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ORIGINAL PAPER

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

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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$^{-3}$, *D*calc is 3.531 g.cm$^{-3}$. The mineral is monoclinic, space group *C*2/*c*, with *a* 10.2380(2), *b* 9.1930(2), *c* 12.2110(3) Å, $\beta$ 95.108(2)°, *V* 1144.71(4) Å$^3$, *Z*=4. The strongest lines in the powder X-ray 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.%) $UO_3$ 48.53, $K_2O$ 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 $UO_2(CO_3)_3$ 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.

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## 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 $SiO_2$ 16.67,

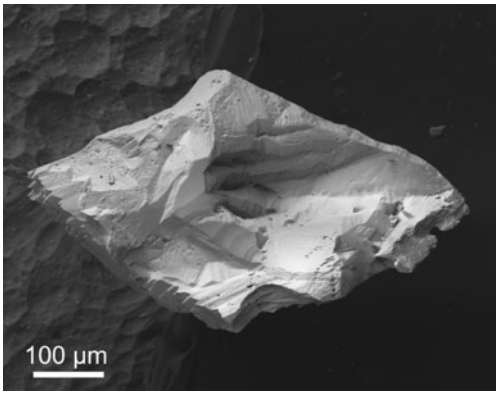


**Fig. 1** Scanning electron microscope image of an isolated grain of agricolaite representing a complex aggregate of crystals

$Bi_2O_3$ 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-ray-amorphous 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

**Table 1** Summary of the analytical data for agricolaite (ten electron microprobe analyses)

| Constituent | Wt.% | Range | Stand. dev. | Probe standard |
|---|---|---|---|---|
| $Na_2O$ | 0.02 | 0.00–0.05 | 0.02 | albite |
| $K_2O$ | 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 2** X-ray powder data for agricolaite

