ORIGINAL PAPER

Agricolaite, a new mineral of uranium from Jáchymov, Czech Republic

Roman Skála • Petr Ondruš • František Veselovský • Ivana Císařová • Jan Hloušek

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Abstract The new mineral agricolaite, a potassium uranyl carbonate with ideal formula $K_4(UO_2)(CO_3)_3$, occurs in vugs of ankerite gangue in gneisses in the abandoned Giftkiesstollen adit at Jáchymov, Czech Republic. The name is after Georgius Agricola (1494–1555), German scholar and scientist. Agricolaite occurs as isolated equant irregular translucent grains to 0.3 mm with yellow color, pale yellow streak, and vitreous luster. It is brittle with uneven fracture and displays neither cleavage nor parting. Agricolaite is non-fluorescent. Mohs hardness is ~4. It is associated with aragonite, brochantite, posnjakite, malachite, rutherfordine, and "pseudo-voglite". Experimental density is higher than 3.3 g.cm⁻³, Dcalc is 3.531 g.cm⁻³. The mineral is monoclinic, space group C2/c, with a

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10.2380(2), b 9.1930(2), c 12.2110(3) Å, β 95.108(2)°, V 1144.71(4) Å³, Z=4. The strongest lines in the powder Xray diffraction pattern are d(I)(hkl): 6.061(55)(002), 5.087 (57)(200), 3.740(100)(202), 3.393(43)(113), 2.281(52) (402). Average composition based on ten electron microprobe analyses corresponds to (in wt.%) UO3 48.53, K2O 31.49, $CO_2(calc)$ 22.04 which gives the empirical formula $K_{3,98}(UO_2)_{1,01}(CO_3)_{3,00}$. The crystal structure was solved from single-crystal X-ray diffraction data and refined to $R_1=0.0184$ on the basis of the 1,308 unique reflections with $F_{o} > 4\sigma F_{o}$. The structure of agricolaite is identical to that of synthetic $K_4(UO_2)(CO_3)_3$ and consists of separate UO₂(CO₃)₃ groups organized into layers parallel to (100) and two crystallographically non-equivalent sites occupied by K^+ cations. Both the mineral and its name were approved by the IMA-CNMNC.

Introduction

In this paper, the new uranyl carbonate mineral agricolaite, found in Jáchymov (Czech Republic), is described. The new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA No. 2009–081). The name agricolaite is after Georgius Agricola (1494–1555), German scholar and scientist, "Father of Mineralogy", and author of the famous book *De re Metallica Libri XII* (1556). Agricola lived in Jáchymov between 1527 and 1531 and wrote there his first scientific work, *Bermannus sive de re Metallica* (1530) discussing matters of geology and mining that were representative of the region around Jáchymov where silver was mined at this time. The name "agricolite" was introduced to the literature in 1873 by Frenzel (Frondel 1943) for a monoclinic mineral of composition SiO₂ 16.67,



Fig. 1 Scanning electron microscope image of an isolated grain of agricolaite representing a complex aggregate of crystals

 Bi_2O_3 81.82, Fe_2O_3 0.90, total 99.39 wt.% found at Schneeberg and Johanngeorgenstadt in Germany. Later, Frondel (1943) showed the identity of "agricolite" with eulytite ($Bi_4(SiO_4)_3$) so the name became obsolete. The name has not been officially in use for more than 50 years. We also suggest using the form "agricolaite" instead of "agricolite"; the former clearly shows the correct Latin root "Agricola" which was not so in the earlier case. The holotype of agricolaite is deposited in the mineral collections of the National Museum in Prague, Czech Republic, under the catalogue number P1p 17/2009.

Occurrence, physical properties, and origin

Agricolaite was found by two of the authors (FV and JH) in the abandoned Giftkiesstollen adit at Jáchymov, Czech Republic. The city of Jáchymov (St. Joachimsthal in German) is located on southern slopes of the Krušné hory Mts. (Erzgebirge) approximately 20 km north of Karlovy Vary, NW Bohemia, Czech Republic. The city lies at the center of the Jáchymov ore district hosting several types of mineralizations. Details on geology and mineralogy may be found elsewhere (Ondruš et al. 1997, 2002, 2003 and references therein).

The new mineral forms small isolated equant irregular translucent grains to 0.3 mm (Fig. 1). It is of yellow color and vitreous luster. Agricolaite is brittle with uneven fracture, displays a pale yellow streak, and neither cleavage nor parting were observed. Agricolaite is non-fluorescent. Mohs hardness is ~4. Density was determined to be higher than that of methylen iodide (3.3 g.cm⁻³). There was not enough material for weighting methods and since the material is water soluble the density cannot be determined by flotation techniques using Clerici solution. The density calculated from empirical formula and unit cell volume is 3.531 g.cm^{-3} . The mean refractive index, obtained from the Gladstone-Dale relationship (Mandarino 1981) using the empirical chemical composition and calculated density, is 1.6.

Agricolaite grains sit on a thin layer of an X-rayamorphous earthy silicate material or on very thin platy crystals of pale blue-green color. The subtle character of these crystals prevents an XRD study. Based on EDX spectroscopic data, the earthy crust contains major K and Si, and subordinate Al and O. The platy crystals are composed of prevailing K, with minor Cu, S, and O. This association occurs in vugs of ankerite gangue or grows on aragonite and malachite. At a distance of the order of tenths of mm other associated minerals occur: aragonite, brochantite, posnjakite, and malachite. Further away (centimeters to decimeters) rutherfordine and "pseudo-voglite" (sensu Ondruš et al. 1997) were identified. Agricolaite represents the youngest member of the mineral assemblage.

