The crystal chemistry of the uranyl carbonate mineral grimselite, $(K,Na)_3Na[(UO_2)(CO_3)_3](H_2O)$, from Jáchymov, Czech Republic

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ABSTRACT

Two crystals of the uranyl carbonate mineral grimselite, ideally $K_3Na[(UO_2)(CO_3)_3](H_2O)$, from Jáchymov in the Czech Republic were studied by single-crystal X-ray diffraction and electron-probe microanalysis. One crystal has considerably more Na than the ideal chemical composition due to substitution of Na into KO_8 polyhedra; the composition of the other crystal is nearer to ideal, and similar to synthetic grimselite. The presence of Na atoms in KO_8 polyhedra, which are located in channels in the crystal structure, reduces their volume, and as a result the unit-cell volume also decreases. Structure refinement shows that the formula for the sample with the anomalously high Na content is $(K_{2.43}Na_{0.57})_{\Sigma3.00}Na[(UO_2)(CO_3)_3](H_2O)$. The unit-cell parameters, refined in space group $P\bar{6}2c$, are $a = 9.2507(1)$, $c = 8.1788(1)$ Å, $V = 606.14(3)$ Å^3 and $Z = 2$. The crystal structure was refined to $R_1 = 0.0082$ and $wR_1 = 0.0185$ with a GOF = 1.33, based on 626 observed diffraction peaks $[I_{obs} > 3\sigma(I)]$.

Introduction

THE dissolution of uraninite (UO_{2+x} with $x = 0-0.67$) in oxidizing conditions can produce high concentrations of uranium-bearing ions. Aqueous uranyl carbonate complexes are important species in circumneutral to alkaline conditions in the presence of dissolved CO_2 (Langmuir, 1978). The $[(UO_2)(CO_3)_3]^{4-}$ complex, which is stable in the pH range $6.5-11.5$, is the primary cause of the mobility of uranium in these solutions (Finch and Murakami, 1999). Uranyl carbonate minerals precipitate from natural solutions where evaporation is significant or where the fugacity of CO_2 is greater than atmospheric (Garrels and Christ,

1959; Finch and Ewing, 1992; Finch, 1997). These conditions are encountered in old mines where hydrothermal veins containing uraninite in a carbonate gangue were exploited. The stability of uranyl carbonate minerals influences the mobility of uranium in natural groundwater and therefore, a detailed knowledge of their crystal chemistry and the conditions in which they are found is of importance.

Here we present two refinements of the crystal structure of the uranyl carbonate mineral grimselite. Single-crystal X-ray diffraction data are supported by quantitative chemical analyses to show an interesting substitution of Na into KO_8 polyhedra.

Previous studies

Grimselite was described as a new mineral from a cable tunnel between Gerstenegg and Sommerloch in the Aar massif, Grimsel area, Bern, Switzerland (Walenta, 1972). It was found as yellowish efflorescences on partially episyenitized aplitic granite with schröckingerite, monohydrocalcite, calcite, gypsum and baylissite (Walenta, 1976). It has subsequently been reported from Krunkelbachtal, Germany (Walenta, 1995) and Jáchymov in the Czech Republic (Pauliš et al., 2007; Tvrdý and Plášil, 2010). Structural investigations of the synthetic analogue of grimselite were carried out by Mazzi and Rinaldi (1960, 1961). They obtained a partial structural solution using the Weissenberg film method and suggested that the composition was $K_3Na[(UO_2)(CO_3)_3]$. The structure was refined to an R index of 0.061 in space group $P\bar{6}2c$ with unit-cell parameters of $a = 9.29$ and $c = 8.26$ Å, but estimated standard deviations for the atom positions were not reported, and no molecular H_2O was located in the structure. In his description of material from the type locality Walenta (1972) noted that grimselite was very similar to the material studied by Mazzi and Rinaldi (1960, 1961), and he concluded that it had the same space group and unit-cell parameters. However, analyses of synthetic and natural material (in Walenta, 1972) suggested that grimselite contained molecular H_2O, although it had not been reported by Mazzi and Rinaldi (1960, 1961). A single-crystal study of synthetic grimselite was undertaken by Li and Burns (2001) using a charge coupled device (CCD) area detector. This located an oxygen atom belonging to molecular H_2O in a channel in the structure, and the formula was rewritten

