

Mines Branch Technical Bulletin TB 31

COMPOSITIONAL VARIATIONS IN PYROCHLORE AND  
NIOBIAN PEROVSKITE FROM A NIOBIUM DEPOSIT  
IN THE OKA DISTRICT OF QUEBEC

by

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SYNOPSIS

The ore from the Columbian Mining Products Limited property at Oka consists largely of calcite, pyroxene, biotite and apatite, with calcite predominating. The niobium-bearing minerals are pyrochlore and niobian perovskite. Pyrochlore is more abundant in the higher-grade samples, while niobian perovskite predominates in the lower-grade samples. The  $Nb_2O_5$  content of the pyrochlore ranges from 39.7% to 55.2%, and that of the perovskite varies from 14.5% to 44.9%. A number of chemical relationships and physical properties of these minerals have been investigated with a view to relating niobium content to other determinable features. It was found that the niobium content of the pyrochlore is related inversely to its radioactivity and titanium content, and that the niobium content of the perovskite is related directly to the  $Nb_2O_5:TiO_2$  ratio in the ore.

Other minerals found in the ore include dolomite, magnesite, siderite, strontianite, monticellite, nepheline, analcite, natrolite, garnet, magnetite, hematite, pyrite, pyrrhotite, chalcopyrite, feldspar, zircon, barite, and fluorite.

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Direction des mines

Bulletin technique TB 31

VARIATIONS DE LA COMPOSITION DU PYROCHLORE  
ET DE LA PÉROVSKITE À NIOBIUM EN PROVENANCE  
D'UN GÎTE DE NIOBIUM DE LA RÉGION D'OKA, P.Q.

par

E. H. Nickel\*

RÉSUMÉ

Le minerai en provenance de la propriété que possède la Columbian Mining Products Limited, à Oka, se compose principalement de calcite ainsi que de pyroxène, de biotite et d'apatite. Les minéraux niobifères y sont le pyrochlore et la pérovskite à niobium. Le pyrochlore prédomine dans les échantillons de qualité supérieure, la pérovskite à niobium, dans ceux de qualité inférieure. La teneur en Nb<sub>2</sub>O<sub>5</sub> du pyrochlore varie de 39.7 p. 100 à 55.2 p. 100 et celle de la pérovskite, de 14.5 p. 100 à 44.9 p. 100. Un certain nombre de relations chimiques et de propriétés physiques de ces minéraux ont été examinées afin de lier la teneur en niobium aux autres caractéristiques qui peuvent être déterminées. L'auteur a découvert que la teneur en niobium du pyrochlore est fonction inverse de sa radioactivité et de sa teneur en titane, tandis que la teneur en niobium de la pérovskite est fonction directe du rapport Nb<sub>2</sub>O<sub>5</sub>:TiO<sub>2</sub> au sein du minerai.

Les autres minéraux présents dans le minerai comprennent la dolomie, la magnésite, la sidérose, la strontianite, la monticellite, la néphéline, l'analcite, la natrolite, le grenat, la magnétite, l'hématite, la pyrite, la pyrrhotine, la chalcopyrite, le feldspath, le zircon, la barytine et la fluorine.

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## INTRODUCTION

The samples investigated are all from a deposit near Oka, Quebec, currently held by Columbian Mining Products Limited. The majority of the samples were diamond drill core assay rejects crushed to about minus  $\frac{1}{4}$  inch. They had been selected by the company officials to represent a diversity of rock types and to span a wide range of niobium content. Several samples of concentrates produced during the experimental milling of the ore and provided by H.L. Noblitt, metallurgical consultant, were also investigated.

The chief aims of the investigation were to determine the extent of compositional variations in the niobium minerals, to determine whether these variations could be related to physical characteristics of the minerals, and to assess the probable effects of the compositional variations on mining operations and milling procedure.

The work was started toward the end of 1960 and was completed late in 1961. The results of the investigation have been reported in the form of a Mines Branch Investigation Report <sup>(1)</sup>. Because much of the information is of general interest, arrangements were made, through the cooperation of officials of Columbian Mining Products Limited, to reprint the report with minor changes, as a Mines Branch Technical Bulletin, thereby assuring wider distribution.

