

NICKEL MINERALS FROM BARBERTON, SOUTH AFRICA:
III. WILLEMSEITE, A NICKEL-RICH TALCS. A. DE WAAL, *National Institute for Metallurgy,
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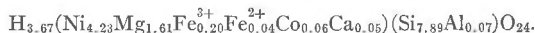
ABSTRACT

Willemseite, a nickel-rich talc, comes from a small tabular body of nickeliferous rock about two miles west of the Scotia Talc Mine in the Barberton Mountain Land, Transvaal. The nickeliferous rock comprises a mixture of nickel-rich talc, nickel-rich chlorite, ferroan tremolite, reevesite, violarite, and millerite.

The willemseite is light green in hand-specimen, and colourless and non-pleochroic in thin section, and has $2V_\alpha = 27^\circ \pm 2^\circ$, $\beta = 1.652 \pm 0.002$, $\alpha = 1.600$, and a measured specific gravity of 3.31. It has a perfect {001} cleavage. It has a monoclinic cell with $a = 5.316 \pm 0.002$ Å, $b = 9.149 \pm 0.003$ Å, $c = 18.994 \pm 0.006$ Å and $\beta = 99.96^\circ \pm 0.06^\circ$. The eight strongest lines, in decreasing order of intensity, have spacings of 9.40, 3.12, 2.503, 4.57, 2.245, 1.524, 3.55, 2.636 Å. The mineral was indexed, a space group Cc being assumed.

The willemseite yields an infrared spectrum similar to that of synthetic nickel-rich talc. The major bands appear at the wavenumbers 383, 413, 452, 465, 668, 705, and 1025 cm^{-1} . The relative intensities of the two bands at 668 and 705 cm^{-1} give a good indication of the magnesium content. A study of the hydroxyl adsorption bands in the region 3600 cm^{-1} strongly suggests that, although the nickel ions show a preference for certain octahedral coordination sites, no cation clustering is present.

The chemical analysis of a purified sample of willemseite gives the cell formula



The name *willemseite* has been proposed for all the talc minerals having nickel as the major element in the octahedral coordination.

INTRODUCTION

As part of a study of the distribution of nickel in serpentinites and related rocks, the author collected and reinvestigated a sample of tremolite and associated silicate minerals from the well-known occurrence approximately two miles west of the Scotia Talc Mine, in the Bon Accord area, Barberton, Transvaal. In addition to violarite and millerite, ferroan tremolite, nickel-rich chlorite, reevesite, and nickel-rich talc were found. The ferroan tremolite and the nickel-rich chlorite, nimitite, have been dealt with in detail (De Waal, 1969, 1970), and have been submitted for publication. This paper is the third in a series in which these nickel-bearing minerals are described.

This paper deals with the nickel-rich talc, believed to be a new nickel mineral.¹ The name *willemseite*, in honour of the late Professor Johannes Willemse, is proposed for this mineral. Professor Willemse, who was the

¹ A preliminary description received limited distribution as *Nat. Inst. Met. Res. Rep.* 352 (1968), and was abstracted in *Chem. Abstr.* 70, 127 (1969); consequently the name will be acted on later by the International Mineralogical Association.

head of the Department of Geology at the University of Pretoria, was a well-known authority on layered mafic intrusions and, in particular, on the Bushveld Igneous Complex.

FIELD RELATIONS AND PETROGRAPHY OF THE NICKEL ORE

The nickel ore under discussion was first reported by Trevor (Partridge, 1944) in 1920. According to the South African Geological Survey (1959), the ore constitutes a tabular body two feet long and is probably a contact deposit along the junction of the Moodie's quartzite and the ultramafic rocks of the Jamestown Igneous Suite. Furthermore, it is stated that the major minerals are nepouite and trevorite. Nepouite was not found, however, in the samples available for the present investigation.

In hand-specimen, the nickel ore has a greenish-grey (5G6/1) appearance on a fresh surface (Rock Color Chart Committee, 1963). The colour, however, tends to be somewhat mottled owing to the patchy distribution of ferroan trevorite in the green silicates. This latter phenomenon strongly simulates brecciation.

