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CANCRINITE WITH A NEW SUPERSTRUCTURE FROM BANCROFT, ONTARIO [1]

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Abstract

Compositionally and structurally unusual cancrinites occur in a nepheline syenite pegmatite and in a skarn at a marble-metasomatic nepheline syenite contact along the York River, Bancroft, Ontario. Associated minerals in the skarn include calcite, nepheline, wollastonite, forsterite, diopside and vesuvianite. Single crystal *x*-ray studies show that the cancrinite displays relatively sharp superstructure reflections which may be indexed on a unit cell with $a = A$ and $c = 11c$, where A and C are substructure translations. Satellite reflections are observable only with $l = 11n \pm 4$, where n is an integer. Materials from both localities differ compositionally from other cancrinites in that they have an unusually high Ca content. High-temperature, single crystal *x*-ray diffractometer studies on these and other crancrinites are consistent with a correlation between superstructure development and volatiles in the structure.

Introduction

Jarchow (1965) reported that cancrinite crystals from Litchfield, Maine, and Ilmengebirge and Barkevitz, Norway, display diffuse satellite reflections with indices $h,k,l \pm 3/7$, based on a subcell with $a = 12.75$ and $c = 5.14$ Å. In addition, Jarchow (written comm.) notes that the superstructure maxima can be attributed to a simple harmonic structural perturbation in the c-axis direction, involving cations and anions in the large channels. His work is based, in part, on studies of synthetic $CO_3^{=}$ — rich cancrinite. However, the precise cause of the superstructure maxima remains to be defined. This paper describes the occurrence and the nature of an unusual cancrinite collected by one of us (DRP) from a skarn in the Bancroft area. In addition, room temperature and high temperature data on the super-structure reflections of a number of specimens from other localities are presented.

Petrology of the Skarn

The cancrinite-bearing deposit is on the east side of the York River, 200 yards north of the Bancroft-Hermon Road (East Road). Exposures

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appear on the hillside directly above the road. The deposit is a relatively narrow skarn zone developed in a Grenville marble unit that directly overlies a band of nepheline gneiss (Hewitt 1953 ; Meen & Gorman 1953). The gneiss has been studied in detail by Osborne (1930), Baragar (1953), Hewitt & James (1956), Tilley (1958), and Hewitt (1961).

The skarn has not been systematically described heretofore. Only listings have been made of the minerals recognized in it. These include (Hewitt 1953 ; Meen & Gorman 1953) : calcite, diopside, garnet (« essonite »), vesuvianite, wollastonite, forsterite, chlorite, feldspar (peristerite), zircon, spinel, and cancrinite.

Our studies have resulted in the recognition of the following species : Essential constituents (some of which are only locally abundant) : calcite, garnet, diopside, forsterite, serpentine, chlorite, vesuvianite, wollastonite, sodic plagioclase, cancrinite, nepheline, and spinel. Accessories : zircon, sphene, pyrrhotite, apatite, and sericite.

The skarn shows extreme variations in texture and mineralogy. Some parts are pegmatoidal in texture with many grains an inch or more across. Much of the rock is heterogranular with the silicate species appearing as small euhedral metacrysts or large anhedral metacrystic aggregates in a calcite matrix.

The most widespread assemblage is garnet-diopside-calcite, usually with orange garnet and green diopside as crystals or anhedral aggregates in a matrix of dominant white calcite. Many of the unaltered euhedral metacrystic species (garnet, diopside, spinel) are characterized by slightly undulatory or embayed crystal faces displaying a highly vitreous luster (« fire-polished »).

The widespread calcite-garnet-diopside rock locally grades into massive garnetite and pyroxenites. Other assemblages include :

calcite-diopside-vesuvianite
calcite-garnet-diopside-vesuvianite
calcite-garnet-diopside-vesuvianite-wollastonite
calcite-garnet-diopside-cancrinite
calcite-garnet-diopside-cancrinite-nepheline

Less common are the forsterite skarns. The assemblage is calcite-forsterite-spinel. The forsterite may be partly or largely replaced by coarse platelets of bright green chlorite, and the remaining olivine is serpentinized to varying degrees. Thus, calcite-forsterite rocks grade into calcite-chlorite rocks.

