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Drugmanite, $Pb_2(Fe^{3+},Al)(PO_4)_2(OH)\cdot H_2O$, a new mineral from Richelle, Belgium

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SUMMARY. Drugmanite occurs as rare colourless transparent platy crystals, up to 0.2 mm, aggregated in bunches, in vugs of a mineralized and silicified limestone. Hardness < 6. Crystals monoclinic, forms {001} {110}, parameters from indexed X-ray powder pattern (and monocrystal measurements): $a = 11.110\ (11.111)$ Å, $b = 7.976\ (7.986)$, $c = 4.644\ (4.643)$, $\beta = 90°18'\ (90.41°)$. Space group $P2_1/a$ with $Z = 2$ giving $D_{calc} = 5.55$. Strongest lines are 4.63 Å (9), 3.752 (10), 3.350 (8), 3.247 (8), 2.912 (9). Mean refractive index 1.88 from reflectance measurements. Strong dispersion $r < v$, optic axial plane // (010), $2V_\alpha = 33 \pm 2°$. Electron microprobe analysis gave P 8.89, Al 0.85, Fe 6.19, Pb 59.76 %, leading to $Pb_{4.02}(Fe^{3+}_{1.55}Al_{0.45})P_{4.00}O_{17.02}\cdot 3H_2O$ or $Pb_2(Fe^{3+}_{0.78}Al_{0.22})(PO_4)_2(OH)\cdot H_2O$. Associated minerals are pyromorphite, anglesite, corkite and phosphosiderite. Named for J. Drugman, Belgian mineralogist (1875-1950).

SITUATED 15 km north of Liège, in the direction of Visé, Richelle represents, for Belgium, a locality of exceptional mineralogical interest. From it some forty mineral species have been recorded and three relatively uncommon minerals, i.e. koninckite, destinezite, and richellite, were discovered and investigated in the past century (Mélon *et al.*, 1976).

The geological background in Richelle is well known for its great complexity. In the part of the outcrops still visible limestone and calcareous breccias of Visean age lie unconformably on Frasnian limestone (Pirlet, 1967). The stratigraphic limit between Visean and Namurian is characterized by an ante-Namurian karst phenomenon, the sink-holes containing breccias, generally composed of Visean limestone fragments and Namurian sediments. Moreover the ancient terraces of the river Meuse crop out at the top of the quarries.

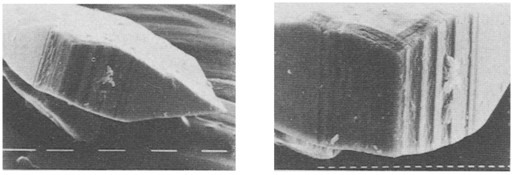
Percolating waters moved many chemical elements and concentrated them, not only into the confined environment of sink-hole breccias, but also into fissures and the cavities of the Visean material. The oxidation and weathering processes of disseminated sulfides (sphalerite, galena, pyrite, and chalcopyrite), the appreciable amount of phosphorus (probably originating from the Namurian sediments), the proximity of partly silicified limestones are a few particular conditions allowing crystallization of a surprising mineralogical variety. Most species frequently occur in very small amounts and were formed at low temperatures.

Different assemblages of minerals, lining vugs in silicified crinoidal limestones or in black resistant phtanites included in the breccias, have recently been the subject of a resurgence of interest, which led to a preliminary minerals list (Fransolet *et al.*, 1974*a*). A more detailed investigation on some rare minerals, i.e. fluellite, minyulite, scholzite, corkite, wulfenite has been undertaken (Fransolet *et al.*, 1974*b*, *c* and *d*, 1977). Another mineral, drugmanite, a new species, is now added to them.

Drugmanite seems to be very rare in the mineralized limestones of Richelle. In spite of a careful examination of numerous specimens with a binocular microscope, only a small amount of this new mineral has been detected in one specimen (generously donated by M. Fouassin, Mining Engineer, Brussels). This specimen, which constitutes the basis of the study, shows three small cavities (1-3 mm), lined with drugmanite, accompanied by colourless microcrystalline anglesite, brown globular corkite, colourless splinters of pyromorphite, and milky crusts of phosphosiderite.

