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NEW OCCURRENCE AND DATA OF NOLANITE

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ABSTRACT

Nolanite, a vanadium iron oxide, occurs in metamorphosed and altered greenstones closely associated with native gold and numerous tellurides in the Kalgoorlie mining district, Western Australia. Typically, it occurs in euhedral tabular prismatic crystals along or near fractures filled with native gold and coloradoite.

Chemical analysis done with the electron microprobe gave: V, 34.52; Fe, 24.32; Ti, 1.70; Al, 0.61; Zn, 0.33; Si, 0.19; Sn, 0.09; O, 38.24; with oxygen by difference; average weight percent from 17 grains. Iron is present as Fe^{3+} and vanadium as V^{4+} and V^{5+} with $V_2O_5/V_2O_4=1.57$.

Nolanite is hexagonal; $a=5.846$ Å, $c=9.254$ Å, cell volume 273.8 Å^3; cell contents $[Al_{0.17}Si_{0.05}Ti_{0.27}V_{5.16}Fe_{3.31}Zn_{0.04}Sn_{0.01}O_{18.00}]$; calculated density 4.60 g cm^{-3}. Average measured specific gravity is 4.69, hardness 5–5½, and in reflected light nolanite shows strong and distinct bireflectance and anisotropism.

INTRODUCTION

Electron microprobe examination of polished sections of gold ores from the Kalgoorlie district, Western Australia, showed the presence of nolanite, a vanadium iron oxide mineral, associated with the ore minerals. Although nolanite was identified in ore samples from many mines in the Kalgoorlie district, the mineral was most abundant in specimens from the Middle Lode, 865-foot level, South Kalgoorlie mine. All data presented in this paper pertain to material from this specific location.

Recognition of nolanite at Kalgoorlie marks the second reported occurrence of the mineral. Prior to this, nolanite associated with uranium minerals had been identified and described from several mines of the Goldfields or Beaverlodge region, Saskatchewan (Barnes and Qurashi, 1952; Robinson *et al*, 1957). Hanson (1958) studied the crystal structure of nolanite using the chemical analyses of Robinson *et al*, (1957) and assuming 16 oxygen atoms per unit cell.

Due to the relatively large grain size of nolanite and the lack of magnetic phases intergrown with it, in the material from Kalgoorlie, it was possible to make clean mineral separations. Based on quantitative chemical analyses made with the electron microprobe analyzer, supported by X-ray diffraction data and measured density, the chemical composition is redefined and certain changes in unit-cell contents are suggested.

Occurrence and Associations

Nolanite at Kalgoorlie is closely associated with massive native gold and numerous telluride minerals in highly altered and metamorphosed greenstones. No sulfide minerals were recognized in samples containing nolanite. Minerals identified from the 865-foot level, South Kalgoorlie mine, include pyrite, chalcopyrite, sphalerite, tennantite-tetrahedrite, altaite, coloradoite, calaverite, krennerite, petzite, sylvanite, native gold, calcite, dolomite, and quartz.

Chemical analyses determined from electron microprobe spectral scans show native gold to be 93 percent Au and 7 percent Ag by weight. Com-

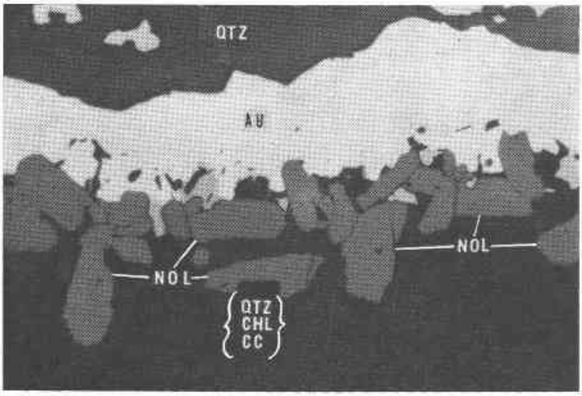

Fig. 1. Small subhedral nolanite grains (NOL) in wallrock along margin of fracture filled with native gold (AU). Gangue at top is massive quartz (QTZ). Gangue at bottom with nolanite is quartz (QTZ), chlorite (CHL) and calcite (CC). 275×.

positions of telluride minerals calaverite, krennerite, petzite, coloradoite, altaite, and sylvanite correspond closely to those reported for Kalgoorlie minerals by Palache, Berman and Frondel (1958). Quantitative data on all telluride minerals, including several with gold to tellurium ratios unreported to date, are included in a manuscript in preparation by Radtke and Taylor.

