

The crystal chemistry of nolanite, $(V,Fe,Ti,Al)_{10}O_{14}(OH)_2$, from Kalgoorlie, Western Australia

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Abstract

Nolanite crystals associated with gold mineralization in the “green leader” deposits of Kalgoorlie, Western Australia, show large local variations in vanadium, titanium and iron contents. The structures have been refined for two compositions with $V/\Sigma M$ atomic fractions of 0.69 and 0.52. Cell parameters (space group $P6_3mc$, $Z = 1$) are $a = 5.890(4)$, $c = 9.255(5)\text{\AA}$ and $a = 5.897(2)$, $c = 9.256(3)\text{\AA}$ respectively. Final weighted R factors were 0.039 and 0.049 for 737 and 604 reflections with $F > 4\sigma(F)$, collected on an automatic diffractometer using $MoK\alpha$ radiation. The structure is based on a closest-packed anion framework with a double hexagonal stacking sequence, ABCBA, *i.e.*, (*ch*) and with cations ordered into 2 tetrahedral and 8 octahedral sites. Valence sum calculations are consistent with nolanite being an oxyhydroxide, $(V,Fe,Ti,Al)_{10}O_{14}(OH)_2$, and with predominately trivalent vanadium and mixed divalent and trivalent iron. Based on a comparison of refined site occupancies and bond lengths for the two structures, plausible cation ordering schemes have been proposed and the intergrain compositional variations have been confirmed to be due to substitutions of the type $V^{3+} \leftrightarrow Fe^{3+}$ and $2(V^{3+},Fe^{3+}) \leftrightarrow (Fe^{2+}+Ti^{4+})$ in the octahedral sites.

Introduction

A new iron vanadate with hexagonal symmetry, $a = 5.854$ and $c = 9.295\text{\AA}$ from Goldfields, Saskatchewan, was first reported by Barnes and Qurashi (1952). The mineral was subsequently described in detail and named nolanite by Robinson *et al.* (1957). Chemical analyses led to inconclusive results regarding the formula because of the difficulty of removing impurities, but Robinson *et al.* used crystal-chemical arguments to propose that the structure was based on a closest-packed anion lattice with 16 anions and 10 cations per unit cell. They suggested unit cell compositions in the range $Fe_{2.5}^{2+}V_{1.5}^{3+}V_{3.5}^{4+}O_{16}$ to $Fe_{2.8}^{2+}V_{1.5}^{3+}V_{3.5}^{4+}O_{16}$. Subsequently their model was confirmed by Hanson (1958) from a single-crystal structure analysis using Weissenberg intensity data. He showed that the structure comprised a closest-packed anion framework with a stacking sequence ABCBA, and with metal ions occupying one 6-fold octahedrally coordinated site and

two 2-fold sites, one of octahedral and one of tetrahedral coordination. He proposed an ordering of cations $(V^{4+})_6^{[6]}(0.78Fe^{2+} + 0.22V^{3+})_2^{[6]}(0.47Fe^{2+} + 0.53V^{3+})_2^{[4]}O_{16}$ but noted that the unit cell composition was unbalanced by 1.5 electrons.

A new occurrence of nolanite, in metamorphosed greenstones associated with native gold and tellurides at Kalgoorlie, was reported by Taylor and Radtke (1967). They carried out electron microprobe analyses, supported by wet chemical analysis on purified material which gave the valence states of vanadium as V^{4+} and V^{5+} with $V_2O_5/V_2O_4 = 1.57$, and proposed a unit cell composition based on 18 anions and a cation to anion ratio of 1:2 *i.e.*, $Al_{0.17}Si_{0.05}Ti_{0.27}V_{5.16}Fe_{3.31}Zn_{0.04}Sn_{0.01}O_{18}$. This composition was in conflict with the results of the structure refinement of Hanson (1958).

