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Perhamite, a new calcium aluminum silico-phosphate mineral, and a re-examination of viséite

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SUMMARY. A new calcium aluminum silico-phosphate mineral has been found at two locations on Newry Hill, Newry, Maine, U.S.A. Its composition closely approximates to $3CaO.3{\cdot}5Al_2O_3.3SiO_2.2P_2O_5.18H_2O$ ($Z = 1$). Perhamite is uniaxial (+), $\varepsilon = 1{\cdot}577$, $\omega = 1{\cdot}564$, density = 2·64 g/cm^3. The mineral is hexagonal, probably *P6/mmm*, with $a = 7{\cdot}02$ Å, $c = 20{\cdot}21$ Å. The colour is light brown to white, the habit is as aggregates of discoidal hexagonal crystals. Cleavage is perfect {0001}, the lustre is vitreous, and the streak white. The mineral is named for a pegmatite miner and geologist, Frank C. Perham of West Paris, Maine, U.S.A.

The most similar species is viséite. A re-examination of viséite indicates that the composition previously given is incorrect. A new form of viséite, also from Visé, Liège, Belgium is also examined and found to differ in composition from the type material.

A NEW calcium aluminum silico-phosphate mineral has been discovered at the Bell Pit, Newry Hill, Newry, Maine. The mineral occurs as rare, isolated brown spherulitic masses (about 1 mm across) of platy crystals, associated with siderite, colourless wardite, amblygonite, eosphorite, and sphalerite in a vuggy amblygonite-rich pegmatite zone.

A second occurrence of this material has been found on material provided by Mr. Vandall King of Darling Center, Maine. This second occurrence is a very soft delicate white botryoidal cluster in the Dunton Gem mine (also known as the Nevell mine) atop Newry Hill. Although this mineral with a pearly lustre does not obviously resemble the brownish brittle perhamite from the Bell Pit, the X-ray powder patterns of these specimens are identical. The white material is exceedingly rare and was not analysed. This study was carried out using the Bell Pit specimens.

We have named the new mineral perhamite for Frank C. Perham, geologist and pegmatite miner of West Paris, Maine, in honour of his dedicated labours in the recovery of mineral specimens. The mineral and the name were approved by the Commission on New Minerals and New Mineral Names, IMA, prior to publication. Type material is in the U.S. National Museum of Natural History, Smithsonian Institution, Washington, D.C. 20560 under catalogue no. 135740 and in the British Museum (Natural History), BM 1976, 424.

Physical description. Perhamite from the Bell Pit is brown with hue and intensity similar to brown eosphorite. It forms as rough spherules with a dull surface, comprised of discoidal, platy hexagonal crystals radiating from a common source. The spherules are quite brittle and cleave readily into tabular fragments due to an imperfect, easy cleavage on {0001}. The lustre of cleavage surfaces is vitreous. The specific gravity, determined by flotation, is $2{\cdot}64 \pm 0{\cdot}01$, Mohs hardness is approximately 5, and the streak is white.

Optical properties. Perhamite is uniaxial (+) with $\varepsilon = 1{\cdot}577$ ($\pm 0{\cdot}004$), $\omega = 1{\cdot}564$ ($\pm 0{\cdot}002$). The perfect {0001} cleavage induces a preferred orientation in immersions, and due to the extreme thinness of the crystal plates, ε is determined only with great difficulty. Dispersion is $r > v$, moderate. Absorption: $\omega > \varepsilon$ for the brown material from the Bell Pit. The mineral is not luminescent in either long- or short-wave ultra-violet.

TABLE I. *Indexed powder diffraction data (third index omitted) for perhamite from the Bell Pit, Newry, Maine.* Cu-$K\alpha$ *radiation, Gandolfi-type camera, diameter 114·56 mm. Refined cell dimensions:* $a = 7{\cdot}022$ Å, $c = 20{\cdot}182$ Å, *hexagonal, P6/****