The source of uranium for the mineral formation may be either rutherfordine or weathered uraninite. Ankerite, forming thin veinlets and rock impregnations, most likely

Constituent	Wt.%	Range	Stand. dev.	Probe standard
Na ₂ O	0.02	0.00-0.05	0.02	albite
K ₂ O	31.49	29.6-32.64	1.00	sanidine
MgO	0.01	0.00-0.03	0.01	spinel
CaO	0.01	0.00-0.06	0.02	andradite
FeO	0.02	0.00-0.07	0.02	andradite
PbO	0.03	0.00-0.14	0.05	vanadinite
Al_2O_3	0.01	0.00-0.04	0.01	sanidine
$CO_2(calc)$	22.04	20.52-22.91	0.80	by stoichiometry
SiO ₂	0.03	0.00-0.11	0.04	sanidine
UO ₃	48.58	46.95-49.9	0.89	rutherfordine
Total	102.24	99.45-104.32	1.74	

Table 1Summary of theanalytical data for agricolaite(ten electron microprobeanalyses)

 Table 2
 X-ray powder data for agricolaite

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18.2 2.11/2 2.11/2 2.11/2 2.11/2 2.11/2 2.11/2 2.11/2 2.11/2 2.11/2 2.11/2 2.11/2 3 4 5.3 0.7 1.43/3 1.44/3 5 3 4 14.3 49.7 2.66178 2.6705 $\overline{1}$ 3 2 7.4 1.7 1.43/3 1.43/3 5 3 4 5.5 7.1 2.6121 2.6146 $\overline{3}$ 1 3 12.1 2.9 1.43/3 1.43/3 1.43/3 6 0 4 6 0 6 7 6.5 1.4148 1.4149 7 1 1 1 5 7 1.5 1.43/3 1.32/1 4 2 7 7 1 3 3 5.3 1.5 1.249/1 1.249/1 6 0 6 <td>5.9</td> <td>/.6</td> <td>2.8659</td> <td>2.8704</td> <td>1</td> <td>3</td> <td>1</td> <td>6.9</td> <td>1.5</td> <td>1.4430</td> <td>1.4441</td> <td>1</td> <td>1</td> <td>1</td>	5.9	/.6	2.8659	2.8704	1	3	1	6.9	1.5	1.4430	1.4441	1	1	1
14.349.72.66782.67051327.41.71.43741.43815345.57.12.61212.6146 $\overline{3}$ 1312.12.91.43031.43076045.98.62.53472.53610247.12.41.32181.32174275.41.42.51342.51522046.80.31.32011.320371333.09.82.40832.41083135.31.51.24911.249160614.025.32.33792.3410 $\overline{2}$ 245.97.11.21621.2161001017.510.52.33322.3356 $\overline{1}$ 15 7.2 2.71.20861.20863195.617.92.25992.2806402 7.1 1.21621.2161001017.71.32.15072.1500025 7.2 2.71.20861.20863195.617.92.2494115 7.2 2.71.20861.208631910.58.72.04382.0431422 7.4 1.71.43741.44112.426.52.05142.05292411	18.2	32.3	2.7172	2.7199	2 1	0	4	6.3	0.7	1.4430	1.4435	6	2	3
5.5 7.1 2.6121 2.6146 3 1 3 12.1 2.9 1.4303 1.430/ 6 0 4 8.0 2.7 2.5485 2.5501 4 0 0 6.7 6.5 1.4148 1.4149 7 1 1 5.9 8.6 2.5347 2.5361 0 2 4 7.1 2.4 1.3218 1.3217 4 2 7 5.4 1.4 2.5132 2 0 4 6.8 0.3 1.3201 1.3203 7 1 3 33.0 9.8 2.4083 2.4108 3 1 3 5.3 1.5 1.2491 1.2491 6 0 6 14.0 25.3 2.3379 2.3410 2 2 4 5.9 7.1 1.2162 1.2161 0 0 10 7.5 2.62 2.2805 2.2806 4 0 2 7 1.2086 1.2086 3 1 9 5.6 17.9 2.2477	14.3	49.7	2.6678	2.6705	1	3	2	7.4	1.7	1.4374	1.4381	5	3	4
8.02.72.54852.55014006.76.51.41481.41497115.98.62.53472.53610247.12.41.32181.32174275.41.42.51342.51522046.80.31.32011.32037133.09.82.40832.41083135.31.51.24911.249160614.025.32.33792.34102245.97.11.21621.2161001017.510.52.33322.33561157.22.71.20861.208631951.926.22.28052.280640271.21621.2161001017.510.52.33322.35072.1500025772.62.11402.1144314417.719.32.15072.15000255552.31402.1144314410.58.72.04382.043142225557.31.52.02602.026906610.317.92.02112.021442334Chemical analyses of agricolaite were carried out with a <td>5.5</td> <td>7.1</td> <td>2.6121</td> <td>2.6146</td> <td>3</td> <td>1</td> <td>3</td> <td>12.1</td> <td>2.9</td> <td>1.4303</td> <td>1.4307</td> <td>6</td> <td>0</td> <td>4</td>	5.5	7.1	2.6121	2.6146	3	1	3	12.1	2.9	1.4303	1.4307	6	0	4
5.98.62.53472.33610247.12.41.32181.32174275.41.42.51342.51522046.80.31.32011.320371333.09.82.40832.41083135.31.51.24911.249160614.025.32.33792.34102245.97.11.21621.2161001017.510.52.33322.3356T157.22.71.20861.20863195.617.92.25992.2590041711.719.32.15072.15000255.72.62.11402.1144314411.719.32.15072.15000255.72.62.05142.052924110.58.72.04382.04314227.31.52.02602.02690610.317.92.02112.02144237.94.71.99071.99335118.94.01.93721.93895118.94.01.93721.93895118.94.01.93721.93895118.9<	8.0	2.7	2.5485	2.5501	4	0	0	6.7	6.5	1.4148	1.4149	7	1	1
5.41.42.51342.51522046.80.31.32011.320371333.09.82.40832.41083135.31.51.249160614.025.32.33792.3410 $\overline{2}$ 245.97.11.21621.2161001017.510.52.33322.3356 $\overline{1}$ 157.22.71.20861.208631951.926.22.28052.2806402 $\overline{7}$ 1.71.20861.20863195.617.92.25992.2590041 $\overline{7}$ $\overline{7}$ 2.62.1402.14431411.719.32.15072.1500025 $\overline{7}$ $\overline{7}$ 2.6C.11402.114431412.426.52.05142.052924115 $\overline{7}$	5.9	8.6	2.5347	2.5361	0	2	4	7.1	2.4	1.3218	1.3217	4	2	7
