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Kittatinnyite and wallkilldellite, silicate/arsenate analogues containing calcium and manganese, from Franklin and Sterling Hill, New Jersey

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Abstract

Kittatinnyite and wallkilldellite are isostructural silicate/arsenate analogues containing Mn and Ca, from Franklin and Sterling Hill, New Jersey, respectively. Both species are rare.

Kittatinnyite is hexagonal, space group $P6_3/mmc$, $P6_3mc$, or $P\bar{6}2c$, with $a = 6.498(4)$ and $c = 22.78(2)$Å. The formula is $Ca_4Mn^{3+}_4Mn^{2+}_2Si_4O_{16}(OH)_8\cdot 18H_2O$ for the idealized end member. Kittatinnyite is bright yellow with perfect {0001} cleavage; D (meas) = 2.61 g/cm^3; and yellow streak. Optically, kittatinnyite is uniaxial negative with $\omega = 1.727(3)$. Kittatinnyite is associated with bostwickite and carbonates on samples found in the Franklin Mine, Franklin, New Jersey, in 1874. The name is derived from the Algonquin word *kittatinny* which means "endless-hills" in allusion to the topography of the Franklin area.

Wallkilldellite has lattice parameters $a = 6.506(7)$ and $c = 23.49(3)$Å. The formula is $Ca_4Mn^{2+}_6As^{5+}_4O_{16}(OH)_8\cdot 18H_2O$ for the idealized end-member. Wallkilldellite is dark red with perfect {0001} cleavage; D (meas) = 2.85 g/cm^3. Optically, wallkilldellite is unixial negative with $\omega = 1.728(4)$. It is associated with a manganoan cuproan adamite on one specimen found in the Sterling Hill Mine, New Jersey, approximately in 1974. The name is derived from the *dell* of the *Wallkill* River, in which both ore deposits were first encountered.

Introduction

Although there are many examples of isostructural relations between phosphates and silicates, heretofore the only examples of arsenates isostructural with silicates have been berzeliite and manganberzeliite, which have the garnet structure. We report here on the unusual occurrence of two new minerals which are isostructural, one of which is a silicate and one an arsenate. The unusual nature of the simultaneous recognition of them as new species is even more surprising in that they are from the related Franklin and Sterling Hill deposits, but were found 100 years apart.

Kittatinnyite, $Ca_4Mn^{3+}_4Mn^{2+}_2Si_4O_{16}(OH)_8\cdot 18H_2O$, was found in 1874 in the Taylor Mine, one of many small mines consolidated in 1897 as the Franklin Mine. It is associated with bostwickite, $CaMn^{3+}_6Si_3O_{16}\cdot 7H_2O$ (Dunn and Leavens, 1983), but was found in a quality suitable for investigation on only two of the five known bostwickite specimens. The specimens had been preserved at the Smithsonian Institution and Harvard University and these are the only ones known at this writing. Kittatinnyite is named for the word *kittatinny* which, in the language of the Algonquin Indians who inhabited the Franklin area, meant "endless-hills" in allusion to the topography of the area around Franklin, New Jersey. The Franklin deposit is overlain by the Kittatinny Formation.

Wallkilldellite, $Ca_4Mn^{2+}_6As^{5+}_4O_{16}(OH)_8\cdot 18H_2O$, was found in the related deposit at Sterling Hill approximately in 1974, 100 years after the finding of kittatinnyite. Like kittatinnyite, wallkilldellite is quite rare; it is known from only one specimen and occurs as only a few milligrams on the holotype specimen. Wallkilldellite is named for the *dell* of the *Wallkill* River, where the Franklin and Sterling Hill deposits outcropped in full view.

Both species and their names were approved by the Commission of New Minerals and Mineral Names, IMA. The holotype specimen for kittatinnyite, which is also a type specimen for bostwickite, is in the Smithsonian Institution under catalog # NMNH C4222. Another specimen is in the Harvard University collection. The only known wallkilldellite specimen was divided in three por-

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tions through the courtesy of John L. Baum, the curator of the Franklin Mineral Museum, who had originally preserved this material in his private collection. The holotype portion is in the collection at Harvard University (HU # 113445); additional portions are in the Smithsonian Institution (NMNH # 149767) and in the private collection of John L. Baum.