Descriptive mineralogy. Much resembling cerussite in its appearance, drugmanite occurs in bunched platy aggregates of pale yellow colour but is colourless as isolated crystals. The lustre is adamantine and the streak white. Unlike the cerussite described (Fransolet *et al.*, 1977), this new phosphate is non-fluorescent under long and short ultraviolet wavelengths. No cleavage is obvious. The hardness is moderate, certainly lower than 6. The specific gravity must be distinctly greater than 4.1, since the crystals of drugmanite sink quickly in Clerici solution. Owing to the scanty material, accurate measurements of hardness and specific gravity could not be made.

The crystals reach a maximum size of 0.2 mm and show tiny rhombs normally flattened to [001]. Some of these are slightly warped and most of them are elongated along [010]. Fig. 1 represents a typical crystal of drugmanite observed under the scanning electron microscope. Measurements on a few crystals were carried out with an optical goniometer, under the optical microscope, and on SEM-photographs. {001} is most prominent but always rough and wavy. Minute bright faces (110) and ($1\bar{1}0$), systematically present, are so small that only approximate angles could be measured. With the goniometer, (110):($\bar{1}10$) is 72° ± 2° (calculated value: 71°24′). Under the polarizing microscope and on SEM-views their interfacial angle is 108° ± 2° (calculated value: 108°36′). These faces are striated parallel to [001]. These striae are merely grooves forming a stepped surface which at first glance, without the aid of the scanning electron microscope, could be ascribed to a form {320} and which seems to result from a growth or corrosion phenomenon (fig. 2).



FIGS. 1, 2. SEM-views of a typical drugmanite crystal. FIG. 1 (*left*). One division: 10 μm. FIG. 2 (*right*). Stepped ($1\bar{1}0$) and (110) faces and truncated edges with the (001) face. One division: 1 μm. (Photographs K. Wouters.)

Insoluble in water and soluble in warm HNO_3 (2N), drugmanite forms a white coating with HCl(2N). It is resistant to 110 °C, but decomposes when heated to 450 °C.

Crystallographic data. Rotation method. Initial measurements of the cell parameters were made by the rotation method on three differently oriented crystals. The results led to $a = 7.972$ (3) Å, $b = 11.080$ (5) Å, and $c = 4.631$ (3) Å after a complete indexation of the powder pattern using the Fortran refinement program of Cox (1967) and respecting the orientation commonly used for orthorhombic symmetry (Brasseur, 1975). However, these observations conflict with the chemical content of the cell (Z = 2, see below).

TABLE I. *X-ray powder pattern for drugmanite*

I/I_0	d_{obs}(Å)	*hkl*	d_{calc}(Å)	I/I_0	d_{obs}(Å)	*hkl*	d_{calc}(Å)
2	6.47	110	6.48	2	1.940	520	1.940
5	5.55	200	5.55			511	1.939
9	4.63	001	4.64	5	1.916	$31\bar{2}$	1.914
1	4.00	011	4.01			430	1.920
10	3.752	120	3.753	2	1.902	312	1.905
5	3.558	201	3.552	1	1.875	240	1.877
8	3.350	310	3.356	1	1.847	600	1.850
8	3.247	211	3.245	2	1.832	041	1.832
5	3.020	021	3.025	2	1.806	141	1.807
9	2.912	121	2.916	4	1.772	431	1.772
7*b*	2.714	311	2.714	2	1.741	$41\bar{2}$	1.742
		320	2.712			$24\bar{1}$	1.741
5	2.614	410	2.621	1	1.725	132	1.726
6	2.391	$40\bar{1}$	2.387	4*b*	1.667	232	1.666
1	2.339	321	2.338	2	1.580	$62\bar{1}$	1.581
2	2.314	002	2.321			150	1.579
		031	2.307			332	1.579
2	2.268	$13\bar{1}$	2.260	1	1.551	003	1.548
6*b*	2.128	231	2.129	1	1.518	630	1.519
1	1.992	040	1.994			013	1.520
3	1.969	122	1.973	2	1.497	142	1.498
						$15\bar{1}$	1.495

Debye-Scherrer camera with a 114.6 mm diameter; Straumanis's method; Mn-filtered Fe-radiation; internal $Pb(NO_3)_2$ standard; film corrected for shrinkage; I/I_0 visually estimated; b = broad.