33.09.82.40832.41083135.31.51.24911.249160614.025.32.33792.3410 $\overline{2}$ 245.97.11.21621.2161001017.510.52.33222.3356 $\overline{1}$ 157.22.71.20861.208631951.926.22.28052.28064027.22.71.20861.20863195.617.92.25992.259004157.22.71.20861.208631911.719.32.15072.150002557.22.62.11402.114431410.58.72.05142.052924115served as a source of CO2.Potassium came most probably7.86.62.04062.0393 $\overline{2}$ 25from micas, one of the main constituents of the gneissesnosting the mineralization.10.317.92.02112.0214 $\overline{4}$ 23346.52.31.92631.92772255.27.51.87551.8767 $\overline{3}$ 346.52.31.92631.92772255.27.51.87551.86073156.52.31.92631.927	5.4	1.4	2.5134	2.5152	2	0	4	6.8	0.3	1.3201	1.3203	7	1	3
14.025.32.33792.34102245.97.11.21621.2161001017.510.52.33322.3356 $\overline{1}$ 157.22.71.20861.208631951.926.22.28052.28064027.22.71.20861.20863195.617.92.25992.259004116.13.52.24772.249411155.72.62.11402.114431444441155.72.62.11402.11443144	33.0	9.8	2.4083	2.4108	3	1	3	5.3	1.5	1.2491	1.2491	6	0	6
17.510.52.33322.33561157.22.71.20861.208631951.926.22.28052.28064025.617.92.25992.25900416.13.52.24772.24941157.72.62.15072.15000255.72.62.11402.114431412.426.52.05142.052924110.58.72.04382.04314227.86.62.04062.03932257.31.52.02602.026900610.317.92.02112.02144237.94.71.99071.93335118.94.01.93721.93895116.52.31.92631.92772255.27.51.87551.876733440.37.11.87291.87364047.82.41.85951.86073155.27.51.87551.87673346.52.31.92631.92772255.27.51.87551.86073155.23.11.85411.854702	14.0	25.3	2.3379	2.3410	2	2	4	5.9	7.1	1.2162	1.2161	0	0	10
51.926.22.28052.28064025.617.92.25992.25900416.13.52.24772.249411511.719.32.15072.15000255.72.62.11402.114431412.426.52.05142.052924110.58.72.04382.04314227.86.62.04062.03932257.31.52.02602.026900610.317.92.02112.02144237.94.71.99071.99335118.94.01.92772255.27.51.87551.876733440.37.11.87291.87364047.82.41.85951.86073155.27.51.87551.8767334Chemical analyses of agricolaite were carried out with aCAMECA SX-100electron microprobe in wavelength-7.82.41.85470261.85421.82872062.351.7894267.41.85551.7894267.51.87551.8287267.61.82821.82872 <td< td=""><td>17.5</td><td>10.5</td><td>2.3332</td><td>2.3356</td><td>1</td><td>1</td><td>5</td><td>7.2</td><td>2.7</td><td>1.2086</td><td>1.2086</td><td>3</td><td>1</td><td>9</td></td<>	17.5	10.5	2.3332	2.3356	1	1	5	7.2	2.7	1.2086	1.2086	3	1	9
5.617.92.25992.259004116.13.52.24772.24941151.719.32.15072.15000255.72.62.11402.114431412.426.52.05142.052924110.58.72.04382.04314227.86.62.04062.0393 $\overline{2}$ 257.31.52.02602.02690610.317.92.02112.0214 $\overline{4}$ 237.94.71.99071.9933 $\overline{5}$ 118.94.01.93721.93895118.94.01.93721.93895116.52.31.92631.92772255.27.51.87551.8767 $\overline{3}$ 3440.37.11.87291.876404CAMECA SX-100 electron microprobe in wavelength-7.82.41.85951.8607315dispersive mode. Accelerating voltage was 15 kV, beam5.23.51.82821.8287206content was calculated by stoichiometry. Since the proposed6.52.31.85411.8547026content was calculated by stoichiometry. Since the proposed6.52.31.85411.8547026 <t< td=""><td>51.9</td><td>26.2</td><td>2.2805</td><td>2.2806</td><td>4</td><td>0</td><td>2</td><td>Dine 178</td><td>additional 1</td><td>ince with inte</td><td>ncity bolow 4</td><td>on a n</td><td>proont a</td><td></td></t<>	51.9	26.2	2.2805	2.2806	4	0	2	Dine 178	additional 1	ince with inte	ncity bolow 4	on a n	proont a	
6.13.52.24772.2494115 $\int_{calc} calculated from the refined crystal structure of agricolate with the program DIAMOND v. 3.2 g (Crystal Impact GbR, Bonn, Germany)11.719.32.15072.15000255.72.62.11402.114431412.426.52.05142.052924110.58.72.04382.04314227.86.62.04062.03932257.31.52.02602.02690610.317.92.02112.02144237.94.71.99071.99335118.94.01.93721.93895118.94.01.93721.93895116.52.31.92631.9277225.27.51.87551.8767346.41.85951.86073155.24.31.85411.8547026.52.31.85411.8547026.52.31.85411.8547026.51.82821.82872066.51.82821.82872066.52.31.85411.8547027.82.41.85470267.82.4.31.8541$	5.6	17.9	2.2599	2.2590	0	4	1	I colo	adultional i	the refined or	ustal atmusture	of agric		th the