In thin section, the rock consists of clusters of minute opaque grains embedded in the willemseite. The nimite forms irregular veins in the talc and opaque ore.

The grain size of the ferroan trevorite varies considerably—from about 0.5 mm to less than 10 μm in diameter. Polished sections further revealed the presence of violarite and millerite. The violarite is intergranular to the ferroan trevorite whereas the other sulphide appears as minute inclusions in the ferroan trevorite. The amount of sulphide varies markedly from one hand-specimen to another.

Secondary alteration of the ore is manifested by the formation of opal and moderate greenish-yellow (10Y7/4) reevesite in druses. These minerals have been mildly stained by iron oxide, and small amounts of goethite are present.

EXPERIMENTAL METHODS

The experimental methods used in this paper are in all respects similar to those already described in a paper on nimite (De Waal, 1970).

The infrared absorption spectrum of the willemseite was run on a Perkin-Elmer model 521 grating-type infrared spectrometer. For this spectrometer an accuracy of 0.5 cm^{-1} is claimed. For the detailed work in the hydroxyl stretching region, the absorption bands of the willemseite were standardized against the water-vapour band at 3656.3 cm^{-1} .

RESULTS

The physical and optical properties of willemseite are provided in Table 1. In the same table are given some data on the 'green silicate,' after Partridge (1944). The poor correlation of the two sets of data indicates that the optical data presented by Partridge are a combination of

TABLE 1. OPTICAL AND PHYSICAL PROPERTIES OF WILLEMSEITE
 COMPARED WITH THOSE OF THE 'GREEN SILICATE,' AFTER PARTRIDGE

	Willemseite	'Green silicate'
Colour	Light green (5G7/4) Colourless and nonpleochroic in thin section	Dark to apple green
Mohs' hardness	2	2-2½
Cleavage	{001} perfect	
Optical axial angle	$2V_{\alpha} = 27^{\circ} \pm 2^{\circ}$	$2V_{\alpha} = 14^{\circ} \pm 2^{\circ}$
Specific gravity	Berman balance: 3.281 (1) Clerici cell: 3.31 (1) Calculated: 3.348 (adsorbed water not considered)	Pyknometer: 3.037 ± 0.002
Refractive index	$\beta = 1.652 \pm 0.002$ $\alpha = 1.600$ [γ is close to β and calculated to be 1.655]	$\beta = \gamma = 1.650 \pm 0.002$ $\alpha = 1.605 \pm 0.003$
Cell constants	$a = 5.316 \pm 0.002 \text{ \AA}$ $b = 9.149 \pm 0.003 \text{ \AA}$ $c = 18.994 \pm 0.006 \text{ \AA}$ $\alpha = 90.00^{\circ}$ $\beta = 99.96^{\circ} \pm 0.06^{\circ}$ $\gamma = 90.00^{\circ}$ Volume = 909.85 \AA^3	

the optical properties of the willemseite and those of nimite, a nickel-rich chlorite (De Waal, 1970).

The values of specific gravity cited for the willemseite show quite a variation, and this phenomenon will be discussed later.

The chemical composition of the willemseite is very close to that of minnesotaite (Table 2), except that the iron is replaced by nickel.

X-ray diffraction data for willemseite are presented in Table 3.

The infrared spectrum of willemseite in the region from 300 to 800 cm^{-1} is shown in Figure 1. The absorption band of the same mineral in the region of 1000 cm^{-1} is shown in Figure 2. To a high degree, both these spectra correspond with the same spectra of synthesized nickel-rich talc (Figure 3).