hkl	*I*	$d_{(obs)}$	$d_{(calc)}$	*hkl*	*I*	$d_{(obs)}$	$d_{(calc)}$	*hkl*	*I*	$d_{(obs)}$	$d_{(calc)}$
001			20·18	118	6	2·052	2·049	226	3	1·5551	1·5563
002	13	10·12	10·09	300			2·027	315			1·5562
003	35	6·71	6·73	0010			2·018	0013			1·5525
100	50	6·08	6·08	301			2·017	400			1·5203
101	71	5·80	5·82	215	6	1·996	1·997				
								1112			1·5168
102	13	5·21	5·21	302			1·987	2110	13	1·5165	1·5165
004	4	5·04	5·05	208	35	1·942	1·941	401			1·5160
103			4·51	303			1·941	316			1·5077
005			4·04	1010	4	1·916	1·915	1013			1·5042
104	6	3·889	3·883	216			1·898				
								309			1·5037
110	50	3·510	3·511	119			1·890	402			1·5033
111			3·459	304	35	1·881	1·881	227	6	1·5003	1·4994
006	9b	3·369	3·364	0011	6	1·834	1·835	403	6	1·4831	1·4829
105			3·363	305	6	1·811	1·811	2012	18	1·4715	1·4717
112			3·316	209			1·805				
								317	4	1·4566	1·4558
113	50	3·115	3·113	217			1·797	404			1·4556
200			3·041	1011	50	1·757	1·757	0014	6	1·4425	1·4416
201	35	3·005	3·007	220			1·755	228			1·4409
106	35	2·947	2·943	1110			1·750	2111			1·4339
202			2·911	221			1·749				
								3010			1·4302
007	100	2·882	2·883	306			1·736	405	3	1·4219	1·4227
114			2·882	222			1·729	1113			1·4198
203	25	2·773	2·771	218			1·699	1014			1·4027
115	25	2·650	2·649	223			1·699	318			1·4021
				310			1·687				
107	13	2·606	2·605					320			1·3951
204			2·604	0012	9	1·684	1·682	321			1·3918
008	18	2·524	2·523	2010			1·681	406			1·3853
116	25	2·429	2·429	311			1·681	2013	13	1·3837	1·3827
205			2·429	312			1·663	229			1·3823
				307			1·658				
108	9	2·330	2·330					322			1·3819
210			2·298	224			1·658	323			1·3660
211			2·284	313			1·636	3011			1·3603
206	25b	2·252	2·256	1111			1·626	2112			1·3573
009			2·242	1012			1·621	319	4	1·3483	1·3479
				225			1·610				
212			2·241					0015			1·3455
117			2·228	219	9	1·604	1·605	407			1·3448
213	18	2·175	2·175	314			1·600	324			1·3446
109	35	2·104	2·104	308			1·5801	1114			1·3335
207			2·092	2011			1·5709	410	6	1·3272	1·3270
214			2·092								
								2210			1·3245
								411			1·3241
								325			1·3186
								412			1·3157
								1015			1·3137

X-ray crystallography. Five single crystals of perhamite from the Bell Pit were studied with the Buerger precession camera, using Mo-$K\alpha$ radiation and a film-to-crystal distance of 60 mm. The results show that perhamite is hexagonal, with cell dimensions $a = 7{\cdot}02 \pm 0{\cdot}02$ Å and $c = 20{\cdot}21 \pm 0{\cdot}04$ Å. Very long exposures of zero and upper-level nets normal to a, a^*, and c reveal the diffraction symmetry $6/mmmP$---($P6/***$), compatible with space groups $P622$, $P6mm$, $P\bar{6}m2$, $P\bar{6}2m$, or $P6/mmm$. We cannot presently say which of these is the true space group, but $P6/mmm$ is most probable on the evidence of the very few oxide compounds known to crystallize in the other four groups (cf. Nowacki, 1967).

Powder diffraction data for perhamite (Table I) were obtained with Cu-$K\alpha$ radiation, using Gandolfi-type cameras of 114·56 mm diameter and samples consisting of a few crushed fragments. The measured 2θ values were indexed using the computer program of Appleman *et al.* (1972). Final refined cell dimensions and least-squares errors (1σ) are: $a = 7{\cdot}022 \pm 0{\cdot}001$ Å, $c = 20{\cdot}182 \pm 0{\cdot}005$ Å. Similar refinement of powder diffraction data for specimens from the Dunton mine yielded parameters in excellent agreement (2σ on a, less than $0{\cdot}5\sigma$ on c).

