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THE COMPOSITION AND CRYSTALLOGRAPHY OF NIOCALITE[1]

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ABSTRACT

Niocalite is monoclinic with $a = 10.83$, $b = 10.42$, $c = 7.38$ Å, and $\beta = 109°40'$. On the basis of two chemical analyses, the generalized formula is $(Ca, Nb)_{16}Si_8(O, OH, F)_{36}$. The similarity of niocalite to woehlerite, hiortdahlite, and låvenite is discussed.

Introduction

Some time ago, the mineral niocalite was introduced in a brief note (Nickel, 1956), which included a partial chemical analysis and a description of the optical properties. Since that time, complete chemical analyses have been performed, and further optical and *x*-ray determinations have been made. A paper on the crystallography of niocalite was presented at the first Annual Meeting of the Mineralogical Association of Canada, and was subsequently published in the Journal of the Canadian Institute of Mining and Metallurgy (Rowland *et al*, 1957).

Occurrence

Niocalite was first identified in diamond drill core from the Oka, Quebec, property of Quebec Columbium, Limited. Surface rock containing this mineral was subsequently found in an open pit made on the upward extension of the deposit.

The rock in which the niocalite occurs is essentially a coarse, crystalline strontian calcite containing niocalite, magnetite, and apatite. Other niobium-bearing minerals, notably pyrochlore and niobian perovskite, although occurring in the area, are characteristically absent in the niocalite rock itself. The niocalite occurs as randomly oriented, coarse, prismatic crystals up to one centimetre in length, and occasionally even longer, embedded in the calcite. In some of the higher grade sections, niocalite constitutes about 10% of the rock.

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Morphology and Twinning

Practically all the niocalite observed occurs as prismatic crystals with a nearly square cross section (Fig. 1a). On close examination, it is seen that most of the crystal faces are uneven and curved, and that the larger crystals tend to be tapered at both ends (Fig. 1b). It is therefore very difficult to obtain accurate goniometric measurements on the external crystal faces. The prism faces of the best crystals available cannot be indexed satisfactorily, possibly because the external faces are composite due to twinning and/or parallel growth. The prism faces correspond fairly closely (within 1°) to (504) of the pseudo-orthorhombic cell determined by x-ray studies of twinned crystals, and to $(\bar{2}54)$ of the true monoclinic cell.

All the niocalite crystals observed so far exhibit twinning. Most of the twins are intimately intergrown (Fig. 1b) and consist of irregular domains which have one of two orientations. Observations on the universal stage show that the twinned members have in common the optical direction X, which corresponds to the crystallographic b-axis.

Some of the small crystals consist simply of contact twins (Fig. 2) also having the b-axis in common. The relationship of the twinning to