Of special interest are the intensity ratios of the two absorption bands at 668 and 705 cm^{-1} . These two bands, according to Stubican and Roy (1961) and Wilkens and Ito (1967), give a good indication of the nickel-magnesium ratio in the talc structure. Both these pairs of investigators worked on synthesized material, and the relevant findings of Stubican

TABLE 2. THE CHEMICAL DATA FOR WILLEMSEITE, COMPARED WITH THOSE OF MINNESOTAITE

	Willemseite ^a	Minnesotaite ^b
SiO ₂	51.83	51.29
TiO ₂	—	0.04
Al ₂ O ₃	0.38	0.61
Fe ₂ O ₃	1.77	2.00
FeO	0.31	33.66
NiO	34.55	—
MnO	0.00	0.12
MgO	7.09	6.26
CoO	0.46	—
CaO	0.28	0.00
Na ₂ O	—	0.08
K ₂ O	—	0.03
H ₂ O ⁺	3.61	5.54
H ₂ O ⁻	0.05	0.24
Total	100.33	99.87
	Number of ions per	
	24(O, OH)	20(O) and 4(OH)
Si	7.890	7.874
	7.96	7.95
Al	0.068	0.074
Fe ³⁺	0.203	0.231
Fe ²⁺	0.040	4.323
Ni	4.230	—
Mn	0.000	0.016
Mg	1.609	1.432
	6.18 ^c	6.00
Co	0.056	—
Ca	0.046	—
Na	—	0.024
K	—	0.006
(OH)	3.67	4.00

^a Analyst: Analytical Chemistry Division, National Institute for Metallurgy.

^b After Deer, Howie, and Zussman (1962).

^c See Discussion ('Unit-Cell Formula').

and Roy are presented in Figure 3a and 3b. From these data it can be deduced that, when the two absorption bands (in the region of approximately 700 cm⁻¹) have equal intensities, the nickel-magnesium ratio

TABLE 3. X-RAY-DIFFRACTION DATA FOR WILLEMSEITE

<i>I</i>	<i>hkl</i>	<i>d</i> (meas) Å	<i>d</i> (calc) Å	<i>I</i>	<i>hkl</i>	<i>d</i> (meas) Å	<i>d</i> (calc) Å
100	002	9.40	9.36	2	241	1.700	1.698
<1	004	4.68	4.68	2	208	1.609	1.611
16	020	4.57	4.57	2B	0.0.12	1.560	1.559
3	114	3.55	3.53	7	060	1.524	1.525
28	006	3.12	3.12	1	1.3.11	1.488	1.489
3	130	2.636	2.635	3	247	1.379	1.378
3	132	2.599	2.596	2	0.0.14	1.336	1.336
23	133	2.503	2.507	3	260	1.318	1.318
1	008	2.338	2.339	2	262	1.289	1.290
8	135	2.245	2.249	1	424	1.270	1.269
2	117	2.165	2.166	2	425	1.257	1.258
3	028	2.085	2.082	2B	0.0.16	1.170	1.169
1	137(?)	1.957	—	1	281	1.051	1.051
<1	0.0.10	1.873	1.871	1	0.0.18	1.039	1.039
1	242	1.729	1.729	3		0.9938	

would be slightly higher than 2 to 1. This, in fact, is in close correspondence with the findings on the willemseite, if it is taken into account that the willemseite also accommodates small amounts of cobalt, iron, and calcium that were most probably not present in the synthesized talc minerals. The intensity ratio of these two peaks therefore gives a good indication of the magnesium content of the willemseite.

The hydroxyl stretching vibrations of the willemseite in the region from 3600 to 3700 cm^{-1} yielded further valuable information on the grouping of cations round the hydroxyl group. It has been shown by Vedder (1964), Wilkens (1967), and Wilkens and Ito (1967), that, in this region, the hydroxyl stretching fundamental peak for talc can split into as many as four peaks, depending on the degree of substitution of the magnesium in the octahedral layer by other divalent ions such as iron, nickel, and cobalt. Furthermore, it is known that the substitution of silicon by aluminium in the tetrahedral layer causes the hydroxyl dipole to tilt with respect to the layering of the sheet-like minerals. When all the octahedral sites are occupied by magnesium and all the tetrahedral sites by silicon, this hydroxyl dipole is perpendicular to the layering.

