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WICKSITE, A NEW MINERAL FROM NORTHEASTERN YUKON TERRITORY

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Abstract

Wicksite $NaCa_2(Fe^{2+},Mn)_4MgFe^{3+}(PO_4)_6 \cdot 2H_2O$ is orthorhombic, space group *Pbca*, with refined cell parameters *a* 12.896(3), *b* 12.511(3), *c* 11.634 (3) Å; $Z = 4$. The strongest eight lines in the X-ray-diffraction powder pattern [*d* in Å (I)(*hkl*)] are 3.502(20)(230), 3.015(80)(411), 2.910(80) (004), 2.868(30)(420), 2.837(30)(104), 2.753 (100)(412,042), 2.571(40)(422) and 2.118(60) (343,610). Wicksite occurs as blue plates in nodules in bedded ironstone and shale along the Big Fish River in northeastern Yukon Territory. The new mineral is dark blue or dark green in thin fragments; large fragments are opaque. It has a hardness of 4½–5, good {010} cleavage and density 3.54 g/cm³ (meas.), 3.58 g/cm³ (calc.). Wicksite is biaxial positive, α 1.713(3), β 1.718(3), γ 1.728(3), $2V$ 66°. It is strongly pleochroic: *X* blue, *Y* greenish blue and Z pale yellowish brown, with absorption $X = Y > Z$. Microprobe analysis, DTA–TGA and titration with potassium dichromate yield Al_2O_3 0.51, Fe_2O_3 7.98, Na_2O 3.08, FeO 22.66, MgO 3.77, MnO 4.72, CaO 11.05, P_2O_5 41.64, H_2O 3.70, sum 99.11%, whence the calculated formula $Na_{4.00}Ca_{7.85}Fe^{2+}_{12.64}Mn_{2.65}Mg_{3.77}Fe^{3+}_{4.01}Al_{0.39}P_{23.46}O_{102.38}H_{16.45}$. The name honors Dr. Frederick John Wicks, Curator of Mineralogy at the Royal Ontario Museum.

Keywords: wicksite, phosphate, new mineral, Yukon.

Sommaire

La wicksite $NaCa_2(Fe^{2+},Mn)_4MgFe^{3+}(PO_4)_6 \cdot 2H_2O$ est orthorhombique, groupe spatial *Pbca*, et possède les paramètres affinés *a* 12.896(3), *b* 12.511(3), *c* 11.634(3) Å pour $Z = 4$. Les huit raies les plus intenses du cliché de poudre [*d* en Å (I) (*hkl*)] sont: 3.502(20)(230), 3.015 (80)(411), 2.910(80)(004), 2.868(30)(420), 2.837(30)(104), 2.753(100)(412,042), 2.571(40)(422) et 2.118(60) (343,610). On trouve la wicksite en plaquettes bleues dans des nodules des formations ferrugineuses et des shales stratifiés le long de la rivière Big Fish (dans le Nord-Est du territoire du Yukon). Cette espèce nouvelle est bleu foncé ou vert foncé en sections minces, opaque en fragments épais. Dureté 4½-5, clivage {010} bon, densité 3.54 (mesurée), 3.58 (calculée). Elle est biaxe positive, α 1.713(3), β 1.718(3), γ 1.728(3), $2V$ 66°; fortement pléochroïque, *X* bleu, *Y* bleu verdâtre, *Z* brun jaunâtre pâle, absorption $X = Y > Z$. Les données analytiques (microsonde, ADT–ATG, titration avec le dichromate de potassium) donnent Al_2O_3 0.51, Fe_2O_3 7.98, Na_2O 3.08, FeO 22.66, MgO 3.77, MnO 4.72, CaO 11.05, P_2O_5 41.64, H_2O 3.70, total 99.11% (en poids), d'où la formule calculée $Na_{4.00}Ca_{7.85}Fe^{2+}_{12.64}Mn_{2.65}Mg_{3.77}Fe^{3+}_{4.01}Al_{0.39}P_{23.46}O_{102.38}H_{16.45}$. Espèce dédiée au Dr Frederick John Wicks, conservateur de minéralogie au Royal Ontario Museum.

(Traduit par la Rédaction)

Mots-clés: wicksite, phosphate, minéral nouveau, Yukon.

Introduction

Since 1973, when the first specimens of phosphate minerals were brought to the Royal Ontario Museum for identification, five new minerals have been described from an iron formation in northeastern Yukon Territory. Specimens with large, well-developed crystals of phosphate minerals were collected in the area along Rapid Creek, whereas in the nearby area along the Big Fish River, the phosphate minerals are developed mostly as aggregates or as nodules. Two new minerals have been found in the specimens from the Big Fish area: maricite $NaFePO_4$ (Sturman *et al.* 1977) and satterlyite $(Fe,Mg)_2PO_4(OH)$ (Mandarino *et al.* 1978). The new

mineral *wicksite* was found as minute grains during the study of the paragenesis of satterlyite, but detailed investigation was postponed until specimens containing larger grains were collected.