Chemical analytical methods

Kittatinnyite and wallkilldellite were chemically analyzed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μA, standardized on brass. The standards used were hornblende (Si,Ca,Fe,Mg), cuprite (Cu), olivenite (As), manganite (Mn), and synthetic ZnO (Zn). Wavelength-dispersive microprobe scans indicated the absence of any additional elements with atomic number greater than 8. Samples were checked for homogeneity with a very small diameter beam and then analyzed with a 25 μm beam spot to minimize volatilization. Both kittatinnyite and wallkilldellite are stable under the electron microprobe beam and homogeneous from sample to sample. Schallerite and kolicite were employed as control standards. There was inadequate material for the direct determination of water; we have calculated it by difference. Analyses of both kittatinnyite and wallkilldellite, together with theoretical end-member compositions, are presented in Table 1.

Kittatinnyite

Crystallography

Crystals of kittatinnyite are very small, exceptionally thin, and invariably distorted. Only one single-crystal was found which could serve as a source for single-crystal data, and the diffraction patterns have reflections which are exceptionally weak and diffuse. Nevertheless, standard Weissenberg methods showed that the Laue symmetry is *6/m 2/m 2/m* and that reflections are extinct which obey the relations: 00*l*, *l* = 2n + 1; *hhl*, *l* = 2n + 1. Although the extinction rules are based on photographs of poor quality, and therefore subject to some question, they are consistent with space groups $P6_3/mmc$, $P6_3mc$ or $P\bar{6}2c$. The lattice parameters, *a* = 6.498(4) and *c* = 22.78(2)Å, were obtained by least-squares refinement of the powder diffraction data, as obtained using a 114.6 mm diameter Gandolfi camera, polycrystalline sample, and Si as an internal standard. The powder data are presented in Table 2. Kittatinnyite crystals are extremely thin and composed of the forms $\{0001\}$ and $\{10\bar{1}l\}$. The *l* index of the latter form could not be directly determined as no reflection from the very narrow faces could be detected using an optical goniometer. Crystals are 0.2 mm in diameter.

Table 1. Microprobe analyses of kittatinnyite and wallkilldellite

	Kittatinnyite		Wallkilldellite	
	Analysis	Theory*	Analysis	Theory**
FeO	0.0	0.00	0.3	0.00
CaO	17.3	17.01	12.4	14.89
ZnO	0.3	0.00	0.0	0.00
MgO	0.0	0.00	0.9	0.00
CuO	0.0	0.00	3.3	0.00
MnO	10.6	10.76	27.0	28.26
Mn_2O_3	23.6	23.95	0.0	0.00
SiO_2	18.2	18.24	1.7	0.00
As_2O_5	0.8	0.00	27.4	30.52
H_2O***	[29.2]	30.04	[27.0]	26.33
Total	100.0	100.00	100.0	100.00

* Theoretical composition for $Ca_4Mn^{3+}_4Mn^{2+}_2Si_4O_{16}(OH)_8 \cdot 18H_2O$.

** Theoretical composition for $Ca_4Mn^{2+}_6As^{5+}_4O_{16}(OH)_8 \cdot 18H_2O$.

*** Water by difference.

Accuracy of data: ± 4 percent of the amount present for major elements.

Table 2. X-ray powder diffraction data for kittatinnyite and wallkilldellite

KITTATINNYITE				WALLKILLDELLITE			
I/Io*	d (obs.)	d (calc.)	hkl	I/Io*	d (obs.)	d (calc.)	hkl
100	11.2	11.39	002	100	11.5	11.74	002
60	5.61	5.63	100	90	5.61	5.63	100
30	5.03	5.05	102	10	5.05	5.08	102
				40	4.56	4.57	103
5	4.00	4.00	104	5	4.06	4.07	104
30	3.80	3.80	006	2	3.92	3.91	006
30	3.25	3.25	110	40	3.25	3.25	110
				10	2.936	2.936	008
50	2.822	2.822	114	60	2.844	2.846	114
		2.817	107				
		2.814	200				
				1	2.810	2.817	200
60	2.733	2.732	202	50	2.748	2.740	202
2	2.637	2.638	203				
40	2.525	2.523	204	50	2.545	2.540	204
5	2.313	2.308	109				
40	2.279	2.278	0.0.10	40	2.349	2.349	0.0.10
				20	2.182	2.179	118
30	2.133	2.128	207	30	2.136	2.130	120
		2.127	210				
20	2.090	2.091	212	20	2.101	2.095	212
2	2.050	2.048	213				
2	2.002	2.001	208				
2	1.949	1.943	1.0.11				
5	1.885			2	1.886		
10	1.784			5	1.794		
				2	1.727		
2	1.704						
1	1.673						
30	1.628			5	1.611		
2	1.609						
10	1.574						
20	1.412			2	1.492		
				5	1.446		
				2	1.425		
5	1.324			5	1.341		