The willemseite yielded altogether four bands of hydroxyl stretching vibrations (Table 4, Figure 4). The relative intensities of these absorption bands, which are relatively sharp ($\Delta\nu_{\frac{1}{2}} = 5 \text{ cm}^{-1}$), are very close to the ratio predicted by the formula of Vedder, a random distribution of the ions in the octahedral sites being assumed: $N_A:N_B:N_C:N_D::1:3x/1-x$

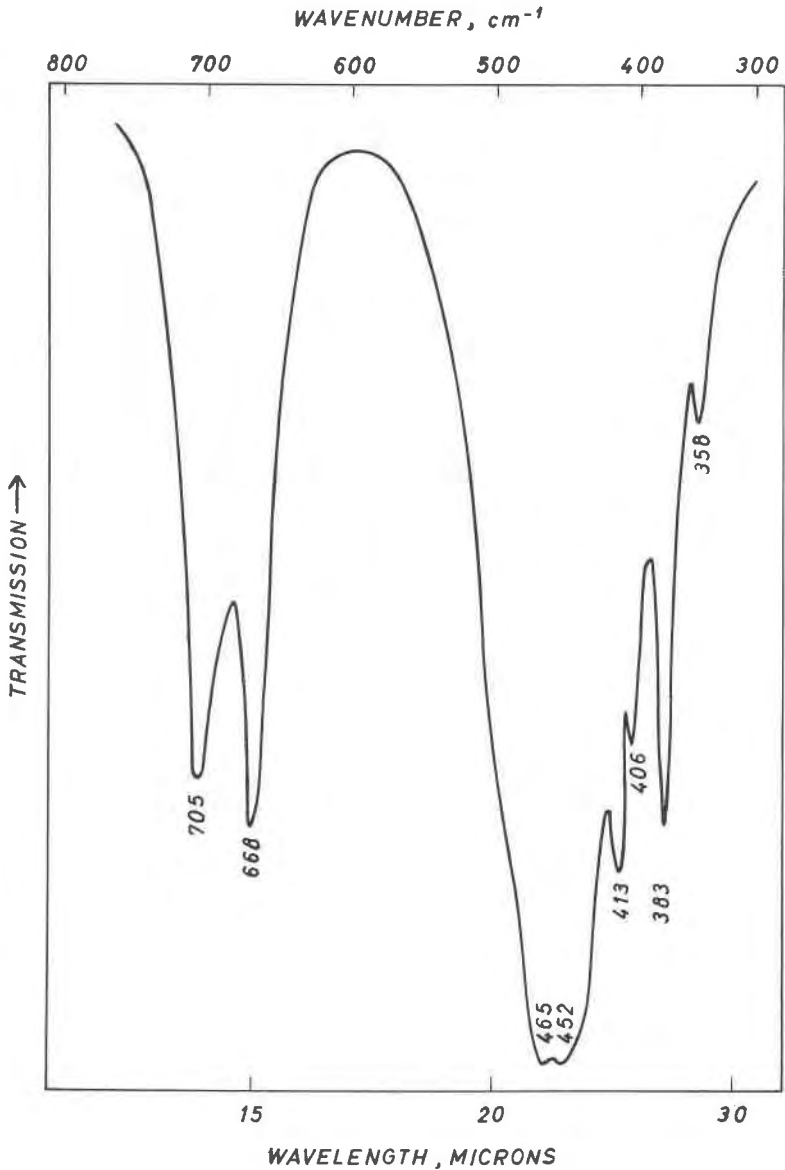


FIG. 1. Infrared spectrum of willemsite in the region 300 cm^{-1} to 800 cm^{-1} .

$:3x^2/(1-x)^2:x^3/(1-x)^3$ where $(1-x)$ = magnesium concentration and x = concentration of replacing divalent ions. The observed deviations of the predicted and measured intensities may have different reasons, one of which is cation clustering. This will be discussed in due course.