## PROCEDURE

Since the chief aim of the investigation was to determine variations in the niobium content of the pyrochlore, the method of investigation was directed primarily toward obtaining, for analysis, pyrochlore concentrates as free as possible from other minerals. A number of the largest fragments were first removed from the samples and made into polished sections for microscopic examination. The remainder of each of the samples was then crushed to minus 65 mesh. After cutting out portions from each of them for analysis, the -65 + 200 mesh fractions were screened out and used for mineral separations.

The mineral separations were made by a combination of heavy liquid and high intensity magnetic procedures. The heavy liquids used were tetrabromoethane, methylene iodide, and Clerici solution, with specific gravities of 2.96, 3.33, and 3.70, respectively. The resulting mineral fractions were examined in oil immersion under a petrographic microscope to evaluate their mineral compositions. The final sink products, namely those which sank in liquid of 3.70 specific gravity and which contained the heavy minerals including pyrochlore and perovskite, were separated on a Frantz isodynamic separator. In some cases, repeated separations were necessary to produce relatively pure concentrates.

The pyrochlore concentrates were then investigated in the

following manner: They were all analyzed chemically for niobium, and selected ones were also analyzed for titanium, uranium, and thorium. The degree of radioactivity of the concentrates, as well as that of the original samples, was measured radiometrically by a gamma-ray equilibrium counter. X-ray powder diffraction patterns were made from each of the concentrates, to determine their diffraction characteristics. Densities of selected pyrochlore concentrates were determined. The results of the various findings were then critically analyzed in an effort to determine what characteristics (or properties) are significant and of possible help in distinguishing different grades of pyrochlore.

During the course of the investigation it was discovered that the perovskite also contained large amounts of niobium. Therefore this mineral also was concentrated for chemical analysis.

The chemical determinations made on the pyrochlore and perovskite concentrates were in many cases restricted by the small amount of material concentrated. This paucity of material was due to the small amount of pyrochlore and perovskite in some of the samples and to the necessity of attaining a high degree of purity in the concentrates. Most concentrates were too small to permit more than a niobium determination to be made and, in some instances, not enough could be concentrated even for that.

This investigation leans heavily on the contributions of



other officers in the Mines Branch. Individual acknowledgments are given in the text.

## RESULTS OF INVESTIGATION

### General Mineralogy

The ore is fine-grained, with practically all of the individual mineral grains smaller than 1 mm in diameter. The principal minerals in the ore are calcite, pyroxene, biotite and apatite, with calcite generally predominating. The proportions of these minerals are extremely variable, and any given ore fragment may consist largely of only one of these minerals, or a mixture of them. The minor minerals are distributed unevenly among the samples, generally as disseminated grains. Minerals such as pyrochlore, perovskite, magnetite, pyrrhotite, pyrite, dolomite and monticellite occur in most of the samples; others, such as nepheline, feldspar, hornblende, analcite, natrolite, garnet, zircon, barite, fluorite, hematite, magnesite, siderite, strontianite and chalcopyrite, were found in small amounts in only a few of the samples.

### Niobium Mineralization

$Nb_2O_5$  analyses of the samples as shown in Table 1 were provided by officials of Columbian Mining Products Limited. During the course of the mineralogical investigations it became apparent that analyses for  $TiO_2$  and radioactivity might be of value, and these results are also listed in Table 1.

The niobium content of the ore can be attributed largely, if not entirely, to pyrochlore and niobian perovskite. Although both minerals are found in practically all of the samples investigated, their relative proportions vary greatly, with pyrochlore predominating in some samples and perovskite in others. Because of this variability it is impossible to establish precisely their over-all ratio. However, from the samples examined, the ore as a whole appears to contain more pyrochlore than perovskite.

TABLE 1

Analysis of Ore Samples

Sample No.	Nb <sub>2</sub> O <sub>5</sub> (%) <sup>*</sup>	TiO <sub>2</sub> (%) <sup>**</sup>	Gamma-radioactivity <sup>***</sup> (counts/sec/100 g)
393	0.60	0.51	1.40
395	0.29	--	1.51
396	0.55	0.49	0.98
399	0.33	1.04	3.35
400	0.88	0.54	0.20
435	0.54	1.04	4.44
441	1.11	2.02	98.04
442	0.43	0.51	2.56
447	0.37	0.56	8.59
636	0.68	1.06	3.91
637	0.47	2.21	38.79
643	0.51	0.59	12.58
644	0.16	--	11.83
650	0.39	0.66	9.82
MC-137	0.34	--	15.33
MC-138	0.56	5.77	27.30
MC-160	0.99	0.83	8.93
MC-233	0.16	0.74	6.95
MC-245	0.19	--	11.12
MC-249	0.16	0.52	15.22
MC-254	0.19	0.48	16.19

\* Analyses supplied by Columbian Mining Products Limited.