$K_3Na[(UO_2)(CO_3)_3](H_2O)$. The crystal structure of the Rb-bearing analogue of grimselite was subsequently determined by Kubatko and Burns (2004); it has a formula $Rb_6Na_2[(UO_2)(CO_3)_3]_2(H_2O)$. Thermodynamic data from solubility measurements of uranyl minerals including grimselite were reviewed by Gorman-Lewis et al. (2008).

Occurrence and sample description

The grimselite specimens used in this study were found in old galleries at the 90 m level at the Rovnost shaft, Jáchymov ore district, Krušné Hory Mountains, Western Bohemia, Czech Republic (50º22′18.421″N, 12º53′32.83″E). Two specimens were studied; each is about $10 \times 5 \times 3.5$ cm, and made up of gangue minerals covered by Fe and Mn oxyhydroxides, which are X-ray amorphous. Rich aggregates of translucent light to grass green grimselite crystals to ~1 mm are present on the surfaces (Fig. 1) and prismatic čejkaite (confirmed by XRD) is also present.

Experimental

X-ray crystallography and crystal structure determination

Two samples were selected for analysis by single-crystal X-ray diffraction. Sample A is a $0.21 \times 0.14 \times 0.08$ mm fragment of a prismatic single crystal of grimselite, which was analysed using monochromatic Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å on an Oxford Diffraction Gemini single-crystal diffractometer equipped with an Atlas CCD area detector. The least squares unit cell refinement used 10,062 reflections and produced a hexagonal unit cell with $a = 9.2507(1)$, $c = 8.1788(1)$ Å and $V = 606.14(3)$ Å^3. Out of a total of 12,561 measured reflections, 664 were unique and 626 classified as observed [$I_{obs} > 3\sigma(I)$]. Data were corrected for background, Lorentz and polarization effects, and an analytical correction for absorption was applied (Clark and Reid, 1995), leading to a value of R_{int} for the merged data of 0.024. The structure of the synthetic analogue of grimselite determined by Li and Burns (2001) was used as a starting model, and the data refined using Jana2006 (Petříček et al., 2006) which produced values of $R_{obs} = 0.0082$ and $wR_{obs} = 0.0185$ with a GOF of 1.33. Despite the low R values the hydrogen atoms were not located in the structure. The absolute structure of this grimselite crystal was determined following the procedure of

Fɪɢ. 1. Grimselite crystals (thick prismatic, greenish) in association with čejkaite (fine crystalline acicular aggregates) on gangue. Field of view 4 mm; photo P. Škácha.

Flack (1983). Details of data collection and structure refinement are listed in Table 1. Final atom coordinates and displacement parameters are listed in Table 2. Selected interatomic distances and a bond valence analysis for sample A are provided in Tables 4 and 5, respectively.

Sample B is a $0.25 \times 0.20 \times 0.10$ mm fragment of a prismatic single crystal of grimselite. It was mounted in a Lindemann capillary and structural determinations made using monochromatic Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature on a Nonius KappaCCD diffractometer. The unit cell was refined on the basis of 9710 reflections, giving a hexagonal cell with $a = 9.3001(1)$, $c = 8.8294(2)$ Å and $V = 621.24(2)$ Å^3. A total of 12,084 reflections were measured up to $\theta_{max}=$ 27.5º; 514 were unique ($R_{int} = 0.065$) and 492 classified as observed [$I_{obs} > 3\sigma(I)$]. The structure was refined as above and converged to $R_{obs} =$ 0.0220 and $wR_{obs} = 0.0623$ with a GOF of 2.67 (see Table 1). Final atom coordinates and displacement parameters are listed in Table 3. Selected interatomic distances and a bond valence analysis for sample B are provided in Tables 6 and 7, respectively.

