90	8.44/ 103.0	24.52/ 90
$Al[(UO_2)_2(V_2O_8)](OH)(H_2O)_8$	metavanuralite	*P-1*	10.46/ 75.9	8.44/ 102.8	10.43/ 90
$Na_2[(UO_2)_2(V_2O_8)](H_2O)_5$	strelkinite	*Pnmm*	10.64/ 90	8.36/ 90	32.73/ 90
$Na_2[(UO_2)_2(V_2O_8)](H_2O)_2$	metastrelkinite I	*$P2_1/n$*	10.50/ 90	8.28/ 97.6	16.24/ 90
$Na_2[(UO_2)_2(V_2O_8)](H_2O)_2$	metastrelkinite II	*$P2_1/a$*	10.48/ 90	8.51/ 113.2	7.72/ 90
$Na_2[(UO_2)_2(V_2O_8)]$	metastrelkinite III	*$P2_1/a$*	10.42/ 90	8.34/ 100.5	6.02/ 90

* Space group unknown. *O*= orthorhombic, *M*= monoclinic

274 **TABLE 2.** Calorimetric cycles for enthalpy of formation calculations for uranyl vanadate minerals

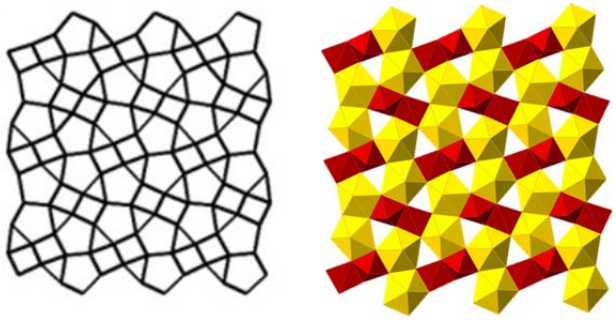
Carnotite
$\Delta H_{f\text{-}ox}$ (carnotite) = -ΔH1 + ΔH5 + 2ΔH4 + ΔH6
$2UO_3$ (xl, 298K) + K_2O (xl, 298K) + V_2O_5 (xl, 298K) = $K_2(UO_2)_2(VO_4)_2$ (xl, 298K)
ΔH_f^0 (carnotite) = -ΔH1 + ΔH5 + 2ΔH4 + ΔH6 + ΔH11 + 2ΔH10 + ΔH12
2K (xl, 298K) + 2U (xl, 298K) + 2V (xl, 298K) + $6O_2$ = $K_2(UO_2)_2(VO_4)_2$ (xl, 298K)

Curienite
$\Delta H_{f\text{-}ox}$ (curienite) = -ΔH3 + ΔH9 + 2ΔH4 + ΔH6 + 4.5ΔH7
$2UO_3$ (xl, 298K) + PbO (xl, 298K) + V_2O_5 (xl, 298K) + $4.5H_2O$ (l, 298K) = $Pb(UO_2)_2(VO_4)_2$•$4.5H_2O$ (xl, 298K)
ΔHf^0 (curienite) = -ΔH3+ ΔH9 + 2ΔH4 + ΔH6 + 4.5ΔH7 + ΔH15 + 2ΔH10 + ΔH12 + 4.5ΔH13
Pb (xl, 298K) + 2U (xl, 298K) + 2V (xl, 298K) + $4.5H_2$ (g, 298K) + 16.5/2 O_2 = $Pb(UO_2)_2(VO_4)_2$•4.5H2O (xl, 298K)