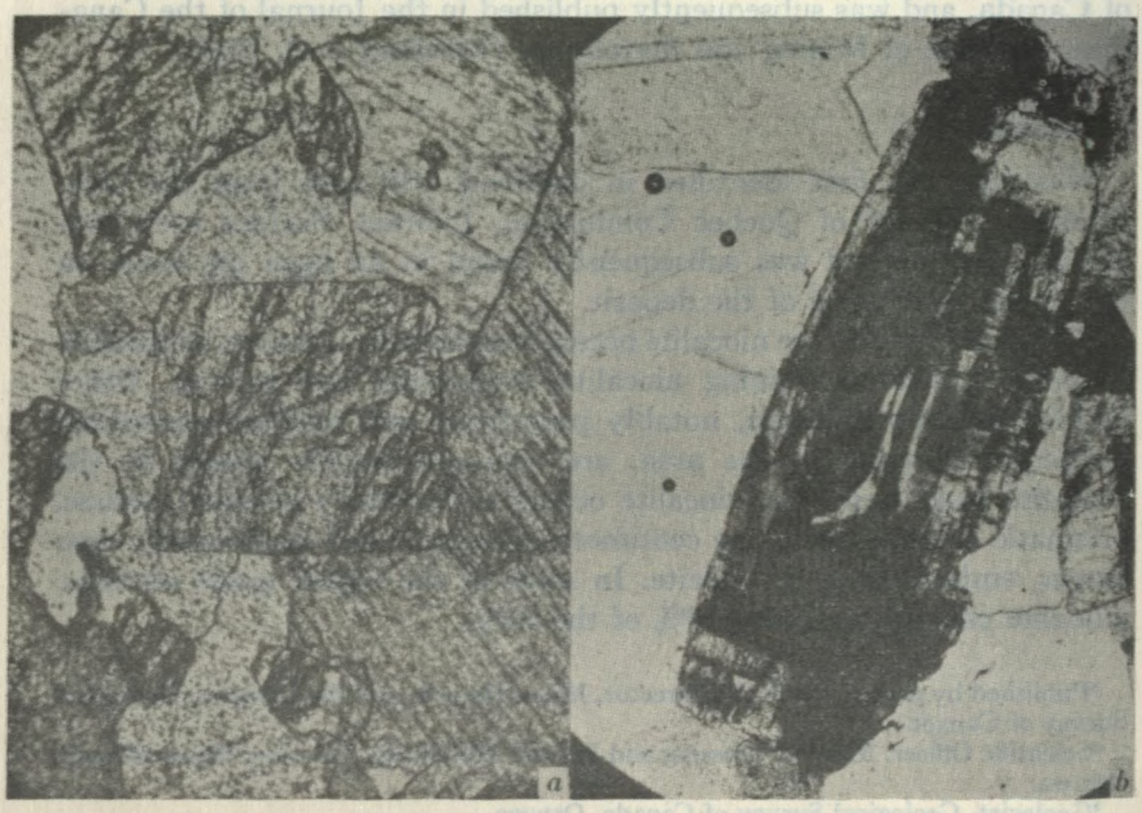

FIG. 1. Niocalite crystals in thin-section. x35. (*a*) Basal section of niocalite crystal in calcite. (*b*) Longitudinal section of crystal between crossed nicols, showing intricate twinning.