Electron-probe microanalysis

The chemical composition of grimselite samples from Jáchymov was studied using a Cameca

SX100 electron microprobe operating in wavelength-dispersive mode. An accelerating voltage of 15 kV, a beam current of 5 nA and a beam diameter of 20 μm were used to minimize the damage to the specimen. The following X-ray lines and standards were selected to minimize overlaps; $K\alpha$ lines: K (sanidine), Na (albite), Al (sanidine), Fe (andradite), Zn (ZnS), Si (sanidine) and P (fluorapatite); $M\alpha$ lines: U (rutherfordine). The elements Ca, Mg and Pb were sought, but their concentrations were below detection limits (0.02−0.10 wt.%). Counting times on the peaks were 10−20 s; the background counting times were half of the peak counting times. The measured intensities were converted to element concentrations using the PAP correction routine (Pouchou and Pichoir, 1985).

Results

Chemical composition

The chemical composition of sample A using the mean of 10 point analyses and calculated on the basis of (U + K + Na + Zn) = 5 a.p.f.u. is expressed by the empirical formula: $(K_{2.37}Na_{0.63})_{\Sigma3.00}(Na_{0.91}Zn_{0.01})_{\Sigma0.92}[(UO_2)_{1.082}$ $(CO_3)_{3.01}](SiO_4)_{0.01}(PO_4)_{0.01}(H_2O)_{1.00}$. This sample is characterized by Na$_2$O contents of up to 7.80 wt.% (with a mean of 7.31 wt.%), and these are significantly larger than the 5.17 wt.%

TABLE 1. Summary of data collection and refinement parameters for grimselite.

	Sample A $(K_{2.43}Na_{0.57})_{\Sigma 3.00}Na[(UO_2)(CO_3)_3](H_2O)$	Sample B $K_{3.00}Na[(UO_2)(CO_3)_3](H_2O)$
Structural formula		
Crystal data		
Unit-cell parameters (range, software)	(based on 10,062 reflections, $3.55° < \theta < 30.42°$, *CrysAlis Pro*)	(based on 9710 reflections, $1.00° < \theta < 27.50°$, *Collect*)
a (Å)	9.2507(1)	9.3000(1)
c (Å)	8.1788(1)	8.2940(2)
V (Å^3)	606.14(3)	621.24(2)
Z	2	2
Space group	$P\bar{6}2c$	$P\bar{6}2c$
Data collection		
Temperature	293 K	293 K
Collection mode	ω rotational scans to fill Ewald sphere	φ and ω rotational scans to fill Ewald sphere
Limiting θ angles	3.53–30.55°	3.53–27.5°
Limiting Miller indices	$-12 < h < 12$, $-13 < k < 13$, $-11 < l < 11$	$-12 < h < 12$, $-11 < k < 12$, $-10 < l < 10$
No. of reflections	12,561	12,084
No. of unique reflections	664	514
No. of observed reflections (criterion)	626 $[I_{obs}>3\sigma(I)]$	492 $[I_{obs}>3\sigma(I)]$
R_{int}, coverage	0.0243, 99.52%	0.0650, 99.0%
Absorption correction (mm^{-1}), method,	14.52, analytical (Clark and Reid, 1995)	14.16, Gaussian (Coppens, 1970),
T_{min}/T_{max}	0.158/0.425	0.0795/0.3185
F_{000}	539	549
Refinement details		
Parameters refined, constraints	41, 5	43, 0
R_1, wR_1	0.0082, 0.0185	0.0220, 0.0623
R_2, wR_2	0.0094, 0.0189	0.0230, 0.0627
GOF	1.33	2.67
Extinction type; coefficient		Gaussian; 0.022(7)
Friedel pairs, Flack parameter	274, $-0.01(1)$	212, 0.00(2)
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	-0.30, 0.36	-1.16, 2.19
Weighting scheme, details	σ, $w = 1/(\sigma^2(I) + 0.0001I^2)$	σ, $w = 1/(\sigma^2(I) + 0.0004I^2)$

TABLE 2. Atom positions, site occupancies, equivalent displacement parameters and anisotropic displacement parameters (Å^2) for grimselite sample A.

