

Session 9: Crystal structure

MO1: The Crystal Chemistry of the Zippeite Group

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Hydrated uranyl sulfates are relatively widespread, and occur where sulfur is oxidized in the presence of uranium and acidic water. They impact the mobility of uranium in acid-mine drainage, and may also be important for understanding the fate of radionuclides in a geologic repository for nuclear waste. Despite their importance, the chemistries and structures of uranyl sulfates are poorly understood. To date, the structures have only been reported for schröckingerite, johannite, uranopilite, and zippeite (K).

There are at least seven zippeite-group minerals with the general formula $M_x(\text{H}_2\text{O})_z[(\text{UO}_2)_2(\text{SO}_4)\text{O}_{2-x}(\text{OH})_x]$, $M = \text{Na, K, Mg, Zn, Ni, Co}$. Several synthetic zippeite-group materials have also been reported, including those with $M = \text{NH}_4$ and Mn. We have completed more than 100 mild hydrothermal syntheses experiments in the M-U-S-H₂O system, and have been successful in growing many crystals of zippeite-group minerals that are suitable for single-crystal studies. The structures of Na, Zn, Co, Mn, two NH₄, and two Mg zippeites have been solved and refined using X-ray diffraction data collected with a Bruker APEX CCD-based detector system. Most crystals are twinned and pseudo-orthorhombic, although many have monoclinic symmetry. Each zippeite-group structure contains a uranyl sulfate sheet with uranyl square bipyramids that share equatorial edges, forming double-wide zigzag chains. Adjacent chains are linked by the sharing of equatorial vertices with sulfate tetrahedra, resulting in sheets of composition $[(\text{UO}_2)_2(\text{SO}_4)\text{O}_{2-x}(\text{OH})_x]$, with all four vertices of the sulfate tetrahedra shared with different uranyl polyhedra. The interlayer constituents differ significantly within the group. Divalent interlayer cations are octahedrally co-ordinated by H₂O groups and oxygen atoms of the uranyl ions (O_{Ur}). However, we have found three distinct structure types, which involve (a) $M\phi_6$ (ϕ : O, H₂O) octahedra that are attached to the sheets on either side by incorporating O_{Ur} atoms, (b) $M\phi_6$ octahedra that are attached to one sheet by incorporation of a O_{Ur} atom, and (c) $M\phi_6$ octahedra that are not attached to the uranyl sulfate sheets, but rather are held in the interlayer by hydrogen bonding only. Monovalent interlayer cations are in large, irregular co-ordination polyhedra involving H₂O groups and O_{Ur} atoms. In most cases there are additional H₂O groups that are held in the interlayers by hydrogen bonding only.

MO2: Arrojadite: variations in space group and composition based on four new refinements.

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Published data on arrojadite show one monoclinic space group (C2/c), a range of compositions, and disorder among cation sites. Four new structure determinations for arrojadites from Rapid Creek, Yukon, Canada, Palermo Mine and Chandlers Mill, NH, USA and Nickel Plate Mine, SD, USA show that arrojadite can occur in either of two monoclinic space groups, Cc (Rapid Creek and Palermo) or C2/c (Chandlers Mill and Nickel Plate). Each has nearly identical cell parameters. Single crystal intensity data were obtained using a CCD based system and for the former two samples, R-values are ~3% while for the later R-values are ~5% with some disorder within one PO₄ and one Na site. The important structural and compositional difference between samples from the two space groups is the number and location of Na sites: Cc arrojadites - AlCaKN₅(Fe,Mn,Mg)₁₃(PO₄)₁₂F and C2/c arrojadites - AlCaKN₄(Fe,Mn,Mg)₁₃(PO₄)₁₂OH. Na sites in Cc arrojadite are well defined based on thermal parameters while in C2/c arrojadite, one Na can be split and shows some correlation with the disordered phosphate.