Nolanite is confined to and localized in the greenstone along the margins of small fractures (Figs. 1 and 2). In some areas, fragments of shattered greenstone containing nolanite grains are isolated in the fissures (Fig. 3). Nolanite formed early in the paragenesis before the late fracturing and subsequent massive flood of precious metal mineralization (Fig. 4). Textural evidence and the general lack of native gold and telluride inclusions in nolanite indicate that nolanite formed before the ore minerals.

Polished section examination shows nolanite to be present in sufficient

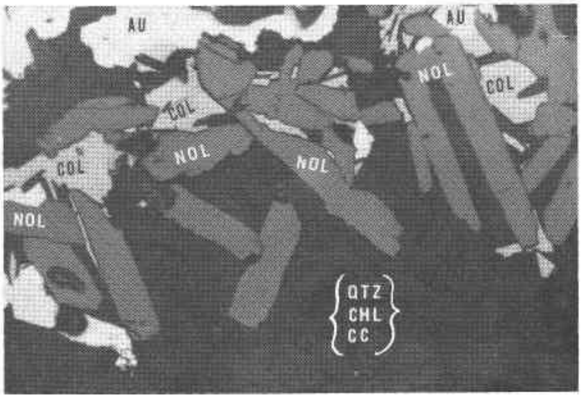

FIG. 2. Large euhedral nolanite grains (NOL) in wallrock along margin of shear zone. Note fracture and breakage of nolanite grains protruding into zone of shearing. Dark gangue is mixture of quartz (QTZ), chlorite (CHL) and calcite (CC). Late coloradoite (COL) and native gold (AU) cement broken nolanite and wallrock. 275×.

amounts to be an ore mineral of vanadium at least locally. The abundance of vanadium in local areas warrants a mineralogical study on a regional basis to determine the extent of this stage of ore mineralization.

PHYSICAL AND OPTICAL PROPERTIES

Physical and optical properties of nolanite from Kalgoorlie correspond closely to those reported by Robinson *et al*, (1957) for nolanite from Beaverlodge, Saskatchewan. The mineral occurs in subhedral to euhedral

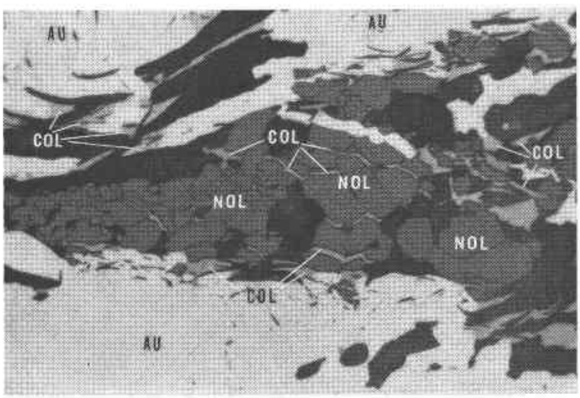

FIG. 3. Photomicrograph showing fragment of broken wallrock containing nolanite (NOL) caught in shear zone. Fractured nolanite grains are cemented by minor amounts of coloradoite (COL) with late native gold (AU) surrounding broken fragments. 275×.

tabular prismatic grains from 10 to 50 microns in width and up to several hundred microns in length. It is opaque, brownish black in powder, and submetallic in luster.

In polished section under reflected light nolanite is strongly bireflectant with colors from medium brown to blue gray in sections parallel to the *c*-axis. Sections perpendicular to the *c*-axis show no bireflectance and have a uniform medium-brown color. Under crossed nichols in sections containing the *a* and *c*-axis, it is strongly anisotropic with polarization colors from deep red to midnight blue.

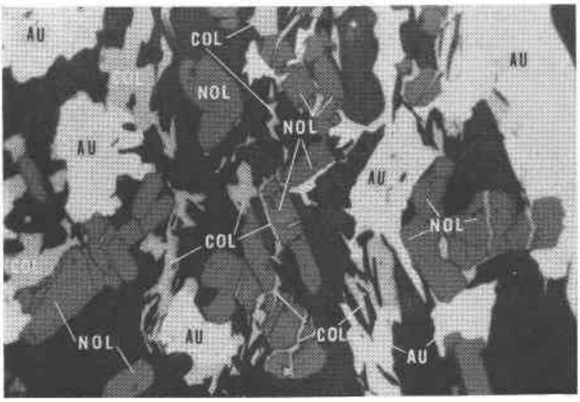

FIG. 4. Photomicrograph showing strongly shattered greenstone containing grains of nolanite (NOL). Many nolanite grains broken out from the greenstone are surrounded and outlined by coloradoite (COL). Note late veinlet of native gold (AU) at right side with native gold cementing fractured greenstone. 275×.