Our interest in this material arose from a systematic study of hōgbomite–nigerite polytypes (Grey and Gatehouse, 1979; Gatehouse and Grey, 1982), which we have

shown to consist of elements of a nolanite-type structure intergrown with elements of a spinel-type structure. Structure analyses for these minerals suggested that the anion lattice in the nolanite-like segments contained hydroxyls. The possibility of hydroxyls in nolanite had not been considered in previous studies by Robinson *et al.* (1957) or Taylor and Radtke (1967).

In an attempt to resolve the inconsistencies in the reported compositions for nolanite we carried out comparative crystal-chemical analyses on two samples with different cation ratios, using data obtained from precise structure refinements.

Occurrence and physical properties

Nolanite was examined in samples from four gold mines in Kalgoorlie, Western Australia. All samples represent the "green leader" type of mineralization (Nickel, 1977) which is characterized by the pervasive presence of green vanadium-bearing muscovite in a quartz stockwork carrying rich gold telluride mineralization. The samples are as follows: 5996—Lake View Mine; 9996—New North Boulder Mine; 9997—Associated Mine; and 17796—Chaffers Shoot.

The nolanite in all these samples occurs mainly in the form of small tabular crystals, generally less than 0.05 mm in longest dimension, and rarely approaching 0.3 mm; a photomicrograph illustrating its typical occurrence is given in Figure 1 of Nickel (1977).

Electron microprobe analyses of grains from the four localities are given in Table 1. The analyses of sample

5996 were made on crystal spectrometers, using metal standards for all elements except Mg and Na, for which MgO and nepheline were used. The other analyses given in Table 1 were made with an energy-dispersive procedure (Ware, 1981). Analyses of several crystals by both methods showed that the results agreed to within the margin of analytical error for all elements except Na, which tended to give spuriously high values by the energy-dispersive method. All results shown in Table 1 are the average of two or three separate point analyses.

Some of the nolanite crystals in sample 5996 were considerably larger than those in the other samples, and several of these crystals were therefore chosen for crystal-structure analysis and determination of physical properties. A preliminary examination showed that the composition of the nolanite varied considerably from grain to grain, and it was therefore decided to make crystal-structure determinations of two crystals as different as possible; these are designated as 5996(1) and 5996(2) in Table 1 and will hereafter be referred to as crystals 1 and 2. This sample also contained the oxyhydroxide mineral tivanite, $TiVO_3(OH)$, (Grey and Nickel, 1981) and is, in fact, the holotype specimen for this mineral. The physical and optical properties of grains with compositions typified by crystal 2 are summarized in Table 1.

Two samples of 9996 were available, designated as A and B in Table 1. In 9996A, no other oxide minerals were found, but in 9996B small scattered grains of tivanite were observed; the high titanium content of this sample, compared with 9996A is notable.

In sample 9997, only a few nolanite crystals, in their typical tabular forms, were present, and no other oxide minerals were detected. The analyses for individual grains were similar to those of grains in sample 9996B (see Table 1).

Sample 17796 was atypical, inasmuch as it contained abundant hematite, magnetite and tourmaline, all of which contain substantial amounts of vanadium (Nickel and Grey, 1982). Most of the nolanite in this sample occurred as tiny tabular crystals in tourmaline, together with some finely disseminated tivanite. Some of the nolanite, however, occurred as fine exsolution lamellae in vanadian magnetite (Nickel and Grey, 1982). At the margins of these exsolution intergrowths the nolanite was coarser, and this was the material from which the analysis shown in Table 1 was obtained. This nolanite composition is notable for its very high Fe and low Ti content.

Atomic proportions in the different nolanite grains, normalized to 10 cations per unit cell, have been calculated and are presented in Table 1. (Mg, Mn and Na, for which the analyses were close to the detection limits for these elements are omitted). A variety of cation substitution patterns occur, *e.g.*, in the samples 5996 from the Lake View Mine, the substitution is vanadium for iron plus titanium. Between samples A and B from the north Boulder Mine the main substitution is vanadium for titanium whereas a comparison of samples from the

Table 1. (a) Results of electron microprobe analyses of nolanite; (b) properties of sample 5996.