| $I_{meas}$ | $I_{calc}$ | $d_{meas}$ | $d_{calc}$ | $h$ | $k$ | $\ell$ |
|---|---|---|---|---|---|---|
| 10.9 | 27.6 | 6.814 | 6.830 | 1 | 1 | 0 |
| 22.0 | 100.0 | 6.085 | 6.112 | $\bar{1}$ | 1 | 1 |
| 55.0 | 52.2 | 6.061 | 6.081 | 0 | 0 | 2 |
| 29.8 | 82.4 | 5.793 | 5.810 | 1 | 1 | 1 |
| 57.3 | 49.4 | 5.087 | 5.100 | 2 | 0 | 0 |
| 8.2 | 22.7 | 4.593 | 4.598 | 0 | 2 | 0 |
| 6.1 | 16.0 | 4.297 | 4.301 | 0 | 2 | 1 |
| 15.5 | 20.1 | 4.087 | 4.091 | $\bar{2}$ | 0 | 2 |
| 100.0 | 39.9 | 3.740 | 3.747 | 2 | 0 | 2 |
| 6.5 | 17.2 | 3.657 | 3.667 | 0 | 2 | 2 |
| 9.3 | 17.9 | 3.575 | 3.581 | $\bar{1}$ | 1 | 3 |
| 6.7 | 12.4 | 3.4110 | 3.4151 | 2 | 2 | 0 |
| 43.5 | 56.3 | 3.3932 | 3.3985 | 1 | 1 | 3 |
| 22.6 | 44.2 | 3.2339 | 3.2381 | 2 | 2 | 1 |
| 24.7 | 40.4 | 3.1436 | 3.1499 | $\bar{3}$ | 1 | 1 |
| 5.3 | 9.5 | 3.0522 | 3.0562 | $\bar{2}$ | 2 | 2 |
| 21.2 | 8.4 | 3.0360 | 3.0403 | 0 | 0 | 4 |
| 17.5 | 15.7 | 3.0199 | 3.0237 | 3 | 1 | 1 |
| 5.9 | 7.6 | 2.8659 | 2.8704 | $\bar{1}$ | 3 | 1 |
| 18.2 | 32.3 | 2.7172 | 2.7199 | $\bar{2}$ | 0 | 4 |
| 14.3 | 49.7 | 2.6678 | 2.6705 | $\bar{1}$ | 3 | 2 |
| 5.5 | 7.1 | 2.6121 | 2.6146 | $\bar{3}$ | 1 | 3 |
| 8.0 | 2.7 | 2.5485 | 2.5501 | 4 | 0 | 0 |
| 5.9 | 8.6 | 2.5347 | 2.5361 | 0 | 2 | 4 |
| 5.4 | 1.4 | 2.5134 | 2.5152 | 2 | 0 | 4 |
| 33.0 | 9.8 | 2.4083 | 2.4108 | 3 | 1 | 3 |
| 14.0 | 25.3 | 2.3379 | 2.3410 | $\bar{2}$ | 2 | 4 |
| 17.5 | 10.5 | 2.3332 | 2.3356 | $\bar{1}$ | 1 | 5 |
| 51.9 | 26.2 | 2.2805 | 2.2806 | 4 | 0 | 2 |
| 5.6 | 17.9 | 2.2599 | 2.2590 | 0 | 4 | 1 |
| 6.1 | 3.5 | 2.2477 | 2.2494 | 1 | 1 | 5 |
| 11.7 | 19.3 | 2.1507 | 2.1500 | 0 | 2 | 5 |
| 5.7 | 2.6 | 2.1140 | 2.1144 | 3 | 1 | 4 |
| 12.4 | 26.5 | 2.0514 | 2.0529 | 2 | 4 | 1 |
| 10.5 | 8.7 | 2.0438 | 2.0431 | 4 | 2 | 2 |
| 7.8 | 6.6 | 2.0406 | 2.0393 | $\bar{2}$ | 2 | 5 |
| 7.3 | 1.5 | 2.0260 | 2.0269 | 0 | 0 | 6 |
| 10.3 | 17.9 | 2.0211 | 2.0214 | $\bar{4}$ | 2 | 3 |
| 7.9 | 4.7 | 1.9907 | 1.9933 | $\bar{5}$ | 1 | 1 |
| 8.9 | 4.0 | 1.9372 | 1.9389 | 5 | 1 | 1 |
| 6.5 | 2.3 | 1.9263 | 1.9277 | 2 | 2 | 5 |
| 5.2 | 7.5 | 1.8755 | 1.8767 | $\bar{3}$ | 3 | 4 |
| 40.3 | 7.1 | 1.8729 | 1.8736 | 4 | 0 | 4 |
| 7.8 | 2.4 | 1.8595 | 1.8607 | 3 | 1 | 5 |
| 5.2 | 4.3 | 1.8541 | 1.8547 | 0 | 2 | 6 |
| 20.1 | 8.5 | 1.8282 | 1.8287 | 2 | 0 | 6 |
| 5.2 | 3.5 | 1.7895 | 1.7904 | $\bar{2}$ | 2 | 6 |
| 13.4 | 10.0 | 1.7715 | 1.7725 | 3 | 3 | 4 |
| 5.6 | 8.0 | 1.7412 | 1.7423 | $\bar{1}$ | 5 | 2 |
| 20.3 | 3.8 | 1.7293 | 1.7292 | 5 | 1 | 3 |
| 9.4 | 8.2 | 1.7083 | 1.7082 | $\bar{1}$ | 1 | 7 |
| 7.5 | 2.8 | 1.7000 | 1.7001 | 6 | 0 | 0 |
| 7.8 | 6.2 | 1.6979 | 1.6992 | 2 | 2 | 6 |
| 5.7 | 8.4 | 1.6979 | 1.6984 | 5 | 3 | 0 |
| 5.4 | 5.2 | 1.6764 | 1.6773 | 4 | 4 | 1 |
| 6.1 | 6.1 | 1.6764 | 1.6764 | $\bar{6}$ | 0 | 2 |
| 9.3 | 3.5 | 1.6599 | 1.6603 | 1 | 1 | 7 |
| 5.9 | 2.2 | 1.6251 | 1.6252 | 0 | 2 | 7 |
| 5.2 | 5.3 | 1.6105 | 1.6110 | $\bar{5}$ | 1 | 5 |
| 8.3 | 0.6 | 1.6041 | 1.6053 | 5 | 3 | 2 |
| 5.4 | 5.8 | 1.6041 | 1.6035 | 5 | 1 | 4 |
| 10.6 | 4.4 | 1.6010 | 1.6009 | 6 | 0 | 2 |
| 7.4 | 1.0 | 1.5746 | 1.5750 | $\bar{6}$ | 2 | 2 |
| 7.3 | 3.0 | 1.5221 | 1.5223 | 4 | 0 | 6 |
| 14.8 | 2.1 | 1.4792 | 1.4794 | 5 | 1 | 5 |
| 7.6 | 0.0 | 1.4742 | 1.4749 | 3 | 1 | 7 |
| 7.4 | 2.3 | 1.4451 | 1.4451 | 4 | 2 | 6 |
| 6.9 | 1.5 | 1.4430 | 1.4441 | $\bar{7}$ | 1 | 1 |
| 6.3 | 0.7 | 1.4430 | 1.4435 | 6 | 2 | 3 |
| 7.4 | 1.7 | 1.4374 | 1.4381 | 5 | 3 | 4 |
| 12.1 | 2.9 | 1.4303 | 1.4307 | 6 | 0 | 4 |
| 6.7 | 6.5 | 1.4148 | 1.4149 | 7 | 1 | 1 |
| 7.1 | 2.4 | 1.3218 | 1.3217 | 4 | 2 | 7 |
| 6.8 | 0.3 | 1.3201 | 1.3203 | 7 | 1 | 3 |
| 5.3 | 1.5 | 1.2491 | 1.2491 | 6 | 0 | 6 |
| 5.9 | 7.1 | 1.2162 | 1.2161 | 0 | 0 | 10 |
| 7.2 | 2.7 | 1.2086 | 1.2086 | 3 | 1 | 9 |

