Canadian Mineralogist
Vol. 23, pp. 247-249 (1985)

A WICKSITE-LIKE MINERAL FROM THE BULL MOOSE MINE, SOUTH DAKOTA

DONALD R. PEACOR
Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

PETE J. DUNN
Department of Mineral Sciences, Smithsonian Institution, Washington D.C. 20560, U.S.A.

ROBERT A. RAMIK
Department of Mineralogy and Geology, Royal Ontario Museum, Toronto, Ontario M5S 2C6

THOMAS J. CAMPBELL AND WILLARD L. ROBERTS
Museum of Geology, South Dakota School of Mines, Rapid City, South Dakota 57701, U.S.A.

ABSTRACT

An unnamed wicksite-like mineral is described from the Bull Moose mine in South Dakota, where it is found associated with barbosalite, pyrite, and secondary Fe-phosphates. Chemical analysis yields: Fe_2O_3 17.2, FeO 9.2, MgO 0.2, CaO 12.0, Na_2O 0.8, MnO 16.9, P_2O_5 40.9, H_2O 4.2, total 101.4 wt.%. X-ray studies (precession method and powder data) confirm a relation to wicksite; the unit-cell parameters are *a* 12.77(1), *b* 12.59(1), *c* 11.709(8) Å. A general formula is $(Mn,Fe^{3+},Fe^{2+},Na,Ca)_7Ca_2(PO_4)_6(OH,H_2O)_4$, with $Z = 4$. This phase is likely the Mn-analogue of wicksite.

Keywords: wicksite, manganese analogue, chemical and crystallographic data, South Dakota.

SOMMAIRE

On décrit un minéral sans nom qui ressemble à la wicksite et qui provient de la mine Bull Moose au Dakota du Sud, où il est associé à la barbosalite, la pyrite et des phosphates de fer secondaires. L'analyse chimique donne 17.2% Fe_2O_3, 9.2% FeO, 0.2% MgO, 12% CaO, 0.8% Na_2O, 16.9% MnO, 40.9% P_2O_5, 4.2% H_2O, totalisant 101.4% (en poids). Les études aux rayons X (méthodes de précession et de poudre) confirment la relation avec la wicksite: les dimensions de la maille sont: *a* 12.77(1), *b* 12.59(1), *c* 11.709(8)Å. La formule chimique générale est $(Mn,Fe^{3+},Fe^{2+},Na,Ca)_7Ca_2(PO_4)_6(OH,H_2O)_4$, où $Z = 4$. Cette phase semble être l'équivalent manganifère de la wicksite.

(Traduit par la Rédaction)

Mots-clés: wicksite, analogue manganifère, données chimiques et cristallographiques, Dakota du Sud.

INTRODUCTION

A green druse coating on barbosalite from the Bull Moose mine, in South Dakota, was noted by one of the authors (WLR) in 1959 during an investigation of minerals from this locality (Roberts & Rapp 1965). As part of a recent study of phosphates from the Black Hills, we have re-examined this material and note that its X-ray powder-diffraction pattern is very similar to that of wicksite (Sturman *et al.* 1981). Our study of this mineral has confirmed this relationship and indicates that the new material may be the Mn-analogue of wicksite. However, because the cation site-assignments in wicksite are still slightly speculative, and because the composition of this material can be recast in a number of different forms that are consistent with different assumptions regarding site occupancies, we have chosen not to name this phase pending a determination of the crystal structure of wicksite. Our data are presented for the record, as a report on an unnamed mineral. The studied samples are deposited in the Smithsonian Institution under catalogue #NMNH 159890 and 159892.

CRYSTALLOGRAPHY

The wicksite-like mineral was studied using single-crystal precession techniques. Precession photographs were obtained with the principal cleavage parallel to the film; these show reflections that are extremely elongated parallel to arcs of equivalent powder-diffraction circles, indicating that the apparent single crystals consist of a mosaic of crystallites. These have the cleavage plane in common orientation but are misoriented about an axis normal to that plane. Because the reflections are so diffuse, they do not permit unambiguous determination of the unit cell and space group. However, as we suspect that this phase is isostructural with wicksite, we directly compared the poor-quality photographs of this phase with photographs of equivalent orientation for wicksite. The relative positions and intensities of reflections for both phases are equivalent. Powder-diffraction patterns of both phases were also compared and found to be so similar as to also strongly imply an isostructural relation. The unit-cell parameters were refined from X-ray powder-diffraction data obtained using a Gandolfi 114.6-mm-diameter powder camera, Fe*Kα* radiation, and a polycrystalline sample, employing Si as an internal standard. This mineral is orthorhombic, with *a* 12.77(1), *b* 12.59(1), and *c* 11.709(8) Å, $V = 1881(2)$ Å^3. These parameters compare closely with those for wicksite: *a* 12.896, *b* 12.511, *c* 11.634 Å. The space group is implied by analogy with wicksite as systematic extinctions could not be determined with certainty owing to a lack of high-quality single-crystal diffraction patterns. Indexing of the powder pattern is consistent with the space group of wicksite, *Pbca*. The powder diffraction data are presented in Table 1.