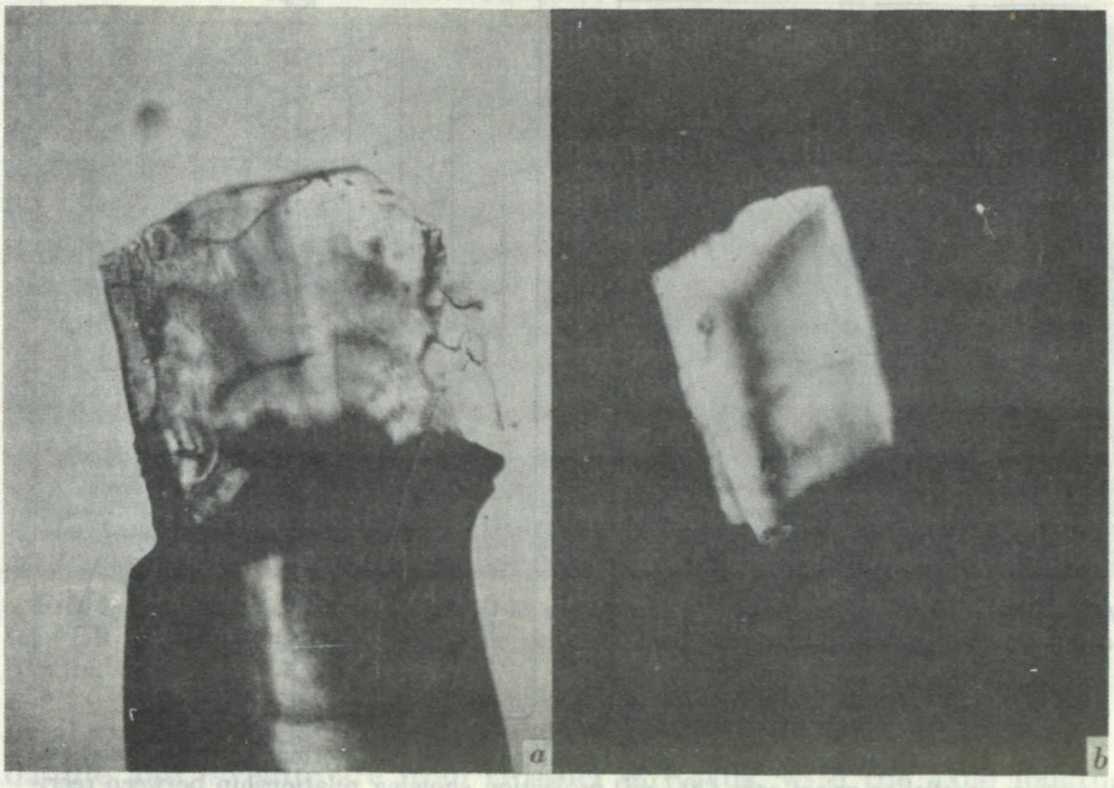

FIG. 2. Niocalite crystal exhibiting simple contact twinning, with the *b*-axis normal to the plane of the paper. x140. (*a*) In plane polarized light. (*b*) Same crystal between crossed nicols, with one of the twins in position of extinction.

the optical and crystallographic directions is illustrated in Fig. 3a, showing that the twin axis, which is normal to the composition plane in the contact twinning, is approximately parallel to the crystallographic *c*-axis. *X*-ray diffraction data enabled the composition plane to be identified as $(\bar{1}02)$, and the normal to this plane (the twinning axis) makes an angle of 15 minutes with the crystallographic *c*-axis (Fig. 3b).

X-ray Crystallography

Single crystal photographs were made using both Weissenberg and precession cameras. The crystals used were "half twins" produced from the contact twins by grinding away one member, leaving the other for the *x*-ray determinations.

Niocalite is monoclinic, space group C_s^2 (Pa) or C_{2h}^4 $(P2/a)$, with $a = 10.83$, $b = 10.42$, $c = 7.38$ Å, and $\beta = 109°40'$. Twinned crystals show a pseudo-orthorhombic symmetry with apparent cell dimensions of $a = 10.42$, $b = 20.39$, and $c = 7.38$ Å. Precession photographs (Fig. 4) show projections of the true monoclinic cell of niocalite and the pseudo-orthorhombic cell of a twinned crystal.

The relationship of these lattices is shown diagrammatically in Fig. 3b. The points in reciprocal space are so related that the twinning can

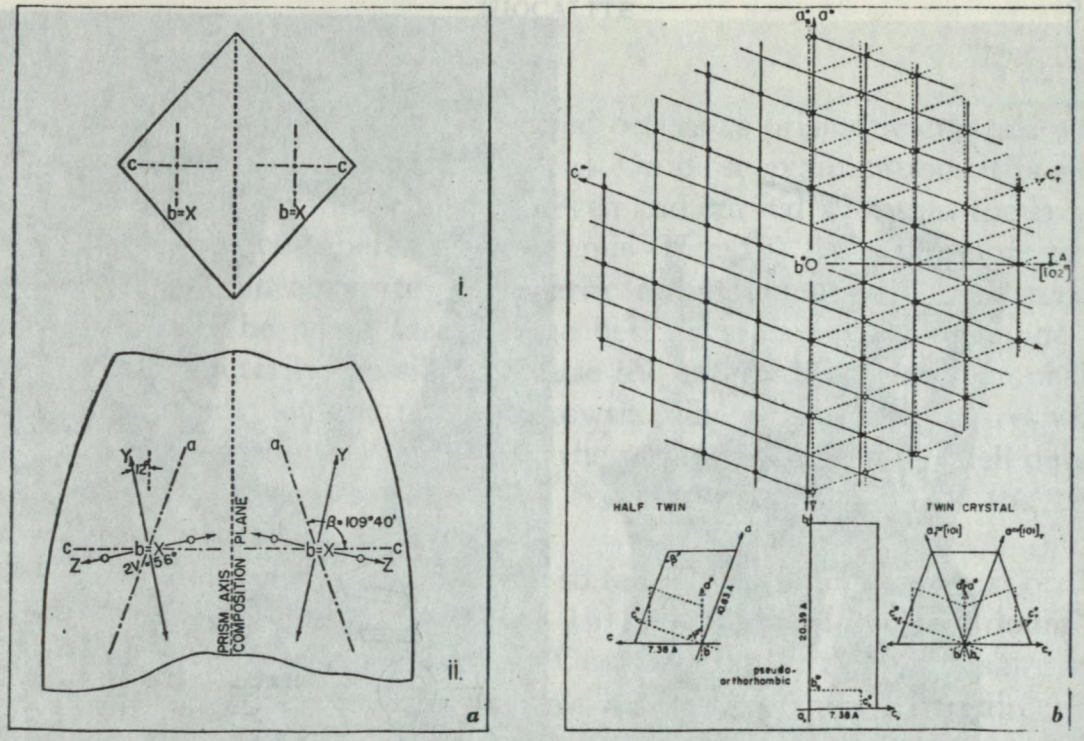

FIG. 3. (*a*) Orientation diagrams of niocalite: (*i*) section normal to prism axis; (*ii*) section parallel to prism axis. (*b*) (*h*0*l*) projection showing relationship between recriprocal lattices of niocalite twin members.