\*\* Chemical analyses by R.W. Buckmaster, Analytical Chemistry Subdivision, Mineral Sciences Division.

\*\*\* Radiometric determinations by C.M. McMahon, Physics and Radiotracer Subdivision, Mineral Sciences Division.

## 1. Pyrochlore

Pyrochlore is a complex niobium oxide of variable composition, and with a general formula expressed by  $A_{16-x}B_{16}(O,OH)_{48}(F,OH)_8^{(2)}$ . The A position is most commonly occupied by sodium or calcium, although a number of other elements, including uranium, thorium and rare earths, may also occupy this site. The B position is occupied chiefly by niobium, although other elements - commonly titanium and tantalum - may substitute for niobium.

The presence of both pyrochlore and betafite is noted in the drill core logs supplied by the company. Hogarth<sup>(2)</sup> has shown that these two minerals have the same structure and form a continuous series, with no sharp compositional break. He suggests that the name betafite be restricted to members of the pyrochlore group that contain more than 15% uranium. Since, as will be shown later, none of the pyrochlore investigated was found to contain more than 15% uranium, it is doubtful if the use of the name betafite is fully justified in reference to the mineral from Columbian Mining Products Limited. The writer therefore prefers to use the name pyrochlore throughout this report.

The pyrochlore in the samples under consideration occurs principally as small disseminated grains which vary in size from a few microns (Fig. 1) to about 1 millimetre (Fig. 2) in diameter. The grains tend to be equidimensional, and vary in form from

anhedral grains to almost perfect octahedral crystals. Some of the larger grains have abundant gangue inclusions (Fig. 2). Zonal growth was observed in the pyrochlore in a few of the samples (Fig. 3), and probably represents changes in composition during growth of the crystal.

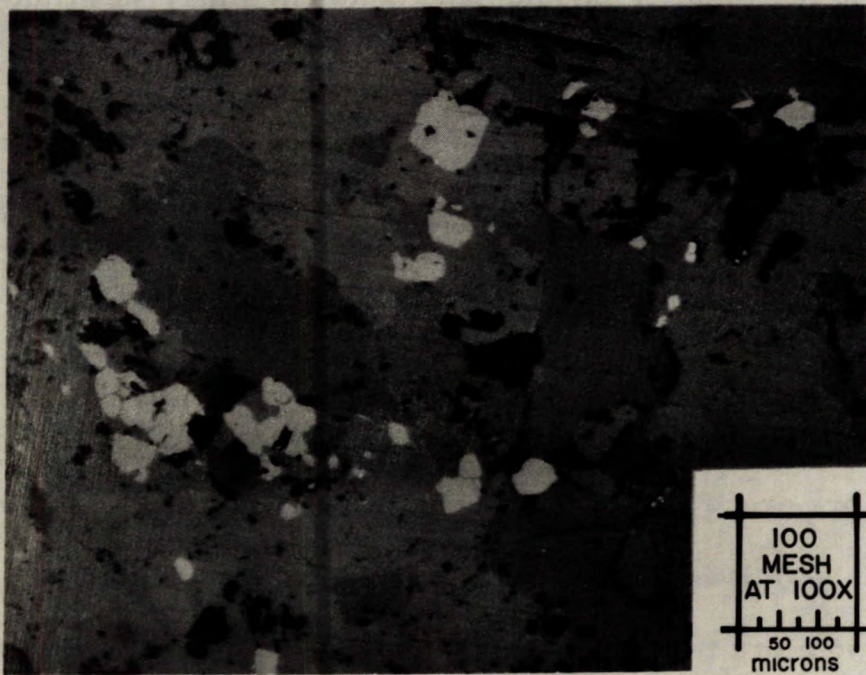


Figure 1 - Photomicrograph of polished section of sample No. 396, showing small disseminated grains of pyrochlore (white) in a matrix of calcite and dolomite (grey). Pits are black.