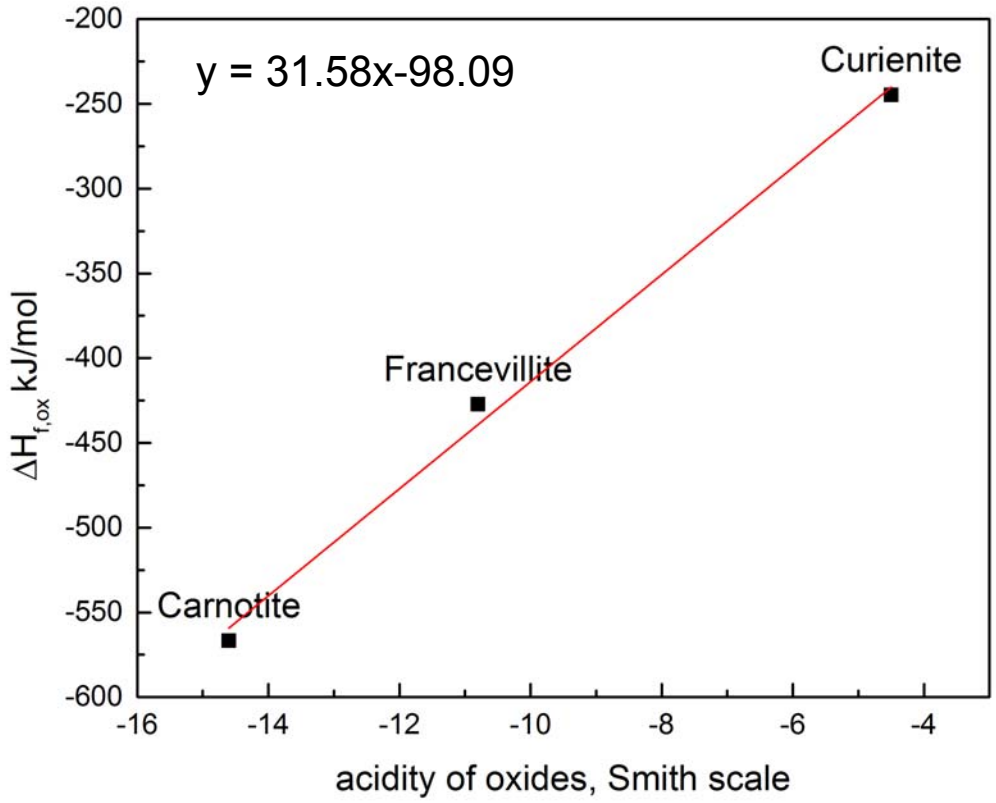
Francevillite
ΔHf-ox (francevillite) = -ΔH2 + ΔH8 + 2ΔH4 + ΔH6 + 5ΔH7
$2UO_3$ (xl, 298K) + BaO (xl, 298K) + V_2O_5 (xl, 298K) + $5H_2O$ (l, 298K) = $Ba(UO_2)_2(VO_4)_2$•$5H_2O$ (xl, 298K)
ΔHf^0 (francevillite) = -ΔH2 + ΔH8 + 2ΔH4 + ΔH6 + 5ΔH7 + ΔH14 + 2ΔH10 + ΔH12 + 5ΔH13
Ba (xl, 298K) + 2U (xl, 298K) + 2V (xl, 298K) + $5H_2$ (g, 298K) + 17/2 O_2 = $Ba(UO_2)_2(VO_4)_2$•$5H_2O$ (xl, 298K)