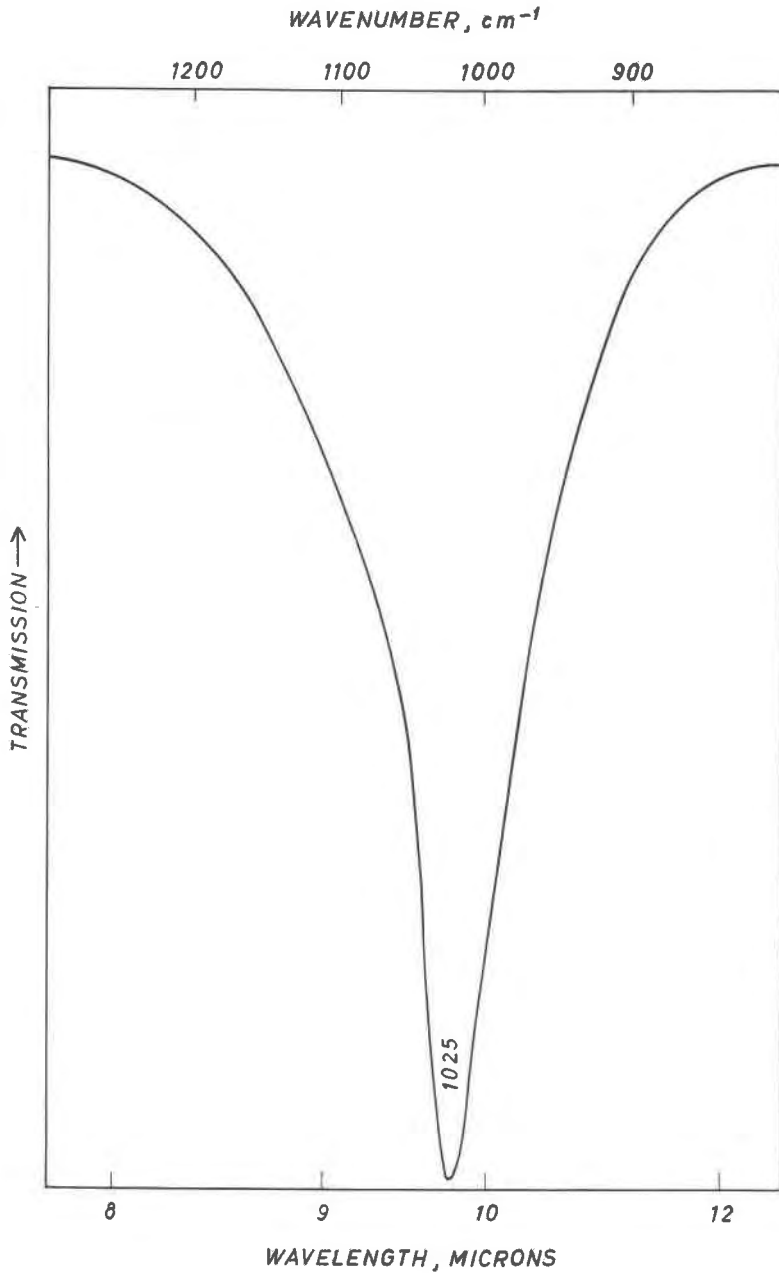


FIG. 2. Infrared absorption band of willemseite in the region 800 cm^{-1} to 1300 cm^{-1} .

A study of Table 4 makes it evident that the magnesium concentration of the willemseite, as predicted by the infrared method, differs from the analysed value by only one percent. This illustrates the usefulness of this method in mineralogy.

DISCUSSION

The Name 'Willemseite.' From the data presented in this paper, it is obvious that a distinct talc mineral is being discussed. Nickel-rich talc, to the author's knowledge, has not previously been described as a natural mineral, although it is rather easily synthesized.