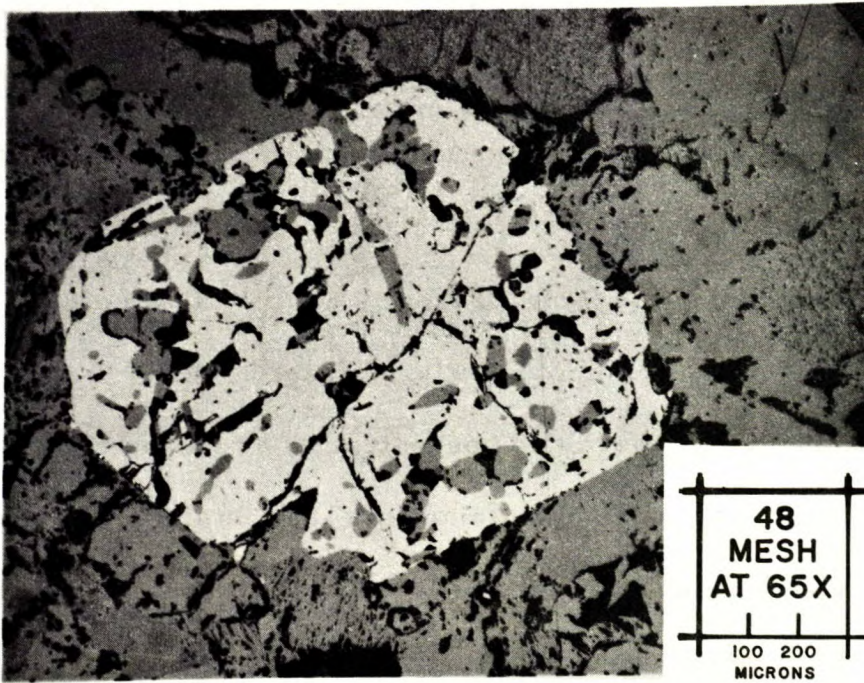


Figure 2 - Photomicrograph of polished section of sample No. 393, showing a relatively large crystal of pyrochlore (white) in calcite (grey). The pyrochlore crystal contains abundant inclusions of calcite. Pits are black.

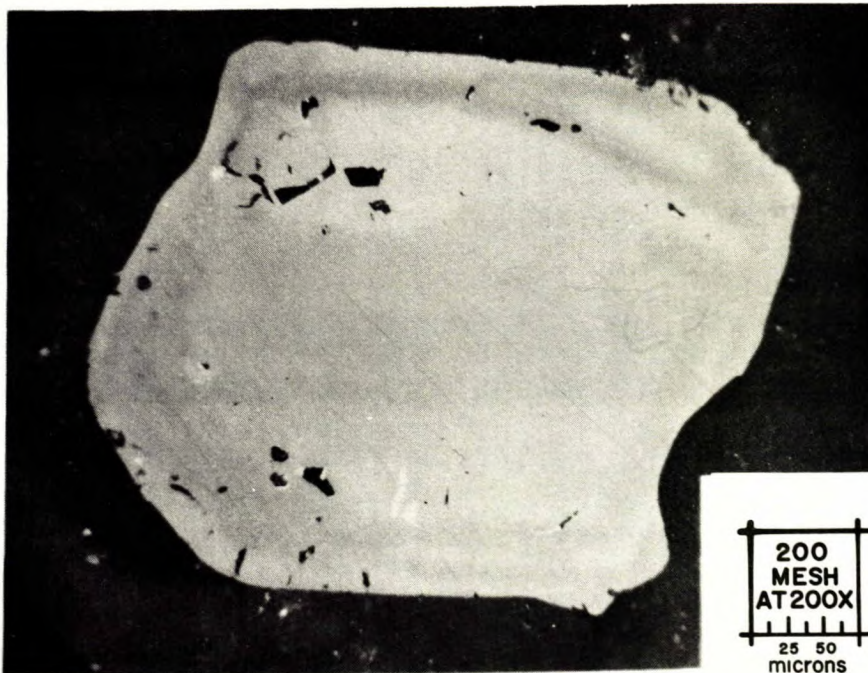


Figure 3 - Photomicrograph (oil immersion) of polished section of a zoned pyrochlore crystal from sample No. 447. The zones are roughly parallel to the external faces of the crystal.

The pyrochlore varies in colour from dark reddish-brown to a relatively light yellowish-brown. This colour variation occurs not only from sample to sample but also within the same sample.

