THE AMERICAN MINERALOGIST, VOL. 42, SEPTEMBER–OCTOBER 1957

NOLANITE, A NEW IRON-VANADIUM MINERAL FROM BEAVERLODGE, SASKATCHEWAN

S. C. Robinson, *Geological Survey of Canada, Ottawa*, and H. T. Evans, Jr., W. T. Schaller, and J. J. Fahey, *U. S. Geological Survey, Washington, D. C.*

Abstract

A new iron vanadium oxide mineral from Fish Hook Bay, Beaverlodge region, Saskatchewan, has been named nolanite, after Dr. Thomas B. Nolan, Director of the U. S. Geological Survey. The mineral occurs as small, black, opaque, hexagonal plates with a submetallic luster, usually intimately associated with another unidentified iron vanadium oxide mineral. The unit cell is hexagonal, with $a = 5.85_4$, $c = 9.29_5$ Å, and space group $P6_3/mmc$, $P6mc$, or $P\bar{6}2c$. Chemical analyses of samples of nolanite, extracted by differential solubility in acid and by hand picking, lead to inconclusive results regarding the formula, owing to the great difficulty experienced in removing impurities. On crystal chemical grounds, it is proposed that Fe substitutes for V in the crystal structure and that the formula may be approximately $Fe_{2.5}^{+2}V_{1.7}^{+3}V_{5.5}^{+4}O_{16.0}$, or $Fe_{2.8}^{+2}V_{1.5}^{+3}V_{5.5}^{+4}O_{16.0}$. The mineral is best identified by its x-ray powder pattern.

Introduction

A small hand specimen from the "A" zone of Eldorado Mining and Refining Limited, on the shore of Fish Hook Bay, Lake Athabaska, in the Beaverlodge region[1] of Saskatchewan, was found to contain a new mineral, an iron vanadium oxide. This specimen and several others from the same area were x-rayed in Washington and in Ottawa and gave identical patterns unlike that of any known mineral.

The new mineral has been named nolanite in honor of Dr. Thomas B. Nolan, Director of the U. S. Geological Survey, and geologist in the Survey since 1924, in recognition of his outstanding geological work and his constant appreciation of the value of mineralogical data in geological problems.

Occurrence

In addition to the original discovery, nolanite has been identified from the first level of the No. 2 mine of Consolidated Nicholson Mines Limited, from several levels of the Ace Mine, and from the main showing on the Pitche group of claims on the southwest shore of Beaverlodge Lake. In the Pitche group vanadium assays were high enough to raise hopes that the element might be recovered economically. It is possible that nolanite may be found in sufficient quantity to become an ore mineral of vanadium.

---

[1] The Beaverlodge region was referred to as the Goldfields region in some earlier publications.

All the deposits containing nolanite are thought to be hydrothermal in origin. They are described in a bulletin on the mineralogy of the region by Robinson (1955). Although fissure filling has been the dominant mechanism in most deposits of the Beaverlodge region it is noteworthy that evidence of replacement has been observed in three of the four deposits in which nolanite has been identified.

The typical occurrence of nolanite is as concentrations of discrete subhedral to euhedral hexagonal plates from 10 to 20 microns in diameter. Locally these plates have coalesced into massive material containing residual inclusions. In the dolomite matrix of the Fish Hook Bay deposit, nolanite crystals attain diameters up to 1 mm. (Fig. 1). In leached zones some of these crystals have been freed by differential weathering of the dolomite. In the Nicholson Mine, nolanite forms radiating crusts on the dolomitized walls of the veins. Pitchblende, calcite, and sulfides in turn form an inner layer toward the center of the vein and fill interstices in the nolanite crust.

Minerals intimately associated with nolanite are dolomite, quartz, calcite, pyrite, hematite, pitchblende, chalcopyrite, ilmenite, and galena. Nolanite fills cracks in euhedral pyrite but is mantled or cemented by massive pyrite. It is also mantled by chalcopyrite, pitchblende, dolomite, and quartz. Hematite in part is veined by nolanite, but crystals of hematite, together with crystals of nolanite, are embedded in chalcopyrite and pyrite (Fig. 2). Ilmenite and nolanite in coalescing subhedral grains occur together, cemented by quartz, calcite, and pitchblende. In the Pitche group showing, carnotite has been identified, presumably having been formed as a weathering product of nolanite and pitchblende.