WEIGHT PERCENT						
	5996 (1)	5996 (2)	9996A	9996B	9997	17796
V	45.0	33.5	42.4	35.0	36.3	37.4
Fe	15.9	24.0	21.7	20.1	20.7	29.7
Ti	3.7	6.7	1.9	10.9	8.8	0.5
Al	0.9	0.8	0.9	1.3	1.2	0.6
Mg	<0.1	0.1	0.3	0.2	0.2	0.3
Mn	<0.1	0.1	<0.1	<0.1	0.1	<0.1
Na	0.1	0.2	0.5	0.5	0.4	0.3
ATOMIC PROPORTIONS (Σ cations = 10)						
V	6.91	5.23	6.43	5.19	5.43	5.65
Fe	2.23	3.42	3.00	2.72	2.83	4.10
Ti	0.60	1.11	0.31	1.72	1.40	0.08
Al	0.26	0.24	0.26	0.37	0.34	0.17
PHYSICAL AND OPTICAL PROPERTIES, SAMPLE 5996						
Color:	black					
Luster:	sub-metallic					
Specular reflectance color:	grey; against hematite - dark greyish violet; against magnetite and tivanite - darker grey					
Birefringence:	faint					
Anisotropism:	moderate, light to dark grey					
Reflectivity (SiC standard):						
	470 nm:	12.7% (max.)	11.0% (min.)			
	546 nm:	13.5	11.8			
	589 nm:	14.0	12.3			
Microhardness (20 g weight):	VHN 734 \pm 25					
Specific gravity (calc.):	4.60					

Associated Mine with those from Chaffers Shoot shows that the main cation variations correspond to iron-titanium substitution.

Crystal structure refinement

The samples chosen for structure refinements were grains 5996(1) and 5996(2) in Table 1. The quality of the crystals was first checked using precession and oscillation photographs. The approximate cell dimensions and symmetry reported by Hanson (1958) were confirmed. The only observed systematic absence was $(hhl), l = 2n + 1$, consistent with space groups $P6_3mc$, $P\bar{6}2c$ or $P6_3/mmc$. The intensity-data collections were carried out using a Philips PW1100 4-circle automatic diffractometer. The conditions are summarized in Table 2. Scattering factor curves for Al, Fe, V, Ti and O neutral atoms were those of Cromer and Mann (1968). Anomalous dispersion corrections were from Cromer and Liberman (1970). All computing was performed on the Monash University Burroughs 6700 and the CSIRO CDC 7600 computers using the X-ray system of programs (Stewart, 1976) and the SHELX program (Sheldrick, 1976).

The refinements were initialized in space group $P6_3mc$, using Hanson's (1958) atomic coordinates and an average scattering curve for all metals corresponding to the cation distributions determined from the microprobe analyses. First, the coordinates and scale factor were refined, then the isotropic temperature factors and coordinates for all atoms (except z of M(3) which was held invariant to fix the origin) were refined with the scale factor fixed. Next, all coordinates, isotropic temperature factors and metal-atom site-population parameters were refined until convergence was achieved. Finally the temperature factors were converted to anisotropic, and refined, together with coordinates, metal-atom population parameters and

scale. The final R -values are listed in Table 2. Sign reversal of all coordinates was carried out to check the absolute configuration but it was found to have a negligible effect on the R -value.

The final atomic coordinates and isotropic thermal parameters are given in Table 3, anisotropic thermal parameters in Table 4 and the observed and calculated structure factors are compared in Table 5.¹ The refined values of the population parameters are included in Table 3. The refinements were repeated using a vanadium scattering curve for all metals, to place the population parameters for the two refinements on the same scale. The coordinates and thermal parameters agreed with those from the first refinement within the associated errors. The population parameters for sites M(1), M(2) and M(3) in Table 3 were 0.98(1), 1.00(1), 1.14(1) and 0.99(1), 1.03(2), 1.13(1) for crystals 1 and 2 respectively, relative to neutral vanadium.