The least common type of skarn is the calcite-peristerite combination in which crystals of red peristerite (« fire-polished » faces) may reach a length of as much as two inches.

In hand specimen the cancrinite appears as pale pink blocky crystals as large as one by three inches in section. In thin section cancrinite appears blocky to boat-shaped, and is commonly associated with calcite, garnet, diopside, and nepheline. Some garnet metacrysts appear to be corroded marginally by adjacent cancrinite. In other garnets cancrinite appears as small inclusions. Cancrinite is veined by sericite, and both it and garnet may be partly replaced by a turbid, very fine-grained calcite. Marginal parts of some cancrinite crystals show shearing and granulation with veinlets of secondary calcite formed along the cleavage planes. Parts of many of the cancrinite crystals exhibit what appears to be crude multilamellar twinning (Fig. 1), with the lamellae parallel to (0001). The cancrinite is clearly a primary constituent of the skarn and was not formed by replacement of the associated nepheline.

Indices of refraction of the cancrinite are: $\omega = 1.525 \pm .001$, $\varepsilon = 1.502 \pm .001$. These indices are very close to those measured by Meen (1938) for a chemically similar cancrinite from the nearby Davis quarry: $\omega = 1.528$, $\varepsilon = 1.503$.

Contact-metasomatic cancrinites are far less common than those formed either as primary phases or by replacement of nepheline in alkalic subsilicic rocks. However, contact metasomatic cancrinites are not especially rare either. Deer, Howie & Zussman (1963, p. 318) list: (1) Hsianghualing, Lingiva, Hunan, China. Cancrinite-corundum rock at granite-limestone contact. (2) Kishengarh, Rajputana, India. Cancrinite-calcite-tremolite-humite (?) rock along nepheline syenite. To these should be added: (3) Mt. Vesuvius, Italy. Calcite-wollastonite-garnet-cancrinite rock in limestone ejectamenta. (4) Delaware River, New Jersey. Nepheline-cancrinite hornfels at contact of Byram diabase. (5) York River, Ontario (this paper).

The presence of nepheline and cancrinite in recrystallized, metasomatized marble overlying the band of nepheline syenite provides additional support for the postulated metasomatic origin of the nepheline syenite.

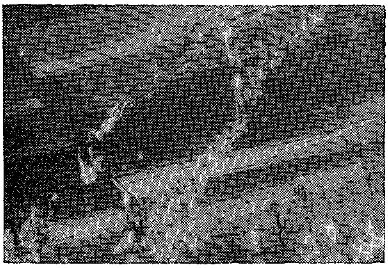

FIG. 1. Twin lamellae in cancrinite.

X-RAY CRYSTALLOGRAPHY

Cleavage fragments, which were examined optically and selected free from inclusions of other phases, were studied by means of precession and Weissenberg methods. X-ray photographs displayed a substructure with lattice parameters and reflection intensities equivalent to those of cancrinite. Consideration of only these strong substructure reflections results in a unit cell with $A = 12.62$ Å and $C = 5.13$ Å. Upon cursory examination the superstructure reflections appear to define a unit cell with $a = A$ and $c = 3C$. However, careful measurements of c-axis rotating crystal photographs and a-axis precession photographs show that they define a cell with $a = A$ and $c = 11C$, but with reflections present only with indices having $l = 11n \pm 4$, where n is an integer. The l indices, when referred to the subcell, correspond to $L \pm 4/11$. The values of these indices were further verified by measuring 2θ for zero-level reflections using an a-axis mounted crystal on a Weissenberg diffractometer. The d-values so determined yielded l indices for superstructure reflections equal to $L \pm 0.362$. Within the error of measurement, $0.362 \sim 4/11 = 0.364$, and this was taken as confirmation of the results previously obtained using film data.