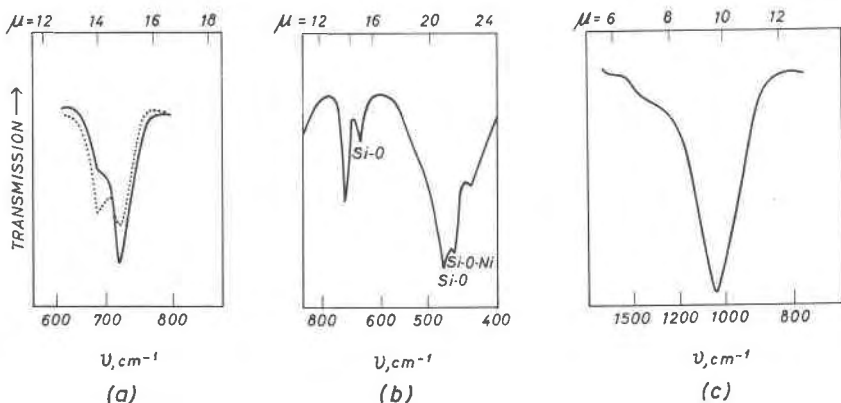


FIG. 3. Infrared spectra of synthetic talcs. (a) The region 600 cm^{-1} to 800 cm^{-1} , for Mg_2Ni talc (full line) and MgNi_2 talc (dotted line). (b) Ni talc in the region 400 cm^{-1} to 800 cm^{-1} . (c) The region 800 cm^{-1} to 1500 cm^{-1} (after Stubican and Roy, 1961).

The name *willemseite* is proposed for all talc minerals in which nickel is the major element in the octahedral coordination. In this way, also, the author wishes to honour the name of a dedicated mineralogist and petrologist, Professor Johannes Willemse.

Specific Gravity. In Table 1, three values of the specific gravity of the willemseite are listed. The determination with the Berman balance had a relatively high reproducibility, but the value of 3.281 obtained by it is obviously very low when it is compared with the value of 3.348 calculated from the unit-cell formula and cell volume. The values obtained with the Clerici cell had a lower reproducibility. However, the value of 3.31 obtained with it is considered more accurate than the 3.281 obtained with the Berman balance. This result illustrates once again the extreme difficulty in the determination of the specific gravities of platy minerals. The fine grain size of the willemseite obviously provides a great deal of oppor-

TABLE 4. INFRARED DATA ON THE WILLEMSEITE AS DERIVED FROM THE HYDROXYL STRETCHING VIBRATIONS

Line notation ^a	N_A	N_B	N_C	N_D
Closest three cations (R = two-valent cations other than Mg)	Mg, Mg, Mg	Mg, Mg, R	Mg, R, R	R, R, R
Theoretical intensity ratios ^b	1	$\frac{3x}{1-x}$	$\frac{3x^2}{(1-x)^2}$	$\frac{x^3}{(1-x)^3}$
Measured wavenumber in cm^{-1} ^c	3676.7	3662.4	3645.4	3624.8
Measured intensity ratios (integrated peak areas)	i) 1.0 ii) 2.1 ± 0.4	9.0 18.8 ± 1.2	17.9 37.6 ± 0.9	19.8 ^d 41.6 ± 1.1 ^e
Calculated intensity ratios from cell formula	i) 1.0 ii) 1.8	8.5 15.0	24.2 42.8	22.9 ^d 40.3 ^e
Mg concentration calculated from	$N_A:N_B$ 0.248	$N_B:N_C$ 0.333		$N_C:N_D$ 0.231
Average value	0.271			
Mg concentration from cell formula	0.260			

^a After Wilkins (1967).

^b After Vedder (1964), where $(1-x)$ = Mg concentration, and x = the concentration of the ions replacing Mg in the octahedral site.

^c Error of measurement: $\pm 0.1 \text{ cm}^{-1}$; Accuracy of Perkin-Elmer spectrometer is claimed to be 0.5 cm^{-1} .

^d Intensity ratio where intensity of N_A equals 1.

^e Intensity ratio where total intensities of $N_A + N_B + N_C + N_D = 100$.

tunity for trapping air, especially with the Berman balance where a grain size of plus 100 mesh (Tyler) was used. In the Clerici cell, this factor of trapped air is markedly reduced since very small grains are used in this experiment.

Unit-Cell Formula. The unit-cell formula (Table 2) calculated from the chemical analysis shows a discrepancy in that the total number of ions (6.18) in the octahedral coordination site is slightly higher than the maximum permissible number of 6.00. This may be partly due to small