DESCRIPTION

Massive nolanite is black, but in powdered form it is brownish black. In polished section it is pleochroic from dark brown to deep blue. Plates with the *c* crystallographic axis normal to the surface are virtually isotropic, but sections containing the *a* and *c* axes are markedly anisotropic with parallel extinction. Charles Milton of the U. S. Geological Survey, in a polished section of the sample from the "A" zone of the Eldorado Mining and Refining Limited, observed two phases, one with a brownish reflection and the other with a bluish reflection. The two phases were in the ratio of approximately four to one in abundance. The chemical analysis by Fahey tended to confirm the presence of two phases by differential solubility, nolanite being the phase of greater abundance.

In thin section nolanite is opaque, but thin splinters are slightly translucent. The hardness is approximately 5; the determination was difficult owing to very small grain size. The specific gravity, as determined by

FIG. 1. Boxwork of nolanite (gray) in chalcopyrite (white) and dolomite (black). Polished section of weathered specimen, Zone "A," Eldorado Mining and Refining Ltd., Fish Hook Bay. Magnification 100×.

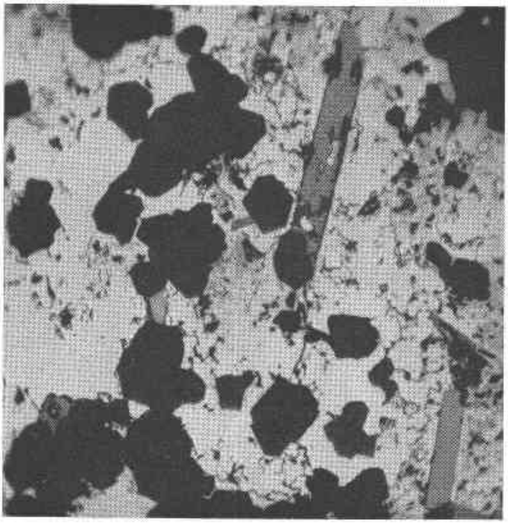

FIG. 2. Crystals of nolanite (dark gray) and laths of hematite (gray) in chalcopyrite and pyrite (white). Polished section under oil immersion. Main showing, Pitche Group, S.W. shore of Beaverlodge Lake. Magnification 500×.

Alice D. Weeks of the U. S. Geological Survey on a crushed sample from the Pitche group, is 4.65. On crystals from Fish Hook Bay the forms $c\ \{0001\}$, $m\ \{10\bar{1}0\}$, and $p\ \{10\bar{1}1\}$ were identified.

Barnes and Qurashi (1952) published results of preliminary *x*-ray studies of nolanite ("iron vanadate . . . from Goldfields, Saskatchewan," unnamed at the time) in which they show that the unit cell is hexagonal, with $a=5.854\pm0.005$ Å and $c=9.295\pm0.010$ Å and the space group $P\bar{6}2c$, $P6mc$ or $P6/mmc$. The axial ratio based on these *x*-ray measurements is $a:c=1:1.588$.

Table 1 lists the calculated spacings based on the unit-cell data of Barnes and Qurashi, the observed spacings and intensities from a film made by F. A. Hildebrand of the U. S. Geological Survey using CrKα radiation, and the observed spacings of Miss A. P. Sabina of the Geological Survey of Canada using CuKα radiation.

It should be noted that identification of nolanite as reported by Robinson (1955) rests on *x*-ray powder diffraction patterns. The same *x*-ray powder pattern has been obtained from approximately a dozen different specimens from Canada.

CHEMICAL SEPARATION

It was obvious, because of the intimate intergrowth of nolanite and the other opaque mineral, that separation of the two species by mechanical means would be impossible. In an effort to find a solvent for these two opaque minerals, and if possible to find a differential solvent, various concentrations of acetic, hydrochloric, nitric, and sulfuric acids were tried. Portions of the ground sample were treated with these acids at room temperature, at the temperature of the steam bath, and at boiling temperatures for periods of time ranging from a few minutes to several months. A solution of one volume of concentrated sulfuric acid in four volumes of water, cooled to room temperature, was found to be a suitable differential solvent. The treatment of the sample was as follows:

To a 2.000-gm. sample in an Erlenmeyer flask, from which the air had been displaced by CO_2, 100 ml. of the (1+4) H_2SO_4 at room temperature was added, and the flask lightly stoppered until the evolution of CO_2, due to the dolomite, ceased. The flask was then tightly closed.