Description of the structure

A (110) section of the structure is represented in Figure 1 in which all metal and oxygen atoms are labelled according to Table 3. The refinements confirm the original structural model established by Hanson (1958), based on a closest-packed anion framework with (hc) stacking, *i.e.*, ABCBA, and with cations ordered into six-fold and two-fold octahedral sites and into a two-fold tetrahedral site. Nolanite is isostructural with the $M_2Mo_3O_8$ group of synthetic compounds (McCarroll *et al.*, 1957; Ansell and Katz, 1966), although it does not have strong metal-metal

¹ To obtain a copy of Tables 4 and 5, order Document AM-83-225 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D. C. 20009. Please remit \$1.00 in advance for the microfiche.

Table 2. Summary of data collection parameters

	Crystal # 1	Crystal # 2
V/M atomic fraction	0.69	0.52
Crystal dimensions (mm)	0.075 x 0.075 x 0.137	0.037 x 0.05 x 0.088
Unit cell parameters	$\underline{a} = 5.890(4) \text{ \AA}$ $\underline{c} = 9.255(5) \text{ \AA}$	$\underline{a} = 5.897(2) \text{ \AA}$ $\underline{c} = 9.256(3) \text{ \AA}$
Data collection parameters (common to both crystals)	Mo-K α radiation; variable scan width scan rate = $0.04^\circ \text{ s}^{-1}$	$\omega - 2\theta$ scan, 3-45°, $\Delta\theta = 1.3 + 0.3\tan\theta$,
Number of reflections	1831 $\underline{h} \ \underline{k} \ \pm 1$	1818 $\underline{h} \ \underline{k} \ \pm 1$
Number of unique reflections	915	908
R-value for equivalent reflections	0.042	0.061
Linear absorption coefficient	88.9 cm^{-1}	86.5 cm^{-1}
Max. and min. transmission factors	0.596, 0.510	0.762, 0.595
Number of reflections used in refinement, $F > 4\sigma(F)$	737	604
Final R, R_w	0.036, 0.039	0.064, 0.049

Table 3. Nolanite: final atomic coordinates, equivalent isotropic temperature factors and valence sums

Atom	Population Parameter	x	y	z	Ueq*	ESi†
<u>Crystal 1, V/VM = 0.69</u>						
M(1) [#]	0.968(3)	0.16559 (7)	-0.16559 (7)	0.6370 (1)	60 (2)	3.09
M(2)	0.982(7)	1/3	2/3	0.3497 (3)	55 (3)	2.89
M(3)	1.114(7)	1/3	2/3	0.9579	74 (3)	2.66
O(1)		0	0	0.0129 (7)	73(13)	1.36
O(2)		1/3	2/3	0.7521 (6)	67(14)	2.19
O(3)		0.1684 (4)	-0.1684 (4)	0.2395 (5)	103(15)	1.79
O(4)		0.5177 (3)	-0.5177 (3)	0.0036 (3)	77(10)	1.97
<u>Crystal 2, VEM = 0.52</u>						
M(1)	0.963(7)	0.1669 (2)	-0.1669 (2)	0.6357 (3)	57 (3)	3.09
M(2)	0.996(4)	1/3	2/3	0.3453 (4)	53 (5)	2.95
M(3)	1.096(3)	1/3	2/3	0.9579	72 (5)	2.64
O(1)		0	0	0.0153(14)	137(24)	1.39
O(2)		1/3	2/3	0.7514(10)	4(19)	2.21
O(3)		0.1681 (11)	-0.1681 (11)	0.2384 (8)	128(18)	1.79
O(4)		0.5181 (5)	-0.5181 (5)	0.0017 (6)	55(12)	1.96

* Ueq = 1/3 $\sum_{ij} U_{ij} a_i^* a_j^* a_i a_j$

† Valence sums calculated using Zachariasen's bond lengths - bond strength functions (Zachariasen, 1978; Muller et al (1979) (empirical parameter for iron)). Empirical parameter for aluminium from Brown and Wu (1976).

