

Wooldridgeite, $\text{Na}_2\text{CaCu}_2^{2+}(\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_{10}$: A new mineral from Judkins Quarry, Warwickshire, England

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ABSTRACT

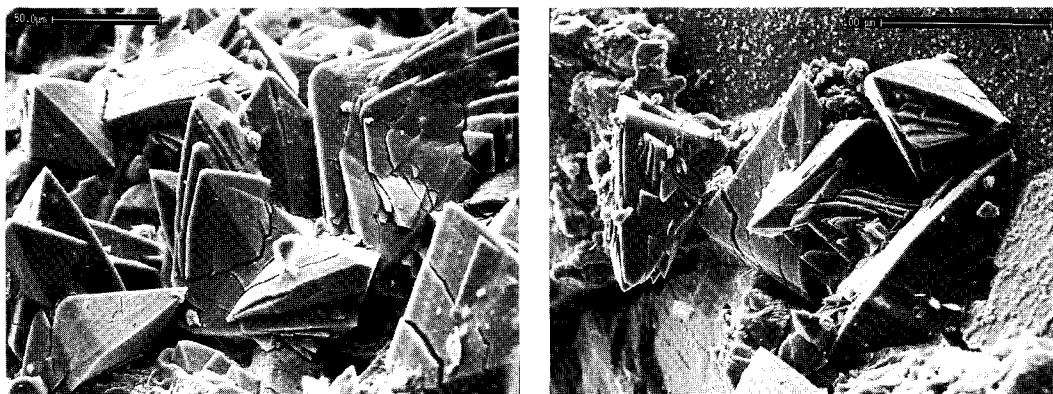
Wooldridgeite, ideally $\text{Na}_2\text{CaCu}_2^{2+}(\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_{10}$, orthorhombic, $a = 11.938(1)$, $b = 32.854(2)$, $c = 11.017(1)$ Å, $V = 4321.2(8)$ Å³, $a:b:c = 0.3634:1:0.3353$, space group $Fdd2$, $Z = 8$, is a new mineral from Judkins Quarry, Nuneaton, Warwickshire, England. Associated minerals are calcite, chalcopyrite, bornite and baryte. It occurs as equant crystals forming rhombic dipyramids; no twinning was observed. It is transparent blue-green with a very pale-blue streak, a vitreous lustre, and does not fluoresce under long- or short-wave ultraviolet light. Wooldridgeite has a Mohs hardness of 2–3, is brittle with an irregular fracture, and has no cleavage. The calculated density is 2.279 g/cm³. In transmitted light, wooldridgeite is colourless, non-pleochroic, and shows no dispersion. It is biaxial negative with $\alpha = 1.508(1)$, $\beta = 1.511(1)$, $\gamma = 1.517(1)$, $2V(\text{meas.}) = 76.2(5)$, $2V(\text{calc.}) = 71(10)^\circ$, $X = b$, $Y = c$, $Z = a$. The strongest five reflections in the X-ray powder diffraction pattern are [$d(\text{Å})$, (h), (kl)]: 8.23(30)(040), 6.52(100)(131), 4.05(40)(260), 3.255(40)(262); 2.924(40)(371). Electron-microprobe analysis of wooldridgeite gave P₂O₅ 39.37, CuO 20.24, MgO 0.24, CaO 7.73, Na₂O 8.33, K₂O 0.17, H₂O(calc.) 24.72, sum 100.80 wt.%; the corresponding unit formula (based on 24 anions) is $(\text{Na}_{1.96}\text{K}_{0.03})\text{Ca}_{1.00}(\text{Cu}_{1.85}\text{Mg}_{0.04})\text{P}_{4.04}\text{O}_{14}(\text{H}_2\text{O})_{10}$ where the H₂O groups were assigned from knowledge of the crystal structure; the infrared absorption spectrum also indicates the presence of H₂O in the structure. The mineral is named for James Wooldridge (1923–1995), a fervent amateur mineral collector who discovered this mineral.

KEYWORDS: wooldridgeite, new mineral, pyrophosphate, Judkins Quarry, Warwickshire, England.