Jarchow (1965) had observed superstructure reflections with indices $h,k,l \pm 3/7$ on specimens from Litchfield, Maine. For comparison, we examined single-crystals from other localities. Rotating-crystal and precession photographs of crystals from Litchfield, Maine and Bancroft, Ontario, showed, with the exception of two crystals, diffuse superstructure reflections. Substructure reflections were sharp. The superstructure reflections of the Litchfield samples, although relatively diffuse, all yielded l indices with $L \pm 3/7$, as reported by Jarchow. Portions of [110]-axis zero-level MoKα precession photographs of a Litchfield, Maine crystal and of a specimen from the York River, Bancroft, Ontario are shown in Figure 2 for comparison, and illustrate the differences in positions of the superstructure reflections. In addition, they show that reflections with $l = L - 4/11$ or $L - 3/7$ are much more intense than those with $l = L + 4/11$ or $L + 3/7$. Despite the differences between indices, intensities of corresponding superstructure reflections in the two kinds of crystals are approximately the same. There is also significant variation in the relative diffuseness of superstructure reflections from specimen to specimen for both Litchfield and Bancroft material. Although the superstructure reflections are present in planes with restricted values of l, there are no systematic absences within a plane, but there is a marked decrease in the average intensity with increasing diffraction angle.

Both Debye-Scherrer and powder diffractometer patterns of the York River skarn material were obtained. Independent least-squares refinement of lattice parameters, using each set of data with only those reflections which could be indexed unambiguously, gave substructure lattice parameters $A = 12.615 \pm .005$ Å and $C = 5.127 \pm .003$ Å. Table 1 contains the indexed Debye-Scherrer data. Visually estimated intensities were compared with a set of intensities obtained using a Weissenberg diffractometer. Despite overexposure of the powder photographs, no superstructure lines were observed. Some extra weak lines on patterns obtained from somewhat cloudy material could be indexed and correlated with natrolite, although natrolite was not observed in thin section or hand specimen.

At this point, it appeared that the skarn cancrinite was unique in both its paragenesis and diffraction characteristics, and that its unique chemistry and/or structure might be directly related to the unusual conditions of formation. We therefore collected a number of additional samples both at the skarn and at nearby nepheline syenite localities. In particular, samples were obtained from the Davis Quarry, where samples of white to pink cancrinite several inches across occur as a replacement of primary pegmatitic nepheline. The cancrinite from this locality was described in detail by Meen (1938) and was shown to have an unusual composition. A specimen which had been among those studied by Meen was provided by Dr. J. Mandarino from the collection of the Royal Ontario Museum. Precession photographs of these specimens duplicated those from the skarn material in all respects, including position, intensity and relative sharpness of the

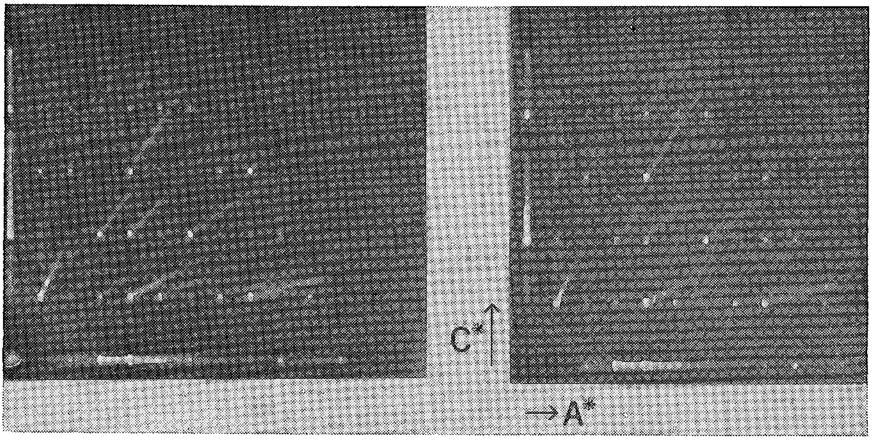

FIG. 2. Portions of zero-level [110]-axis, MoK_α precession photographs of cancrinite from the York River skarn (left) and Litchfield, Maine (right). The magnitudes of the substructure translations, A^* and C^* are shown.