Within a few minutes the acid solution assumed a faintly blue green color that gradually deepened for about five days. After this time there was no visual evidence of further solution of the sample. The flask was allowed to stand for two weeks, with frequent agitation, and then the blue green solution was carefully decanted into another flask from which the air had been displaced by CO_2. From this flask aliquots (25 ml. =0.500 g. sample) were pipetted and analyzed (Analysis 1, Table 2).

TABLE 1. *X*-RAY POWDER DATA FOR NOLANITE

Calculated spacings based on hexagonal unit cell, space group $P6_3/mmc$, $a=5.85_4$, $c=9.29_5$ Å

Evans measured spacings in Å based on Hildebrand's film no. 5865, CrKα radiation (2.2909 Å), 114.7 mm. diameter camera, cutoff at 20.0 Å

Sabina measured spacings in Å based on film made with CuKα radiation (1.5418 Å), 114.7-mm. diameter camera, cutoff at 12.0 Å

b indicates broad line

hkl	*d* (*calc.*) Å	Evans *d* (*obs.*) Å	Evans *I*(100)	Sabina *d* (*obs.*) Å	Sabina *I*(10)
10.0	5.07	5.09	16		
00.2	4.65	4.66	55	4.63	3
10.1	4.45	4.47	8		
10.2	3.43	3.44	100	3.43	6
11.0	2.93	2.95	16	2.92	1
10.3	2.63	2.66	90	2.64	5
20.0	2.54	2.55	16	2.54	½
11.2	2.48	2.49	90	2.47	10
20.1	2.45	2.46	40	2.44	6
00.4	2.32	2.33	6		
20.2	2.23	2.23	50	2.23	3
10.4	2.11	2.12	1		
20.3	1.962	1.969	30	1.962	4
21.0	1.916				
21.1	1.913				
11.4	1.818				
21.2	1.772	1.779	9	1.777	½
10.5	1.745	1.750	6		
20.4	1.713	1.719	20	1.718	2
30.0	1.690				
30.1	1.663				
21.3	1.630	1.636	25	1.634	4
30.2	1.588	1.595	13	1.594	1
00.6	1.549	1.543	4	1.541	½
20.5	1.499	1.495	60	1.503	6
30.3	1.484				
10.6	1.482				
21.4	1.478			1.470*b*	3
22.0	1.454	1.461*b*	22		
31.0	1.406				
31.1	1.390				
22.2	1.387				
11.6	1.369				
30.4	1.367	1.357	1		
31.2	1.346	1.346	3		
21.5	1.334	1.333	6		
20.6	1.322	1.320	6		
10.7	1.285	1.282*b*	20	1.287	2
31.3	1.280				
40.0	1.268	1.269	1		
40.1	1.256	1.256	4	1.261*b*	1
30.5	1.251				
22.4	1.232	1.238	3		
40.2	1.223	1.223	3		
21.6	1.205				
31.4	1.203				
20.7	1.176	1.176	5		

After displacing with CO_2 the air in the flask containing the undissolved portion of the sample, an additional 100 ml. of (1+4) H_2SO_4 at room temperature was added and the flask tightly stoppered. For about two weeks the acid remained colorless. Then a faint blue green color appeared that slowly deepened for about two weeks, after which no further increase in depth of color was noticed. After another period of two weeks (total time six weeks), the solution was carefully decanted into another flask that had been filled with CO_2. From this flask aliquots were pipetted as before and analyzed (Analysis 2, Table 2).

To determine whether all of the vanadium and iron had been dissolved, another 100 ml. of (1+4) H_2SO_4 at room temperature was added to the remaining undissolved portion of the sample after displacing the air in the flask with CO_2. The flask was tightly stoppered and allowed to stand for two weeks at room temperature, with frequent shaking. Aliquots were then taken and analyzed colorimetrically for iron and vanadium.