Introduction

WOOLDRIDGEITE, ideally $\text{Na}_2\text{CaCu}_2^{2+}(\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_{10}$, is a newly recognized mineral species which was first encountered during a study of the

mineralization at Judkins Quarry, Nuneaton, Warwickshire, England (national grid reference SP 346 930). A suite of samples collected by RES and the late Jim Wooldridge in September 1989 yielded a number of specimens bearing distinct



FIGS. 1 and 2. FIG. 1 (*left*). Intergrown crystalline aggregates of wooldridgeite showing rhombic dipyramidal forms; note the curved edges of the crystals in the centre of the photomicrograph (scale bar = 50 μm). FIG. 2 (*right*). Crystals of wooldridgeite perched on an earlier-formed coarse scalenohedron of calcite (scale bar = 100 μm).

pale-blue crystals up to 0.2 mm across. Several visits were made to the quarry to collect additional material for study, but only a relatively small number of specimens have been confirmed as bearing wooldridgeite. The mineral name is for the late James 'Jim' Wooldridge (1923–1995), a keen amateur mineralogist and gemmologist who first discovered the mineral in September 1989. The new mineral and mineral name have been approved by the International Mineralogical Association Commission on New Minerals and Mineral Names. Type material is deposited at the Manchester Museum, Manchester, England, accession number MANCH:N13200.

Physical properties

Wooldridgeite occurs as both intergrown crystalline aggregates (Fig. 1) and as isolated well-formed crystals up to 50–200 μm in maximum dimension; no twinning was observed. The isolated crystals have a simple rhombic-dipyramidal form and sometimes display subtly curved faces (Fig. 1). Wooldridgeite crystals are perched on earlier-formed coarse colourless scalenohedral calcite (Fig. 2), weathered botryoidal clots of chalcopyrite, corroded bornite pseudomorphs after chalcocite and light pink 'desert-rose' aggregates of baryte. Wooldridgeite is transparent blue-green with a very pale-blue streak and a vitreous lustre; it does not fluoresce under long-wave or short-wave ultraviolet light. It is brittle with an irregular fracture and no cleavage; Mohs hardness is 2–3 and the calculated density is 2.279 g/cm^3 .

Optical properties

In transmitted light, wooldridgeite is colourless, non-pleochroic and shows no dispersion. The optical orientation is $X = b$, $Y = c$, $Z = a$; $2V$ was measured by the Tobi method, and the indices of refraction were measured in monochromatic light ($\lambda = 590 \text{ nm}$). The measured and calculated optical properties are listed in Table 1.

Chemical composition

Crystals were analysed chemically with a Cameca SX-50 electron microprobe operating in wavelength-dispersion mode with an accelerating

TABLE 1. Optical properties, chemical composition and unit formula of wooldridgeite

α	1.508(1)	$2V(\text{obs})^\circ$	76.2(5)
β	1.511(1)	$2V(\text{calc})^\circ$	71(10)
γ	1.517(1)		
P_2O_5	39.37	P	4.04
CuO	20.24		
MgO	0.24	Cu	1.85
CaO	7.73	Mg	0.04
Na_2O	8.33		
K_2O	0.17	Ca	1.00
$(\text{H}_2\text{O})(\text{calc})$	24.72		
Sum	100.80	Na	1.96
		K	0.03
		H	10.00