be adequately explained by the following twin law: composition plane = ($\bar{1}02$), twin plane ($\bar{1}02$).

The axial ratio of niocalite is $a:b:c = 1.038:1:0.708$, and the cell volume is 784 Å^3. The measured specific gravity is 3.32, and the calculated molecular weight is 1568.

Niocalite is crystallographically and chemically similar to woehlerite, hiortdahlite, and låvenite, which are considered to be members of the woehlerite group (Gossner & Kraus, 1934). The cell dimensions and

TABLE 1. CELL DIMENSIONS AND AXIAL ANGLES OF WOEHLERITE, HIORTDAHLITE, LÅVENITE, AND NIOCALITE

	Woehlerite				
	Present work	Gossner & Kraus	Hiortdahlite	Låvenite	Niocalite
a	10.87	10.82	10.93	10.95	10.83
b	10.27	10.28	10.31	10.01	10.42
c	7.32	7.27	7.33	7.19	7.38
α	90°	90°	90°29′	90°	90°
β	109°05′	108°57′	108°50′	110°18′	109°40′
γ	90°	90°	90°08′	90°	90°

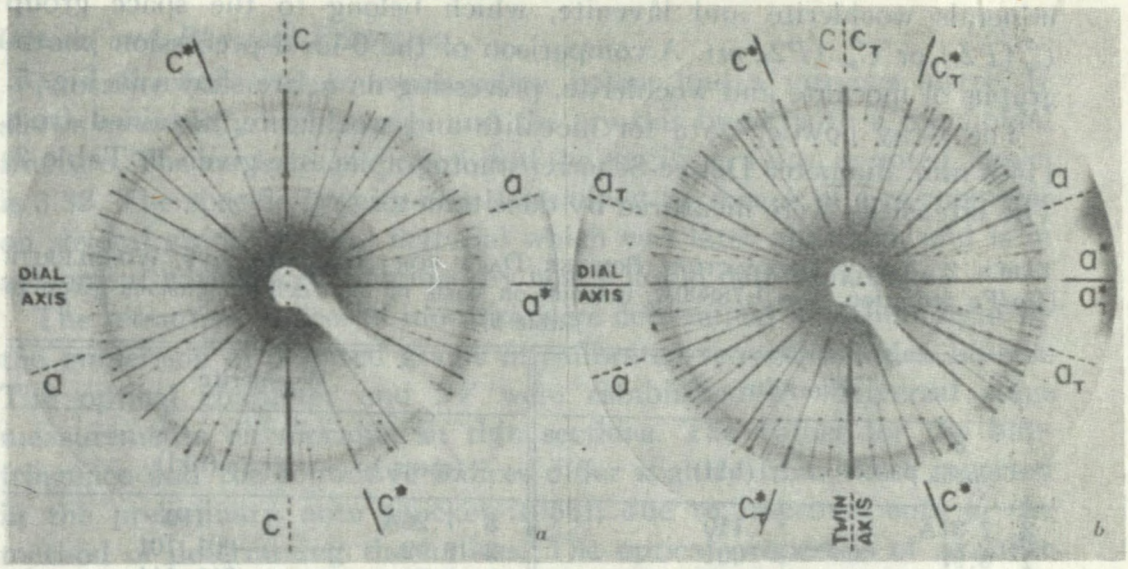

FIG. 4. Niocalite recriprocal lattice, 0-level projection, precession on [*b*], Mo/-radiation. (*a*) Half twin showing true monoclinic cell. (*b*) Twinned grain showing pseudo-orthorhombic cell.

axial angles of these minerals are shown in Table 1. The data for hiortdahlite and låvenite are from Gossner & Kraus, with the axial lengths converted to Ångstroms from their published values, which are assumed to be in *kX* units. The woehlerite data were derived from our *x*-ray study of crystals from Langesfiord, Norway, kindly supplied by Dr. R. M. Thompson of the University of British Columbia.