Site	Occupancy	x/a	y/b	z/c	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	2c		⅔	⅓	¾	0.01364(3)	0.01371(4)	0.01371(4)	0.01350(6)	0	0.00685(4)	0
K1	6g	0.821(5)	0.2897(1)	0	0	0.0355(3)	0.0420(4)	0.0335(4)	0.0282(4)	0.0168(4)	0.0047(2)	0.0095(4)
Na1	6g	0.179(5)	0.2897(1)	0	0	0.0355(3)	0.0420(4)	0.0335(4)	0.0282(4)	0.0168(4)	0.0047(2)	0.0095(4)
Na2	2d		⅓	⅔	¾	0.0283(3)	0.0347(5)	0.0347(5)	0.0154(6)	0.0173(5)	0	0
O1	6h		0.9697(2)	0.4800(5)	¾	0.0282(9)	0.0154(7)	0.021(1)	0.0499(9)	0.011(1)	0	0
O2	6h		0.8497(2)	0.6324(2)	¾	0.0314(9)	0.022(1)	0.025(1)	0.050(1)	0.0138(7)	0	0
O3	4f		⅔	⅓	0.9686(2)	0.0352(4)	0.0451(8)	0.0451(8)	0.0155(4)	0.0226(4)	0	0
O4	6h		0.1293(3)	0.7588(3)	¾	0.0341(8)	0.0208(9)	0.022(1)	0.051(1)	0.0045(8)	0	0
O5	4e	0.5	0	0	0.1122(1)	0.090(2)	0.093(3)	0.093(3)	0.084(5)	0.046(5)	0	0
C	6h		0.9887(4)	0.6296(4)	¾	0.024(1)	0.019(1)	0.021(1)	0.032(1)	0.010(1)	0	0

TABLE 3. Atom positions, site occupancies, equivalent displacement parameters and anisotropic displacement parameters (Å^2) for grimselite sample B.

Site	Occupancy	x/a	y/b	z/c	U^*_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	2c		⅔	⅓	¾	0.0165(2)	0.0149(2)	0.0149(2)	0.0197(3)	0.0075(11)	0	0
K	6g		0.2922(3)	0	0	0.0368(9)	0.0420(1)	0.036(1)	0.031(1)	0.01787(7)	0.0043(5)	0.009(1)
Na	2d		⅓	⅔	¾	0.027(1)	0.029(2)	0.029(2)	0.022(3)	0.0143(8)	0	0
O1	6h		0.9677(5)	0.478(1)	¾	0.026(3)	0.010(2)	0.020(4)	0.048(3)	0.008(3)	0	0
O2	6h		0.8475(8)	0.6299(9)	¾	0.023(3)	0.018(4)	0.036(3)	0.035(4)	0.017(3)	0	0
O3	4f		⅔	⅓	0.965(1)	0.031(2)	0.030(2)	0.030(2)	0.034(4)	0.015(4)	0	0
O4	6h		0.1281(9)	0.759(1)	¾	0.026(3)	0.023(3)	0.024(3)	0.050(5)	0.008(3)	0	0
O5	4e	0.5	0	0	0.130(2)	0.071(7)	0.083(9)	0.083(9)	0.05(1)	0.04(1)	0	0
C	6h		0.989(1)	0.632(1)	¾	0.022(3)	0.021(5)	0.016(4)	0.028(4)	0.009(3)	0	0

TABLE 4. Selected bond and interatomic distances (Å), and bond angles (°) for grimselite sample A.