Four-circle diffractometer method. A crystal (0.1 × 0.04 × 0.02 mm) was selected for redetermination of the cell dimensions on a four-circle diffractometer using graphite-monochromatized Mo-$K\alpha$ radiation ($\lambda = 0.71069$ Å). The symmetry is in fact monoclinic and the parameters, calculated from measurements of twenty-two reflections, are $a = 11.111$ (5), $b = 7.986$ (5), $c = 4.643$ (3) Å, $\beta = 90.41$ (3)°. The reflections *hol* with *h* odd and *oko* with *k* odd are systematically absent and suggest the space group $P2_1/a$. Oscillation photographs taken about both the *a* and *c* axes point to an orthorhombic pseudosymmetry.

Indexation of the powder pattern. The completely indexed powder pattern (Table I) following the Fortran program of refinement least-squares procedure (Cox, 1967) led to the cell dimensions given in Table II, column 2.

Chemical composition. Preliminary qualitative analyses by optical spectrography and microchemical tests showed the presence of P, Pb, and Fe. The electron microprobe confirmed them and detected, except for Al, no other elements with atomic number greater than 11.

Refined electron microprobe analyses were performed with a slightly defocused electron beam (Cambridge Microscan MK V, acceleration voltage 20 KV, sample current 30 nA, and beam diameter ≃ 10 μm) at eight points on a polished crystal

TABLE II. *Cell criteria for drugmanite*

	1	2
a (Å)	11.111 (5)	11.100 (6)
b (Å)	7.986 (5)	7.976 (4)
c (Å)	4.643 (3)	4.644 (3)
β	90.41 (3)°	90°18 (2)′
V (Å^3)	412 (1)	411 (1)
a:b:c	1.391:1:0.581	1.392:1:0.582
Space group	$P2_1/a$	
Composition	$Pb_2(Fe^{3+}_{0.78}Al_{0.22})(PO_4)_2(OH)\cdot H_2O$	
Z	2	
D_{calc} (g/cm^3)	5.55	

1. Four-circle diffractometer method (King and Sengier, priv. comm.).
2. Refinement from the complete indexed powder pattern.

(50 × 100 µm) selected for optical measurements and for crystallographic investigation. Synthetic standards $Pb_5(PO_4)_3Cl$, Fe_2O_3 and Al_2O_3 were used for Pb, P, Fe, and Al. The ZAF corrections (Duncumb and Reed, 1968; Heinrich, 1967; Philibert, 1963; and Reed, 1965) were made with the equations of Yarowitz *et al.* (1973) for the emission energies, absorption edges, and mass absorption coefficients.

The crystal examined was homogeneous throughout, as the microprobe gave constant Pb:P:(Fe+Al) ratios. The average of the eight measurements for each element appears in Table III.

Optical properties. The optical properties of drugmanite have been established on isolated grains. Under the microscope the mineral is completely colourless and anisotropic with abnormal interference colours due to strong dispersion $r < v$. The refractive indices, measured on oriented crystals, are all undoubtedly greater than 1.74 (immersion in methylene iodide). Drugmanite is biaxial, negative with $2V_\alpha = 33° \pm 2°$ measured by Mallard's method with sodium light. The optic axial plane is // (010). The angle between α and c could not be observed; α is approximatively perpendicular to (001) (see fig. 3*a*). The measured birefringence γ-β on sections (001) is 0.020 (2). The morphology of the crystals (fig. 1) and their high refraction hinder any other optical measurements in transmitted light.