Average scattering curves for M: crystal 1, 0.69V + 0.22 Fe + 0.06 Ti + 0.03 Al; crystal 2, 0.53V + 0.34 Fe + 0.11 Ti + 0.02 Al.

bonding, as occurs in the molybdates. Two types of cation (001) layers alternate in nolanite; the six-fold sites form a layer of edge-shared octahedra identical with the (111) octahedral layers in spinel (O-layer) and the two-fold sites form a layer of corner-shared octahedra and tetrahedra (T1-layer). The interlayer articulations of the metal atom polyhedra are illustrated in Figure 2. The two-fold octahedrally coordinated M(2) shares corners with a

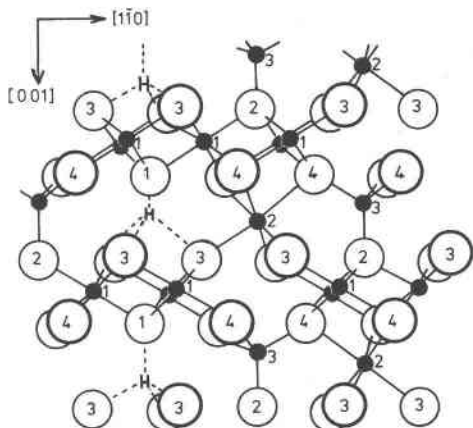


Fig. 1. Ball and spoke representation of a (110) section of the structure of nolanite. The numbering of the anions and cations corresponds to that given in Table 3.

six-membered ring of M(1) octahedra in one layer and shares edges with a triangular cluster of M(1) octahedra in the opposite layer. Two types of tetrahedral sites occur. That occupied by M(3) has an interlayer articulation identical to that in spinel (Fig. 2b). The other tetrahedral site (Fig. 2c) is like that in olivine, with edge-sharing of the tetrahedral base to a triangular cluster of M(1) octahedra. This site is unoccupied in the $M_2Mo_3O_8$ compounds and is occupied by the small Be^{2+} cation in the T1 layer of taaffeite (Peng and Wang, 1963). We propose that in nolanite, as in högbomite (Gatehouse and Grey, 1982) and nigerite (Grey and Gatehouse, 1979), this site is occupied, at least partially, by hydrogen, (see below).

Bond lengths and angles in nolanite, crystals 1 and 2, are compared in Table 6. In spite of the quite large compositional variations between the two samples, the mean M-O bond lengths agree to within the associated errors. The only significant structural change accompanying the replacement of V by (Fe, Ti) from crystal 1 to crystal 2 is an increase in the trigonal distortion of the octahedrally coordinated M(2). In both crystals there is an axial displacement of M(2) away from the triangular grouping of anions, O(4), associated with edge-sharing to M(1) octahedra, towards the triangle of O(3), which are involved in corner-sharing to M(1). There are corresponding decreases in O(4)-M(2)-O(4) and increases in the O(3)-M(2)-O(3) angles.

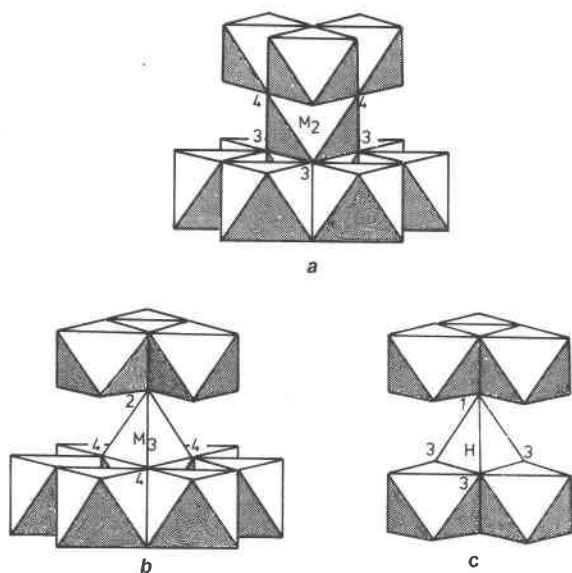


Fig. 2. Polyhedral representations of interlayer articulations in nolanite. (a) About octahedral site M(2). (b) About tetrahedral site M(3). (c) About the second tetrahedral site in the T1 layer (occupied by H).