Plus 178 additional lines with intensity below 5 on a percent scale

$I_{calc}$ calculated from the refined crystal structure of agricolaite with the program *DIAMOND* v. 3.2 g (Crystal Impact GbR, Bonn, Germany)

The correction term applied to the data was $\cos\theta \times \cot\theta/\lambda^2$

served as a source of $CO_2$. Potassium came most probably from micas, one of the main constituents of the gneisses hosting the mineralization.

## Chemical data

Chemical analyses of agricolaite were carried out with a CAMECA SX-100 electron microprobe in wavelength-dispersive mode. Accelerating voltage was 15 kV, beam current 5 nA and beam diameter 20 μm. Carbon dioxide content was calculated by stoichiometry. Since the proposed mineral is identical with synthetic $K_4(UO_2)(CO_3)_3$ (Anderson 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 | $K_4UO_2(CO_3)_3$ | |
| Formula weight | 606.46 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system, space group | monoclinic, *C*2/*c* | |
| Unit-cell dimensions | $a$=10.2380(2) Å | $\alpha$=90° |
| | $b$=9.1930(2) Å | $\beta$=95.108(2)° |
| | $c$=12.2110(3) Å | $\gamma$=90° |
| | $V$=1144.71(4) Å$^3$ | |
| *Z*, Calculated density | 4, 3.519 g/cm$^3$ | |
| Absorption coefficient | 15.687 mm$^{-1}$ | |
| *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 [$F_o > 4\sigma F_o$] | $R_1$=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$^{-3}$ | |

$R_1 = \sum ||F_o| - |F_c|| \sum |F_o|$

$wR_2 = \left\{\sum \left[w\left(F_o^2 - F_c^2\right)^2\right] / \Sigma w\left(F_o^2\right)^2\right\}^{1/2}$

$\text{GooF} = \left\{\sum \left[w\left(F_o^2 - F_c^2\right)^2\right] / (n-p)\right\}^{1/2}$ where $n = 1308$ and $p = 89$