Sufficient pyrochlore for radiometric and partial chemical analyses was isolated from 13 of the 21 samples investigated. In general, only those samples with at least 0.3%  $\text{Nb}_2\text{O}_5$  were found to be amenable to pyrochlore concentration by means of the laboratory methods used. In those containing less than this, the pyrochlore was not sufficiently abundant, or was too finely intergrown with other minerals, to permit concentration. The analyses of the pyrochlores and their observed colours are listed in Table 2. It is evident that the niobium content of the pyrochlore cannot be correlated either with its colour or with the niobium content of the ore samples.

TABLE 2

Niobium Content of Ore Samples and Pyrochlore Concentrates

Sample No.	Nb <sub>2</sub> O <sub>5</sub> Content (Wt %)		Colour of Pyrochlore
	Ore Sample*	Pyrochlore**	
441	1.11	42.5	Dark reddish-brown + yellowish-brown
MC-160	0.99	53.5	Reddish-brown
400	0.88	55.2	Reddish-brown
636	0.68	53.7	Reddish-brown
393	0.60	52.2	Reddish-brown
396	0.55	54.4	Reddish-brown
435	0.54	52.2	Medium brown
643	0.51	39.7	Dark reddish-brown
637	0.47	50.0	Yellowish-brown + minor reddish- brown
442	0.43	54.0	Dark reddish-brown
650	0.39	45.7	Dark reddish-brown
447	0.37	47.5	Dark reddish-brown
399	0.33	52.0	Yellowish-brown + minor reddish- brown

\* From Table 1, arranged in order of decreasing Nb<sub>2</sub>O<sub>5</sub>.

\*\* Chemical analyses by H.R. Lauder and R.W. Buckmaster,  
Analytical Chemistry Subdivision, Mineral Sciences Division.



Examination of the X-ray powder diffraction patterns of the analyzed pyrochlores revealed that those with the lowest niobium contents gave diffraction patterns that were weak and diffuse. Since this is characteristic of partially metamict minerals, and since metamictization is generally due to the presence of radioactive elements, it was suspected that there might be some correlation between the niobium content of the pyrochlore and its degree of radioactivity. The radioactivity of the concentrates was therefore measured, with the results listed in Table 3. It can readily be seen that a fair degree of correlation exists and that the radioactivity of the pyrochlore increases with decreasing niobium content. This is shown graphically in Fig. 4. The degree of correlation between the  $\text{Nb}_2\text{O}_5$  content of the pyrochlore and the radioactivity of the corresponding ore samples from which the pyrochlore was concentrated is much poorer (see Table 3). In a general way, those samples with a low radioactivity contain pyrochlore with a relatively high  $\text{Nb}_2\text{O}_5$  content, and vice versa, as shown in Fig. 5.

TABLE 3

Nb<sub>2</sub>O<sub>5</sub> Content of Pyrochlore as Related to Radioactivity of the Pyrochlore and that of the Ore Samples

Sample No.	Nb <sub>2</sub> O <sub>5</sub> Content* of Pyrochlore (%)	Gamma-Radioactivity	
		Pyrochlore** (counts/sec/g)	Ore Sample*** (counts/sec/100 g)
400	55.2	0.51	0.20
396	54.4	1.34	0.98
442	54.0	2.20	2.56
636	53.7	4.09	3.91
MC-160	53.5	7.69	8.93
393	52.2	2.92	1.40
435	52.2	7.35	4.44
399	52.0	8.75	3.35
637	50.0	9.09	38.79
447	47.5	17.13	8.59
650	45.7	Not determined.	9.82
441	42.5	45.51	98.04
643	39.7	56.77	12.58