Nolanite has a Mohs hardness of 5 to $5\frac{1}{2}$, polished easily, and shows uneven fracture. Three determinations of specific gravity gave values of 4.70, 4.67 and 4.70, for an average of 4.69. Under high-energy electron bombardment (30 KV), nolanite shows no cathode luminescence. No microchemical tests were made due to the small grain size and the close association with the more reactive native gold and various tellurides.

X-RAY DATA

X-ray powder diffraction data for nolanite from Kalgoorlie are given in Table 1. The X-ray data for nolanite from Beaverlodge, Saskatchewan, reported by Robinson *et al*, (1957) is included in Table 1 for comparison. Unit-cell constants determined in the present study are: $a=5.846$ Å and $c=9.254$ Å with $c/a=1.583$. Robinson *et al*, (1957) reported $a=5.854$ Å and $c=9.295$ Å for nolanite from Beaverlodge, Saskatchewan.

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR NOLANITE FROM KALGOORLIE, AUSTRALIA

Calculated[1]		Observed		Observed	
		Nolanite South Kalgoorlie Mine Kalgoorlie Western Australia[2]		Nolanite Fish Hook Bay Beaverlodge Saskatchewan[3]	
hkl	d_{hkl}	d_{hkl}	*I*	d_{hkl}	*I*
100	5.06	5.05	20	5.09	16
002	4.63	4.62	60	4.66	55
101	4.44	4.44	15	4.47	8
102	3.42	3.41	85	3.44	100
110	2.92	2.92	35	2.95	16
103	2.63	2.63	100	2.66	90
200	2.53	2.53	40	2.55	16
112	2.47	2.47	100	2.49	90
201	2.44	2.44	80	2.46	40
004	2.31			2.33	6
202	2.22	2.22	60	2.23	50
104	2.10			2.12	1
203	1.957	1.955	65	1.969	30
210	1.913				
211	1.874				
114	1.814	1.812	25		
212	1.768	1.769	40	1.779	9
105	1.738	1.738	20	1.750	6
204	1.708	1.710	40	1.719	20
300	1.688				
301	1.660	1.659	5		
213	1.626	1.628	60	1.636	25
302	1.585	1.587	45	1.595	13
006	1.542	1.541	25	1.543	4
205	1.494	1.494	60	1.495	60
303	1.480				
106	1.475				
214	1.474				
220	1.461	1.463	85	1.461	22B
310	1.404				

[1] Indices from least-squares refinement of X-ray powder data using digital computer program (Evans *et al*, 1963).

[2] Mount of nolanite grains 1 to 10; chemical analysis Table 2. Specimen 0D24907, Ore Deposits Collection, Stanford University; Film 311, 1964; Cu/Ni; radiation $CuK_\alpha = 1.5418$ Å; camera diameter 114.6 mm.

[3] Film 5865, F. A. Hildebrand, U. S. Geological Survey; CrK_α radiation = 2.2909 Å; 114.7 mm diameter camera; (Robinson *et al*, 1957).

TABLE 1—(*continued*)

Calculated[1]		Observed		Observed	
		Nolanite South Kalgoorlie Mine Kalgoorlie Western Australia[2]		Nolanite Fish Hook Bay Beaverlodge Saskatchewan[3]	
hkl	d_{hkl}	d_{hkl}	*I*	d_{hkl}	*I*
222	1.394	1.393	5		
311	1.388				
116	1.364				
304	1.363			1.357	1
312	1.344	1.346	5	1.346	3
215	1.330	1.332	10	1.333	6
206	1.317	1.315	5	1.320	6
107	1.279	1.279	40	1.282	20B
313	1.278				
400	1.266			1.269	1
401	1.254	1.255	20	1.256	4
305	1.247				
224	1.236	1.236	25	1.238	3
402	1.221			1.223	3
				1.176	5
		1.170	15		
		1.128	20		
		1.111	5		
		1.088	35		
		1.076	40B		
		1.060	20		
		1.046	45		
		0.967	20		
		0.956	15		
		0.873	20B		
		0.854	35B		

ELECTRON MICROPROBE ANALYSIS

Polished sections containing nolanite grains were prepared for electron microprobe analysis following the procedures outlined by Taylor and Radtke (1965). Both the analysis section and the standard polished section were carbon coated simultaneously to uniform thicknesses. The general method followed in the quantitative microprobe analysis corresponds to the procedure described by Birks (1963). Qualitative spectral scans and quantitative analyses were made at the Materials Analysis Company with the Model 400 electron microprobe analyzer. All elements detected from spectral scans except oxygen were analyzed quantitatively; oxygen was determined by difference.