U−O3	1.788(2) (2×)	C−O1	1.305(6)
U−O2	2.428(3) (2×)	C−O2	1.299(5)
U−O2	2.428(5)	C−O4	1.251(3)
U−O4	2.416(3) (3×)	O1−C−O4	122.49(4)
<O3−U−O3>	180	O2−C−O4	123.23(3)
<U−O$_{eq}$>	2.422	O1−C−O2	114.28(4)
		<O−C−O>	120
		<C−O>	1.285
		ECoN*	2.957
U−C	2.867(4)		
U−C	2.867(5) (2×)		
K1/Na1−O1	2.802(3) (2×)	Na2−O1	2.914(3) (2×)
K1/Na1−O2	2.700(2) (2×)	Na2−O1	2.914(5)
K1/Na1−O4	2.838(2) (2×)	Na2−O3	2.301(3) (2×)
K1/Na1−O5	2.860(3) (2×)	Na2−O4	2.428(3)
<K1/Na1−O>	2.800	Na2−O4	2.428(4)(2×)
ECoN*	7.838	<Na2−O>	2.579
		ECoN*	5.362
O1−O2	2.199(5)	O2−O4	2.244(4)
O1−O2	2.664(4)	O2−O5	3.141(4) (2×)
O1−O3	3.015(3) (2×)	O4−O5	3.190(4) (2×)
O1−O4	2.241(5)	O5−O5	2.00(1)
O1−O4	3.143(5)	O5−O5	2.09(1)
O2−O3	3.006(3) (2×)		

* ECoN is the effective coordination number after Hoppe (1979).

Na_2O that would be found in ideal $K_3Na[(UO_2)(CO_3)_3](H_2O)$. The composition of sample B was similar to synthetic (ideal stoichiometric) grimselite with an empirical formula using the mean of 4 point analyses and calculated on the basis of (U + K + Na + Zn) = 5 a.p.f.u. of $K_{3.06}(Na_{0.90}Fe_{0.01}Al_{0.01})_{\Sigma 0.92}$ $[(UO_2)_{1.02}(CO_3)_{3.00}](H_2O)_{1.00}$.

TABLE 5. Bond valence analysis* for the crystal structure of grimselite sample A.

	O1	O2	O3	O4	O5	ΣBV
U	0.47 ×3→	0.48 ×3→	1.65 ×2→			6.15
C	1.26	1.28		1.46		4.00
K1**	0.15 ×2↓→	0.19 ×2↓→		0.13 ×2↓→	0.13 ×3↓	1.07
Na2	0.05 ×3→		0.26 ×2→	0.18 ×3→		1.21
ΣBV	2.08	2.14	1.91	1.90	0.39	

* Values are expressed in valence units (vu). ΣBV, bond-valence sums; ×2↓→, multiplicity; U^{6+}−O bond strengths (r_0 = 2.042, b = 0.506) from Burns *et al*. (1997); C^{4+}−O, K−O and Na−O bond strengths are from Brown and Altermatt (1985).
** The site occupancy ratio K1/Na1 of 0.826/0.174 was used in calculations.

TABLE 6. Selected interatomic distances (Å), and bond angles (º) for the crystal structure of grimselite sample B.

U−O3	1.785(8) (2×)	C−O1	1.35(2)
U−O2	2.425(4) (2×)	C−O2	1.30(2)
U−O2	2.43(2)	C−O4	1.25(1)
U−O4	2.408(7)	O1−C−O2	112.2(8)
U−O4	2.408(8)	O1−C−O4	122.7(13)
U−O4	2.41(1)	O2−C−O4	125.1(3)
<O3−U−O3>	180	<O−C−O>	120
<U−O$_{eq}$>	2.418	<C−O>	1.298
		ECoN*	2.875
U−C	2.890(9)		
U−C	2.89(2) (2×)		
K−O1	2.809(9) (2×)	Na−O1	2.945(4) (2×)
K−O2	2.730(6)	Na−O1	2.95(2)
K−O2	2.730(7)	Na−O3	2.362(8) (2×)
K−O4	2.869(5)	Na−O4	2.45(1) (3×)
K−O4	2.869(7)	<Na−O>	2.615
K−O5	2.925(8) (2×)	ECoN*	5.563
<K−O>	2.826		
ECoN*	7.785		
O1−O2	2.20(2)	O2−O5	3.16(1) (2×)
O1−O2	2.27(1)	O2−O3	2.80(1)
O1−O3	3.011(6) (2×)	O4−O5	3.18(1) (2×)
O1−O3	3.01(1)	O5−O5	1.98(3)
O1−O4	2.27(1)	O5−O5	2.16(3)
O1−O4	3.17(1)		
O2−O4	2.26(1)		
O2−O5	3.156(9)		

* ECoN is the effective coordination number after Hoppe (1979).