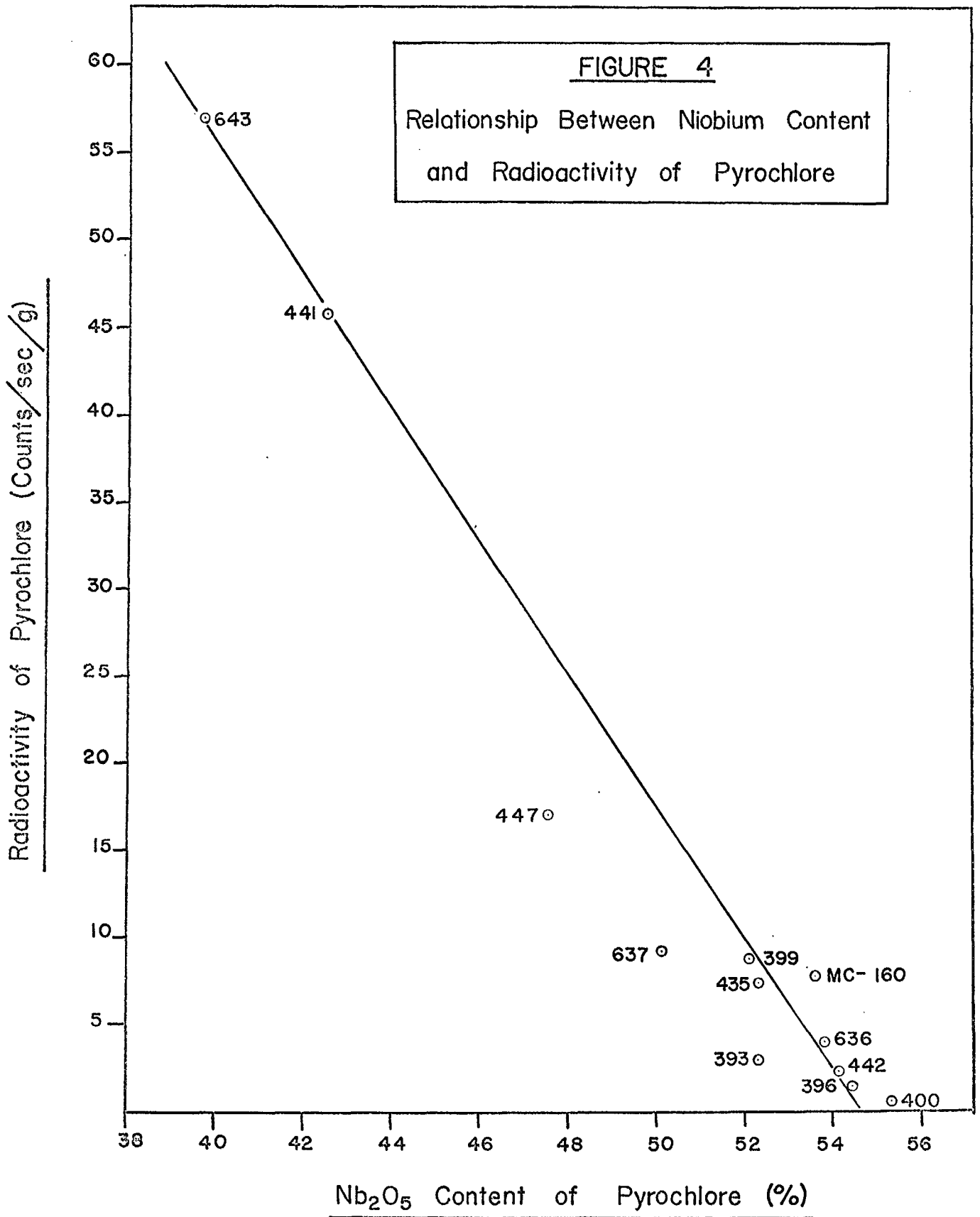
\* From Table 2, arranged in order of decreasing Nb<sub>2</sub>O<sub>5</sub> content.

\*\* Radiometric analyses by C.M. McMahon, Physics and Radio-tracer Subdivision, Mineral Sciences Division.

\*\*\* From Table 1.

It should be noted that the radioactivity of the ore samples is given in counts per 100 grams, whereas that of the pyrochlore concentrates is given in counts per gram. Since the figures in columns 3 and 4, Table 3, are of the same order of magnitude, it is evident that the radioactivity of the pyrochlore is, in general, about 100 times as high as that of the ore, which indicates that the pyrochlore is in large part responsible for the radioactivity of the ore. When the radioactivity of the individual pyrochlore concentrates is compared with the radioactivity of the ore samples from which the pyrochlore was concentrated (Table 3, columns 3 and 4), a general correlation of the degree of radioactivity in the pyrochlore and in the corresponding sample is evident, although there are some obvious discrepancies in individual cases. These discrepancies indicate that pyrochlore alone is not entirely responsible for the radioactivity, this explains the rather poor correlation between the  $\text{Nb}_2\text{O}_5$  content of the pyrochlore and the radioactivity of the ore.

FIGURE 4  
Relationship Between Niobium Content  
and Radioactivity of Pyrochlore





In order to determine the elements chiefly responsible for the radioactivity in the pyrochlore, the amounts of uranium and thorium were estimated radiometrically using the gamma-ray spectrometer. The results (Table 4) show quite conclusively that the proportion of uranium to thorium is extremely variable, with uranium predominating in some samples and thorium in others.