We are pleased to name this mineral in honor of Dr. Frederick John Wicks, Curator of Mineralogy at the Royal Ontario Museum, Toronto. His contribution to mineralogy, especially in the field related to serpentine minerals, has been recognized by the Mineralogical Association of Canada, which awarded him and his coauthor Dr. E.J. Whittaker the Hawley medal for the best paper published in *The Canadian Mineralogist* in 1977 and again in 1978.

The mineral and the name were approved by the Commission on New Minerals and Mineral Names, I.M.A. The type specimen (grams) is preserved in the collections of the Royal Ontario Museum, Toronto (*M*37364), and the fragments from this specimen are preserved in the Smithsonian Institution, Washington, D.C. (*NMNH* 145607) and the National Mineral Collection, Geological Survey of Canada, Ottawa (61309).

Paragenesis

Wicksite is found in ironstone and shale units of Cretaceous sediments along the Big Fish River in northeastern Yukon Territory. The geology of the area was described by Young (1977). The type specimen was collected at the locality known as Big Bend, located on the west shore of the Big Fish River (latitude 68°28′30″ N and longitude 136°29′ W). There, the phosphate minerals, including wicksite, are found in nodules in shale beds. Many of the nodules have an outline that suggests formation by the replacement of fossil ammonites. The major constituents of the nodules are wolfeite, satterlyite, maricite and pyrite; some nodules are composed of only one or two of these minerals. Of several hundred nodules examined, only about ten contain wicksite, always as a minor constituent.

Wicksite is intimately associated with wolfeite, satterlyite and maricite. These apparently all formed contemporaneously. Wicksite is usually found along the edges of nodules or interstitially, filling the spaces between the radial aggregates of satterlyite, maricite and wolfeite, or admixed with the minerals in these aggregates. Pyrite and quartz are also found in the nodules with wicksite; in some nodules all minerals are coated with a thin layer of ludlamite or vivianite.

Crystallography

A single-crystal X-ray-diffraction study of a small cleavage plate of wicksite showed that it is orthorhombic, space group *Pbca* with unit-cell parameters *a* 12.91(2), *b* 12.54(2), *c* 11.64(2) Å. An X-ray-diffraction powder pattern was obtained with a Guinier–de Wolff camera and Cu $K\alpha$ radiation. Intensities of the reflections on precession and Weissenberg camera films were used as an aid in indexing the powder pattern. Least-squares refinement of the unit-cell parameters, based on 19 reflections in the powder pattern (Table 1), yielded the refined unit-cell parameters *a* 12.896(3), *b* 12.511(3), *c* 11.634(3) Å.

Physical and Optical Properties

Wicksite is dark blue, almost black, tending toward blue or green and transparent in thin fragments. The streak is green, and the lustre, submetallic. Cleavage {010} is good. The hardness (Mohs) is 4½–5. Wicksite is platy parallel to {010}; some specimens are massive. Striations parallel to the *a* axis are developed on many plates. No forms other than {010} were observed.

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR WICKSITE

I	d_{obs}	d_{calc}	hkl	I	d_{obs}
10	6.47	6.448	200	5	2.085
10	6.28	6.256	020	10	2.041
10	5.83	5.817	002	1	1.991
10	4.50	4.500	220	5	1.962
5	4.33	4.319	202	5	1.909
5	4.19	4.189	221	1	1.893
1	4.05	4.045	122	1	1.852
1	3.556	3.560	113	5	1.834
		3.554	222	5	1.776
20	3.502	3.502	230	10	1.748
80	3.015	3.015	411	10	1.718
20	2.942	2.941	141	5	1.662
80	2.910	2.908	004	5	1.647
30	2.868	2.866	420	10	1.632
30	2.837	2.837	104	1	1.604
20	2.820	2.820	402	1	1.595
100	2.753	2.755	042	1	1.569
		2.751	412	10	1.553
10	2.736	2.735	241	5	1.534
20	2.693	2.694	142	5	1.505
40	2.571	2.571	422	1	1.477
20	2.491	2.491	431	5	1.433
10	2.467	2.469	511	10	1.336
10	2.429	2.432	413	10	1.285
5	2.332	2.333	250		
1	2.252	2.252	115		
1	2.146	2.150	125		
60	2.118	2.118	343		
		2.118	610		

Guinier camera; CuKα radiation; intensities estimated visually; indexed with orthorhombic unit cell a=12.896, b=12.511, c=11.634 Å, space group *Pbca*.

The density, measured with a Berman microbalance, is 3.54(2) g/cm³. It compares well with the density (3.58 g/cm³) calculated from the ideal formula, the refined unit-cell parameters and $Z = 4$.