TABLE 1. X-RAY POWDER DATA FOR CANCRINITE FROM YORK RIVER SKARN, BANCROFT, ONTARIO

CuK_{α}, Ni filter; 114.59 mm diameter camera; $a = 12.615$, $c = 5.127$Å

hkl	*d*(calc.)Å	*d*(obs.)Å	*I*	*hkl*	*d*(calc.)Å	*d*(obs.)Å	*I*
100	10.92	10.92	40	430	1.796	1.791	20
110	6.31	6.28	5	322*	1.792		
200	5.46	5.45	5	520	1.749	1.746	25
101	4.64	4.64	90	412	1.746		
210	4.13	4.11	15	601	1.716	1.713	5
300	3.64	3.64	70	411	1.695	1.691	10
211	3.22	3.21	100	103	1.689		
310	3.03	3.02	10	521*	1.656	1.654	10
301	2.969	2.950	10	113	1.650		
400	2.731	2.730	40	203	1.631	1.629	10
311	2.609	2.607	30	332	1.626		
002	2.564	2.560	30	422	1.608	1.605	5
320	2.506	2.498	20	611	1.585	1.579	40
102	2.498			213	1.579		
401	2.411	2.408	40	440	1.577		
112	2.375	2.365	1	530*	1.561	1.555	10
202	2.321	2.321	1	700	1.561		
321	2.252	2.249	25	512	1.558		
500	2.185	2.166	20	303	1.547		
212	2.178			701	1.493	1.488	50
411*	2.162			313	1.489		
330	2.103	2.099	70	602	1.485		
302	2.096			621	1.453	1.447	50
501*	2.010	2.010	20	203	1.449		
222	1.989			710	1.447		
510	1.962	1.953	2	522	1.445		
132	1.957			323	1.412	1.411	5
331	1.945			630	1.376	1.376	2
421	1.915	1.914	10	503	1.346	1.342	25
402	1.869	1.868	20	442*	1.343		

* Comparison with single-crystal intensity values suggests that this index most likely corresponds to the observed *d*.

There are approximately 50 additional observed lines at higher values of θ.

superstructure reflections. This indicates that there is no direct relationship between the unusual paragenesis and diffraction effects exhibited by the skarn material.

CHEMICAL ANALYSIS

York River material was carefully selected for chemical analysis from the sample which had been used as a source of specimens for *x*-ray analysis. The analysis was carried out by J. C. DeVine and J. B. Bodkin, Pennsylvania State University, using standard wet-chemical methods and the results are presented in Table 2. Qualitative spectrographic and *x*-ray flourescence analyses indicated that no other elements were present in detectable amounts. A duplicate analysis gave results within the estimated

TABLE 2. CHEMICAL ANALYSES OF CANCRINITE FROM THE YORK RIVER SKARN[1] AND DAVIS QUARRY (MEEN, 1938), BANCROFT, ONTARIO

	Davis Quarry	York River Skarn	
	Wt. %	Wt. %	Atoms per Cell[2]
SiO_2	35.38	34.16	6.02
TiO_2		0.011	
Al_2O_3	28.42	28.75	5.98
FeO		<.01	
Fe_2O_3		<.01	
MgO		<.01	
CaO	11.66	10.10	1.91
Na_2O	9.82	16.02	5.48
K_2O	1.23	0.14	0.03
H_2O^+	6.39	3.43	2.02
H_2O^-	0.60	0.12	0.07
SO_3	0.19	<.01	
Cl	0.08	0.12	0.04
CO_2	6.18	6.70	1.61
F_2		0.02	
$O \equiv Cl$		—.03	
TOTAL	99.95	99.54	

