HIORTDAHILITE FROM KIPAWA RIVER, VILLEDEU TOWNSHIP, TEMISCAMING COUNTY, QUÉBEC, CANADA

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ABSTRACT

Hiortdahlite, a member of the inadequately studied wüthlerite 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 10.91, c 7.89 Å, α 90°19’, β 109°02’, γ 90°05’, V = 778.0 Å³. It is polysynthetically twinned but the twin law has not been resolved. Optical data are: nα 1.639(3), nβ 1.63, nγ 1.646(4), nγ-nα 0.007, 2V+80’ to 93’, no detectable pleochroism or dispersion, D = 3.256 g/cm³. The principal powder lines with intensities (CuKα 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, wüthlerite, niocaite 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 (Ca0.63 Na0.65 Y0.12 Ti0.10) (Zr0.85 Nb0.15 Mn0.05 Ti0.01 Fe0.01 Mg0.01 Al0.01) [Si2.06 O4] (F1.30 O6.31 OH4.18). 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, microcline 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 wüthlerite group, rinkite, mosandrite, eudialyte, vlasovite, britholite, miserite and at least one new mineral (agrellite).

OCCURRENCE

A characteristic mode of occurrence of hiortdahlite and other wüthlerite group minerals is in streaks and veinlets 1/2 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 1/2 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:

- 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

<table>
<thead>
<tr>
<th>Reciprocal Lattice (Å⁻¹)</th>
<th>Direct Lattice (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>a</td>
</tr>
<tr>
<td>0.0564±0.00015</td>
<td>0.000015</td>
</tr>
<tr>
<td>b</td>
<td>0.10±0.0015</td>
</tr>
<tr>
<td>c</td>
<td>0.0970±0.00015</td>
</tr>
<tr>
<td>d</td>
<td>0.0971±0.00015</td>
</tr>
<tr>
<td>e</td>
<td>0.0972±0.00015</td>
</tr>
<tr>
<td>f</td>
<td>0.0973±0.00015</td>
</tr>
</tbody>
</table>

Table 2. Cell Constants of Members of the Wöhlerite Group

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4*</th>
<th>5*</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>10.43</td>
<td>10.42</td>
<td>10.47</td>
<td>10.40</td>
<td>10.31</td>
</tr>
<tr>
<td>c</td>
<td>7.54</td>
<td>7.38</td>
<td>7.32</td>
<td>7.19</td>
<td>7.33</td>
</tr>
<tr>
<td>d</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>e</td>
<td>110°04'</td>
<td>109°40'</td>
<td>109°05'</td>
<td>108°50'</td>
<td>109°02'</td>
</tr>
<tr>
<td>f</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

6. Hiortdahlite, Kipawa River, Villefieu Township, Quebec; present study.

* Converted from kX units in which the original data were given.
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Type locality in Norway with which they are compared in Table 2, together with data for other members of the wohlerite 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 Brøgger using optical goniometry in order to show the relationship to the monoclinic members of the wohlerite 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 pseudo-symmetry has been reported in other members of the wohlerite group. Thus Portnov et al. (1966) were misled into choosing an orthorhombic cell for lavenite 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 $\alpha$ and $\gamma$ to $90^\circ$ (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 $P2_1/a$. 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.

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 resembles the twinning of niocalite (Nickel et al. 1958).

Niocalite is twinned by reflection across (102) and so [102]* must be common to both individuals of the twin and result in a single row of reflections (Fig. 3). Because of its similarity to

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**Fig. 2.** Three cells of the hiortdahlite reciprocal lattice.

**Fig. 3.** Reciprocal lattice of niocalite twinned about [102]* (= twinning across the (102) plane of the direct lattice) (after Nickel et al. 1958).

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**TABLE 3. PSEUDO-ORTHORHOMBIC SYMMETRY IN THE WÖHLERITE GROUP**

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>20.70Å</td>
<td>20.40Å</td>
<td>21.01Å</td>
</tr>
<tr>
<td>$b$</td>
<td>10.31Å</td>
<td>10.42Å</td>
<td>10.05Å</td>
</tr>
<tr>
<td>$c$</td>
<td>7.33Å</td>
<td>7.36Å</td>
<td>7.29Å</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>90°20'</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td>$\beta$</td>
<td>90°37'</td>
<td>90°30'</td>
<td>90°</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>89°47'</td>
<td>90°</td>
<td>90°</td>
</tr>
</tbody>
</table>

1. Hiortdahlite, Sheffield, Villiedieu Township, Quebec; present study.
2. Niocalite, Oka, Quebec; 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 [102]* row (Fig. 4). Furthermore, if [102]* 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 20 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 (CaF₂) 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 hiortdahlite, 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 cannot be used to distinguish between hiortdahlite, wöhlerite, niocalite and seidozerite. Single crystal and chemical data are also necessary.