Powder data obtained using a 114.6 mm diameter Gandolfi camera, Si as internal standard, Cu Kα X-radiation, and polycrystalline sample.
* - intensities visually estimated.

Chemical composition

Calculation of the number of cations per unit cell based on the observed density, unit-cell volume, and chemical analysis (Table 1) results in the values, exclusive of hydrogen: $Ca_{4.04}Mn_{5.88}Zn_{0.05}Si_{3.97}As_{0.09}$. In order to determine the numbers and kinds of anions, we first assume that because kittatinnyite is isostructural with wallkilldellite, an arsenate, and because no briding oxygens are found between arsenate tetrahedra in natural minerals, arsenic must be in insular tetrahedra in kittatinnyite. The Si:O ratio is therefore 1:4. Additional anions are required for charge balance, but the relative number of OH and O is in turn dependent upon the oxidation state of Mn, a value which cannot be directly determined. We assume that significant Mn^{3+} is present for three reasons: (1) Calculations for the Gladstone–Dale relationship yield superior values based on the presence of considerable Mn^{3+}. (2) The brilliant yellow color is compatible with Mn^{3+}. (3) Mn^{3+} is present in the intimately associated bostwickite (Dunn and Leavens, 1983), implying that the chemical conditions of formation at least permit the occurrence of Mn^{3+}. We have chosen the Mn^{3+}:Mn^{2+} ratio of 4:2 based on charge-balance considerations, and using the Gladstone–Dale relationship as a guide. This results in the ideal formula $Ca_4Mn_4^{3+}Mn_2^{2+}Si_4O_{16}(OH)_8 \cdot 18H_2O$, for which Z = 1. This formula must be regarded as tentative, due to the assumptions on which it is based. This is especially true for the H_2O content which is based on calculation only by difference.

Physical and optical properties

Kittatinnyite is bright yellow and has a highly vitreous luster. Reflectivity is enhanced by internal reflections from cleavage surfaces. Kittatinnyite looks very much like native gold in hand specimen; the translucency is apparent only under microscopic examination, in part due to small crystal size. The hardness is approximately 4 (Mohs), but could not be determined with certainty due to the small crystal size and high degree of brittleness. Crystals occur as composite, subparallel aggregates up to 0.5 mm in diameter, flattened on {0001} and approximately 2.0 μm in thickness. The density, determined using heavy-liquid techniques, is 2.61 g/cm^3, in excellent agreement with the calculated value of 2.62 g/cm^3. The streak is light yellow. The {0001} cleavage is perfect and easily produced. Kittatinnyite is not fluorescent in ultraviolet radiation. Optically, kittatinnyite is uniaxial (−) with $\omega = 1.727(3)$; ϵ could not be determined due to the extreme thinness of platy crystals. Kittatinnyite is very weakly pleochroic with O = medium yellow, E = medium yellow, and $E \geq O$.

Occurrence

Kittatinnyite was found in the Franklin Mine, Franklin, Sussex County, New Jersey, in that part of the mine formerly known as the Taylor Mine, prior to the consolidation of many small mines into the Franklin Mine at the end of the last century. It was found in 1874 and preserved because of the presence of an associated mineral thought to be arseniosiderite (Palache, 1935) and now known as bostwickite (Dunn and Leavens, 1983). Kittatinnyite occurs coating fractures on a massive, granular, franklinite ore which is coated with secondary calcite and, in turn, by kittatinnyite and bostwickite, both of which appear to have formed contemporaneously. The franklinite–fluorite ore is in itself very unusual at Franklin.