Of these four minerals, all are monoclinic except hiortdahlite, which is triclinic, with α and γ quite close to 90°. Niocalite, with space group C_s^2 (Pa) or C_{2h}^4 $(P2/a)$, is distinguished from the other two monoclinic

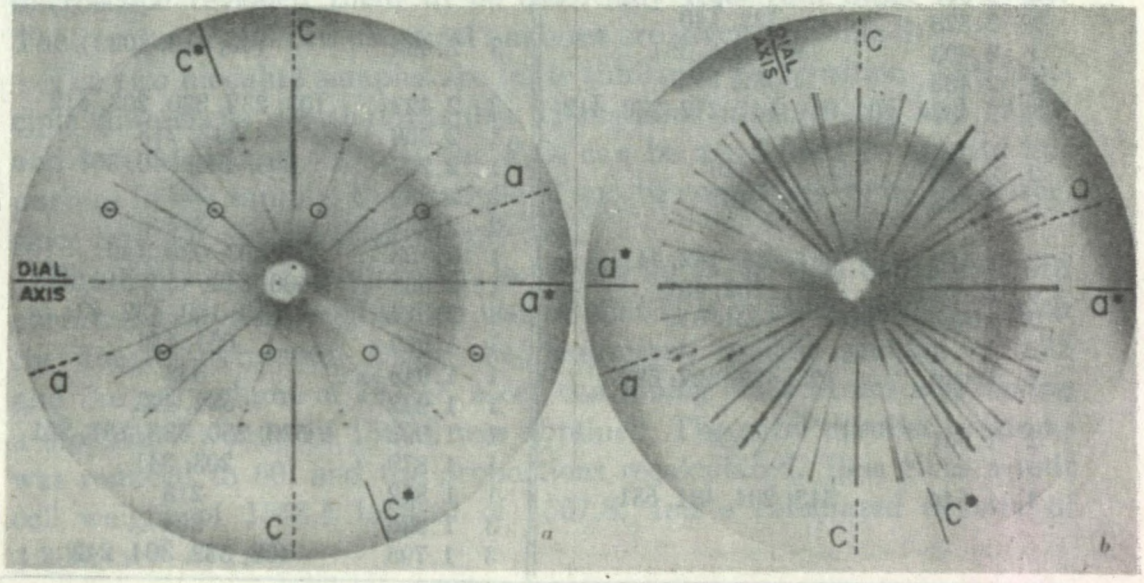

FIG. 5. Reciprocal lattice, 0-level projection, precession on [*b*], Co/-radiation. (*a*) Niocalite, (*h*0l) $h = 2n$. (Extra diffractions due to twinning are circled). (*b*) Woehlerite, (*h*0l) all present.

minerals woehlerite and låvenite, which belong to the space group C_2^2 ($P2_1$) or C_{2h}^2 ($P2_1/m$). A comparison of the 0-level precession photographs of niocalite and woehlerite, precessing on b, are shown in Fig. 5.

The x-ray powder data for niocalite and woehlerite, obtained from 114.6 mm. diameter Debye-Scherrer photographs, are given in Table 2. The intensities were measured by densitometer.

TABLE 2. X-RAY DIFFRACTION POWDER DATA FOR NIOCALITE AND WOEHLERITE (Co/Fe radiation, $\lambda = 1.78890$Å, indexed on basis of unit cell dimensions given in Table 1)