Description of the crystal structures

The crystal structure of natural grimselite is similar to the structure determined by Li and Burns (2001) for synthetic $K_3Na[(UO_2)(CO_3)_3](H_2O)$. However, in contrast to the synthetic analogue, the corresponding MO_8 polyhedra in sample A contain both Na and K (see below).

TABLE 7. Bond valence analysis* for the crystal structure of grimselite sample B.

	O1	O2	O3	O4	O5	ΣBV
U	0.47 ×3→	0.49 ×3→	1.66 ×2→			6.20
C	1.13	1.26		1.48		3.87
K	0.16 ×2↓→	0.21 ×2↓→		0.14 ×2↓→	0.12 ×3↓	1.14
Na	0.05 ×3→		0.22 ×2→	0.17 ×3→		1.10
ΣBV	1.97	2.17	1.88	1.93	0.36	

* Values are expressed in valence units (vu). ΣBV, bond-valence sums; ×2↓→, multiplicity; U^{6+}−O bond strengths (r_0 = 2.042, b = 0.506) from Burns *et al.* (1997); C^{4+}−O, K−O and Na−O bond strengths are from Brown and Altermatt (1985).
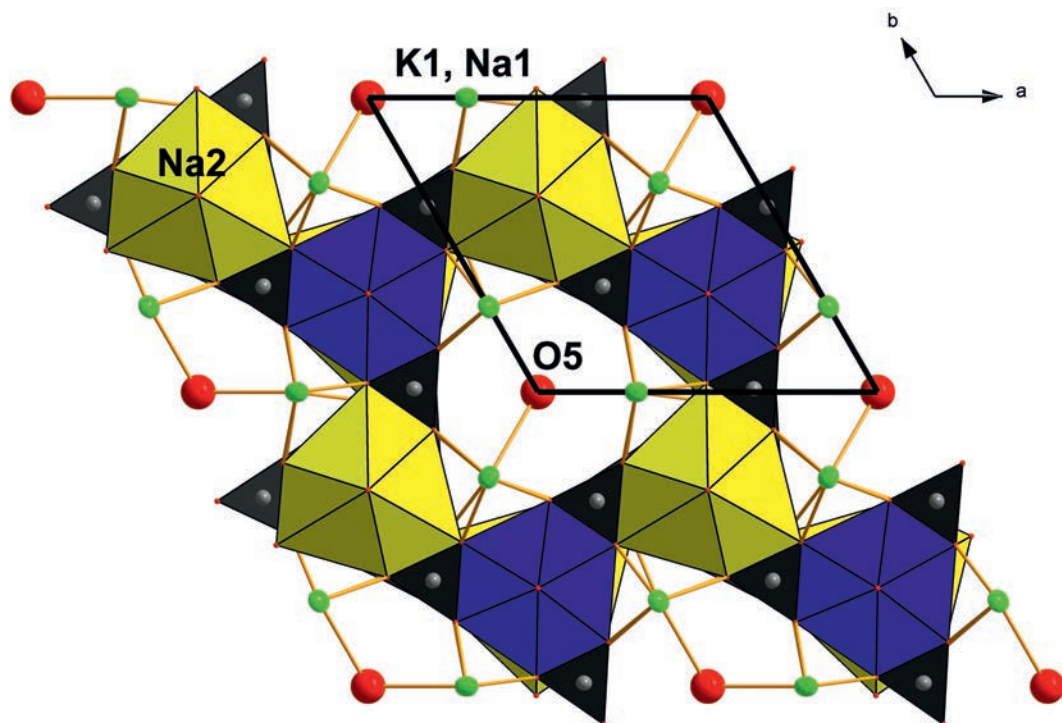
FIG. 2. The heteropolyhedral framework of grimselite projected along [001]. Uranyl hexagonal bipyramids are blue; adjacent planar CO_3^{2-} groups are black (with a grey central C atom); NaO_8 hexagonal bipyramids are yellow and the K1 (or Na1) position is green; and oxygen atoms are red. The unit-cell edges are outlined using a solid black line.
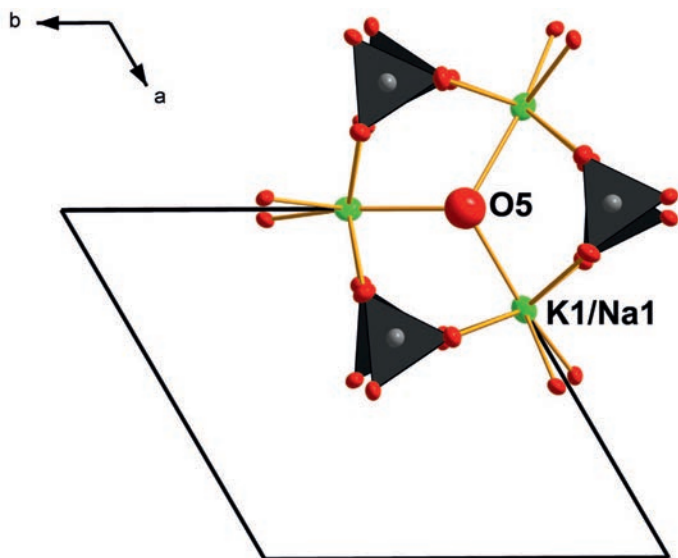