11.719.32.15072.15000255.72.62.11402.114431412.426.52.05142.052924110.58.72.04382.04314227.86.62.04062.0393 $\overline{2}$ 257.31.52.02602.026900610.317.92.02112.0214 $\overline{4}$ 237.94.71.99071.9933 $\overline{5}$ 118.94.01.93721.93895118.94.01.93721.93895116.52.31.92631.9277225.27.51.87551.8767 $\overline{3}$ 3440.37.11.87291.87364047.82.41.85951.86073155.24.31.85411.854702662.018.51.82821.8287206content was calculated by stoichiometry. Since the proposed5.23.51.78951.7904 $\overline{2}$ 265.23.51.78951.7904 $\overline{2}$ 266666667.87.91.78951.7904 $\overline{2}$ 26666667.87	6.1	3.5	2.2477	2.2494	1	1	5	program	DIAMOND	v. 3.2 g (Crv	stal Impact G	bR. Bor	in. Gern	nanv)
5.72.62.11402.114431412.426.52.05142.052924110.58.72.04382.04314227.86.62.04062.0393 $\overline{2}$ 257.31.52.02602.02690610.317.92.02112.0214 $\overline{4}$ 237.94.71.99071.9933 $\overline{5}$ 118.94.01.93721.93895116.52.31.92631.92772255.27.51.87551.8767 $\overline{3}$ 3440.37.11.87291.87364047.82.41.85951.86073155.24.31.85411.85470266.52.31.82821.82872067.82.4.31.85411.85470267.81.8551.82821.82872067.81.85411.8547026content was calculated by stoichiometry. Since the proposed5.23.51.78951.7904 $\overline{2}$ 26mineral is identical with synthetic K.(UO2)(CO2). (Anderson)	11.7	19.3	2.1507	2.1500	0	2	5	The corr	ection term	applied to the	data was cos	$s\theta \times \cot\theta$	∂/λ^2	
12.426.52.05142.052924110.58.72.04382.04314227.86.62.04062.0393 $\overline{2}$ 257.31.52.02602.026900610.317.92.02112.0214 $\overline{4}$ 237.94.71.99071.9933 $\overline{5}$ 118.94.01.93721.93895118.94.01.93721.93895116.52.31.92631.92772255.27.51.87551.8767 $\overline{3}$ 3440.37.11.87291.87364047.82.41.85951.86073155.24.31.85411.85470265.24.31.85411.8547026current 5nA and beam diameter 20 μ m. Carbon dioxidecontent was calculated by stoichiometry. Since the proposed5.23.51.78951.7904 $\overline{2}$ 26	5.7	2.6	2.1140	2.1144	3	1	4	1110 0011		applied to the	adda wab cos	0010		
10.58.72.04382.043142227.86.62.04062.0393 $\overline{2}$ 257.31.52.02602.026900610.317.92.02112.0214 $\overline{4}$ 237.94.71.99071.9933 $\overline{5}$ 118.94.01.93721.93895116.52.31.92631.92772255.27.51.87551.8767 $\overline{3}$ 3440.37.11.87291.87364047.82.41.85951.86073155.24.31.85411.8547026current 5nA and beam diameter 20 μ m. Carbon dioxidecontent was calculated by stoichiometry. Since the proposed5.23.51.78951.7904 $\overline{2}$ 26	12.4	26.5	2.0514	2.0529	2	4	1							
7.86.62.04062.0393 $\overline{2}$ 25Solved as a source of Copy Foldssham came most producty7.81.52.02602.026900610.317.92.02112.0214 $\overline{4}$ 237.94.71.99071.9933 $\overline{5}$ 118.94.01.93721.93895116.52.31.92631.92772255.27.51.87551.8767 $\overline{3}$ 3440.37.11.87291.87364047.82.41.85951.86073155.24.31.85411.85470265.23.51.82821.8287206current 5 nA and beam diameter 20 μ m. Carbon dioxidecontent was calculated by stoichiometry. Since the proposed5.23.51.78951.7904 $\overline{2}$ 26	10.5	8.7	2.0438	2.0431	4	2	2	served	as a source	e of CO ₂ P	otassium ca	ame mo	ost prol	hahlv
7.31.52.02602.026900610.317.92.02112.0214 $\overline{4}$ 237.94.71.99071.9933 $\overline{5}$ 118.94.01.93721.93895116.52.31.92631.92772255.27.51.87551.8767 $\overline{3}$ 34Chemical analyses of agricolaite were carried out with a40.37.11.87291.8736404CAMECA SX-100 electron microprobe in wavelength-7.82.41.85951.8607315dispersive mode. Accelerating voltage was 15 kV, beam5.24.31.85411.8547026content was calculated by stoichiometry. Since the proposed20.18.51.82821.8287206mineral is identical with synthetic K $_{4}(UO_{2})(CO_{2})_{5}$ (Anderson	7.8	6.6	2.0406	2.0393	$\overline{2}$	2	5	from m	icas, one	of the main $\frac{1}{2}$	1 constituer	nts of t	he gne	eisses
10.317.92.02112.0214 $\overline{4}$ 237.94.71.99071.9933 $\overline{5}$ 118.94.01.93721.93895116.52.31.92631.92772255.27.51.87551.8767 $\overline{3}$ 34Chemical analyses of agricolaite were carried out with a40.37.11.87291.8736404CAMECA SX-100 electron microprobe in wavelength-7.82.41.85951.8607315dispersive mode. Accelerating voltage was 15 kV, beam5.24.31.85411.8547026current 5 nA and beam diameter 20 μ m. Carbon dioxide20.18.51.82821.8287206content was calculated by stoichiometry. Since the proposed5.23.51.78951.7904 $\overline{2}$ 26mineral is identical with synthetic K 4(UOs)(COs) (Anderson)	7.3	1.5	2.0260	2.0269	0	0	6	hosting	the miner	alization.			B	