Niocalite			Woehlerite		
I	d (meas.)	(hkl)	I	d (meas.)	(hkl)
3	7.31Å	110	3	7.26Å	110
1	6.97	001	2	6.92	001, $\bar{1}01$
2	5.77	011, $\bar{1}11$	1	5.75	011, $\bar{1}11$
			2	5.151	200, 020
1	5.015	$\bar{2}01$	3	5.022	101, $\bar{2}01$
1	4.677	120			
1	4.595	210	3	4.601	210, 120
1	4.535	111, $\bar{2}11$	3	4.502	111, $\bar{2}11$
2	4.174	021, $\bar{1}21$	3	4.113	021, $\bar{1}21$
			3	3.582	201, 121, $\bar{2}21$, $\bar{3}01$
1	3.473	$\bar{1}12$, 002, 030, $\bar{2}02$	1	3.453	002, $\bar{1}12$
1	3.395	211, $\bar{3}11$	1	3.377	211, $\bar{3}11$
5	3.240	310	6	3.253	$\bar{2}12$, 310, 130
1	3.117	031, $\bar{1}31$	3	3.066	031, $\bar{1}31$
10	3.012	$\bar{1}22$	7	2.998	102
			5	2.965	$\bar{3}02$
6	2.891	022, $\bar{2}22$			
6	2.852	131, $\bar{2}31$, 320	10	2.839	$\bar{3}12$, 320, 230, 131
1	2.613	$\bar{4}11$, 040, 122	1	2.625	$\bar{4}11$
3	2.557	400	2	2.570	122, $\bar{3}22$, 400, 040
1	2.528	$\bar{1}32$, 140			
1	2.493	$\bar{4}02$, 231, $\bar{3}31$	3	2.494	140, 410, $\bar{4}02$
1	2.460	032, $\bar{2}32$			
3	2.433	$\bar{2}03$, 041, $\bar{1}41$, 212, 330, $\bar{4}12$	3	2.422	$\bar{1}03$, $\bar{2}32$, 330, $\bar{2}03$, $\bar{4}12$
			1	2.358	$\bar{1}13$, $\bar{2}13$
2	2.292	420	1	2.297	003, 420, 240, $\bar{3}03$
2	2.268	132	2	2.259	222
			2	2.232	$\bar{3}13$
2	2.130	331, $\bar{4}31$, $\bar{1}42$, 411	1	2.103	103, 023, $\bar{1}42$
3	2.031	232, $\bar{4}32$	1	2.050	500, 340, 430, $\bar{5}12$, $\bar{4}13$
2	2.006	421, 510	4	2.014	510, 150, $\bar{4}32$, 421
			1	1.969	051, $\bar{1}51$
1	1.949	123, $\bar{4}23$, 322, $\bar{5}22$	1	1.945	$\bar{3}42$
			1	1.932	$\bar{5}22$, $\bar{4}23$
2	1.901	520	1	1.903	520, 250, $\bar{3}33$, 151, $\bar{2}51$
			1	1.879	203, 341
4	1.844	$\bar{5}13$, $\bar{2}04$, 431, $\bar{5}31$	1	1.852	213
			3	1.826	$\bar{2}04$
			3	1.795	402, 332, $\bar{3}04$, 242

Optical and Physical Properties

Niocalite has a clear lemon-yellow colour and a vitreous lustre. It shows essentially no cleavage and the crystals break with a conchoidal fracture. The hardness is about 6, and the specific gravity, as noted above, is 3.32. The specific gravity was determined by means of a pycnometer on several grams of pure material which was later analyzed, and is in agreement with results obtained by heavy liquid determinations.

The refractive indices of niocalite were determined in sodium light by the immersion of oriented grains in calibrated refractive index liquids. The optical character and $2V$ were established by universal stage measurements on niocalite in thin sections. The values for the birefringence and the refractive indices differ slightly from those reported in the preliminary note (Nickel, 1956), due to improvements in the method of determining the indices. The optical properties of niocalite are:

$\alpha = 1.701; \beta = 1.714; \gamma = 1.720$
$2V_X = 56°$
Birefringence $\gamma - a = 0.019$
Optical orientation: $X = b$; $Z \wedge c = 12°$

Composition

Niocalite was concentrated from a diamond drill core and from a rock sample taken from the open pit, crushed to -65 mesh. The concentration was effected by repeated heavy liquid separation using liquids with specific gravities of 3.31 and 3.33, which eliminated the associated minerals, as well as niocalite grains combined with lighter or heavier minerals. Examination of the resulting concentrates under a petrographic microscope revealed them to be essentially free from other minerals. The results of the two chemical analyses are given in Table 3.

The two niocalite samples are quite similar in composition. The principle differences are that number II contains more Nb_2O_5 and MgO, and less Al_2O_3 and P_2O_5. If the P_2O_5 can be attributed to apatite impurities in the sample, then sample II can be considered to be the purer, since its P_2O_5 content is extremely low.