**Table 4. X-ray powder diffraction data for hiortdahlite**

<table>
<thead>
<tr>
<th>Film</th>
<th>Diffraoctometer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d(meas)</td>
</tr>
<tr>
<td>1</td>
<td>6.30</td>
</tr>
<tr>
<td>2</td>
<td>5.77</td>
</tr>
<tr>
<td>3</td>
<td>5.17</td>
</tr>
<tr>
<td>4</td>
<td>4.66</td>
</tr>
<tr>
<td>5</td>
<td>4.13</td>
</tr>
<tr>
<td>6</td>
<td>3.77</td>
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<tr>
<td>7</td>
<td>3.61</td>
</tr>
<tr>
<td>8</td>
<td>3.41</td>
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<td>9</td>
<td>3.00</td>
</tr>
<tr>
<td>10</td>
<td>2.87</td>
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<tr>
<td>11</td>
<td>2.69</td>
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<td>12</td>
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<td>13</td>
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<td>14</td>
<td>2.31</td>
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<tr>
<td>15</td>
<td>2.26</td>
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<tr>
<td>16</td>
<td>2.19</td>
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<td>17</td>
<td>2.03</td>
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<tr>
<td>18</td>
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<tr>
<td>19</td>
<td>1.84</td>
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<tr>
<td>20</td>
<td>1.70</td>
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<tr>
<td>21</td>
<td>1.60</td>
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<tr>
<td>22</td>
<td>1.55</td>
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<tr>
<td>23</td>
<td>1.49</td>
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<tr>
<td>24</td>
<td>1.47</td>
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<tr>
<td>25</td>
<td>1.42</td>
</tr>
<tr>
<td>26</td>
<td>1.37</td>
</tr>
<tr>
<td>27</td>
<td>1.33</td>
</tr>
</tbody>
</table>

For values of d lower than 2.26 the number of possibilities becomes too large to permit indexing by this method.
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. Cal-
culated density of the unaltered mineral is 3.221.

**Optical Properties**

For unaltered hiortdahlite the optical proper-
ties measured in sodium light are: \( n_\alpha = 1.639(3) \),
\( n_\gamma = 1.646(4) \), \( n_\gamma - n_\alpha = 0.007 \), 2V + 80°
to \(-83° \) (± 2°). No pleochroism or disper-
sion are detectable. The effect of alteration is to
lower the refractive indices; the lowest value of
\( n_\alpha \) recorded was 1.625. Birefringence is also re-
duced 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 variabili-
ty of the unaltered mineral is 3.221. Birefrin-
gence is also reduced but could not be deter-
dined because of

**Chemical Study**

The analytical chemistry of such minerals as
the wöhlertite group is fraught 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 mem-
ers of the rare earth group. Accordingly, a
scheme of analysis was devised in conjunction
with Dr. J. C. Van Loon to afford the best

to interpret the composition of hiortdahlite in
terms of the structure of the wöhlertite group.

Although the structure of hiortdahlite has not
been determined the structures of several other
members of the wöhlertite group are known:
cuspidine (Belo 1961), wöhlertite (Shibayeva &
Belov 1962), titanolävenite (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

The general formula of the group is written
\( X_1 [\text{Si}_2 \text{O}_7] \) \((\text{OH,F})_2\) where \( X \) represents mett-
alic ion and is exemplified by the simplest
member, cuspidine: \( \text{Ca}_2[\text{Si}_6 \text{O}_{15}] \) \((\text{OH,F})_2\). In the
other members metallic cations are seen as re-
placing calcium and a further refinement of the
general formula is written \( \left(X_rX_s\right)_4[\text{Si}_2\text{O}_7] \)
\((\text{OH,F})_2\) where \( X_r \) represents relatively large
ions and \( X_s \) represents relatively small ions.

Using the weight of the unit cell \( M_0 \) the num-
ber of ions per unit cell for hiortdahlite is cal-
culated and gives the following formula :

\[
\left(\text{Ca}_2,\text{Na}_{0.88}\text{Y}_{0.12}\text{Zr}_{0.04}\right)\left(\text{Si}_2\text{O}_7\right)\left(\text{OH,F}\right)_2
\]

Ideally there should be 4 metallic cations, 2 sili-
con ions, and 9 anions, but it can be seen that
in the calculated formula the metallic cations
have a 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 de-
ficiency appears to be real and to be a charac-
teristic feature of hiortdahlite.

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

\[
(X_rX_s)_{4-2x}[\text{Si}_2\text{O}_7] \left(\text{OH,F}\right)_2
\]
or, since in the case of the Kipawa River mineral
the deficiency appears to be concentrated on zir-
conium, as

\[
\text{Ca}_2(\text{Na},\text{Y},\text{Zr})_1\text{Zr}_{1-x}[\text{Si}_2\text{O}_7] \left(\text{OH,F}\right)_2
\]

The formula of the altered fraction can not be
calculated on the same basis because the crys-
tallographic parameters and density can not be
determined owing to the variable degree of al-
teration from grain to grain. Accordingly, the
formula was calculated on the basis of 9(\text{OH,F})
with the following result :

\[
M_0 = V_\rho /1.66 \text{ where } V \text{ is the cell volume}
\]

and density of the mineral.
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). Lävenite 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 P1. This deficiency appears to be a characteristic of hiortdahlite 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.

Acknowledgments

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References