$w = 1/\left[\sigma^2\left(F_o^2\right) + (0.0225 \times P)^2 + 3.98 \times P\right]$

where $P = \left[2F_c^2 + \text{Max}\left(F_o^2, 0\right)\right]/3$

determination of $CO_2$ 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 $K_{3.98}(UO_2)_{1.01}(CO_3)_{3.00}$. The simplified formula is $K_4(UO_2)(CO_3)_3$ which requires (in wt.%): $K_2O$ 31.07, $UO_3$ 47.16, $CO_2$ 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°2θ, step size 0.02°2θ 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** Atomic coordinates, equivalent isotropic displacement parameters and anisotropic displacement parameters (Å$^2$) for agricolaite. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor. The anisotropic displacement factor exponent takes the form: $-2\pi^2\left(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}\right)$.

| Atom | *x* | *y* | *z* | $U_{eq}$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 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 |
| O1 | 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) |
| O2 | 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) |
| O3 | 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) | 0.0009(9) |
| O4 | 0.5 | 1.1431(4) | 0.25 | 0.0235(8) | 0.035(2) | 0.0109(18) | 0.027(2) | 0 | 0.0120(17) | 0 |
| O5 | 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) |
| O6 | 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) |

**Table 5** Selected bond lengths (Å) and angles (°) for agricolaite

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| U1–O6 | 1.799(3) | 2× | K1–O3 | 2.742(3) | 1× | C1–O5 | 1.235(5) 1× |
| U1–O1 | 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× |
| U1–O2 | 2.440(3) | 2× | K1–O3 | 2.797(3) | 1× | <C1–O> | 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> | 1.289 |
| O1–U1–O1 | 53.80(9) | | <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× | C2–O1–U1 | 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> | 2.898 | | | |
| O2 … O3 | 2.191(4) | 2× | | | | O3 … O3 | 2.643(4) 1× |
| O1 … O1 | 2.193(4) | 1× | | | | O1 … O2 | 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, $\beta$ 95.095 (6)°, $V$ 1145.3(1) Å$^3$. 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 single-crystal data are $a$ 10.2380(2), $b$ 9.1930(2), $c$ 12.2110(3) Å, $\beta$ 95.108(2)°, $V$ 1144.71(4) Å$^3$. 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 agricolaite

| | O1 | O2 | O3 | O4 | O5 | O6 | Σ |
|---|---|---|---|---|---|---|---|
| U1 | 0.487 $^{\times 2\rightarrow}$ | 0.473 $^{\times 2\rightarrow}$ | 0.486 $^{\times 2\rightarrow}$ | | | 1.625 $^{\times 2\rightarrow}$ | 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 $^{\times 2\rightarrow}$ | | | 1.464 | | | 3.960 |
| Σ | 2.066 | 2.159 | 2.160 | 1.765 | 2.065 | 1.957 | |

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

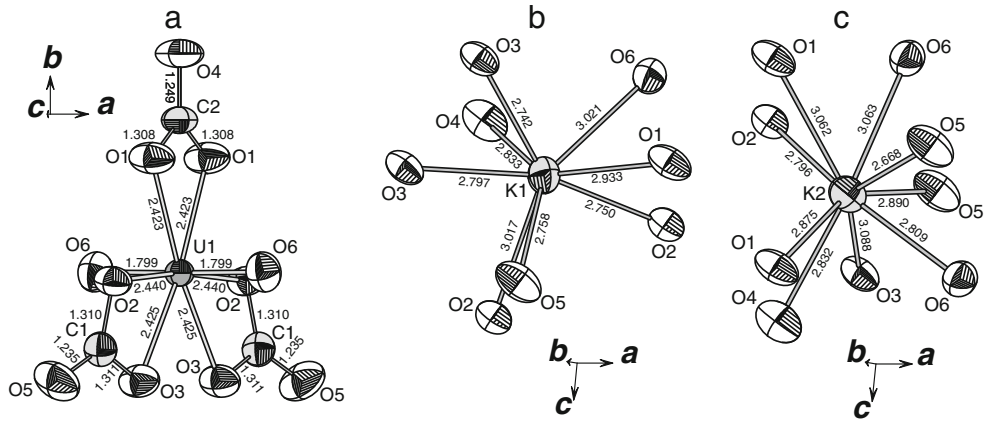


**Fig. 2** Coordination environment of uranium (**a**) and potassium (**b**, **c**) in the crystal structure of agricolaite. Thermal ellipsoid probability 90%