Electron probe analyses show slightly less than 5 and 4 Na atoms/48 oxygens for Cc and C2/c arrojadites, respectively, consistent with the structural results. All four samples have ~13 (Fe, Mn, Mg) atoms/48 oxygens although some substitution of these elements must occur into the Na sites. Of the four arrojadites, those with Cc symmetry have very low F while those with C2/c symmetry are F rich. This may be related to symmetry and other compositional changes, but cause/effect is not known. Palermo arrojadite has low Ca but high levels of Sr and Ba that substitute into the Ca site. The Chandlers Mill sample has low K but high Ba and Pb with the former substituting for Ca and K and the latter for K.

For determinative purposes, the cell parameters do not appear to distinguish between the two types of arrojadite. Short of structural determination, electron probe analysis for Na and possibly F appear to be promising in distinguishing between the two arrojadite types. The above results appear to explain at least part of the discrepancies in structure and composition for this complex mineral.

MO3: Structure Solution and Refinement of Various Minerals by *Ab initio* Powder Methods

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The structure solution of a number of minerals has, in the past eluded crystallographers by virtue of their occurrence only as microcrystalline masses, which make them unsuitable to single crystal methods. In such cases, when the symmetry is high, it has often been possible, to establish the crystal structure from the powder diffraction pattern. There remains, however, a group of microcrystalline minerals of monoclinic and triclinic symmetry, for which crystal structure determination has proven to be intractable. The recent development of methods to fit powder diffraction profiles obtained using synchrotron X-ray sources together with the development of new software to accurately extract intensity data from these patterns has made possible the *ab initio* determination of the structure of microcrystalline compounds. We report here the crystal structures of two such minerals, kingite Al₃(PO₄)₂(OH,F)₃·9H₂O and priceite Ca₂B₁₀O₁₉·7H₂O.

Kingite from the Fairview phosphate working near Robertson, South Australia was first described in 1957. In this study a triclinic cell where, $a = 9.3775(1)$, $b = 10.1131(1)$, $c = 7.1377(1)$ Å, $\alpha = 97.598(1)^\circ$, $\beta = 100.879(1)^\circ$, $\gamma = 96.008(1)^\circ$ was refined to the powder diffraction pattern. The structure solution showed a layer structure consisting of strips of 3 corner-linked AlO₆ octahedra which are inter-linked by PO₄ tetrahedra.

Priceite was described in 1873 from an occurrence in Oregon, U.S.A. We obtained a monoclinic cell $a = 12.356(1)$, $b = 6.980(1)$, $c = 11.627(1)$ Å, and $\beta = 110.677(2)^\circ$. The structure solution from direct methods showed chains of Ca polyhedra linked by oxygen bridges, the Ca polyhedra are additionally linked via BO₃ and BO₄ groups.

MO4: The Crystal Structure and Crystal Chemistry of a New Uranyl Carbonate With Composition K₄Ca₆(UO₂)₄(CO₃)₁₂(H₂O)₇

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Crystals of K₄Ca₆(UO₂)₄(CO₃)₁₂(H₂O)₁₃ were synthesized by evaporation of a solution containing uranyl nitrate, calcium nitrate, and potassium carbonate at 21°C. The crystal structure, orthorhombic, space group *Pnmm*, a 17.015(2), b 18.048(2), c 18.394(2), V 5684.32, $Z=4$, was solved by direct methods and refined by least squares techniques to an agreement index (R_1) of 3.86% and a goodness of fit (S) of 0.859 for 12,221 unique reflections ($(F_o) > 4\sigma(F)$). Data were collected using a Bruker Platform three circle X-ray diffractometer equipped with a 4K APEX CCD detector and graphite monochromated MoK α radiation. The structure consists of uranyl hexagonal bipyramids that share edges with three carbonate triangles, resulting in the well-known uranyl tri-carbonate cluster of composition $[(\text{UO}_2)(\text{CO}_3)_3]^{4+}$. As is common in other uranyl carbonates with U:C ratios of 1:3, the structure of K₄Ca₆(UO₂)₄(CO₃)₁₂(H₂O)₁₃ consists of uranyl tricarbonate clusters that are not directly linked, rather they are connected through bonds to lower valence cations. There are three symmetrically independent U⁶⁺ positions, seven unique carbonate groups, and four calcium polyhedra. Along the [001] direction there are bands of isolated uranyl tri-carbonate clusters that are linked to three Ca ϕ_7 , two K ϕ_8 , and four K ϕ_6 polyhedra (ϕ : H₂O or O²⁻). The structure contains six independent K sites that are from 20 to 80% occupied. K₄Ca₆(UO₂)₄(CO₃)₁₂(H₂O)₇ belongs to the group of uranyl carbonate compounds with the uranyl carbonate complex being the only anion.