Wallkilldellite

X-ray crystallography

No crystals of wallkilldellite could be found which are suitable for single-crystal X-ray diffraction. The powder diffraction pattern (114.6 mm diameter Gandolfi camera, Cu$K\alpha$ X-radiation, polycrystalline sample, Si as internal standard) is very similar to that of kittatinnyite, however, indicating that these minerals are isostructural. Starting with the lattice parameters of kittatinnyite, the powder diffraction data of wallkilldellite were easily indexed, and least-squares refinement of the lattice parameters gave rise to the values $a = 6.506(7)$ and $c = 23.49(3)$Å. All reflections are satisfactorily indexed using these parameters. The powder data are presented in Table 2, together with those for kittatinnyite.

Chemical composition

The chemical composition of wallkilldellite (Table 1), calculated on the basis of 14 cations, exclusive of H, as for kittatinnyite, yields: $(Ca_{3.31}Cu_{0.62}Fe_{0.06})_{\Sigma 3.99}(Mn_{5.69}^{2+}Mg_{0.33})_{\Sigma 6.02}(As_{3.56}Si_{0.42})_{\Sigma 3.98}O_{16}(OH)_{7.50} \cdot 18.65H_2O$ or ideally, $Ca_4Mn_6^{2+}As_4O_{16}(OH)_8 \cdot 18H_2O$, the As and Mn^{2+} analogue of kittatinnyite. The presence of considerable Si for As in solid solution is unusual, but not unreasonable, as it is known to occur, for example, in members of the apatite group. The presence of Cu is more problematical, however. We have assumed a valence of 2+ in the absence of direct evidence to the contrary, even though Cu^{2+} generally requires unusual coordination polyhedra. This chemical formula, like that of kittatinnyite, is tentative pending the discovery of material of adequate quality for structure analysis.

Physical and optical properties

Wallkilldellite is dark red. It appears very similar to kraisslite and mcgovernite but is slightly redder than either of these minerals. It is visually indistinguishable from the unnamed Fe^{3+} analogue of hematolite (Dunn and Peacor, 1983) also known from Sterling Hill. On the only specimen known, wallkilldellite occurs as flattened, radial clusters of platy crystals without obvious morphological characteristics other than the extremely platy habit. Crystal size is approximately 0.1 mm. The hardness could not be accurately determined due to the extremely small crystal size, but we estimate that wallkilldellite is approximately 3 in hardness (Mohs). It lacks the brittleness of kittatinnyite. The luster is vitreous on cleavage surfaces and tends to appear slightly resinous on fracture surfaces. The density, measured using heavy liquid techniques, is 2.85(5) g/cm^3, compared with the calculated value of 2.90 g/cm^3. The streak is light orange. The {0001} cleavage is perfect and easily produced. Wallkilldellite is not fluorescent in ultraviolet radiation. Optically, wallkilldellite is uniaxial (−) with $\omega = 1.728(4)$; ϵ could not be determined due to the extreme thinness of the platy crystals. Wallkilldellite is pleochroic with O = reddish orange, E = light orange-pink, and moderate absorption, $O > E$.

Occurrence

Wallkilldellite occurs in the Sterling Hill Mine, Ogdensburg, Sussex County, New Jersey. The one occurrence known was discovered in the mid-1970's and preserved for posterity by John L. Baum. The matrix consists of typical, massive, granular, franklinite/willemite ore which also has abundant calcite. This matrix is nearly identical to that for ogdensburgite (Dunn, 1981) and both minerals may have come from the same paragenesis. The surface of the ore is covered with carbonates, followed by a very atypical, finely-fibrous, light yellowish-green adamite-group mineral with approximate cation ratios for Zn:Cu:Mn = 2:2:1. Wallkilldellite is the last mineral to form in this assemblage and occurs as radial, irregular aggregates of platy crystals approximately 0.5 mm in maximum diameter, but most are considerably smaller. This mineral is extremely rare.

The occurrence of such a unique arsenate at Sterling Hill is not entirely surprising inasmuch as many secondary arsenates and arsenites, as well as complex arsenosilicates such as kraisslite, mcgovernite, kolicite, and holdenite are known to occur there. Because of the chemical complexity of both the Sterling Hill and Franklin orebodies, additional unique arsenates may await discovery.

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