Reactions	ΔH (kJ/mol)	ΔH (kJ/mol)	ΔH (kJ/mol)	REF
1	ΔH_{ds} (Carnotite)	$K_2(UO_2)_2(VO_4)_{2\ (xl,\ 298K)}$ = $K_2O_{\ (soln,\ 976K)}$ + $2UO_{3\ (soln,\ 976K)}$ + $V_2O_{5\ (soln,\ 976K)}$	407.62 ± 11.12	
2	ΔH_{ds} (Francevillite)	$Ba(UO_2)_2(VO_4)_2$•$5H_2O$ (xl, 298k) = BaO (soln, 976K) + $2UO_3$ (soln, 976K)+ V_2O_5 (soln, 976K)+ $5H_2O$ (g,976K)	746.58 ± 19.26	
3	ΔH_{ds} (Curienite)	$Pb(UO_2)_2(VO_4)_2$•4.5H2O (xl, 298K) = PbO (soln, 976K) + $2UO_3$ (soln, 976K)+ V_2O_5 (soln, 976K)+ $4.5H_2O$ (g, 976K)	698.80 ± 11.27	
4	ΔH_{ds} (UO_3)	UO_3 (xl, 298K) = UO_3 (soln, 976K)	9.5 ± 1.50	(Helean et al., 2002)
5	ΔH_{ds} (K_2O)	K_2O (xl, 298K) = K_2O (soln, 976K)	-318 ± 3.10	(Molodetsky et al., 2000)
6	ΔH_{ds} (V_2O_5)	V_2O_5 (xl, 298K) = V_2O_5 (soln, 976K)	140 ± 2.10	(Navrotsky, 2014)
7	ΔH_{hc} (H_2O)	H_2O (l, 298K) = H_2O (g, 976K)	69 ± 0	(Robie and Hemingway, 1995)
8	ΔH_{ds} (BaO)	BaO (xl, 298K) = BaO (soln, 976K)	-184.6 ± 3.2	(Robie and Hemingway, 1995)
9	ΔH_{ds} (PbO)	PbO (xl, 298K) = PbO (soln, 976K)	-15.4 ± 1.10	(Navrotsky, 2014)
10	ΔH_f^0 (UO_3)	U (xl, 298K) + 3/2 O_2 (g, 298K) = UO_3 (xl, 298K)	-1224 ± 0.80	(Robie and Hemingway, 1995)
11	ΔH_f^0 (K_2O)	2K (xl, 298K) + 1/2 O_2 (g, 298K) = K_2O (xl, 298K)	-363.2 ± 2.10	(Robie and Hemingway, 1995)
12	ΔH_f^0 (V_2O_5)	2V (xl, 298K) + 5/2 O_2 (g, 298K) = V_2O_5 (xl, 298K)	-1550.6 ± 6.30	(Robie and Hemingway, 1995)
13	ΔH_f^0 (H_2O)	H_2 (g, 298k) + 1/2 O_2 (g, 298K) = H_2O (l, 298K)	-285.8 ± 0.10	(Robie and Hemingway, 1995)
14	ΔH_f^0 (BaO)	Ba (xl, 298K) + 1/2 O_2 (g, 298K) = BaO (xl, 298K)	-548.1 ± 2.10	(Robie and Hemingway, 1995)
15	ΔH_f^0 (PbO)	Pb (xl, 298K)+ 1/2 O_2 (g, 298K) = PbO (xl, 298K)	-219.41 ± 0.80	(Robie and Hemingway, 1995)

FIGURE 1. The francevillite anion topology (left) and population of the francevillite anion topology (right) by pentagonal bipyramids of uranium and square pyramids of vanadium. Modified from Burns (Burns, 2005).



293 **FIGURE 2.** Enthalpies of formation from oxides for carnotite, curienite, and francevillite as a
294 function of acidity of oxides (Smith, 1987).



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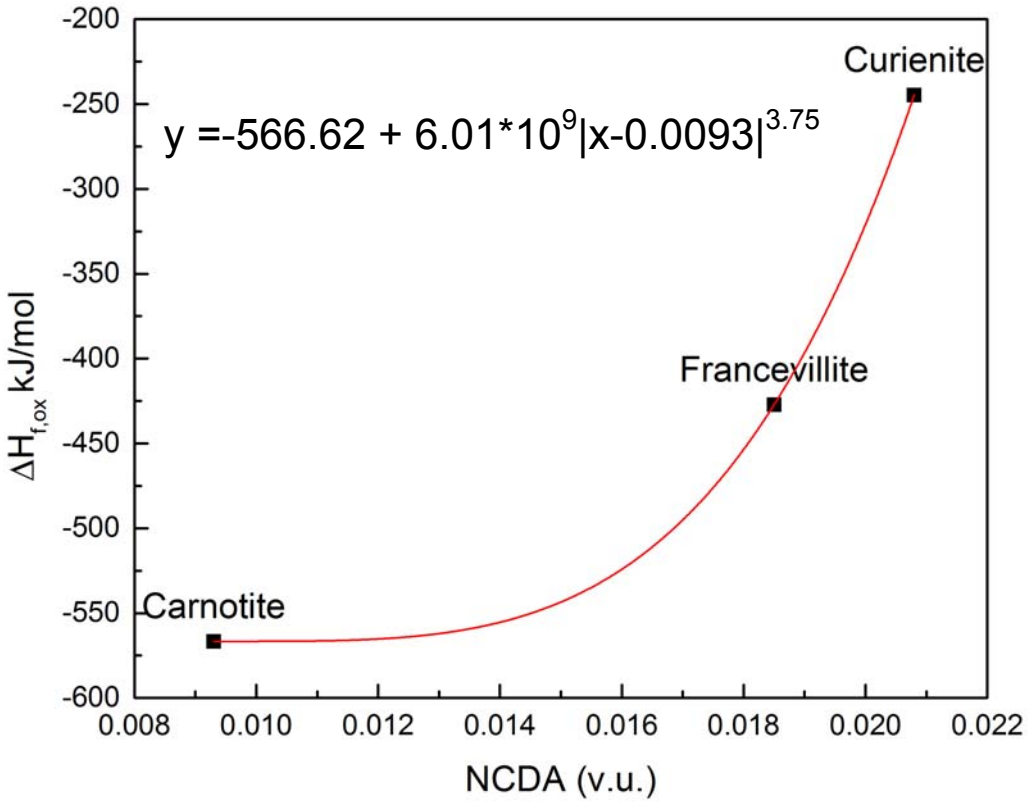
303 **FIGURE 3.** Enthalpies of formation from oxides for carnotite, curienite, and francevillite as a