CHEMICAL ANALYSES

The chemical analyses of the first and second leachings of the mineral, as described above, are given in Table 2, analyses 1 and 2, respectively, in terms of weight percentages of the original sample. The aliquot taken of the third leaching was also analyzed for iron and vanadium, giving V_2O_4 0.40 per cent and FeO 0.10 per cent (percentages of original sample). The ratio of V_2O_4 to FeO in this third leaching indicates that it corresponds to the mineral dissolved in the second leaching. The mol ratios obtained from these analyses indicate that the formula of the mineral dissolved in the first leaching, corresponding to the crystallized nolanite, is $4FeO \cdot V_2O_3 \cdot 4V_2O_4$; and that the formula of the mineral dissolved in the second leaching is $FeO \cdot 2V_2O_4$.

Twenty-five milligrams of nolanite crystals were hand-picked from a dolomitic specimen from the Fish Hook Bay deposit. A microchemical analysis by A. M. Sherwood of the U. S. Geological Survey is listed in Table 1, analysis 3. This analysis indicates that water is absent and suggests the formula $3FeO \cdot V_2O_3 \cdot 3V_2O_4$ for nolanite.

The formula $4FeO \cdot V_2O_3 \cdot 4V_2O_4$ computed from analysis 1, Table 2, by Fahey and that, $3FeO \cdot V_2O_3 \cdot 3V_2O_4$, obtained from Sherwood's microchemical analysis 3, Table 2, are not greatly different. When one considers that more than 40 per cent of the sample analyzed by Fahey was made up of minerals other than nolanite, and that Sherwood analyzed only 25 milligrams of sample, the agreement is notably close. However, the correct formula will probably not be known until a complete structural study of nolanite has been made.

TABLE 2. CHEMICAL ANALYSES OF NOLANITE

(*a*) Wt. per cent analysis
(*b*) Mol ratios calculated from (*a*)

	1		2		3	
	a	*b*	*a*	*b*	*a*	*b*
V_2O_3	8.18	1.05	none		16.5	0.96
V_2O_4	34.40	3.97	10.86	1.96	59.8	3.14
FeO	14.90	3.97	2.50	1.04	24.0	2.90
Total	57.48		13.36		100.3	

1. Analysis of first (1+4) H_2SO_4 leaching of 2-gram sample of material from Fish Hook Bay, Beaverlodge, Saskatchewan. J. J. Fahey, analyst.
2. Analysis of second leaching of the same sample. J. J. Fahey, analyst.
3. Microanalysis of 25-mg. hand-picked sample from Fish Hook Bay. A. M. Sherwood, analyst.

Table 3 contains the gross chemical analysis of the sample from Fish Hook Bay, from another portion of which nolanite and the other vanadium mineral (Table 2, Nos. 1 and 2) had been separated by differential solution. The component minerals, computed from the analysis in Table 3, are listed in Table 4. Due to the organic matter present, the figure for H_2O+(110° C.) in Tables 3 and 4 is probably a little high.

TABLE 3. CHEMICAL ANALYSIS OF THE GROSS SAMPLE FROM FISH HOOK BAY, BEAVERLODGE REGION, SASKATCHEWAN, CANADA
By J. J. Fahey

	Per cent
V_2O_3	8.18
V_2O_4	45.66
FeO	17.50
CaO	4.78
MgO	3.64
CO_2	9.61
U_3O_8	1.26
H_2O- (110° C.)	1.50
H_2O+ (110° C.)	3.32
Inorganic insoluble (1+4) H_2SO_4	1.13
Organic insoluble (1+4) H_2SO_4	2.30
SO_3	0.03
Total	98.91

TABLE 4. PROBABLE MINERAL COMPOSITION OF ANALYZED SAMPLE COMPUTED FROM TABLE 3

	Per cent
More soluble mineral (nolanite)	57.48
Less soluble mineral ($FeO \cdot 2V_2O_4$)	13.86
Dolomite (computed from 4.78% CaO)	15.74
MgO (excess)	0.23
CO_2 (excess)	2.06
U_3O_8	1.26
H_2O- (110° C.)	1.50
H_2O+ (110° C.)	3.32
Inorganic insoluble (1+4) H_2SO_4	1.13
Organic insoluble (1+4) H_2SO_4	2.30
SO_3	0.03
Total	98.91

CRYSTAL CHEMICAL CONSIDERATIONS

In the absence of conclusive chemical data, the principal criteria for the identification of nolanite are its characteristic crystallography and *x*-ray powder diffraction pattern. The unit-cell dimensions and symmetry place rather severe restrictions on the chemical constitution of nolanite, although, unfortunately, they do not in themselves lead to a unique chemical formula for the mineral.