WOOLDRIDGEITE, A NEW MINERAL

TABLE 2. X-ray powder-diffraction data for wooldridgeite

$I_{est.}$	$I_{calc.}$	$d\text{\AA}_{(meas.)}$	$d\text{\AA}_{(calc.)}$	h	k	l	$I_{est.}$	$I_{calc.}$	$d\text{\AA}_{(meas.)}$	$d\text{\AA}_{(calc.)}$	h	k	l	
30	24	8.23	8.203	0	4	0								
10	5	7.92	7.859	1	1	1	3	1	2.022	2.028	2	14	2	
100	100	6.52	6.507	1	3	1	*	8	3	1.999	2.001	3	11	3
40	16	4.05	4.030	2	6	0	5	1	1.961	1.968	1	7	5	
10	3	3.91	3.930	2	2	2	*	3	1	1.939	1.939	2	16	0
	5		3.882	0	6	2	*	5	3	1.910	1.914	5	5	3
*	5	2	3.719	3	1	1								
	3	3	3.623	2	4	2	5	2	1.892	1.893	4	12	2	
*	5	4	3.537	3	3	1								
			3.538	3	3	1	5	1	1.869	1.870	6	0	2	
*	15	6	3.345	1	3	3								
			3.344	1	3	3	5	1	1.869	1.863	1	9	5	
*	40	25	3.255	2	6	2	*	5	3	1.842	1.843	3	13	3
*	10	4	3.097	1	5	3	*	10	3	1.817	1.815	4	8	4
	3	1	2.979	4	0	0								
			2.981	4	0	0	7	2	1.747	1.754	1	11	5	
*	40	27	2.924	3	7	1								
			2.923	3	7	1	2	2	1.746	1.746	2	2	6	
*	25	8	2.807	1	7	3	*	3	2	1.708	1.710	2	14	4
*	5	3	2.755	0	0	4								
			2.756	0	0	4	3	2	1.697	1.699	3	15	3	
*	3	1	2.687	3	1	3								
			2.689	3	1	3	3	1	1.697	1.691	1	17	3	
	5		2.620	3	3	3								
			2.620	3	3	3	5	2	1.665	1.672	2	6	6	
	20	6	2.614	0	4	4								
			2.613	0	4	4	5	1	1.665	1.662	2	18	2	
*	5	5	2.594	4	2	2	*	3	1	1.645	1.645	1	13	5
*	5	5	2.553	2	10	2	*	3	2	1.631	1.631	7	5	1
*	5	4	2.534	1	9	3								
			2.529	1	9	3	3	2	1.618	1.617	5	1	5	
*	10	3	2.496	3	5	3								
			2.496	3	5	3	3	1	1.618	1.615	4	16	2	
*	3	2	2.409	1	13	1								
			2.410	1	13	1	5	1	1.599	1.602	5	3	5	
*	5	4	2.363	4	6	2								
			2.365	4	6	2	5	1	1.599	1.595	5	15	1	
*	5	3	2.325	5	1	1	*	3	1	1.586	1.586	2	16	4
			2.325	5	1	1								
	2		2.275	2	6	4								
			2.275	2	6	4	5	2	1.568	1.572	5	5	5	
15	2		2.276	1	11	3								
			2.273	1	11	3	5	1	1.568	1.570	3	17	3	
	1		2.159	1	1	5	7							
			2.163	1	1	5								
	3	1	2.159	0	14	2								
			2.157	0	14	2								
*	10	4	2.134	2	8	4								
			2.136	2	8	4								
*	10	3	2.087	5	7	1								
			2.087	5	7	1								
*	10	5	2.053	4	10	2								
			2.048	4	10	2								

114.6 mm Debye-Scherrer powder camera; Cu radiation, Ni filter (λ Cu-K α = 1.54178 Å)

Intensities estimated visually; calculated intensities from crystal structure

Not corrected for shrinkage and no internal standard; * = lines used for unit-cell refinement

d -spacings due to admixed quartz and calcite have either been removed or downgraded in intensity

Indexed with $a = 11.925$, $b = 32.81$, $c = 11.024$ Å

voltage of 15 kV, a specimen current of 20 nA, a beam size of 20 μ m and counting times on peak and background of 20 and 10 s, respectively. The following standards were used: P: fluorapatite; Cu: metallic copper; Mg: periclase; K: orthoclase; Ca: wollastonite; Na: jadeite. Data were reduced using the $\phi(\rho Z)$ method of Pouchou and Pichoir (1985); the mean of 10 analyses is given in Table 1. The chemical formula (Table 1) was calculated on the basis of 24 anions including 10 H₂O groups, as derived from solution and refinement of the crystal structure (Cooper and Hawthorne, 1998).