7.94.71.99071.9933 $\overline{5}$ 118.94.01.93721.93895116.52.31.92631.92772255.27.51.87551.8767 $\overline{3}$ 34Chemical analyses of agricolaite were carried out with a40.37.11.87291.8736404CAMECA SX-100 electron microprobe in wavelength-7.82.41.85951.8607315dispersive mode. Accelerating voltage was 15 kV, beam5.24.31.85411.8547026current 5 nA and beam diameter 20 μ m. Carbon dioxide20.18.51.82821.8287206content was calculated by stoichiometry. Since the proposed5.23.51.78951.7904 $\overline{2}$ 26mineral is identical with synthetic K 4(UOs)(COs) (Anderson)	10.3	17.9	2.0211	2.0214	4	2	3	nooting						
8.9 4.0 1.9372 1.9389 5 1 1 Chemical data 6.5 2.3 1.9263 1.9277 2 2 5 5.2 7.5 1.8755 1.8767 $\overline{3}$ 3 4 Chemical analyses of agricolaite were carried out with a 40.3 7.1 1.8729 1.8736 4 0 4 CAMECA SX-100 electron microprobe in wavelength- 7.8 2.4 1.8595 1.8607 3 1 5 dispersive mode. Accelerating voltage was 15 kV, beam 5.2 4.3 1.8541 1.8547 0 2 6 current 5 nA and beam diameter 20 μ m. Carbon dioxide 20.1 8.5 1.8282 1.8287 2 0 6 content was calculated by stoichiometry. Since the proposed 5.2 3.5 1.7895 1.7904 $\overline{2}$ 2 6 mineral is identical with synthetic K (UOc)(COc)). (Anderson	7.9	4.7	1.9907	1.9933	5	1	1							
6.52.31.92631.92772255.27.51.87551.8767 $\overline{3}$ 34Chemical analyses of agricolaite were carried out with a40.37.11.87291.8736404CAMECA SX-100 electron microprobe in wavelength-7.82.41.85951.8607315dispersive mode. Accelerating voltage was 15 kV, beam5.24.31.85411.8547026current 5 nA and beam diameter 20 μ m. Carbon dioxide20.18.51.82821.8287206content was calculated by stoichiometry. Since the proposed5.23.51.78951.7904 $\overline{2}$ 26mineral is identical with synthetic K 4(UOc)(COc).	8.9	4.0	1.9372	1.9389	5	1	1	Chemi	cal data					
5.27.51.87551.8767 $\overline{3}$ 34Chemical analyses of agricolaite were carried out with a40.37.11.87291.8736404CAMECA SX-100 electron microprobe in wavelength-7.82.41.85951.8607315dispersive mode. Accelerating voltage was 15 kV, beam5.24.31.85411.8547026current 5 nA and beam diameter 20 μ m. Carbon dioxide20.18.51.82821.8287206content was calculated by stoichiometry. Since the proposed5.23.51.78951.7904 $\overline{2}$ 26mineral is identical with synthetic K (UOc)(COc) (Anderson	6.5	2.3	1.9263	1.9277	2	2	5	Chemi	cur untu					
40.37.11.87291.8736404CAMECA SX-100 electron microprobe in wavelength-7.82.41.85951.8607315dispersive mode. Accelerating voltage was 15 kV, beam5.24.31.85411.8547026current 5 nA and beam diameter 20 μ m. Carbon dioxide20.18.51.82821.8287206content was calculated by stoichiometry. Since the proposed5.23.51.78951.7904 $\overline{2}$ 26mineral is identical with synthetic K (UOc)(COc). (Anderson	5.2	7.5	1.8755	1.8767	3	3	4	Chemic	al analyse	s of agrico	laite were	carried	out w	vith a
7.82.41.85951.8607315dispersive mode. Accelerating voltage was 15 kV, beam5.24.31.85411.8547026current 5 nA and beam diameter 20 μ m. Carbon dioxide20.18.51.82821.8287206content was calculated by stoichiometry. Since the proposed5.23.51.78951.7904 $\overline{2}$ 26mineral is identical with synthetic K (UQc)(CQc)) (Anderson	40.3	7.1	1.8729	1.8736	4	0	4	CAME	CA SX-10	0 electron	microprol	be in y	vavele	ngth-
5.2 4.3 1.8541 1.8547 0 2 6 current 5 nA and beam diameter 20 μ m. Carbon dioxide 20.1 8.5 1.8282 1.8287 2 0 6 content was calculated by stoichiometry. Since the proposed 5.2 3.5 1.7895 1.7904 $\overline{2}$ 2 6 mineral is identical with synthetic K ₄ (UO ₂)(CO ₂) ₂ (Anderson	7.8	2.4	1.8595	1.8607	3	1	5	disnersi	ive mode	Acceleration	ig voltage	was 14	5 kV	heam
20.1 8.5 1.8282 1.8287 2 0 6 content was calculated by stoichiometry. Since the proposed 5.2 3.5 1.7895 1.7904 $\overline{2}$ 2 6 mineral is identical with synthetic K ₄ (UO ₂)(CO ₂) ₂ (Anderson	5.2	4.3	1.8541	1.8547	0	2	6	current	5 nA and	beam diar	neter 20 11	n. Carl	on di	oxide
5.2 3.5 1.7895 1.7904 $\overline{2}$ 2 6 mineral is identical with synthetic K ₄ (UO ₂)(CO ₂). (Anderson	20.1	8.5	1.8282	1.8287	2	0	6	content	was calcul	lated by sto	ichiometrv	Since f	he proi	oosed
	5.2	3.5	1.7895	1.7904	$\overline{2}$	2	6	mineral	is identica	l with synth	etic K ₄ (UO-)(CO ₂)	(And	erson