In the reduction of electron microprobe intensity data, corrections were made for: (1) drift of the incident electron beam; (2) background from the continuous spectrum; (3) characteristic fluorescence by other K-

TABLE 2. CHEMICAL ANALYSES OF NOLANITE IN WEIGHT PERCENT BY ELECTRON MICROPROBE ANALYZER

Grain No.[1]	Al	Si	Ti	V	Fe	Zn	Sn	O[2]
1	0.60	0.18	2.18	34.15	24.25	0.41	0.11	38.12
2	0.59	0.21	1.94	34.17	24.18	0.40	0.16	38.35
3	0.60	0.16	1.99	34.10	23.93	0.38	0.10	38.74
4	0.71	0.19	2.30	33.80	24.14	0.45	0.11	38.30
5	0.61	0.18	2.10	33.81	24.18	0.40	0.08	38.65
6	0.62	0.16	1.81	34.04	24.76	0.39	0.06	38.17
7	0.55	0.15	1.80	34.31	24.84	0.33	0.08	37.93
8	0.61	0.13	1.76	34.39	24.50	0.32	0.06	38.23
9	0.51	0.13	1.92	33.99	24.68	0.34	0.08	38.35
10	0.58	0.11	1.82	34.25	24.47	0.35	0.06	38.37
Average	0.60	0.16	1.96	34.10	24.39	0.38	0.09	38.32
Standard Dev.	0.05	0.03	0.18	0.19	0.30	0.04	0.03	0.23
11	0.58	0.25	1.26	35.39	24.10	0.24	0.11	38.07
12	0.57	0.22	1.28	35.30	23.67	0.22	0.13	38.61
13	0.57	0.23	1.31	34.71	24.07	0.25	0.08	38.78
14	0.59	0.23	1.20	35.58	24.14	0.26	0.09	37.90
15	0.65	0.24	1.40	34.94	24.51	0.29	0.08	37.89
16	0.80	0.25	1.66	34.38	24.70	0.33	0.13	37.74
17	0.61	0.22	1.13	35.51	24.36	0.31	0.09	37.77
Average	0.62	0.23	1.32	35.12	24.22	0.27	0.10	38.11
Standard Dev.	0.08	0.01	0.17	0.45	0.34	0.04	0.02	0.67

[1] Analyses 1 to 10 and 11 to 17 were taken from nolanite grains concentrated in two distinct areas of the polished section.

[2] By difference.

radiations; (4) absorption effects; and (5) atomic number effects. K_α characteristic lines were used for Al, Si, Ti, V, Fe, Zn and the characteristic line L_α was used for Sn. All analyses were run at 25 KV except that Al and Si were run at 15 KV, and Zn at 30 KV.

The quantitative data was reduced at the Stanford University Computer Center following a program developed by Richard Wolf of the Materials Analysis Company. Compositions of 17 nolanite grains by weight percent and atomic percent are shown in Table 2.

No corrections were made for wavelength shifts for Al K_α and Si K_α. These corrections would raise the weight percent of Al and Si by 5 to 8 percent of the absolute values but would only slightly lower the weight percent value for oxygen.

Wet or Conventional Chemical Analysis

A small piece of ore was crushed and ground to minus 200 mesh to liberate nolanite from other minerals. Heavy minerals were then concentrated using Clerici solution, and after cleaning and drying, a permanent magnet was used to separate the strongly magnetic nolanite. Microscopic examination showed nolanite to be the only phase in the final concentrate. Thirteen milligrams of this concentrate were analyzed by wet chemical techniques.

Using standard wet chemical methods, nolanite was dissolved in H_2SO_4 to determine weight percent of total vanadium and the ratio V_2O_5 to V_2O_4. This analysis was done by Lois M. Jones of the U.S. Geological Survey at Menlo Park. Total weight percent of vanadium was determined as 34.3 percent and the ratio of V_2O_5 to V_2O_4 was 1.57 to 1. Three-fifths of the vanadium is therefore in the +5 valence state.