X-ray diffraction

A single-crystal fragment was mounted on a Siemens P4 four-circle X-ray diffractometer and the unit cell was determined by indexing 40 automatically aligned reflections. Wooldridgeite is orthorhombic, $a = 11.938(1)$, $b = 32.854(2)$, $c = 11.017(1)$ Å, $V = 4321.2(8)$ Å³, $a:b:c = 0.3634:1:0.3353$. The crystal structure was determined in the space group $Fdd2$, and details will be reported elsewhere. The X-ray powder-diffraction pattern is reported in Table 2, together

with the experimental conditions and the corresponding unit-cell dimensions.

Infrared spectroscopy

Experimental methods are identical to those reported by Roberts *et al.* (1994). The infrared spectrum shows a broad absorption of $\sim 3400\text{ cm}^{-1}$ and a sharp weaker absorption at 1657 cm^{-1} , indicating the presence of H_2O in the structure.

Occurrence and associated minerals

Wooldridgeite has been identified on a small number of specimens collected from a rockfall below the disused southwest face of Judkins Quarry, Nuneaton, Warwickshire, England (National Grid Reference SP 346 930). Judkins Quarry exposed a section of about 100 m that contains the well-defined unconformity between Precambrian igneous rocks and overlying Cambrian sediments. An interesting assemblage of sulphide and supergene minerals is found within 10–20 m of the unconformity, and is dominated by a Ca-Ba-Cu suite, with minor Zn-Pb-V components.

The Quarry has been worked for many years to provide roadstone and has been regularly visited by generations of field parties on account of the interesting geological features which are exposed. During the 1980s, the disused eastern part of the quarry was progressively back-filled as a repository for household waste, and active quarrying ceased in December 1996 due to slope-instability problems. Additional information regarding the geology and mineralogy of Judkins Quarry can be found in Ince *et al.* (1991).

Paragenesis

The coarse calcite-baryte-Cu-sulphide assemblage crystallized along fractures during a low-temperature hydrothermal event. Later exposure to surface weathering resulted in the breakdown of the sulphides and release of Cu, which combined with P to form wooldridgeite. There are no other phosphate minerals reported from the quarry, and the source of the P is currently unknown. Wooldridgeite was found 100–200 m from the waste tip, and well above (tens of metres) the level of the tip, negating the possibility of

interaction between the sulphides and seepage from the tip. The land surrounding the quarry is pasture, indicating that the P is very unlikely to be due to agricultural runoff. The most likely source of P is either the normal groundwater or bird droppings.

Related species

Wooldridgeite is only the second pyrophosphate mineral to be discovered; canaphite, $\text{Na}_2\text{Ca}(\text{P}_2\text{O}_7)(\text{H}_2\text{O})_4$, is the only other mineral known to contain (P_2O_7) groups (Rouse *et al.*, 1988). However, apart from the common (P_2O_7) group, the structures are otherwise not related.

Acknowledgements

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References

- Cooper, M.A. and Hawthorne, F.C. (1998) The crystal structure of wooldridgeite, $\text{Na}_2\text{CaCu}_2^+(\text{P}_2\text{O}_7)_2(\text{H}_2\text{O})_{10}$, a novel pyrophosphate structure. *Canad. Mineral.* (submitted).
- Ince, F., Starkey, R.E. and Wooldridge, J. (1991) The geology and mineralogy of Judkins Quarry, Warwickshire. *U.K. J. Mines Minerals*, **10**, 8–13.
- Pouchou, J.L. and Pichoir, F. (1985) 'PAP' $\phi(\rho Z)$ procedure for improved quantitative microanalysis. In *Microbeam Analysis 1985*, San Francisco Press, San Francisco, 104–60.
- Roberts, A.C., Ercit, T.S., Criddle, A.J., Jones, G.C., Williams, R.S., Cureton, F.F. and Jensen, M.C. (1994) Mcalpineite, $\text{Cu}_3\text{TeO}_6 \cdot \text{H}_2\text{O}$, a new mineral from the McAlpine mine, Tuolumne County, California, and from the Centennial Eureka mine, Juab County, Utah. *Mineral. Mag.*, **58**, 417–24.

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