1. Analysts J. C. DeVine and J. B. Bodkin, Pennsylvania State University.
2. Normalized to 12(Si + Al) per unit cell.

errors of the reported values. The formula, normalized to 12(Si + Al) per unit is :

$$Na_{5.48}K_{0.03}Ca_{1.91}Al_{5.98}Si_{6.02}(CO_3)_{1.61}.2.09H_2O$$

This formula has interesting characteristics not found in other members of the cancrinite group. The relative amounts of Ca and CO_3 are high, whereas SO_4 and Cl are present only in trace amounts. Only one other analysis of cancrinite-group minerals is similar in this regard, and that is the one by Meen (1938) (Table 2) on material from the Davis Quarry, Bancroft, Ontario. The formula obtained from this analysis after normalizing to 12(Si + Al) is :

$$Na_{3.30}K_{0.27}Al_{5.83}Si_{6.17}(CO_3)_{1.47}.3.7H_2O$$

This formula, as noted by Meen (1938), is deficient in Na and high H_2O. He noted that the H_2O might be filling vacancies at the Na sites. (The ideally ordered cancrinite unit cell may accommodate $2H_2O$, $2CO_2$, and Na, K, and Ca atoms in two equipoints of rank 2 and 6). Analyses of both the skarn and Davis Quarry specimens are similar in the high proportions of Ca, and this appears to be the only characteristic which contrasts markedly with those of other cancrinites. These two cancrinites have similar superstructure diffraction patterns which differ from those reported for other cancrinites. Thus the unusual superstructure may be related to ordering of the high proportion of Ca over the large cation sites.

THERMAL TREATMENT

The behavior of the superstructure reflection intensity as a function of temperature should provide information on the nature of the ordering mechanism causing the superstructure. For example, sluggish, irreversible decreases in the intensity of superstructure reflections at high temperatures might be attributable to Al-Si disorder. Therefore, cleavage fragments of both the Litchfield and York River materials exemplifying the two kinds of superstructure observed, were studied using a high-temperature furnace mounted on a Weissenberg single-crystal counter-diffractometer (Foit & Peacor 1967).

Integrated intensities of both substructure and superstructure reflections were graphically recorded as a function of temperature, up to 600° C for the Litchfield specimen, and up to 340° C for the York River skarn specimen. After heating to a given temperature, intensities were monitored for up to 36 hours in order to verify that a steady state was attained. When changes in intensity at constant temperature occurred as a function of time, the changes were monitored until no further differences could be observed.

The intensities of all maxima were observed to decrease with an increase in temperature. Similarly, diffuseness increased for both superstructure and substructure reflections. Figures 3-5 show intensity changes which are representative of all reflections studied. They show that, although there were no significant variations in substructure intensities as a function of temperature, the superstructure intensities exhibited considerable change. In particular, the superstructure intensities of the Litchfield sample show little change up to about 120° C. Above this temperature, they rapidly and continuously decrease in intensity up to about 250° C, when they become almost unobservable. The York River sample exhibits equivalent

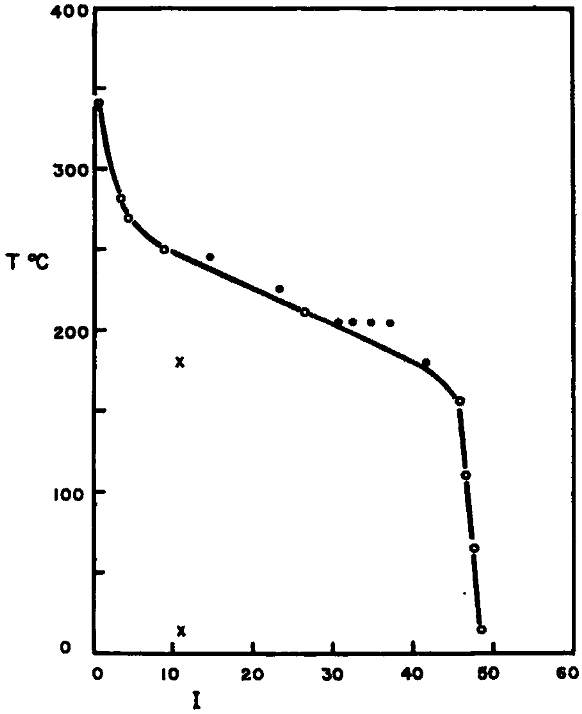

Fig. 3. Integrated intensity (*I*) *of* 114 (indexed on supercell) of York River skarn cancrinite, as a function of temperature. Open circles are points obtained with equilibrium conditions, solid circles correspond to a measurement with intensity changing with time, and crosses were measured with decreasing temperature.

changes in the temperature interval 150-300° C. These changes were sluggish, and periods of up to 10 hours duration were required before no further variation could be observed. Substructure intensities returned to their original values upon cooling the crystal, but superstructure intensities, although increasing with decreasing temperature, returned to only a fraction of their original values.