Chemistry. All analyses in this study were done on an ARL electron microprobe with an operating voltage of 15 kV and a sample current of 0·15 μA. Standards used were NMNH microprobe standards of high reliability, and different standards were used on individual analyses. The partial analyses of perhamite are presented as Table II. There was inadequate material for the determination of water content, and the H_2O content was assigned to give the best fit between calculated and measured densities and to the specific volume of oxygen for similar compounds. An electron microprobe scan indicated no detectable major elements other than calcium, silicon, aluminum, and phosphorus. In order to look for elements lighter than fluorine, we subjected perhamite to analysis by the ion microprobe mass spectrometer at the National Bureau of Standards, Washington, D.C. This analysis showed that the atomic ratio of Be to Si in perhamite is approximately 1:500. Lithium is present only in trace amounts, and boron is entirely absent. The electron microprobe analyses of Table II are confirmed in all other respects. Semi-quantitative ion-probe analysis for hydrogen also confirms the presence of a large number of hydrogen atoms in the perhamite formula. Thus we must conclude that the analyses presented in Table II are reasonably complete, and correct within the limits of accuracy of microprobe techniques.

The Bell Pit perhamite is homogeneous with no zonal concentrations or impurities. The average of our analyses yields the approximate formula $3CaO.3{\cdot}5Al_2O_3.3SiO_2.2P_2O_5.18H_2O$ ($Z = 1$). Based on the average analysis and the refined cell the calculated density is 2·53, compared with the measured value of 2·64.

TABLE II. *Analyses of perhamite, Bell Pit, Newry, Maine*

	1	2	3	Average	Theory‡
SiO_2	13·53	14·06	13·34	13·64	13·73
TiO_2	0·11	0·08	0·09	0·09	—
Al_2O_3	27·09	26·85	27·33	27·09	27·17
FeO*	0·27	0·34	0·18	0·26	—
MgO	0·02	0·00	0·00	0·02	—
CaO	12·29	12·22	12·26	12·26	12·81
Na_2O	0·02	0·02	0·00	0·02	—
P_2O_5	22·06	21·69	21·96	21·90	21·62
F	0·10	—	—	0·10	—
H_2O†	24·51	24·74	24·84	24·62	24·67
Total	100	100	100	100	100·00

* Total iron as FeO.
† By difference.
‡ For the formula $3CaO.3{\cdot}5Al_2O_3.3SiO_2.2P_2O_5.18H_2O$.
Accuracy of data ±2% relative.

Similar species. Perhamite is shown by its distinctive X-ray diffraction pattern and chemical composition to be an entirely new mineral species. The known mineral most similar to perhamite in composition is viséite, a hydrous basic calcium aluminum silico-phosphate first described by Mélon (1942) as a new mineral from Visé, Belgium. Viséite occurs as a botryoidal coating, resembling herderite, associated with a previous deposition of brown opal. The density is 2·20, it is isotropic, and the refractive index (*n*D) is 1·530.

Type viséite, from Visé, Belgium (NMNH no. 106364) was re-examined in the present study, and the sample agrees with Mélon's description. Additional comments on the description of the type material are given here. In thin section, the botryoidal clusters are seen to be comprised of an oolitic aggregate of tiny spherulites with a distinct outer rind of less densely packed spherulites. This outer zone is quite obvious at very high magnifications (200 ×).

The core and outer rind of viséite were analysed separately by the method described above for perhamite, and in the same run of analyses. A tabulation of these analyses is presented as Table III. Although the silica content of the viséite varies considerably (from 6·3 % to 9·0 %), there was no significant compositional zoning in either the core or the rind. Since the microprobe analyses of the present study indicate a much lower silicon content than reported by Mélon, it is quite possible, given the intimate association of opal and the oolitic nature of the botryoids, that his figures for silicon are high due to admixed opal impurities.

The sodium, reported by Mélon in only one of his four analyses (Table III), is obviously in error. Four separate analyses for sodium, in the present study, indicate that it is present only as traces and thus plays no part in the structure. We also find significantly less calcium. Melon proposed, on the basis of his analyses, the formula $3SiO_2.3P_2O_5.5Al_2O_3.5CaO.nH_2O$ $(30 > n > 25)$. This formula was rewritten by McConnell (1952) as $(Na_2Ca_{10})(AlO_2)_{20}(SiO_2)_6(PO_2)_{10}(H_3O_2)_{12}.16H_2O$ to show a proposed relationship of the structure to that of analcime.

The new analyses of type viséite in this study indicate a much lower calcium content, a lower silicon content, and the absence of sodium. Based on these analyses, the approximate formula for the type viséite is: $5CaO.6Al_2O_3.3SiO_2.3{\cdot}5P_2O_5.1{\cdot}5F.36H_2O$. Due to the oolitic nature of the aggregate, the resultant lack of single crystals, and the extremely diffuse powder pattern, this viséite formula cannot be confirmed by single crystal methods and an accurate density determination.