Using the data of Barnes and Qurashi (1952) the unit-cell volume is 275.9 Å³. The cell will just accommodate 16 oxygen atoms, assuming the specific volume of oxygen to be 17.2 Å³. This value of the specific volume is entirely consistent with that found for other oxides of the same type. For example, the specific volume of oxygen in goethite is 17.2 Å³; in montroseite, (V, Fe)O(OH) (Evans and Block, 1953) it is 17.1 Å³; and in duttonite, $VO(OH)_2$ (Evans and Mrose, personal communication), it is 17.2 Å³. On the basis of 16 oxygen atoms in the unit cell, the chemical analyses in Table 2 may be formulated:

$Fe_{2.5}^{+2}V_{1.7}^{+3}V_{5.5}^{+4}O_{16.0}$ (analysis 3)
$Fe_{2.8}^{+2}V_{1.5}^{+3}V_{5.5}^{+4}O_{16.0}$ (analysis 1)

Concerning the structure itself, it seems likely that the 16 oxygen atoms are arranged in closest packing, either purely hexagonal, or half hexagonal and half cubic. An ideal closest packing of oxygen atoms with specific volume 17.2 Å³, four layers high, would have the hexagonal unit cell dimensions $a = 5.80$ Å and $c = 9.46$ Å. As pointed out by Barnes and Qurashi, the permissible space groups provide only 2-, 4-, and 6-fold equipoints for the cations in the structure. The formulations given above consistent with the chemical analytical data suggest that the unit cell probably contains a total of 10 cations (analysis 1 give 9.8, analysis 3 gives 9.7).

The crystal chemical considerations are complicated by the fact that iron may be expected to substitute for vanadium in one or more of the crystallographic sites in the nolanite structure, so that the Fe/V or V^{+3}/V^{+4} ratios need not be rational. In montroseite (Weeks, Cisney and Sherwood, 1953), Fe^{+2} substitutes for V^{+3} to the extent of as much as 8 weight per cent. For these reasons, and also because of the recognized uncertainties in the chemical analyses (mainly because of the difficulty of purifying samples), it is not possible to write a valid chemical formula for nolanite at this time. It is probable that the true formula may be revealed only by a complete crystal-structure determination, which is now in progress (W. H. Barnes, personal communication).

SUMMARY

Although it is not possible at the present time to write a conclusive chemical formula for nolanite, the mineral has been established as a new species on crystallographic evidence. This situation is common among low-valence vanadium oxide minerals because such minerals are frequently intermixed on a fine scale and impossible to separate. The crystals are hexagonal and have a crystal structure based on a close packed arrangement of 16 oxygen atoms in the unit cell. The structure as a whole is unknown, and, especially in view of the possibility of partial substitution of Fe for V, a rational chemical formula cannot be written at the present time. The mineral is most easily characterized by means of its *x*-ray powder pattern, which has been completely accounted for in terms of the single-crystal data.

ACKNOWLEDGMENTS

Grateful acknowledgment is made to W. H. Barnes, National Research Council of Canada, and to J. A. Maxwell, Geological Survey of Canada, for information and helpful criticism of this paper; to the following members of the U. S. Geological Survey: A. M. Sherwood for his analysis of nolanite, Mrs. A. D. Weeks for the determination of its specific gravity, J. M. Axelrod and F. A. Hildebrand for making and measuring many *x*-ray powder diffraction patterns; and to Miss A. P. Sabina, Geological Survey of Canada, for other *x*-ray powder patterns.

REFERENCES

BARNES, W. H., AND QURASHI, M. M. (1952), Unit cell and space group data for certain vanadium minerals: *Am. Mineral.*, **37**, 407–422.

Evans, H. T., Jr., and Block, Stanley (1953), The crystal structure of montroseite, a vanadium member of the diaspore group: *Am. Mineral.*, **38,** 1242–1250.

Robinson, S. C. (1955), Mineralogy of uranium deposits, Goldfields, Saskatchewan: *Geol. Survey Canada Bulletin* **31.**

Weeks, A. D., Cisney, E., and Sherwood, A. M. (1953), Montroseite, a new vanadium oxide from the Colorado Plateaus: *Am. Mineral.*, **38,** 1235–1241.

Manuscript received March 26, 1957.