Weissenberg photographs of the Litchfield specimen, taken after cooling to room temperature verified that : (1) Substructure reflections retained their original, relative intensities. (2) Superstructure reflections are still present, but at a much reduced intensity. (3) Superstructure reflections had become much more diffuse, relative to substructure intensities.

Since the results for both the Litchfield and York River samples are the same except for a small difference in temperature, the basic structural and chemical causes of the different superstructures must be closely related. This was apparent also in the equivalence of intensities for these two structure types, as described above. Furthermore, the nature of the changes as a function of temperature supports Jarchow's conclusions that the intra-framework atoms are primarily responsible for the superstructure maxima. Since changes occur continuously at relatively low temperatures, it is clear that they cannot be due to disordering in the (Si,Al)-O framework.

Jarchow showed that Na and Ca cations occupy both of two kinds of channels aligned parallel to the 6_3 and 3-fold axes between six-rings of tetrahedra. The $CO_3^=$ and H_2O molecules, on the other hand, occupy

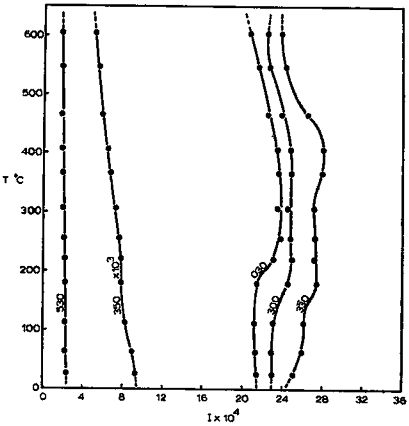

FIG. 4. Integrated intensities (I) of selected substructure reflections of Litchfield cancrinite as a function of temperature.

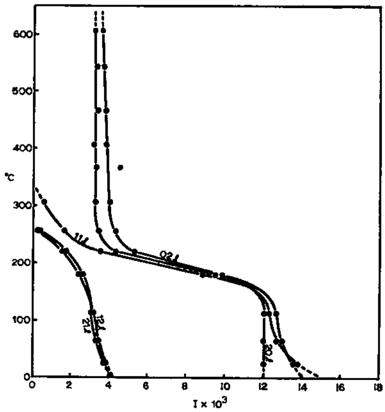

FIG. 5. Integrated intensities (I) of selected superstructure reflections of Litchfield cancrinite as a function of temperature.

the channels along the 6_3 and 3-fold axes, respectively. Jarchow (1965 and written comm.) concluded that CO_3 and, to a lesser extent, H_2O are the major contributors to the formation of the superstructure reflections. His conclusion was based in part on an apparent relationship between $CO_3^=$ content and superstructure periodicity and on the relative amounts of $CO_3^=$ and H_2O obtained from a refinement of the substructure.

The observed irreversibility in the change of the superstructure reflection intensity with temperature is consistent with this interpretation. This, and the fact that intensity change is a continuous function over a temperature range, indicate that the changes occur simultaneously with a change in composition, namely loss of one or more volatile constituents. Kirsch (1956) showed that H_2O is continuously lost over the temperature range 70 to 350° C. Thus the changes in intensity are apparently in part related to the loss of water. Since the temperature at which volatilization of water occurs varies both as a function of the sample composition and of the water vapor pressure present for any given experiment, our observed temperature interval appears to be consistent with that of Kirsch.

However, this does not mean that ordering of H_2O is the principal source of the superstructure. Loss of H_2O should promote interchange or positional adjustments among $CO_3^=$, Ca and Na. A complete analysis of the superstructure, involving a directly crystal-structure determination, will be required to define explicitly the nature of the relative contributions of Ca, Na, H_2O and CO_3 to the superstructure.

ACKNOWLEDGEMENTS

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