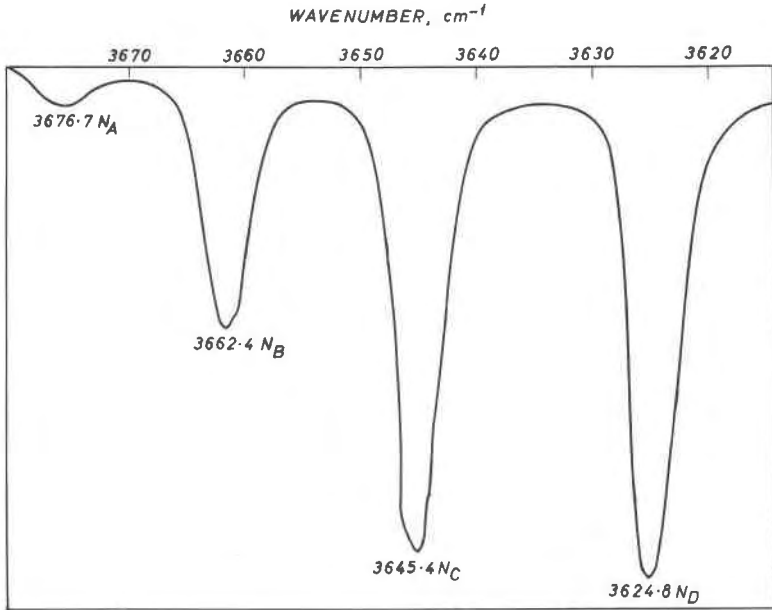


FIG. 4. Hydroxyl vibration bands of willemseite in the region 3620 cm^{-1} to 3680 cm^{-1} .

amounts of goethite, present as a brown coloration on some of the willemseite grains, as well as minor amounts of ferroan trevorite in the powder submitted for analysis. The influence of this brown goethite coloration on the magnetic properties and on the specific gravity was negligibly small. Separation of these grains was not possible. Strictly speaking, the number of trivalent ions accommodated in the octahedral layer must equal the number of trivalent ions that replace the silicon in the tetrahedral layer. This would mean that the total number of trivalent cations in the octahedral sites in the willemseite will be 0.068—that is, the number of aluminium ions that replace the silicon. From this discussion it is evident that 0.135 of the trivalent iron ions must be regarded as an impurity. The total number of cations in the octahedral coordination will therefore be reduced by 0.135 to approximately 6.04, which is an acceptable figure.

X-ray Diffraction. The broad and diffuse lines of the willemseite pattern made accurate measurement of the θ -values extremely difficult. The measured values were indexed according to the Cc space group, but, because of the inaccuracy of measurement, a higher symmetry arrangement, such as $C2/c$, is possible.

Infrared Work. The observations made on willemseite are in good agreement with published work on synthetic nickel-rich talc. Of interest, however, are the intensity ratios of the hydroxyl stretching bands in the region between 3600 and 3700 cm^{-1} . From Table 4 it is evident that there is a pronounced difference in the intensity ratios of the four bands when expressed with the assumptions that the intensity of N_A equals one and the total intensity of the four bands ($N_A + N_B + N_C + N_D$) equals 100. The author contends that the latter system of expression is the better. Because a constant value of 100 for the total intensity of the four bands is used, it is possible to compare directly two or more sets of intensity ratios. This is not possible with the first system of expression, because N_A itself is variable.

Furthermore, it is evident from Table 4, that the measured intensities of the N_A and N_D bands are close to the calculated values. The intensities of the N_B and N_C bands are, respectively, higher and lower than the calculated values. Cation clustering is therefore not significant, because, in such a case, the measured intensities of the N_A and N_D band would be expected to be higher than the calculated intensities.

Strens (1966) showed that, in amphiboles, the ratio $(Bo/Bc)/(Co/Cc)$ (where Bo and Co are the observed intensities, and Bc and Cc the calculated intensities, of N_B and N_C , respectively) gives an indication of preference for certain cations to fill certain sites in the amphibole structure. The ratio $(Bo/Bc)/(Co/Cc)$ for willemseite is greater than unity and therefore indicates that the magnesium shows a preference for certain octahedral coordinated sites. Depending on the stacking of the silicon layers in the talc structure, conditions are obtained where either one out of every three sites in the octahedral coordination has a centre of inversion, or *vice versa*. Because the precise stacking of the silicon layers in the willemseite was not determined in the present investigation, the author is unable to tell precisely which sites of octahedral coordination (i.e., with or without centres of inversion) are favoured by the magnesium and which by the nickel.

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