304 function of normalized charge deficiency per anion (NCDA).



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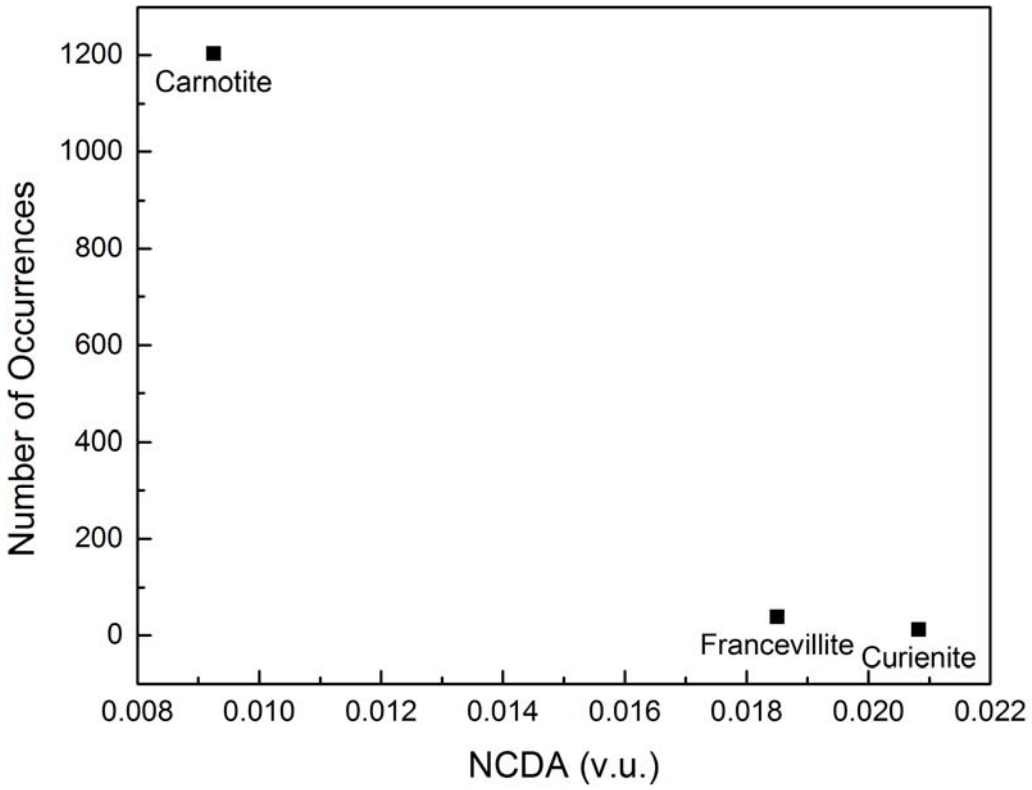
311 **FIGURE 4.** Number of occurrences (2016) plotted as a function of NCDA.



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