et al. 1980; Han et al. 1990) and only limited quantity of

natural material was available for the study, the experimental

 Table 3 Data collection and structure refinement details for agricolaite
 Structural formula $K_4UO_2(CO_3)_3$ 606.46 Formula weight Temperature 293(2) K Wavelength 0.71073Å Crystal system, space group monoclinic, C2/c Unit-cell dimensions $\alpha = 90^{\circ}$ a=10.2380(2) Å b=9.1930(2) Å $\beta = 95.108(2)^{\circ}$ c=12.2110(3) Å $\gamma = 90^{\circ}$ V=1144.71(4) Å³ Z, Calculated density 4, 3.519 g/cm³ 15.687 mm⁻¹ Absorption coefficient *F*(000) 1096 Theta range for data collection 2.98 to 27.49° Limiting indices $-13 \le h \le 13, -11 \le k \le 11, -15 \le l \le 15$ Reflections collected/unique $7409/1308 [R_{int} = 0.0531]$ Completeness to theta = 27.49° 100.0% Refinement method Full-matrix least-squares on F^2 Data/restraints/parameters 1308/0/89 Goodness-of-fit on F^2 1.149 Final *R* indices $[F_0 > 4\sigma F_0]$ $R_1 = 0.0184, wR_2 = 0.0466$ R indices (all data) $R_1 = 0.0186, wR_2 = 0.0467$ Extinction coefficient 0.0093(3)Largest diff. peak and hole 1.243 and -1.341 e.Å-3 $R_1 = \sum ||F_0| - |F_c|| \sum |F_0|$

 $wR_2 = \left\{ \sum \left[w \left(F_o^2 - F_c^2 \right)^2 \right] / \Sigma w \left(F_o^2 \right)^2 \right\}^{1/2}$ GooF = $\left\{\sum \left[w(F_0^2 - F_c^2)^2\right]/(n-p)\right\}^{1/2}$ where n = 1308 and p = 89 $w = 1/[\sigma^2(F_0^2) + (0.0225 \times P)^2 + 3.98 \times P]$ where $P = [2F_{c}^{2} + Max(F_{0}^{2}, 0)]/3$

determination of CO2 was not carried out. Analytical data and probe standards are given in Table 1. The empirical formula of agricolaite based on five cations per formula unit is K_{3.98}(UO₂)_{1.01}(CO₃)_{3.00}. The simplified formula is $K_4(UO_2)(CO_3)_3$ which requires (in wt.%): K_2O 31.07, UO_3 47.16, CO₂ 21.77. Agricolaite, based on its chemical composition, belongs to the class of uranyl carbonates with ratio $UO_2:CO_3 = 1:3$ (code 5.E) in the Strunz classification scheme (Strunz and Nickel 2001).

X-ray diffraction study

The X-ray powder diffraction pattern of agricolaite was collected with a Philips X'Pert diffractometer. Copper radiation was monochromatized with a secondary graphite monochromator. The angular range was 10 to $120^{\circ}2\theta$, step size $0.02^{\circ}2\theta$ and counting time per step 15 s. The diffraction data demonstrated identity of the mineral with synthetic $K_4(UO_2)(CO_3)_3$. Peak positions and intensities