FIG. 3. Details of coordination of the O5 atom within the channel voids in the structure of grimselite. Planar CO_3^{2-} groups are black (with a grey central C atom); the K1 (or Na1) position is green; and oxygen atoms are red. The unit-cell edges are outlined using a solid black line. Thermal ellipsoids are drawn at the 50% probability level.
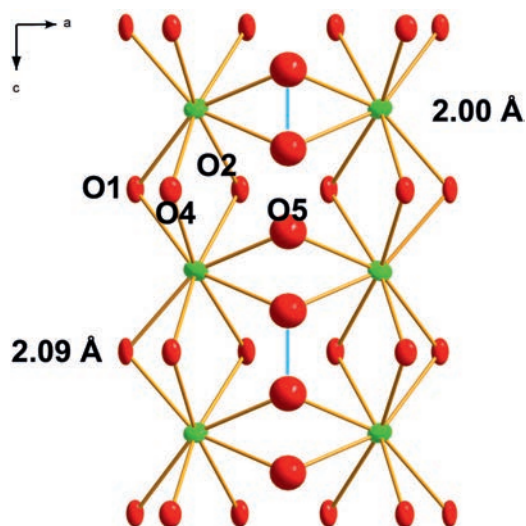
FIG. 4. The coordination environment around K1/Na1 (light green) in the structure of grimselite. The short separation distance between O5 atoms of molecular H_2O is apparent. Thermal ellipsoids are drawn at the 50% probability level.

The crystal structure of grimselite is a heteropolyhedral framework that consists of uranyl tricarbonate clusters linked in layers parallel to (001) by sharing polyhedral elements with NaO_8 hexagonal bipyramids (Fig. 2). Each