Electrostatic valence sums

Electrostatic valence sums, calculated from the bond length–bond strength parameters of Zachariassen (1978) are given in Table 3. As expected from the similar bond lengths in Table 6, the Σsi values are almost identical for

the two nolanite compositions. The anions O(1) and O(3) are severely undersaturated. These anions form tetrahedral coordination as shown in Figure 2c. Examination of the difference Fourier maps showed no indication of occupation of this site by metal atoms. However a small positive peak was observed on the three-fold axis near 0, 0, 0.41 in both maps, *i.e.*, the peak was $\sim 0.95\text{\AA}$ from O(1) and was reasonably interpreted as a hydrogen atom. We have accordingly normalized the unit cell composition to $14\text{ O} + 2(\text{OH})$, although we acknowledge atom site O(1) may not be fully hydroxylated. Σsi for O(1), 1.37–1.39, is higher than the corresponding value for hydroxyl anions in well established oxyhydroxides such as diaspore (Hill, 1979), in which $\Sigma si\text{ O}(2) = 1.29$.

Oversaturation of O(2) occurs for both crystals. This atom was the only one to display appreciable anisotropy of the temperature factor (elongated in the basal plane). It is possible that the local symmetry is lower than that imposed by space group $P6_3mc$ and O(2) is statistically distributed over a series of positions lying off the three-fold axis. This would result in longer M–O(2) bonds (and hence lower Σsi values) than the average values established in the refinement.

The valence sum calculations for the metal atom sites gave values close to 3 for the octahedral sites M(1) and M(2) and values near 2.6 for site M(3), *i.e.*, corresponding to a 1:2 mixture of divalent and trivalent ions in the tetrahedral site. The valence sums over all cations gave values of 29.6 and 29.7 for crystals 1 and 2, respectively, consistent with the proposed anion assignment of $14\text{ O} +$

Table 6. Bond lengths and angles

	Bonds		Angles	
	Crystal 1	Crystal 2	Crystal 1	Crystal 2
M(1) OCTAHEDRON				
M(1)–O(3) (x2)	1.951 (3)	1.957 (6)		
M(1)–O(2)	2.015 (3)	2.009 (5)		
M(1)–O(1)	2.043 (2)	2.037 (7)		
M(1)–O(4) (x2)	2.040 (4)	2.037 (4)		
Mean	2.007	2.006		
O(4)–O(4)	2.632 (4)	2.628 (7)	O(4)–M(1)–O(4)	80.4 (1)
O(1)–O(3)	2.713 (7)	2.685 (12)	O(1)–M(1)–O(3)	85.5 (2)
O(2)–O(4)	2.757 (5)	2.765 (9)	O(2)–M(1)–O(4)	85.6 (1)
O(3)–O(4)	2.823 (5)	2.833 (10)	O(3)–M(1)–O(4)	90.0 (2)
O(1)–O(4)	2.952 (6)	2.957 (10)	O(1)–M(1)–O(4)	92.6 (1)
O(2)–O(3)	2.947 (4)	2.951 (9)	O(2)–M(1)–O(3)	95.9 (2)
O(3)–O(3)	2.979 (7)	2.974 (15)	O(3)–M(1)–O(3)	99.5 (2)
M(2) OCTAHEDRON				
M(2)–O(3) (x3)	1.965 (4)	1.956 (8)		
M(2)–O(4) (x3)	2.083 (3)	2.097 (5)		
Mean	2.024	2.027		
O(4)–O(4) (x3)	2.632 (4)	2.628 (7)	O(4)–M(2)–O(4)	78.4 (1)
O(3)–O(4) (x6)	2.924 (5)	2.920 (9)	O(3)–M(2)–O(4)	92.4 (1)
O(3)–O(3) (x3)	2.911 (6)	2.923 (10)	O(3)–M(2)–O(3)	95.6 (2)
M(3) TETRAHEDRON				
M(3)–O(2)	1.905 (6)	1.911 (9)		
M(3)–O(4) (x3)	1.928 (3)	1.930 (5)		
Mean	1.922	1.925		
O(2)–O(4) (x3)	2.992 (5)	2.988 (9)	O(2)–M(3)–O(4)	102.7 (1)
O(4)–O(4) (x3)	3.258 (3)	3.269 (5)	O(4)–M(3)–O(4)	115.3 (1)
				102.1 (2)
				115.7 (2)