Wicksite is biaxial positive; $2V_z$ 66(2)° (measured), 72° (calculated). Principal indices of refraction are α 1.713(3), β 1.718(3) and γ 1.728(3). Dispersion of the optic axes is strong, $r < v$. The mineral is strongly pleochroic with absorption $X = Y > Z$; X blue, Y greenish blue, Z pale yellowish brown. The orientation of the indicatrix is $Z = c$ and $Y = a$. Wicksite is not fluorescent under ultraviolet light, and no cathodoluminescence is produced by the beam of the electron microprobe. The specific refractivity K_C calculated from the chemical composition, using the Gladstone–Dale constants given by Mandarino (1976), is 0.202, in excellent agreement with the constant $K_P = 0.203$, calculated from the measured density and indices of refraction.

Many grains of wicksite show anomalous optical effects consistent with monoclinic, rather than orthorhombic, symmetry. For example, a maximum extinction angle $Z \wedge c$ of 5° was observed on many grains. Two adjacent individuals or two zones have identical orientation of the crystallographic elements, but the angle between the two principal vibration directions $Z_1 \wedge Z_2$ may attain 10°, thus suggesting a twin. The anomalous optical behavior is commonly observed on grains in thin section, indicating that it may have been induced by stress. Careful study of such optically anomalous grains with the single-crystal X-ray-diffraction methods showed that they are indeed single crystals with orthorhombic symmetry.

Reflections on the films obtained by the single-crystal X-ray-diffraction method are invariably diffuse and imperfect, and are typical of crystals with a high density of imperfections and a complex mosaic structure. Indeed, the crystals are so imperfect that they are not suitable for a crystal-structure determination.

Chemistry

Wicksite was chemically analyzed with an ARL–SEMQ electron microprobe utilizing an operating voltage of 15 kV and a beam current of 0.15 μA. The data were corrected using standard Bence–Albee factors. The standard used for all elements was chemically analyzed wyllieite. Analyses obtained with other standards yielded very similar results. Titration of type wicksite with potassium dichromate yielded 22.66% FeO. The iron in excess of 22.66% was calculated as Fe_2O_3. Microchemical tests indicated the presence of both ferric and ferrous iron, with the reaction for ferrous iron being the stronger of the two.

TABLE 2. CHEMICAL COMPOSITION OF WICKSITE

Al_2O_3	Fe_2O_3	Na_2O	FeO	MgO	MnO	CaO	P_2O_5	H_2O	Total
0.51	7.98	3.08	22.66	3.77	4.72	11.05	41.64	3.70	99.11%

H_2O determined by DTA-TGA; ferrous iron by titration with potassium dichromate; other elements determined with microprobe; total iron 23.19%; accuracy of data ± 3% of the amount present.

Gravimetric analysis of 13 mg of wicksite in a vacuum showed a weight loss of 3.70%, most of which occurred during heating between 440 and 580°C. Analysis of the evolved gas indicated that the weight loss should be attributed to the loss of H_2O.

Calculation of unit-cell contents for the composition given in Table 2, using the refined unit-cell parameters and observed density, yields $Na_{4.00}Ca_{7.85}Fe^{2+}_{12.64}Mn_{2.65}Mg_{3.77}Fe^{3+}_{4.01}Al_{0.39}P_{23.46}O_{102.38}H_{16.45}$. Semiquantitative analyses of a number of wicksite samples indicate that Mn is not an essential constituent but is likely a substitute for ferrous iron. The above unit-cell contents strongly suggest that Fe^{3+}, Na and Mg are ordered on equipoints of rank four. However, space group *Pbca* has only two special equipoints of rank four and the general equipoint of rank eight. Because there are approximately 36 non-tetrahedral cations in the cell, they can only be distributed on one site of rank four and four sites of rank eight. These observations strongly suggest that one of the three elements Na, Mg or Fe^{3+} is ordered on one site of rank four, but we cannot determine which one on the basis of the extant data. The empirical data suggest a tentative general formula $Na_{1.00}Ca_{1.96}Fe^{2+}_{3.16}Mn_{0.66}Mg_{0.94}Fe^{3+}_{1.00}Al_{0.10}P_{5.86}O_{23.52}\cdot 2.06H_2O$ or, simply stated, $NaCa_2(Fe^{2+}, Mn)_4MgFe^{3+}(PO_4)_6\cdot 2H_2O$, with $Z = 4$.

We emphasize that the apparent ordering of the cations Na, Fe^{3+} and Mg may be only fortuitous; it is not permitted by the space group without the ordered vacancies. On the other hand, the anomalous optical properties indicate that a lower symmetry is possible, which could be consistent with the additional equipoints of rank four. Although the single-crystal X-ray diffraction study gave results that are apparently consistent with space group *Pbca*, a final interpretation of the chemical formula must await a complete crystal-structure determination.

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