Table 4 orthogon	Atomic coordinates alized U_{ij} tensor. The	t, equivalent isotro e anisotropic displa	pic displacement cement factor exp	parameters and an onent takes the for	insotropic displacer m: $-2\pi^2 (h^2 a^{*2} U_{11})$	nent parameters (A + \dots + 2 <i>hka</i> * <i>b</i> * <i>U</i>	 tor agricolaite. ¹₁₂). 	U _{eq} is defined as	one third of the	e trace of the
Atom	x	У	Ν	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U1	0.5	0.694506(17)	0.25	0.01135(10)	0.01226(13)	0.01019(13)	0.01178(13)	0	0.00210(7)	0
K1	0.68394(8)	0.34580(10)	0.34698(7)	0.02091(18)	0.0188(4)	0.0222(4)	0.0217(4)	0.0048(3)	0.0018(3)	-0.0013(3)
K2	0.60216(9)	0.81946(9)	0.54382(7)	0.02047(19)	0.0199(4)	0.0219(4)	0.0200(4)	-0.0034(3)	0.0036(3)	-0.0032(3)
C1	0.6278(3)	0.5382(4)	0.0860(3)	0.0150(6)	0.0150(16)	0.0165(16)	0.0135(15)	0.0002(13)	0.0017(12)	-0.0021(12)
C2	0.5	1.0072(6)	0.25	0.0171(9)	0.019(2)	0.010(2)	0.022(2)	0	0.0045(19)	0
01	0.5423(3)	0.9296(3)	0.1706(2)	0.0210(6)	0.0312(16)	0.0137(13)	0.0198(13)	0.0011(11)	0.0113(12)	0.0011(9)
02	0.6042(3)	0.6780(3)	0.0783(2)	0.0166(5)	0.0208(14)	0.0122(12)	0.0173(13)	0.0015(10)	0.0052(11)	0.0018(9)
03	0.5648(3)	0.4733(3)	0.1611(2)	0.0188(5)	0.0246(14)	0.0147(12)	0.0183(12)	-0.0010(10)	0.0087(11)	(6)6000.0
04	0.5	1.1431(4)	0.25	0.0235(8)	0.035(2)	0.0109(18)	0.027(2)	0	0.0120(17)	0
05	0.7016(3)	0.4733(3)	0.0279(2)	0.0258(6)	0.0310(16)	0.0218(14)	0.0265(14)	0.0080(12)	0.0142(12)	0.0000(11)
90	0.6619(3)	0.6966(3)	0.3205(3)	0.0200(6)	0.0172(14)	0.0230(16)	0.0195(14)	-0.0011(9)	0.0004(12)	0.0016(9)

the

Table 5 Selected bond lengths						
(Å) and angles (°) for agricolaite	U106	1.799(3) 2×	K1–O3	2.742(3) 1×	C1–O5	1.235(5) 1×
	U101	2.423(3) 2×	K1–O2	2.750(3) 1×	C1–O2	1.310(5) 1×
	U1–O3	2.425(3) 2×	K1–O5	2.758(3) 1×	C1–O3	1.311(5) 1×
	U1O2	2.440(3) 2×	K1–O3	2.797(3) 1×	<c1-0></c1-0>	1.285
	$<$ U $-$ O $>$ $_{Ur}$	1.799	K1–O4	2.833(3) 1×		
	$<$ U $-$ O $>_{Eq}$	2.430	K1–O1	2.933(3) 1×	C2-O4	1.249(7) 1×
			K1–O2	3.017(3) 1×	C2-O1	1.308(4) 2×
	O3–U1–O2	53.51(9)	K1–O6	3.022(4) 1×	<c2–o></c2–o>	1.289
	01–U1–O1	53.80(9)	<k1–o></k1–o>	2.857		
	O3–U1–O3	66.04(9)				
	O1–U1–O2	66.70(9)	K2–O5	2.668(3) 1×	O5-C1-O2	123.45(33)
	O6-U1-O3	86.91(12)	K2–O2	2.796(3) 1×	O5-C1-O3	123.11(32)
	O6-U1-O2	87.54(13)	K2-O6	2.809(3) 1×	O2-C1-O3	113.44(31)
	O6-U1-O1	89.36(11)	K2–O4	2.832(1) 1×		
	O6-U1-O1	89.55(11)	K2–O1	2.875(3) 1×	O4-C2-O1	123.05(12)
	O6-U1-O2	92.53(13)	K2–O5	2.890(3) 1×	O1-C2-O1	113.91(16)
	O6-U1-O3	94.12(12)	K2-O1	3.062(3) 1×		
	O2-U1-O2	172.87(9)	K2–O6	3.063(4) 1×	C201U1	96.15(14)
	O1–U1–O3	173.00(9)	K2–O3	3.088(3) 1×	C1-O2-U1	95.24(20)
	O6-U1-O6	178.78(14)	<k2–o></k2–o>	2.898		
	O2 O3	2.191(4) 2×			O3 O3	2.643(4) 1×
	01 01	2.193(4) 1×			01 02	2.674(4) 2×

were extracted from the powder data by the program XFIT which employs a fundamental-parameters approach to profile shape fitting (Coelho and Cheary 1997; Cheary and Coelho 1992, 1998a, b; Cheary et al. 2004). The peak positions were used for unit-cell dimensions refinement by the program of Burnham (1962). Sample displacement was corrected during the procedure. A total of 201 lines were resolved in the pattern and 254 indices assigned to them based on the theoretical diffraction pattern generated from the crystal structure data of Anderson et al. (1980). Three cycles of least square refinement provided unit-cell parameters a 10.2410(6), b 9.196(1), c 12.2096(8) Å, β 95.095 (6)°, V 1145.3(1) Å³. Powder data are listed in Table 2. Although indexing is satisfactory, we observe notable discrepancies between intensities calculated from the structure data and those obtained from powder pattern refinement. They can obviously be attributed to severe preferred orientation. This preferred orientation is not trivial because it cannot be explained with a simple increase or decrease of intensities parallel to a particular crystallographic plane, which indicates, considering lack of observable cleavage, complex shaping of grains after grinding for powder diffraction study.