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 $X_4(UO_2)(CO_3)_3$ 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 ($CO_3$) 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 $\langle U\text{-}O\rangle_{Ur}$ in the uranyl group is 1.80 Å while the average distance in the equatorial plane of the ($UO_8$) dipyramid attains 2.43 Å. These values are close to those given by Burns et al. (1997): $^{[8]}U\text{-}O_{Ur} \sim 1.78(3)$ Å and $^{[8]}U\text{-}\Phi_{Eq} \sim 2.47(12)$ 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 $[(UO_2)(CO_3)_3]^{4-}$ complex is shown in Fig. 2a.

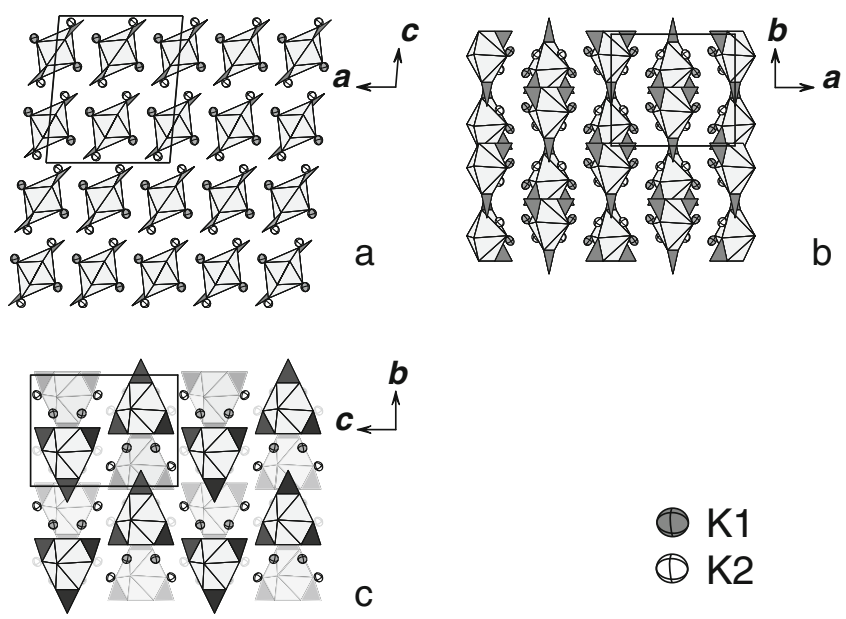


**Fig. 3** Crystal structure of agricolaite projected on the (010) plane (**a**), and viewed down to the [001] axis (**b**) and along the [100] axis (**c**). The equatorial plane of the ($UO_8$) hexagonal dipyramids (shown in *light grey*) is inclined by 26.3° to the **c** axis while the angle between the vertical axis of the ($UO_8$) 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

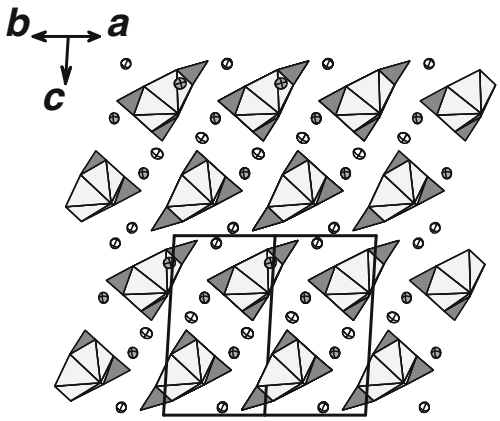


**Fig. 4** Crystal structure of agricolaite viewed along [110]. Structure elements are arranged into columns

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 ($UO_8$) 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 ($UO_8$) 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 $(UO_2)(CO_3)_3$ groups (Fig. 4).

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