Location:	Rapid Creek Yukon, Canada		Palermo New Hampshire		Chandlers Quarry New Hampshire	Nickel Plate Mine South Dakota		
Space Group	Cc		Cc		C2/c	C2/c		
R	0.029		0.033					
<u>Microprobe analyses</u> (average of 7 points; atoms based on 48 oxygens)								
	probe	x-ray	probe	x-ray		x-ray		x-ray
Fe+2	10.421	10.54	8.725	11.04	9.280		8.029	
Mn+2	0.454	“	3.707	“	1.679		4.775	
Mg+2	1.810	2.46	2.46	1.96	1.143		1.766	0.617
[Fe+Mn+Mg]	[12.685]	[13.00]	[13.575]	[13.00]	[12.725]		[13.421]	
Al+3	0.982	1.00	1.003	1.00	0.980		0.953	
Na+1	4.760	4.85	4.493	4.50	3.728		3.599	
K+1	0.821	0.90	0.684	0.79, 0.17	0.521		0.765	
Ca+2	0.976	0.98	0.231	0.23 Fe=0.58	0.937		0.917	
Ba+2	0.0	-	0.020	-	0.221		0.0	
Sr+2	0.007	-	0.118	0.19	0.078		0.0	
Pb+2	0.002	-	0.002	-	0.244		0.017	
P+5	11.978	12.00	11.961	12.00	11.912		11.852	
Si+4	0.001	-	0.001	-	0.006		0.009	
Ti+4	0.050	-	0.003	-	0.0		0.015	
F	0.040	-	0.109	-	0.823		0.712	

X-ray site occupancies

	Mg	[Mn+Fe]	Mg	[Mn+Fe]	Mg	[Mn+Fe]	Mg	[Mn+Fe]
M1	0.11	0.89	0.06	0.94			0.51	0.48
M2a	0.05	0.95	0.04	0.96			0.08	0.92
M2b	0.24	0.76	0.09	0.91				
M3a	0.43	0.57	0.49	0.51			0.29	0.71
M3b	0.57	0.43	0.44	0.56				
M4a	0.28	0.72	0.21	0.79			0.03	0.97
M4b	0.22	0.78	0.15	0.85				
M5a	0.03	0.97	0.02	0.98			0.02	0.98
M5b	0.07	0.93	0.02	0.98				
M6a	0.06	0.94	0.10	0.90			0.10	0.90
M6b	0.08	0.92	0.08	0.92				
M7a	0.08	0.92	0.13	0.87			0.10	0.90
M7b	0.24	0.76	0.13	0.87				
Na1	0.99		0.59				0.92	
Na2a	0.97		0.94				0.98	
Na2b	0.97		0.92					
Na3a	0.96		1.00				0.47	
Na3b	0.96		1.00					
K	0.90		0.78				0.46	
Ca	0.98		1.32				0.58	

Notes:

Rapid Creek: $Fe = Fe + Mn$.

Palermo: $Fe = Fe + Mn$; $Ca = Ca + Sr + Ba + Fe$ where Ca, Sr and Ba taken from probe and Fe = excess Fe in M sites; K split into two sites with occupancies of 0.79 and 0.17; O42 is NPD.

Chandlers Quarry:

Nickel Plate: