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HIORTDAHLITE FROM KIPAWA RIVER, VILLEDIEU TOWNSHIP, TEMISCAMING COUNTY, QUÉBEC, CANADA

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ABSTRACT

Hiortdahlite, a member of the inadequately studied wöhlerite group, is recorded for the first time in Canada from the Kipawa River, Temiscaming County, Québec, at 46°47′49″ N lat. and 78°29′31″ W long. in a regionally metamorphosed alkalic complex. The mineral is triclinic, pseudo-orthorhombic and pseudo-monoclinic. The triclinic cell has a 10.95, b 10.31, c 7.29Å, α 90°19′, β 109°02′, γ 90°05′, $V = 778.0\text{Å}^3$. It is polysynthetically twinned but the twin law has not been resolved. Optical data are: n_α 1.639(3), n_β 1.643, n_γ 1.646(4), n_γ-n_α 0.007, $2V$+80° to —83°, no detectable pleochroism or dispersion, D=3.256 g/cm^3. The principal powder lines with intensities (Cu$K\alpha$ radiation) are: 2.87 (100), 3.00 (100), 3.29 (45), 1.84 (40), 1.80 (30), 4.12 (25), 2.52 (20), 2.44 (20), 1.55 (20). Despite considerable differences in composition the powder data do not distinguish between hiortdahlite, wöhlerite, niocalite and seidozerite, nor in general do the single crystal data. Chemical analysis is necessary for a final distinction to be made. A new analysis, believed to be the most reliable on record, gives the structural formula $(Ca_{2.01}Na_{0.85}Y_{0.12}TR_{0.04})$ $(Zr_{0.58}Nb_{0.02}Mn_{0.02}Ti_{0.01}Fe_{0.01}Mg_{0.01}Al_{0.01})$ $[Si_{2.05}O_{7.0}]$ $(F_{1.34}O_{0.41}OH_{0.18})$. This seems to confirm a deficiency in the Zr site that was suggested by earlier analyses.

INTRODUCTION

Hiortdahlite, not previously known in Canada, occurs in an alkalic rock complex on the Kipawa River in Villedieu Township, Temiscaming County, Québec, at 46°47′49″ N latitude and 78°29′31″ W longitude. The general geology of the complex is imperfectly known but consists essentially of alkalic gneisses composed of plagioclase, microline and alkalic amphibole in which small bodies of pyroxenite and amphibolite are found, some of which are nepheline-bearing. The entire sequence has been traced for one and a half miles in a belt up to one half mile wide but exposure is relatively poor and there is nothing to indicate that these really are the limits of the alkalic rock complex. Nepheline syenites one mile distant are indeed probably part of the complex.

The gneisses with their enclosed pyroxenite and amphibolite bodies have been intensely folded during the Grenville orogeny. K/Ar ages on muscovite and nepheline from various rocks the complex are muscovite: 913 my, 895 my; nepheline: 1286 my, 1276 my, 1309 my.

In all probability this is an alkalic intrusion of pre-Grenville age that has subsequently been regionally metamorphosed. It is one of a rare group of agpaitic intrusions in Eastern Canada that stand in marked contrast to the commoner feldspathoidal rocks of similar age and very simple mineralogy that are found over a considerable area of the Grenville Province of Ontario and Quebec.

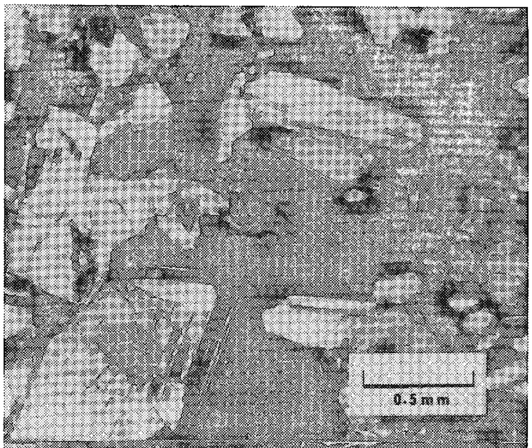
All the rocks of the complex are characterized by enrichment in zirconium, fluorine and rare earths. The rare minerals are concentrated mostly in the pyroxenite-amphibolite bodies and include members of the wöhlerite group, rinkite, mosandrite, eudialyte, vlasovite, britholite, miserite and at least one new mineral (agrellite).

OCCURRENCE

A characteristic mode of occurrence of hiortdahlite and other wöhlerite group minerals is in streaks and veinlets ½ to 4 cm wide and 10 to 20 cm in length within an alkalic amphibolite. These veins are almost purely monomineralic but other minerals in the amphibolite commonly include britholite, calcite, zircon, fluorite, and occasionally albite and nepheline. In hand specimen the mineral is light brown with a grain size of ½ to 1 mm. In thin section (Fig. 1) it is seen as elongate, anhedral polysynthetically twinned crystals of very high relief and low first order birefringence. Because of the nearly monomineralic nature of the veins the high relief is not always immediately apparent with the result that the mineral closely resembles twinned plagioclase. It is colourless and clear for the most part but yellow-brown patches are observed within some of the grains. These discoloured areas are often associated with cracks from which a darkening can be seen to spread into clear, colourless areas. The axial angle and sometimes the optic sign of these discoloured areas are quite different from the clear areas and the two types do not extinguish simultaneously. Twinning, however, continues uninterruptedly across the grain. While this discolouration obviously represents a form of alteration it is distinctly different in appearance from commoner mineral alterations and is best likened to the characteristic appearance of eudialyte in thin section where parts of the same grain display variations of very low first order birefringence.

Depositories of the type material

Specimens of the rock from which the analyzed mineral has been separated have been deposited as follows:



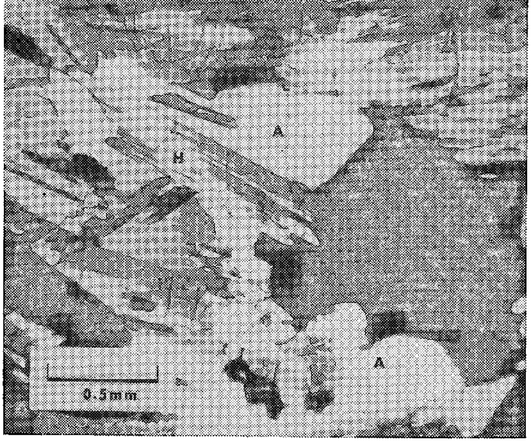


FIG. 1 A. (Top) Hiortdahlite in thin section (crossed polars) showing the characteristic polysynthetic twinning. No other minerals are present in the photograph.

FIG. 1 B. Hiortdahlite (H) and albite (A) in thin section (crossed polars). Note the high relief of hiortdahlite in relation to albite.

The Petrology Collection, University of Toronto	P7-545 to P7-549
The Royal Ontario Museum Mineral Collection	M30637
The Mineral Collection, Department of Mineralogy and Petrology, University of Cambridge	19701
The British Museum Collection	BM 1971, 115
The National Mineral Collection, National Museum, Ottawa, Canada	71/1

X-RAY CRYSTALLOGRAPHIC STUDY

The unit cell

Most grains in the separated powder used for chemical analysis possess part of a crystal face. Only clear colourless grains were used and these were mounted with the aid of a two-circle reflecting goniometer to rotate about the normal to this face which was later found to be (010). The unit cell was determined by precession photography after an initial Weissenberg study.

The six parameters of each of the three direct cells calculated from these data are set down in Table 1. It is apparent that it is the *X* cell whose edges form the three shortest non-coplanar translations in the direct lattice. Accordingly this *X* cell is selected to represent the mineral. The measured reciprocal lattice constants of this cell are also presented in Table 1. Estimated errors of the measurements are expressed as error bounds and are approximately equivalent to three standard deviations. The unit cell data are in close agreement with those of hiortdahlite from the

TABLE 1. UNIT CELL CONSTANTS OF HIORTDAHLITE FROM KIPAWA RIVER

Reciprocal Lattice (Å^{-1})		Direct Lattice (Å)			
	X		*X*	*Y*	*Z*
a^*	0.09644±0.00015	a	10.95 ±0.03	11.02	20.70
b^*	0.09703±0.00015	b	10.31 ±0.02	10.31	10.31
c^*	0.1452 ±0.0003	c	7.29 ±0.03	7.29	7.30
α^*	89°38' ±10'	α	90°19'±10'	90°30'	90°20'
β^*	70°57' ±15'	β	109°02'±15'	110°10'	90°37'
γ^*	89°48' ±10'	γ	90°05'±10'	89°39'	89°47'
V^*	0.001287±0.00001Å^{-3}	V	778.0±5Å^3	778.0Å^3	2x778.0Å^3

TABLE 2. CELL CONSTANTS OF MEMBERS OF THE WÖHLERITE GROUP

	1	2	3	4*	5*	6
a	10.85Å	10.83Å	10.87Å	10.95Å	10.93Å	10.95Å
b	10.43	10.42	10.27	10.01	10.31	10.31
c	7.54	7.38	7.32	7.19	7.33	7.29
α	-	-	-	-	90°29'	90°19'
β	110°04'	109°40'	109°05'	110°18'	108°50'	109°02'
γ	-	-	-	-	90°08'	90°05'

1. Cuspidine, Mt. Vesuvius, Italy. Smirnova *et al.* (1955); Wilson & Leary (1961).
2. Niocalite, Oka, Quebec, Canada. Nickel *et al.* (1958).
3. Wöhlerite, Langesundsfjord, Norway. Nickel *et al.* (1958).
4. Låvenite, Isle of Laven, Langesundsfjord, Norway. Gossner & Kraus (1934).
5. Hiortdahlite, Langesundsfjord, Norway. Gossner & Kraus (1934)
6. Hiortdahlite, Kipawa River, Villedieu Township, Quebec; present study.

* Converted from kX units in which the original data were given

type locality in Norway with which they are compared in Table 2, together with data for other members of the wöhlerite group. The agreement is indeed close among all members of the group. The present study has shown that the slightly triclinic character of hiortdahlite can not be detected in *b* axis Weissenberg photographs; the systematic offset of levels parallel to the a^* c^* plane is too small to be detected.

The setting for hiortdahlite was chosen by Brögger using optical goniometry in order to show the relationship to the monoclinic members of the wöhlerite group in which $a > c$ according to accepted practice. The same setting was retained by Gossner & Kraus (1934) using *x*-ray methods. Single crystal photographs of the dusky, yellowish-brown grains can be superimposed directly on photographs of the clear colourless grains but they are of poorer quality, confirming that the difference is the degree of alteration.

Pseudo-symmetry

The present study shows the presence of a pseudo-orthorhombic *B*-faced-centred lattice (case Z of Table 1 and Fig. 2). Similar pseudosymmetry has been reported in other members of the wöhlerite group. Thus Portnov *et al.* (1966) were misled into chosing an orthorhombic cell for låvenite in preference to a monoclinic cell, and Kern *et al.* (1957) similarly chose an orthorhombic cell for niocalite. Nickel (1961) and Nickel *et al.* (1958) pointed out that both minerals are monoclinic and that the pseudo-orthorhombic character is the result of twinning. The pseudo-orthorhombic symmetry of all three minerals is compared in Table 3. In addition to pseudo-orthorhombic symmetry the Canadian hiortdahlite displays pseudo-monoclinic symmetry because of the closeness of α and γ to 90° (cases *X* and *Y*). This same pseudo-monoclinic symmetry is further apparent in plots of the zero level of the a^* c^* plane of both hiortdahlite and niocalite (Nickel *et al.* 1958). The space group assigned to niocalite by Nickel *et al.* is *Pa* or *P*2/*a*. The *a* glide plane manifests itself in single crystal photographs by the condition $h0l$ present only when *h* is even. Despite its triclinic symmetry hiortdahlite simulates this condition by the fact that when *h* is odd the $[h0l]^*$ rows are either absent or very weak, suggesting that the *a* glide is almost realized in the hiortdahlite structure, thus further emphasizing the pseudo-monoclinic character.

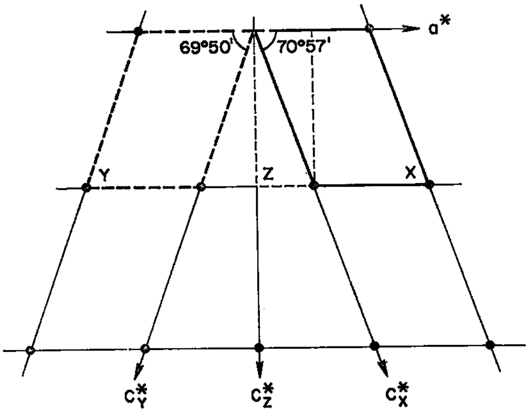


FIG. 2. Three cells of the hiortdahlite reciprocal lattice.

TABLE 3. PSEUDO-ORTHORHOMBIC SYMMETRY IN THE WÖHLERITE GROUP

	1	2	3
a	20.70Å	20.40Å	21.01Å
b	10.31	10.42	10.05
c	7.30	7.38	7.23
α	90°20'	90°	90°
β	90°37'	90°30	90°
γ	89°47'	90°	90°

1. Hiortdahlite, Sheffield, Villedieu Township, Quebec; present study.
2. Niocalite, Oka, Quebec; Nickel *et al.* (1958).
3. Låvenite, North Baikal region, U.S.S.R.; Portnov *et al.* (1966).

Twinning

Doubling of reflections in Weissenberg photographs of the a^* c^* reciprocal lattice plane was initially presumed to be due to the twinning which can be readily seen in thin section but this proves not to be the case. The arrangement ressembles the twinning of niocalite (Nickel *et al.* 1958).

Niocalite is twinned by reflection across $(\bar{1}02)$ and so $[\bar{1}02]^*$ must be common to both individuals of the twin and result in a single row of reflections (Fig. 3). Because of its similarity to

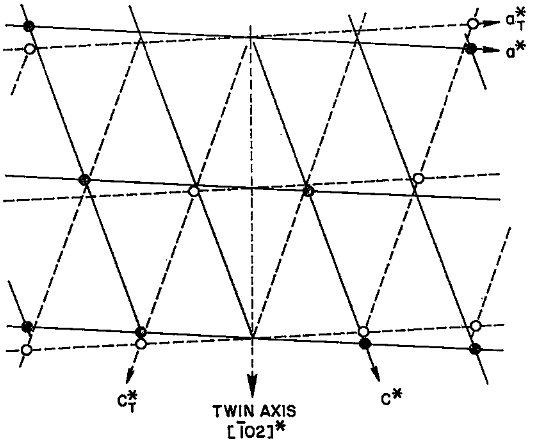


FIG. 3. Reciprocal lattice of niocalite twinned about $[\bar{1}02]^*$ (= twinning across the $(\bar{1}02)$ plane of the direct lattice) (after Nickel *et al.* 1958).

niocalite a similar twin plane might be expected in hiortdahlite but photographs of several crystals all show a multiplicity of reflections along the [$\bar{1}$02]* row (Fig. 4). Furthermore, if [$\bar{1}$02]* of hiortdahlite were a twin axis of the reciprocal lattice the intensities of reflections generated by its operation should be equal on opposite sides. There is no such regularity in the hiortdahlite photographs.

The multiplicity of reflections and their relative intensities might be explained by the presence of two or more crystallites joined along their *b* direction but differing in alignment by about 1°. Because of the indifferent quality of the precession films of layers that are normal to the a^* c^* zero level, detection of the twinning observed in thin section might well be obscured by the multiplicity of spots caused by two such individuals but so far one must conclude that the single crystal study yields no satisfactory explanation of the twinning seen in thin section.

Powder pattern

Exposures of at least 10 hours are necessary to obtain powder lines of sufficient intensity for measurement of 2θ values and even the sharpest pattern obtained with the 57.3 mm diameter camera and Ni-filtered Cu radiation contains some diffuse lines. Diffractometer traces contain only a few sharp peaks, others being small or broad or asymmetrical with jagged edges. However, these traces do yield more measurable reflections than the films. Synthetic fluorite (CaF_2) previously calibrated against diamond was employed as an internal standard in the diffractometer traces. The *d*-values derived from measurement of both films and diffractometer traces are presented in Table 4. The pattern has been indexed by comparing the measured *d*-values with all possible *d*-values computed from the single crystal data. The powder data for hiortdhalite, niocalite, wöhlerite and seidozerite are so similar as to be indistinguishable in practice despite distinct differences in chemical composition and the fact that the seidozerite cell differs markedly from the others. Other members of the wöhlerite group have *d*-values that are similar but yet sufficiently different to allow a distinction being made in practice.

In summary, the powder pattern alone can not be used to distinguish between hiortdahlite, wöhlerite, niocalite and seidozerite. Single crystal and chemical data are also necessary.

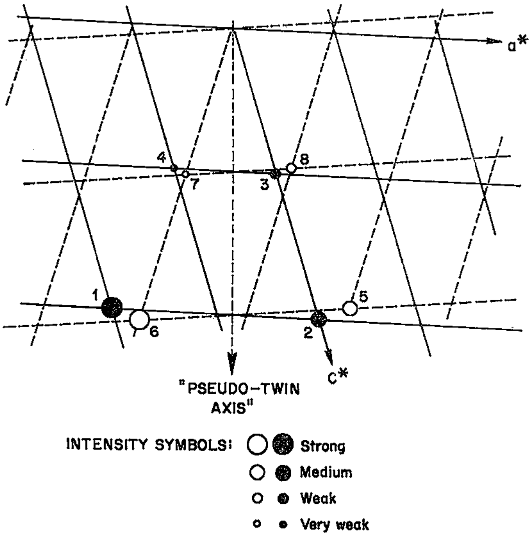


FIG. 4. Hiortdahlite. A hypothetical twinning interpretation of the multiplicity of reflections on the a^* c^* zero level Weissenberg film. If the axis [$\bar{1}$02]* is assumed to be a "twin axis" then reflections 1, 2, 3, and 4 and reflections 5, 6, 7, and 8 respectively represent corresponding reciprocal lattice points in the two individuals of the twin. Thus the intensity ratios $I_1:I_2:I_3:I_4$ of the first individual should equal the intensity ratios $I_5:I_6:I_7:I_8$ for the second individual. Therefore $I_1:I_4$ should equal $I_5:I_8$ in a twin relationship. Such an equality was not found in hiortdahlite.

DENSITY

Suspension in heavy liquids of grains of both the unaltered and the discoloured partly altered fractions, using the same powders that were em-

TABLE 4. *X*-RAY POWDER DIFFRACTION DATA FOR HIORTDAHLITE*

Film		Diffractometer			
I(est)	*d*(meas)	*I*(est)	*d*(meas)	*d*(calc)	*hkl*
		1	6.93		
		6	5.75	5.746	$01\bar{1}$
		8	5.18	5.176	200
		1	4.61	4.608	120
		1	4.51	4.509	111
25	4.12	15	4.13	4.129	$12\bar{1}$
		2	3.65	3.646	$220,10\bar{2}$
		5	3.61	3.612	$201,1\bar{2}1$
		11	3.42	3.415	$2\bar{1}1$
45	3.29	45	3.28	3.276	$3\bar{1}0,01\bar{2}$
100	3.00	90	3.00	2.990	102
100	2.87	100	2.87	2.873	$02\bar{2},3\bar{2}0,2\bar{3}0,112$
		5	2.59	2.594	$1\bar{2}2$
20	2.52	23	2.51	2.512	$4\bar{1}0,410,13\bar{2}$
20	2.44	16	2.44		$212,03\bar{2},3\bar{3}0$
		5	2.31		$2\bar{4}0,420$
15	2.27	10	2.26	2.263	$13\bar{2}$
		6	2.07		
30	2.03	25	2.03	For values of *d* lower than 2.26 the number of possibilities becomes too large to permit indexing by this method	
10	1.96	6	1.96		
40	1.84	30	1.84		
30	1.80	25	1.80		
5	1.78				
45	1.71	40	1.70		
15	1.60	10	1.60		
20	1.55	15	1.55		
5	1.49	2	1.49		
5	1.47	1	1.47		
10	1.42	10	1.42		
5	1.37	2	1.37		
5	1.33	2	1.33		

*CuKα radiation, λ=1.5418Å, 57.3 mm diameter camera and diffractometer ployed in the chemical analysis, gave measured densities of 3.256 gm/cm³ (standard deviation 0.01) and 2.94 gm/cm³ (standard deviation 0.01) respectively. The value for the fresh material is in good agreement with other hiortdahlites. Calculated density of the unaltered mineral is 3.221.

Optical Properties

For unaltered hiortdhalite the optical properties measured in sodium light are: n_α 1.639(3), n_β1.643, n_γ 1.646(4), $n_\gamma - n_\alpha$ 0.007, $2V + 80°$ to $-83°$ ($\pm$ 1.2°). No pleochrosim or dispersion are detectable. The effect of alteration is to lower the refractive indices; the lowest value of n recorded was 1.625. Birefringence is also reduced but could not be determined because of the varying state of alteration from grain to grain. The optic axial angle is reduced to values between $-45°$ and $-29°$. The variability of $2V$ in hiortdahlite was noted by Brögger (1890) in the Norwegian material, where it is probably also a function of incipient alteration.

Chemical Study

The analytical chemistry of such minerals as the wöhlerite group is frought with difficulty and there seem to be very few reliable analyses in the literature. The principal problems are the difficulty of determining silica in the presence of large amounts of fluorine and zirconium, and the difficulty of determining the individual members of the rare earth group. Accordingly, a scheme of analysis was devised in conjunction with Dr. J. C. Van Loon to afford the best approach to the many difficulties and is described fully in Aarden (1969). It consists of classical gravimetric and volumetric analysis supported by atomic absorption, and x-ray fluorescence analysis of the chemically separated rare earth group. The analysis is presented in Table 5.

TABLE 5. CHEMICAL ANALYSES OF HIORTDAHLITE

Weight %	1	2
SiO_2	32.2	34.7
ZrO_2	18.76	20.65
HfO_2	0.27	0.29
Nb_2O_5	0.56	0.58
Fe_2O_3	0.27	0.26
TiO_2	0.30	0.31
SnO_2	0.02	0.02
U_3O_8	0.09	0.10
Y_2O_3	3.50	4.01
TR_2O_3	2.08	2.48
Al_2O_3	0.07	0.08
CaO	29.57	25.54
SrO	0.03	0.08
MnO	0.30	0.33
MgO	0.09	0.10
Na_2O	6.85	4.12
K_2O	0.02	0.08
H_2O^+	0.42	2.75
F	6.69	4.23
O≡F	2.81	1.79
Total	99.28	98.92

Rare Earth Group

Wt. %	1	2
La_2O_3	0.08	0.12
Ce_2O_3	0.23	0.32
Pr_2O_3	0.04	0.04
Nd_2O_3	0.17	0.22
Sm_2O_3	0.07	0.08
Eu_2O_3	0.01	0.03
Gd_2O_3	0.12	0.14
Tb_2O_3	0.04	0.04
Dy_2O_3	0.31	0.36
Ho_2O_3	0.09	0.10
Er_2O_3	0.35	0.40
Tm_2O_3	0.07	0.08
Yb_2O_3	0.44	0.50
Lu_2O_3	0.06	0.05
	2.08	2.48

1. unaltered hiortdahlite 2. altered hiortdahlite

Although the structure of hiortdahlite has not been determined the structures of several other members of the wöhlerite group are known: cuspidine (Belov 1961), wöhlerite (Shibayeva & Belov 1962), titanolåvenite (Simonov & Belov 1960), niocalite (Li Te-Yu *et al.* 1966), and seidozerite (Skrzhat & Simonov 1965). It is then at least a reasonable working basis to attempt to interpret the composition of hiortdahlite in terms of the structure of the wöhlerite group.

The general formula of the group is written $X_4[Si_2O_7]$ (O,OH,F)$_2$ where X represents metallic cation and is exemplified by the simplest member, cuspidine: $Ca_4[Si_2O_7]$ (OH,F)$_2$. In the other members metallic cations are seen as replacing calcium and a further refinement of the general formula is written $(X_L,X_S)_4$ $[Si_2O_7]$ (O,OH,F)$_2$ where X_L represents relatively large ions and X_S represents relatively small ions. Using the weight of the unit cell M_0* the number of ions per unit cell for hiortdahlite is calculated and gives the following formula:

$$(Ca_{2.01}Na_{0.85}Y_{0.12}TR_{0.04})\ (Zr_{0.58}Nb_{0.02}Mn_{0.02}Ti_{0.01}Fe_{0.01}Mg_{0.01}Al_{0.01})\ [Si_{2.05}O_{7.0}]\ (F_{1.34}O_{0.41}OH_{0.18})$$

Ideally there should be 4 metallic cations, 2 silicon ions, and 9 anions, but it can be seen that in the calculated formula the metallic cations total only 3.68 for a deficiency of 8.0%. There is a total anion deficiency of only 0.8% but a silicon excess of 2.4%. The apparent cation deficiency appears to be real and to be a characteristic feature of hiortdahlite.

It appears then that the formula of hiortdhalite may be written as

$$(X_L,X_S)_{4-x}\ [Si_2O_7]\ (O,OH,F)_2$$

or, since in the case of the Kipawa River mineral the deficiency appears to be concentrated on zirconium, as

$$Ca_2(Na,Y,TR)_1Zr_{1-x}\ [Si_2O_7]\ (O,OH,F)_2$$

The formula of the altered fraction can not be calculated on the same basis because the crystallographic parameters and density can not be determined owing to the variable degree of alteration from grain to grain. Accordingly, the formula was calculated on the basis of 9(O,OH,F) with the following result:

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* $M_0 = V\rho/1.66$ where V is the cell volume and density of the mineral.

$(Ca_{1.72}Na_{0.51}Y_{0.13}TR_{0.05})$ $(Zr_{0.63}Nb_{0.02}Mn_{0.02}Ti_{0.01}Fe_{0.01}Mg_{0.01}Al_{0.01})$ $[Si_{2.18}O_{7.0}]$ $(O_{0.01}OH_{1.15}F_{0.84})$

The alteration of hiortdahlite can be described as the loss of Ca and Na accompanied by the loss of F and the replacement of O by OH.

Chemical composition and space group symmetry of the wöhlerite group

Cuspidine has the maximum symmetry of the wöhlerite group because all its metallic cations are calcium and therefore of the same size (Shibayeva & Belov 1962). Låvenite retains the same symmetry because its ratio of relatively large to relatively small cations is close to unity (Belov 1961), but wöhlerite displays lower symmetry because the ratio rises to about 3:1. Niocalite has an even greater imbalance of large and small cations but its symmetry is disputed as noted previously; whether its symmetry is greater than, equal to, or less than that of the other members must be considered as uncertain.

This general relationship between symmetry and the ratio of large to small cations is shown in Table 6.

There are two possible explanations of the cationic deficiency in hiortdahlite. There is clearly a close similarity between the compositions of wöhlerite and hiortdahlite. Some of the sodium in wöhlerite appears to be replaced by rare earths in hiortdahlite. Some of these rare earths have larger ionic radii than sodium or calcium ions and may tend to crowd the neighbouring sites making them too small to accommodate other ions. In addition, all of the rare earth ions have a greater positive charge than either sodium or calcium. Fewer cations are therefore required to maintain the charge balance. It is entirely conceivable that the cation deficiency is due to a combination of both of these factors.

It seems likely that the cationic deficiency and the high ratio of large to small cations serves to reduce the symmetry of hiortdahlite to $P1$ or $P\bar{1}$. This deficiency appears to be a characteristic of hiordahlite but may also characterize other wöhlerite group minerals. Fourteen analyses of wöhlerite group minerals have a mean value of X of 3.93; the five hiortdahlite analyses in this group have a mean value of X of 3.77.

TABLE 6. THE RELATIONSHIP OF SYMMETRY TO THE PROPORTION OF LARGE AND SMALL CATIONS IN THE WÖHLERITE GROUP

	X_L	X_S	X_L X_S	Space Group
Cuspidine	$Ca_{3.9}$	(Al,Fe, *etc.*)$_{0.1}$	39/1	$P2_1/a$
Låvenite	$Na_{1.2}Ca_{1.0}$	$(Zr,Mn,Fe,Ti)_{1.7}$	1.3/1	$P2_1/m$
Wöhlerite	$Ca_{1.9}Na_{1.0}$	$(Zr,Nb)_{1.1}$	2.6/1	$P2_1$
Niocalite	$Ca_{3.4}$	$Nb_{0.7}$	4.9/1	$P2_1$, Pa or $P2/a$
Hiortdahlite	$Ca_{2.0}(Na,TR)_{1.0}$	$Zr_{0.7}$	4.3/1	$P1$ or $P\bar{1}$

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