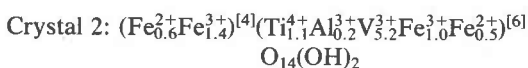
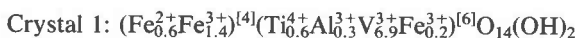
2(OH). The results do not support the cation valence distributions proposed by either Taylor and Radtke (1967) (V^{4+} , V^{5+} , Fe^{3+}) or Robinson *et al.* (1957) (predominantly V^{4+} , Fe^{2+}).

Discussion

The structure refinements for the two nolanite crystals have provided precise estimates of site population parameters and polyhedral bond lengths for the three different cation sites, and have shown how these parameters vary with change in composition. In addition, valence sum calculations have led to the determination of the unit cell compositions as oxyhydroxides, $M_{10}O_{14}(OH)_2$, where the number of each cation type, M, is known from the microprobe analyses. This wealth of experimental data would generally be sufficient to unambiguously establish the crystal-chemistry of a compound, including the cation distributions in the independent crystallographic sites. However, in the case of nolanite, the determination of the cation ordering is complicated by two factors. First the major elements, Ti, V and Fe all have similar scattering factors for X-rays and they can thus be combined in different ways to match the experimentally determined site population parameters. Second, vanadium commonly occurs in three different valence states in oxides, V^{5+} , V^{4+} , V^{3+} and iron in two, Fe^{2+} , Fe^{3+} . Crystal-field stabilization of cations in different crystallographic sites can result in all valence states of a particular cation occurring in the one compound. This is illustrated by the data in Table 7, which lists some structurally characterized iron vanadium oxides, with their established cation distributions. An interesting observation from Table 7 is that V^{3+} and V^{4+} can coexist with Fe^{3+} in the same compound, but only V^{3+} is stable when Fe^{2+} is present; *i.e.*, the assemblage $Fe^{2+} + V^{4+}$ is unstable relative to $Fe^{3+} + V^{3+}$. This is in contrast to iron titanates, where the reverse applies. Thus $FeVO_3$ comprises Fe^{3+} , V^{3+} , whereas $FeTiO_3$ comprises Fe^{2+} , Ti^{4+} (Shirane *et al.*, 1961). Similarly, Fe_2VO_4 contains Fe^{2+} , Fe^{3+} , V^{3+} (Wakihara *et al.*, 1971) whereas Fe_2TiO_4 contains Fe^{2+} , Ti^{4+}

(Forster and Hall, 1965). If we apply this stability relationship to nolanite, some conclusions may be drawn concerning the cation assignments.

The population parameters and valence sums are almost invariant with change of composition for the tetrahedral site M(3), and their values (Table 3) correspond to ordering of iron in this site, with a $Fe^{2+}:Fe^{3+}$ ratio near 1:2. The remaining iron, and the titanium, vanadium and aluminium, are then ordered in the octahedral sites and, since ferrous iron is present, vanadium is restricted to the trivalent state. The unit cell compositions for the two crystals can thus be given as

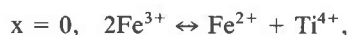


It was not possible to unambiguously determine the cation distributions between the two-fold and six-fold octahedral sites, although the Σsi values in Table 3 suggest that Ti^{4+} is ordered in the six-fold site M(1). The cation substitutions in the octahedral sites in going from crystal 1 to crystal 2 are given by



i.e., the compositional variations are accommodated by direct substitutions of the type $Al^{3+} \leftrightarrow Fe^{3+}$ and $V^{3+} \leftrightarrow Fe^{3+}$, together with the charge compensated substitution, $2 V^{3+} \leftrightarrow Fe^{2+} + Ti^{4+}$.