PHYSICAL AND OPTICAL PROPERTIES

This mineral is dark green when fresh; altered material is a lighter green. The density, determined using heavy-liquid techniques, is 3.64(5)(meas.), 3.766 (calc.) g/cm^3. The lustre is slightly pearly on cleavage surfaces, and decidedly dull on fracture surfaces. Although closely related to wicksite, there is very little physical resemblance between the species. Optically, this wicksite-like mineral is biaxial positive, with $2V$ approximately 75°. The indices of refraction are α 1.781, β 1.787, and γ 1.796 (all ± 0.003). Pleochroism is intense: *X* dark brownish green, *Y* dark green, *Z* medium brownish green; absorption is $X > Y > Z$. Dispersion of the optic axes is strong, $r < v$. The majority of the crystal fragments examined are curved and exhibit wavy extinction. Calculation of the Gladstone–Dale relationship, using the values of Mandarino (1981), yields K_C 0.221 and K_P 0.216, indicating excellent compatibility of the physical and chemical data.

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR THE WICKSITE-LIKE MINERAL

I/Io	d (obs.)	d (calc.)	hkl	I/Io	d (obs.)
40	6.31	6.29	020	5	2.271
50	5.84	5.85	002	2	2.165
20	4.49	4.48	220	60	2.098
5	4.31	4.31	202	10	2.045
1	4.18	4.19	221	20	1.978
20	3.81	3.81	311	10	1.951
30	3.50	3.51	230	10	1.909
10	3.30	3.32	023	10	1.849
		3.29	132	2	1.831
5	3.22	3.22	213	1	1.805
		3.21	123		
90	2.997	3.008	232	10	1.781
		2.991	411	5	1.754
100	2.927	2.927	004	20	1.727
10	2.856	2.853	104	10	1.708
100	2.769	2.772	042	30	1.665
		2.776	421		
2	2.706	2.709	142	5	1.648
2	2.658	2.661	204	2	1.628
		2.654	024	5	1.613
10	2.558	2.560	422	10	1.570
20	2.484	2.482	431	5	1.543
10	2.424	2.424	413	5	1.514
		2.417	151	10	1.472
5	2.334	2.340	502	10	1.426
		2.330	432	5	1.374
				2	1.356
				5	1.339
				2	1.316
				2	1.296
				10	1.283

Intensities estimated visually.

CHEMICAL COMPOSITION

This wicksite-like mineral was chemically analyzed using an ARL-SEMQ electron microprobe utilizing an operating current of 15 kV and a sample current of 0.025 μA, measured on brass. The following standards were used: marićite (Fe,Na, P), manganite (Mn), and arrojadite (Ca,Mg). An emission spectrographic analysis and a wavelength-dispersion microprobe scan indicated the absence of elements other than those reported herein. Fluorine is present as a trace. The oxidation state of iron was determined by titration and yielded 9.2 wt.% FeO; the remainder of the Fe was calculated as Fe_2O_3. The *in vacuo* TGA-Evolved Gas Analysis (EGA) curves of our phase and of wicksite are similar. Wicksite (Sturman *et al.* 1981) evolved 3.7% H_2O between 440 and 680°C, with a maximum rate of loss at 530°C. The wicksite-like phase experienced a weight loss of 6.7% between 120 and 670°C, with a maximum rate of H_2O loss at 595°C. However, although H_2O was the only major volatile detected by EGA of our phase, the TG curve indicated rapid evolution of an additional volatile between 550 and 600°C. This volatile had apparently condensed before reaching the spectrometer. The contribution of H_2O to the total 6.7% loss was estimated to be 4.2%, with a cautious error estimate of ± 1.0%. TGA–EGA were repeated on another sample of this wicksite-like mineral with similar results. An attempt to identify the unknown volatile by comparative semiquantitative microprobe scans of the wicksite-like phase and the resultant breakdown-product was inconclusive. The fusion of wicksite and of the wicksite-like phase are both marked by minor bursts of CO_2 (plus SO_2 in the wicksite-like phase) at 925 and 920°C, respectively. The resultant analysis yields Fe_2O_3 17.2, FeO 9.2, MgO 0.2, CaO 12.0, Na_2O 0.8, MnO 16.9, P_2O_5 40.9, H_2O 4.2, total 101.4 wt.%.