Under these conditions, the mean refraction can be calculated from the measured reflectances of the polished crystal selected for microprobe analysis using the well-known formula

$$R = \frac{(n-n_o)^2+k^2}{(n+n_o)^2+k^2}.$$

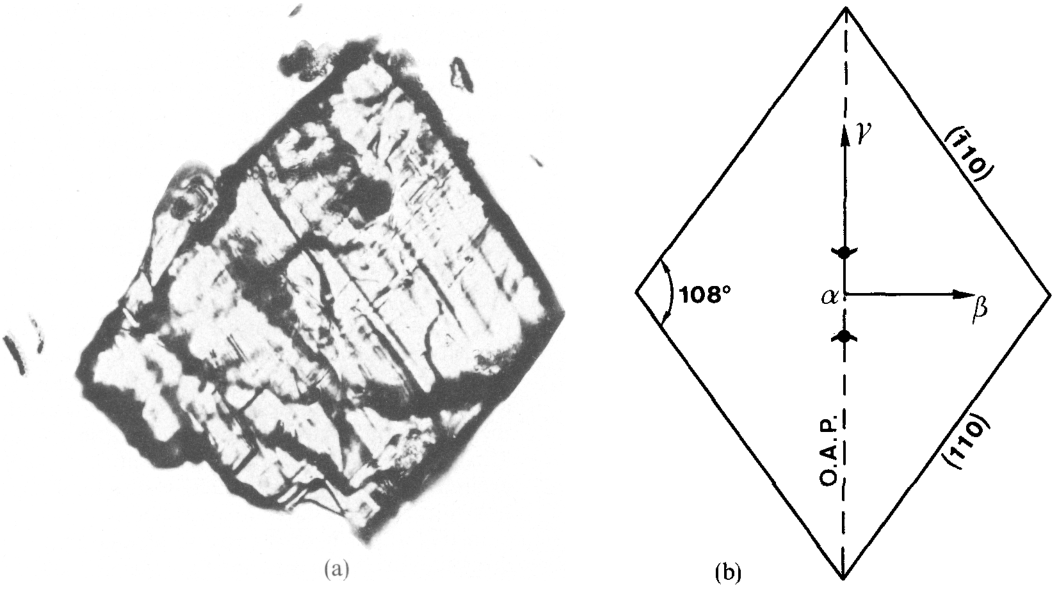


FIG. 3. (*a*). Microscopical view of drugmanite with (001) lamellae (400 ×). (*b*) Optical orientation in a section nearly parallel to (001).

TABLE III. *Chemical composition of drugmanite*

	1		2	3	4	5	6	7
P	8.89±0.04	P_2O_5	20.37	0.144	2.00	4.002	20.56	20.61
Al	0.85±0.17	Al_2O_3	1.61	0.016	0.99	0.446	1.63	1.63
Fe	6.19±0.24	Fe_2O_3	8.85	0.055		1.548	8.93	9.04
Pb	59.76±0.80	PbO	64.37	0.288	4.00	4.016	64.97	64.80
		H_2O*	3.87	0.215	2.99	6.000	3.91	3.92
			99.07				100.00	100.00

1. Average of 8 point measurements with standard deviation (Analyst: K. Abraham);
2. Calculated percentages from 1; * Calculated on the basis of 20 oxygens in the cell;
3. Molecular proportions;
4. Molecular ratios deduced from 3;
5. Numbers of cations calculated on the basis of 17 oxygens in the 'anhydrous' part of the compound;
6. Composition 2 recalculated to 100.00%;
7. Theoretical composition for $Pb_2(Fe^{3+}_{0.78}Al_{0.22})(PO_4)_2(OH)\cdot H_2O$.

With SiC (R = 20.2%) as a standard this method, neglecting k, gave n = 1.88 (1). The dispersion of n in the wavelength range from 625 to 425 nm appears in Table IV.

By the relationship of Gladstone and Dale, $\langle n \rangle$ calc = 1.94, the specific refractive energies for the component oxides being obtained from the recent values of Mandarino (1976) and the density 5.55 g/cm^3 calculated from the crystallographic data.

Figure 3*b* exhibits abundant fracture-like lines // {110} which could be considered as an imperfect cleavage. This feature is more likely due to a stacking of {001} slabs, identically oriented. Moreover the number of lines varies from one aggregate to another and some grains are completely devoid of them, then showing only near the edges, very close thin growth rims, parallel to {110}.

Discussion. The chemical analysis of drugmanite raises two questions, i.e. the oxidation state of iron and the water content.

The total iron content is considered as Fe_2O_3 for two reasons. As a consequence of the environment and the mineral assemblage in which drugmanite occurs the presence of ferrous iron does not seem to be justified. In addition, a particularly suitable stoichiometry of the Pb:(Fe+Al):PO_4 ratio exists if Fe is trivalent and replaces Al.