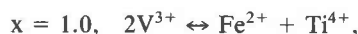
The latter type of substitution may be generalized to explain the observed composition variations listed in Table 1 for nolanite samples from the four different mines, *i.e.*, $2(V_x^{3+}Fe_{1-x}^{3+}) \leftrightarrow Fe^{2+} + Ti^{4+}$ for which the special cases are



corresponding to Fe \leftrightarrow Ti substitution



corresponding to V \leftrightarrow Ti substitution



mixed substitution.

The cation substitutions proposed for nolanite are consistent with the experimental observation that the mean M-O bond lengths are almost unchanged with change of composition, since Fe^{3+} , V^{3+} and $(Fe^{2+} + Ti^{4+})$ have similar ionic radii (Shannon, 1976). The observations would also be compatible with a $Ti^{4+} \leftrightarrow V^{4+}$ substitution, as these two cations also have similar ionic radii. Although this type of substitution is unlikely because of the stability relation $Fe^{2+} + V^{4+} \rightarrow Fe^{3+} + V^{3+}$, some V^{4+} may be stabilized in nolanite in the presence of Fe^{2+} if the two cations are ordered into different crystallographic sites, *e.g.*, V^{4+} in M(1) and Fe^{2+} in M(2), M(3). Yet other cation substitution schemes are possible if we

Table 7. Cation distributions in some iron-vanadium oxides

Compound	Cation Distributions	Reference
$FeVO_3$	Fe^{3+} (octahedral), V^{3+} (octahedral)	Shirane <i>et al.</i> , (1961)
Fe_2VO_4	Fe^{3+} (tetrahedral) $Fe^{2+} + V^{3+}$ (octahedral)	Wakihara <i>et al.</i> , (1971)
FeV_2O_4	Fe^{2+} (tetrahedral), V^{3+} (octahedral)	Wakihara <i>et al.</i> , (1971)
$Fe_2V_4O_{11}(OH)$	V^{5+} (tetrahedral) $Fe^{3+} + V^{3+}$ (octahedral) $Fe^{3+} + V^{4+}$ (octahedral)	Muller <i>et al.</i> , (1979)
$(Fe,V)_{18}O_{35}$	V^{5+} (tetrahedral) V^{4+} (square pyramidal) $Fe^{3+} + V^{3+}$ (octahedral) $Fe^{3+} + V^{4+}$ (octahedral)	Grey <i>et al.</i> , (1981)

allow the O/OH ratio to vary, e.g., $V^{3+} + OH^- \leftrightarrow Ti^{4+} + O^{2-}$. The change in the calculated Σsi values for O(1), 1.36 (low titanium) to 1.39 (high titanium) is qualitatively consistent with this hypothesis, but the magnitude of the change is of the order of the associated errors. (Changes of 0.01 to the bond lengths correspond to changes of ~ 0.1 in Σsi).

The assignment of all the vanadium to the trivalent state and iron to a mixture of ferrous and ferric is in disagreement with earlier proposed composition models for nolanite (Taylor and Radtke, 1967; Robinson *et al.*, 1957) but is consistent with the valences of these two elements in other oxide minerals found in the "green leader" deposits at Kalgoorlie. These include tomichite, $(Fe^{3+}, V^{3+})_4Ti_3As^{3+}O_{13}(OH)$ (Nickel and Grey, 1979), vanadian hematite, $V_{0.8}^{3+}Fe_{1.2}^{3+}O_3$ (Nickel and Grey, 1982) tivanite, $V^{3+}Ti^{4+}O_3(OH)$ (Grey and Nickel, 1981), vanadian muscovite, $K(Al, V^{3+})_2Si_3AlO_{10}(OH)_2$ (Nickel, 1977; vanadian tourmaline, $Na(Fe^{2+}, V^{3+}, Mg, V^{3+})Al_6(BO_3)_3Si_6O_{18}(OH, F)_4$ (Nickel and Grey, 1982) and vanadian magnetite, $(Fe, V)_3O_4$ (Nickel and Grey, 1982), which contains Fe^{2+} , Fe^{3+} and V^{3+} (Wakihara *et al.*, 1971).

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