NaO_8 hexagonal bipyramid shares three equatorial edges with three CO_3^{2-} planar groups, and three equatorial vertices with three UO_2O_6 hexagonal bipyramids. The sheets are linked by the sharing of apical vertices between the UO_8 and NaO_8 bipyramids. The voids in the heteropolyhedral framework contain dominant K^+ cations and H_2O groups (Fig. 3). Site-occupancy refinement of the K position provided significantly reduced occupancy values. The other sites are fully occupied. Taking into account the results of the chemical analysis (Table 8), Na^+ cations were introduced at the K-dominated site and their presence verified by subsequent refinement. The ratio of K:Na atoms, produced by the refinement, is 0.413(5):0.087(5), resulting in a formula which is written $(K_{2.43}Na_{0.57})_{\Sigma3.00}$. Potassium and sodium atoms are coordinated by 8 oxygen atoms, two of which are molecular H_2O (the O5 atoms), on the basis of bond valence analysis (Table 5). The O5−O5 site (4e) separation is quite low [2.09(1) and 2.00(1) Å] for the site with the full occupancy, and hence locally only one of the two sites can be occupied at one time in each $(K,Na)O_8$ polyhedron (Fig. 4).

Effect of cationic substitution

In addition to the synthetic analogue of grimselite *sensu stricto* (Li and Burns, 2001), Kubatko and Burns (2004) reported the Rb analogue of grimselite, with a formula $Rb_6Na_2[(UO_2)$

TABLE 8. Chemical compositions of the grimselite samples.

Oxide	Ideal formula*	– (K,Na) Grimselite (sample A) –			— Grimselite (sample B) —		
		Mean (10 analyses)	Range	SD	Mean (4 analyses)	Range	SD
Na_2O	5.17	7.31	6.70−7.80	0.34	4.74	4.53−4.96	0.18
K_2O	23.57	17.14	16.26−18.11	0.55	24.56	24.31−24.74	0.21
FeO					0.09	0.00−0.29	0.14
Al_2O_3					0.03	0.00−0.09	0.04
ZnO		0.07	0.00−0.21	0.08			
CO_2**	22.03	20.30	19.51−20.91	0.45	22.47	22.19−22.71	0.22
P_2O_5		0.08	0.00−0.18	0.07			
SiO_2		0.11	0.00−0.41	0.14			
UO_3	47.72	47.45	46.16−49.47	0.98	49.62	48.48−50.45	1.16
H_2O	1.50	1.38	1.34−1.42	0.03	1.53	1.53−1.54	0.01
Total	99.99	93.84			103.05		

* Composition (wt.% oxide) of the ideal formula, $K_3Na[(UO_2)(CO_3)_3](H_2O)$.
** The CO_2 content calculated to produce charge balance.

TABLE 9. Comparison of polyhedral volumes and distortion indices for MO_8 polyhedra in crystal structures of natural grimselite and synthetic samples.

Sample	(K,Na) grimselite[1]	Natural grimselite[2]	Synthetic grimselite[3]	$Rb_6Na_2[(UO_2)(CO_3)_3]_2(H_2O)$[4]
V_p (Å^3)	32.670	33.412	33.443	38.478
Δ	0.0173	0.0222	0.0227	0.0306

[1] Mixed $(K,Na)O_8$ polyhedron from Jáchymov, sample A, this paper.
[2] KO_8 polyhedron, Jáchymov, sample B, this paper.
[3] KO_8 polyhedron, synthetic (Li and Burns, 2001).
[4] RbO_8 polyhedron, synthetic Rb^+ analogue of grimselite (Kubatko and Burns, 2004).
The symbol V_p is the polyhedral volume; Δ is the bond-length distortion after Brown and Shannon (1973).

$(CO_3)_3]_2(H_2O)$. Therefore, at least three large univalent cations, Na, K and Rb, can occur at the MO_8 polyhedral site in materials with a grimselite structure. In view of the differences in effective ionic radii (Na is 1.18 Å, K is 1.51 Å and Rb is 1.61 Å; Shannon, 1976), a change in polyhedral volume should be expected. The polyhedral volumes of the relevant polyhedra are listed in Table 9, together with distortion indices. The distortion indices expressed as bond length distortions, defined on the basis of Brown and Shannon (1973), suggest that the mixed $(K,Na)O_8$ polyhedron is more regular, than the larger RbO_8 polyhedron.

Acknowledgements

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