The cell content of niocalite, as shown in Table 4, is based on both chemical analyses (weighted to assume that II is twice as good as I) with the apatite extracted. Using the determined specific gravity of 3.32 and the cell volume of 784 Å^3, a cell containing 60.37 atoms and having a molecular weight of 1567.8 was obtained. The total number of atoms was reduced to 60, and the proportions recalculated. This gives a unit cell weight of 1558.5 instead of 1567.8, and a calculated density of 3.300.

TABLE 3. CHEMICAL ANALYSIS OF NIOCALITE
(J. A. Maxwell, Analyst)

	I Niocalite from diamond drill core	II Niocalite from open pit
CaO^a	47.50	46.96
SiO_2	29.70	29.90
$Nb_2O_5{}^b$	16.56	18.86
$Al_2O_3{}^c$	1.31	0.16
$Fe_2O_3{}^d$	0.54	0.54
TiO_2	0.22	0.26
P_2O_5	0.60	0.07
MgO	0.28	0.70
MnO	1.28	0.99
Na_2O	0.78	0.55
K_2O	0.02	0.00
H_2O	0.16	0.18
F	1.7	1.73
	100.65	100.90
$O \equiv F$	0.71	0.73
	99.94	100.17

[a]Includes some SrO.
[b]Includes a small amount of Ta_2O_5.
[c]Includes rare earths and zirconium.
[d]Total Fe as Fe_2O_3.

In order to compare the niocalite cell content with those of woehlerite, hiortdahlite, and låvenite, the cell contents of these minerals are also included in Table 4. The cell contents have been recalculated to total 60 atoms from the atomic proportions given by Gossner & Kraus (1934).

TABLE 4. CELL CONTENTS OF WOEHLERITE, HIORTDAHLITE, LÅVENITE, AND NIOCALITE

	Woehlerite		Hiortdahlite		Låvenite		Niocalite	
Ca	7.81	11.73	8.65	11.80	2.06	8.10	13.07	13.39
Na	3.92		3.15		6.04		0.32	
Nb	1.49	4.37	—	3.41	0.51	7.46	2.13	2.78
Zr	2.14		2.63		3.94		—	
Fe	0.38		0.26		0.87		0.11	
Mg	0.05		0.04		—		0.25	
Mn	0.23		0.20		1.72		0.24	
Ti	0.08		0.28		0.42		0.05	
Al	—	8.15	—	7.95	—	8.10	0.17	7.94
Si	8.15		7.95		8.10		7.77	
OH	0.66	35.75	0.48	36.84	0.60	36.34	0.15	35.89
F	2.51		4.56		3.33		1.41	
O	32.58		31.80		32.41		34.33	
	60.00		60.00		60.00		60.00	

It is evident from Table 4 that the chief chemical similarity between the four minerals is in the number of (Si, Al) and (O, OH, F) atoms, which are close to 8 and 36, respectively. There does not appear to be a consistent ratio between the alkalis and other ions, nor between ions of similar size. The generalized formula for this group of minerals, therefore, is $A_{15-16}Si_8(O, OH, F)_{36}$, with A representing all the cations except silicon and possibly aluminum. This suggests a relatively rigid $Si_8(O, OH, F)_{36}$ network with the other ions in the structure arranged to maintain electrical neutrality and according to their availability. That the cations are distributed differently in some of the members of this mineral group is shown by the different space groups represented.

The generalized formula of niocalite, on the basis of the above discussion, can be written (Ca, Nb, etc.)$_{16}$Si$_8$(O, OH, F)$_{36}$ or, more simply, 4[(Ca, Nb)$_4$Si$_2$(O, OH, F)$_9$].

Acknowledgments

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Note. Since the preparation of this paper, a short article by R. Kern, A. Rimsky, and J. C. Monier, entitled "Contribution à l'étude de la niocalite" has appeared in *Comptes Rendus des Séances* (1957), **245**, No. 23, 2063–2064. The authors ascribe to niocalite an orthorhombic unit cell with $a = 7.339$kX, $b = 10.432$kX, and $c = 20.285$kX. This cell is similar to the apparent cell we obtained by x-raying twinned crystals, hence the crystallographic work of Kern, Rimsky, and Monier is probably based on twinned crystal fragments.—E. H. Nickel.