Mineral Chemistry

The quantitative electron microprobe analyses, supported by wet chemical analysis on purified material, provide conclusive chemical data on nolanite. Reference to Table 2 shows vanadium and iron to be major constituents, together with significant amounts of titanium. All grains analyzed also contained detectable amounts of aluminum, silicon, zinc and tin.

Analyses 1 to 10 and 11 to 17 in Table 2 represent nolanite grains in two different areas of a polished section. Although the abundances of silicon, titanium, vanadium and zinc in nolanite vary between the two areas, the content is rather uniform and distinct for grains in each area. Comparison of the atomic percents of titanium and vanadium considered with their valence and ionic radii (Ti^{4+}, 0.68 Å and V^{4+}, 0.63 Å) suggests that titanium substitutes for vanadium in the nolanite structure.

The atomic percent of oxygen averages 66.96 (grains 1 to 10) and 66.73 (grains 11 to 17). Nolanite is an AB_2-type mineral with a cation to oxygen ratio of 1:2. The approximate vanadium to iron ratio is 3:2 and the average composition of nolanite in atomic percent is:

$$Al_{0.62}Si_{0.16}Ti_{1.15}V_{18.72}Fe_{12.21}Zn_{0.16}Sn_{0.02}O_{66.96} \text{ (grains 1 to 10)}$$

$$Al_{0.65}Si_{0.23}Ti_{0.77}V_{19.31}Fe_{12.16}Zn_{0.12}Sn_{0.02}O_{66.73} \text{ (grains 11 to 17)}$$

By normalizing oxygen to 66.67 atomic percent the average composition of all 17 grains is:

$$Al_{0.64}Si_{0.19}Ti_{1.00}V_{19.08}Fe_{12.26}Zn_{0.14}Sn_{0.02}O_{66.67}$$

To balance the electrostatic charge between the cations and oxygen, it is necessary to have V^{5+} present in the structure. The presence of V_2O_5 and V_2O_4 in nolanite in a ratio of 1.57:1 was determined by wet chemical techniques. As shown by Garrels and Christ (1965), under any given conditions of Eh, pH, at equilibrium, it is impossible for V^{3+} and Fe^{2+} to coexist with V^{5+}; therefore it is doubtful whether any V^{3+} and Fe^{2+} are present in nolanite as reported by Robinson *et al*, (1957). Nolanite at Kalgoorlie apparently formed under relatively strong and uniform oxidizing conditions. Although vanadium minerals are very sensitive to small variations in Eh and pH no other vanadium minerals were recognized in the ore.

Study of X-ray wavelength shift for iron showed the valence in nolanite to be Fe^{3+}, and the coordination of iron with oxygen to be six-fold. Analyses were run with the electron microprobe at 7 KV using a potassium acid phthalate (KAP) crystal and the Fe L_α spectral line. In a similar study for vanadium, preliminary results show both V^{4+} and V^{5+} are present in nolanite with vanadium probably in six-fold coordination with oxygen. Methods of this work are described in a manuscript in preparation by the authors.

In the original description of nolanite Robinson *et al*, (1957) proposed that iron substituted for vanadium in the crystal structure. The presence of both elements in uniform amounts and ratios in our study suggests that both elements are essential in the nolanite structure and that, at least locally, any substitution is very limited.

Using the calculated unit-cell volume of 273.8 $Å^3$ and 16 oxygen atoms per cell, the calculated specific volume for oxygen is 17.2 Å. Assuming 18 oxygen atoms in the cell, the specific volume per oxygen atom is 15.2 $Å^3$. Although a specific volume of 15.2 $Å^3$ is small for oxygen, this value could be possible due to strong bonds between high valence vanadium atoms and oxygen (oral communication, C. L. Christ, 1966). By normalizing the average composition to 16 oxygen and using a unit-cell volume of 273.8 $Å^3$ and average measured specific gravity of 4.69, the unit cell contains 1.15 formula weights. The calculated specific gravity is only 4.08. Assuming 18 oxygen per unit cell there are 1.02 formula weights per unit cell and the calculated density is 4.60. Therefore it seems likely that nolanite contains 18 oxygen atoms per unit cell and the composition may be written:

$$Al_{0.17}Si_{0.05}Ti_{0.27}V_{5.16}Fe_{3.31}Zn_{0.04}Sn_{0.01}O_{18.00}$$ (average grains 1 to 17).

For three-fifths of the vanadium as +5 vanadium and two-fifths as +4 vanadium, and all other cations in their highest oxidation states, the sum of the charges on the cations is +35.6, in good agreement with the anion charge of −36.0.

Acknowledgments

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