TABLE IV. *Variation with wavelength of the mean reflectivity R and calculated n of drugmanite*

λ(nm)	R (%)	n
625	9.17	1.87
605	9.24	1.87
585	9.24	1.87
565	9.29	1.88
545	9.30	1.88
525	9.42	1.89
505	9.47	1.89
485	9.67	1.90
465	9.69	1.90
445	9.93	1.92
425	10.68	1.97

Without any determination of water content even of a qualitative nature, the establishment of the chemical formula could be hazardous. The amount of material is at present too scanty for any thermogravimetric or infrared analysis. Nevertheless a suggestion can be made by analogy with known minerals.

From a chemical point of view drugmanite seems to be comparable with brackebuschite $Pb_2(Mn,Fe)(VO_4)_2\cdot H_2O$, goedkenite $(Sr,Ca)_2Al(PO_4)_2(OH)$ (Moore *et al.*, 1975), and arsenbrackebuschite $Pb_2(Fe^{3+},Zn)(AsO_4)_2(OH,H_2O)$ (Abraham *et al.*, 1978) if solely the ratios Pb:($R^{2+}+R^{3+}$):ZO_4 = 2:1:2 are considered. On the other hand, the cell dimensions and the X-ray powder patterns of drugmanite and these three compounds are completely different.

The geometrical properties which characterize the cells of gadolinite, of the datolite-homilite series or hydroxyherderite-herderite series members (Strunz, 1978) afford noteworthy similarities with the cell criteria for drugmanite. As can be seen from Table V, the parameters and the identity of space group $P2_1/a$ emphasize possible isostructural relationships between these mineral species.

In this way it is reasonable to assume that the drugmanite cell also contains 20 oxygens leading to the structural formula:

$$Pb_{4.02}(Fe^{3+}_{1.55}Al_{0.45})P_{4.00}O_{17.02}\cdot 3H_2O$$

and to the idealized formula:

$$Pb_2(Fe^{3+}_{0.78}Al_{0.22})(PO_4)_2(OH)\cdot H_2O$$

TABLE V. *Drugmanite and structurally-similar minerals*

Mineral	Chemical composition	Space group	Z	*a* (Å)	*b* (Å)	*c* (Å)	*β*
Drugmanite	$Pb_2(Fe^{3+},Al)(PO_4)_2(OH)\cdot H_2O$	$P2_1/a$	2	11.10	7.98	4.64	90°18′
Gadolinite*	$Y_2Fe^{2+}Be_2[O/SiO_4]_2$	$P2_1/a$	2	9.89	7.55	4.66	90°33½′
Herderite*	$CaBe(F,OH)PO_4$	$P2_1/a$	4	9.82	7.70	4.81	90°06′
Datolite*	$CaB[OH/SiO_4]$	$P2_1/a$	4	9.66	7.64	4.83	90°09′
Homilite*	$Ca_2Fe^{2+}B_2[O/SiO_4]_2$	$P2_1/a$	—	9.67	7.57	4.74	90°22′

* See Strunz (1978).

On the basis of the crystallographic data, the molecular weight of 688.84 g and Z = 2, the calculated density is 5.55 g/cm^3.

The structural analysis of the atomic arrangement in drugmanite, presently in progress in the Laboratory of Crystallography of Professor G. S. D. King, might provide arguments, conclusive or negative, to this discussion and assumption.

Name. The name of the new species is for Dr Julien Drugman (1875–1950), a Belgian mineralogist who was particularly interested in twinning problems. His extended bibliography is given by Denaeyer (1951).

The material described is to be regarded as an aluminium-bearing variant since the pure Fe^{3+} end-member has not yet been found. The name drugmanite is suggested for compositions in which $Fe^{3+} > Al$. The species and the name have received approval from the International Commission on New Minerals and New Mineral Names (IMA). The type specimen (in two parts) is deposited with the Institut royal des Sciences naturelles de Belgique, Brussels (no. RN 5210) and the Institut de Minéralogie, Université de Liège, Liège (no. 19347).

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