The single-crystal X-ray diffraction study was carried out with a Nonius KappaCCD four-circle diffractometer. Details on data collection and refinement are summarized in Table 3. Unit-cell dimensions refined from the singlecrystal data are a 10.2380(2), b 9.1930(2), c 12.2110(3) Å, β 95.108(2)°, V 1144.71(4) Å³. Structure refinement was performed starting from the model of Anderson et al. (1980) with the SHELX-97 package (Sheldrick 2008) operated through the WinGX graphic user interface (Farrugia

Table 6	Bond	valence	analysis
for agri	colaite		

Bond valence parameters taken from Burns et al. (1997) for U and from Brown and Altermatt (1985) for the rest of the elements

	01	02	03	O4	05	O6	Σ
U1	$0.487 \xrightarrow{\times 2 \rightarrow}$	$0.473 \xrightarrow{\times 2 \rightarrow}$	0.486 ^{×2→}			1.625 ^{×2→}	6.142
K1	0.115	0.188 ± 0.091	0.192+0.166	0.150	0.184	0.090	1.176
K2	0.135 ± 0.081	0.166	0.075	0.151	0.236 ± 0.129	0.161 ± 0.081	1.215
C1		1.241	1.241		1.516		3.998
C2	1.248 ^{×2→}			1.464			3.960
Σ	2.066	2.159	2.160	1.765	2.065	1.957	

Fig. 2 Coordination environment of uranium (a) and potassium (b, c) in the crystal structure of agricolaite. Thermal ellipsoid probability 90%



1999). The structural features are identical to those presented for synthetic analog by Anderson et al. (1980) and Han et al. (1990). Final positional and displacement parameters are given in Table 4; selected bond distances are listed in Table 5, and the results of a bond-valence analysis performed with the program VaList (Wills 2010) are given in Table 6.

Description of the structure

The crystal structure of agricolaite is of a cluster type as defined by Burns (2005) and Schindler and Hawthorne (2008).

Agricolaite is isostructural with compounds $X_4(UO_2)$ (CO₃)₃ where X = Cs, Tl, Rb and (NH)₄ (Krivovichev and Burns 2004; Chernorukov et al. 2005). This type of structure consists of $[(UO_2)(CO_3)_3]^{4-}$ complexes which do

not share any common element; in between these clusters there are two symmetrically non-equivalent sites occupied in the case of agricolaite with potassium. In the uranyl tricarbonate complex, each of the carbonate triangular (CO₃) groups shares one of its edges with an equatorial edge of the (UO_8) hexagonal dipyramid. The hexagonal dipyramid is markedly flattened with short interatomic distances along its vertical axis. The average distance $\langle U-O \rangle$ _{Ur} in the uranyl group is 1.80Å while the average distance in the equatorial plane of the (UO_8) dipyramid attains 2.43Å. These values are close to those given by Burns et al. (1997): ^[8]U- $O_{Ur} \sim 1.78(3)$ Å and ^[8]U- $\Phi_{Ea} \sim 2.47(12)$ Å, respectively. The lengths of equatorial edges of the dipyramid depend on whether they are shared with carbonate groups or not: those being shared are shorter by almost 20% (Table 5). The geometry of the whole $[(UO_2)(CO_3)_3]^{4-1}$ complex is shown in Fig. 2a.

Fig. 3 Crystal structure of agricolaite projected on the (010) plane (a), and viewed down to the [001] axis (b) and along the [100] axis (c). The equatorial plane of the (UO₈) hexagonal dipyramids (shown in *light grey*) is inclined by 26.3° to the **c** axis while the angle between the vertical axis of the (UO₈) dipyramids and the **c**-axis is 66.6° (**a**). Uranyl-carbonate complexes are organized to layers parallel to the (100) plane (b). Two adjacent layers of uranyl-carbonate groups display a herringbone-like pattern. The lower layer is dimmed. Carbonate groups are shown as dark grey triangles. (c) Potassium atoms are presented as thermal ellipsoids





Fig. 4 Crystal structure of agricolaite viewed along [110]. Structure elements are arranged into columns

The effective coordination number (ECoN, Hoppe 1979) for uranium is 7.83 demonstrating the fact that this polyhedron is extremely irregular as already noted above. At the same time the ECoN for C1 and C2 sites are 3.01 and 3.00, respectively, illustrating very little departure from ideal geometry. The coordination environment around the K⁺ ions is much more complicated (Fig. 2b, c). ECoNs for sites K1 and K2 are 8.03 and 9.03, respectively. This is in agreement with data of Anderson et al. (1980) and Han et al. (1990). The complex coordination geometry around the K1 and K2 sites is also responsible for notable discrepancies in the bond-valence sums for K1, K2 and O4 (Table 6).

Equatorial planes of individual (UO₈) hexagonal dipyramids are inclined by ~26.3° to the **c** axis (Fig. 3a) which means that they are roughly parallel to the (503) plane. The angle between the vertical axis of the (UO₈) dipyramids and the **c** axis is ~66.6°. Single $[(UO_2)(CO_3)_3]^{4-}$ groups are organized, as indicated by Krivovichev and Burns (2004), into layers parallel to the (100) plane (Fig. 3b). Individual uranyl carbonate groups are arranged in a herringbone-like pattern within these layers (Fig. 3c). Adjacent layers are mutually shifted by [½, ½, 0]. When viewed along [110] individual structure elements appear organized to columns including K1 and K2 sites placed between columns of (UO₂)(CO₃)₃ groups (Fig. 4).

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