During the course of this study, additional specimens of viséite from Visé, Liége, Belgium came to our attention. The new viséite in no way resembles the original material. This viséite is a chalky, blue, friable massive material. This new viséite has also been analysed by microprobe, and the resultant analysis is also given in Table III. The new material is markedly different in composition from the original viséite. It is deficient in silicon, and contains significantly greater amounts of calcium, aluminum, and phosphorus. Water (by difference), is also deficient, relative to the type material. An appropriate formula for this newer blue viséite is: $3CaO.6{\cdot}5Al_2O_3.SiO_2.2P_2O_5.9H_2O$.

Both the type viséite and the new blue material have been examined with X-ray diffraction techniques. Both materials are so poorly crystalline that it is impossible to obtain more than a few weak, extremely broad, and diffuse diffraction lines. The patterns of both the original and the blue viséite are identical, with no discernible differences in spacing or intensity. The results are in substantial agreement with those of McConnell (1952). Direct comparison of our viséite patterns with those of perhamite show significant differences throughout the patterns.

Given the uncertainty of the viséite formula, the diffuse powder pattern, the demonstrated variation in silicon content, and the lack of single crystals, it is our opinion that viséite cannot, at the present time, be more accurately characterized.

TABLE III. *Analyses of viséite, NMNH 106364, and of 'blue viséite'*

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
SiO_2	10·43	9·20	—	10·17	9·93	8·77	8·40	6·35	7·84	7·94	8·03	8·99	7·31	8·07	7·97	8·02	5·30†
Al_2O_3	26·69	26·33	—	25·42	26·14	23·32	29·01	27·10	27·32	27·32	26·12	28·44	26·47	27·08	26·82	27·23	33·62
FeO	—	—	—	—	—	0·46	1·43	—	0·94	0·62	0·56	0·66	—	0·61	0·74	—	0·15
MgO	—	—	—	—	—	0·10	0·20	—	0·15	0·09	0·03	0·20	—	0·10	0·12	—	0·15
CaO	14·90	14·67	—	—	14·78	12·58	12·25	12·80	12·54	12·54	12·51	12·39	12·65	12·52	12·53	12·48	17·16
K_2O	—	—	—	—	—	0·12	0·17	—	0·15	0·14	0·12	0·15	—	0·14	0·14	—	tr.
Na_2O	—	—	1·77	—	1·77	0·01	—	—	0·01	0·02	0·02	—	—	0·02	0·02	—	tr.
P_2O_5	22·11	20·13	—	19·23	20·49	21·97	—	21·30	21·63	21·83	—	—	21·07	21·45	21·54	22·12	28·25
F	—	—	0·67	—	0·67	—	1·27	—	1·27	—	—	1·31	—	1·31	1·29	1·27	—
H_2O	23·78	26·55	—	27·99	26·10	—	—	—	—	—	—	—	—	—	28·82*	28·88	15·37*
MnO	—	—	—	—	—	—	0·01	—	0·01	—	—	0·00	—	0·00	0·01	—	—
Total															100	100·00	100

Accuracy of data ±4% relative.

* By difference.

† Varies from 4·3 to 6·7%.

1–4. J. Mélon, 1942.

5. Average of 1–4.

6–8. Dunn, this study, rind.

9. Average of 6–8.

10–13. Dunn, this study, core.

14. Average of 10–13.

15. Dunn, this study, average of 7 analyses.

16. Theory for empirical formula $3SiO_2.3{\cdot}5P_2O_5.6Al_2O_3.5CaO.1{,}5F.36H_2O$ (simplified average composition).

17. 'Blue viséite.'

ZnO 0·00% in anals. 6, 9, and 15.

TiO_2 0·00% in anals. 7, 9, 10, 11, 12, 14, 15, and 17.

$Cr2O_3$ 0·00% in anals. 10, 11, 14, and 15.

Although the blue material has a markedly different composition, we feel that a new name for this material is not justified at this time in view of the facts that the powder pattern of this blue material is identical to that of viséite and the material comes from the type locality. Although the blue material may indeed be a new mineral, there is, in our opinion, inadequate evidence available at this time to support such an argument. Structural investigations of silico-phosphates may afford new insights into these complex compounds, and we feel that any new names for additional calcium aluminum silico phosphates should await such structural studies.

In summary, perhamite is distinguished from viséite by its characteristic hexagonal, platy morphology; its sharp, distinctive powder diffraction pattern and hexagonal unit cell; its uniaxial (+) optical character and its chemical composition. The strong compositional similarity to viséite should be emphasized. The principal difference between the compositions of perhamite and viséite lies in the silica content.

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