Calculation of the unit-cell contents, using the refined cell-parameters and the observed density, yields: $Fe^{3+}_{8.88}Fe^{2+}_{5.28}Mg_{0.20}Ca_{8.82}Na_{1.06}Mn_{11.05}P_{23.77}H_{19.22}O_{108.23}$. We interpret the formula very tentatively because, as was the case with wicksite, there is some ambiguity in the assignment of specific cations to the individual sites. Some discussion of these relations is warranted here as they relate to whether or not this phase should be given species status. This mineral, like wicksite, has approximately 36 nontetrahedral cations (35.31 in wicksite, 35.29 in this phase). The space group has two special positions of rank 4 and a general position of rank 8. The only way to distribute the 36 cations on these equipoints is to place four cations on a special equipoint and the remaining approximately 32 cations (plus 0.71 vacancies?) on four sites corresponding to the general equipoint. As in wicksite, there are approximately 8 Ca atoms per unit cell, and Ca is therefore inferred to occupy one general equipoint in both structures. In wicksite, there are approximately 4 Fe^{3+}, 4 Na and 4 Mg per cell, and one of those atoms thus occupies the special equipoint. However, none of these elements occur in this wicksite-like phase in similar amounts; we therefore cannot determine which cationic species occupy the special equipoint. The remaining cations are all consistent with octahedral co-ordination and may occur in mutual solid-solution relations. No cations occur in numbers per cell corresponding to equipoint ranks. We are, therefore, severely restricted in writing a formula for this phase; rather than write one with specific site-assignments that may be in error, we simply write it as: $(Mn,Fe^{3+},Fe^{2+},Na,Ca,Mg)_7Ca_2(PO_4)_6(OH,H_2O)_4$, with $Z = 4$. The distinguishing feature of this formula, relative to that of wicksite, is the high Mn content. Wicksite has a high Fe^{2+} content (12.64 atoms per cell). This wicksite-like phase is therefore inferred to be the Mn-equivalent of wicksite, but we have not attempted to assign species status to it because of the ambiguities in site occupancies. Clearly, the broad solid-solution relations implied by the complex compositions of wicksite and this phase indicate that other such apparent end-members may come to light. Until crystal-structure relations are definitively established, with definitions of limits on site occupancies, we recommend that additions to the nomenclature, relating to other apparent isostructural phases, be applied with caution.

OCCURRENCE

This mineral was found in a pegmatite known as the Bull Moose Lode, which is located in the SE ¼, sec. 32, T3S, R5E, five kilometres southeast of Custer, Custer County, South Dakota. The pegmatite dyke is emplaced in granite and schist. The Bull Moose mine, within this pegmatite, has been worked intermittently for microcline, rose quartz, beryl, muscovite and columbite–tantalite. The mineral studied occurs in masses of fine-grained barbosalite up to one metre in diameter; these are derived from graftonite–triphylite–sarcopside intergrowths (Peacor 1969) that have abundant pyrite and sparse arsenopyrite segregations within them. These sulfides persist and are also found in similar proportions in the resultant barbosalite, which is the common type of barbosalite; the MnO content is less than 1.0 wt.%. Subsequent hydrothermal alteration has etched the barbosalite, creating vugs (1–8 cm) lined with secondary barbosalite. Secondary phases that occur in these vugs include gypsum, leucophosphite, strengite and phosphosiderite, all of which form euhedral crystals.

The wicksite-like mineral occurs as compact, lamellar, irregular aggregates intimately associated with the pyrite segregations. The material studied is from these segregations, in which the wicksite-like mineral forms almost wholly within pyrite. Many specimens have large vugs which, we presume, represent areas where pyrite has been dissolved out of the aggregates, leaving remnants of the wicksite-like mineral as vug-linings. These linings consist of a felty green material, the powder pattern of which is identical to the fresh material from the pyrite segregations.

Another assemblage was observed by us, but not examined in detail. In this occurence, also at the Bull Moose mine, a wicksite-like mineral, identified as such by its powder pattern, occurs with green tavorite on massive primary triphylite. This wicksite-like mineral forms reddish brown rosettes up to 0.1 mm in diameter.

ACKNOWLEDGEMENTS

The authors are indebted to Mr. Joseph A. Nelen for the titration for ferrous iron, and to Dr. Richard V. Gaines for spectrographic analyses of this phase. We thank Drs. George Chao, H.D. Grundy, B.J. Burley and Robert F. Martin for constructive suggestions for improvement of the text.

REFERENCES

MANDARINO, J.A. (1981): The Gladstone–Dale relationship. IV. The compatibility concept and its application. *Can. Mineral.* **19**, 441-450.

PEACOR, D.R. (1969): Triphylite–sarcopside–graftonite intergrowths from Custer, South Dakota. *Amer. Mineral.* **54**, 969-972.

ROBERTS, W.L. & RAPP, G.R., JR. (1965): Mineralogy of the Black Hills (leucophosphite). *S. Dak. School Mines Tech. Bull.* **18**, 124-125.

STURMAN, B.D., PEACOR, D.R. & DUNN, P.J. (1981): Wicksite, a new mineral from northeastern Yukon Territory. *Can. Mineral.* **19**, 377-380.

Received July 31, 1984, revised manuscript accepted December 4, 1984.