TABLE 4

Estimated Uranium and Thorium Content of Pyrochlore Concentrates\*

Sample No.	U + Th (%)	U (%)	Th (%)
400	0.10	0.07	0.03
396	0.35	0.12	0.23
393	0.37	0.37	n.d.
442	0.37	0.23	0.14
636	0.72	0.26	0.46
399	1.25	n.d.	1.25
637	1.54	0.1	1.44
447	2.10	2.10	n.d.
435	2.20	0.75	1.45
643	7.26	7.0	0.26
441	9.13	0.63	8.5

\* Estimates made from gamma-ray spectrometer by  
J.L. Horwood, Physics and Radiotracer Subdivision,  
Mineral Sciences Division.

n.d. = not detected

According to the structural formula of pyrochlore discussed earlier, the uranium and thorium should substitute for calcium or sodium in the A position. Since niobium is located in the B position, the inverse relationship between the degree of radioactivity and niobium content of the pyrochlore cannot be due to a simple replacement of niobium by uranium and thorium. However, this relationship can be explained, in part, by a coupled substitution whereby the excess charge introduced by substituting the more highly charged uranium and thorium ions for divalent calcium may be balanced by a simultaneous substitution for 5-valent niobium by some less highly charged cation, probably titanium. This explanation is supported by titanium analyses of three of the pyrochlore concentrates as shown in Table 5. These indicate that the titanium content increases with increasing U + Th and decreasing niobium.

TABLE 5

The Relationship Between Titanium, Niobium, and Uranium + Thorium Contents of Pyrochlore

Sample No.	TiO <sub>2</sub> (%) <sup>*</sup>	Nb <sub>2</sub> O <sub>5</sub> (%) <sup>**</sup>	U + Th (%) <sup>***</sup>
400	5.70	55.2	0.10
435	7.85	52.2	2.20
441	9.65	42.5	9.13

\* Analyst: H.H. Bart, Analytical Chemistry Sub-Division, Mineral Sciences Division.

\*\* From Table 2.

\*\*\* From Table 4.

It might be expected that the  $\text{Nb}_2\text{O}_5:\text{TiO}_2$  ratios in the ore samples would bear a consistent relationship to those in the contained pyrochlore, and therefore provide a guide to the  $\text{Nb}_2\text{O}_5$  content of the pyrochlore. Table 6, however, shows that there is no consistent relationship between the  $\text{Nb}_2\text{O}_5:\text{TiO}_2$  ratio in the ore and the  $\text{Nb}_2\text{O}_5$  content of the pyrochlore. Any relationship that might have existed has probably been obscured by the presence of perovskite, since the latter contains major amounts of both niobium and titanium.

TABLE 6

Relationship Between the  $\text{Nb}_2\text{O}_5:\text{TiO}_2$  Ratio in the Ore and the  $\text{Nb}_2\text{O}_5$  Content of the Pyrochlore

Sample No.	$\text{Nb}_2\text{O}_5:\text{TiO}_2$ * in Ore	, $\text{Nb}_2\text{O}_5$ (%) in** Pyrochlore
400	1.63	55.2
MC-160	1.19	53.5
393	1.18	52.2
396	1.12	54.4
643	0.86	39.7
442	0.84	54.0
447	0.66	47.5
636	0.64	53.7
650	0.59	45.7
441	0.55	42.5
435	0.52	52.2
399	0.32	52.0
637	0.21	50.0

\* Calculated from the values shown in Table 1, and arranged in decreasing order.

\*\* From Table 2.



Attempts were made to correlate the niobium content of the pyrochlore with some of its physical properties, including specific gravity and unit cell parameter. The specific gravities of a number of pyrochlore concentrates were determined by pycnometer, and are shown in Table 7, together with their niobium contents. No consistent correlation can be made.

TABLE 7  
Specific Gravity and Niobium Content of Some  
Pyrochlore Concentrates

Sample No.	Specific Gravity	Nb <sub>2</sub> O <sub>5</sub> (%)**
636	4.32	53.7
441	4.34	42.5
637	4.42	50.0
400	4.44	55.2
442	4.50	54.0
Crystals*	4.63	50.4

\* Large crystals from a mill sample, provided by H.L. Noblitt.

\*\* From Table 2 except for 50.4 for the crystals.

The unit cell parameter of the pyrochlore varies between 10.37 and 10.38 Å, but could not be correlated with variations in niobium content.

In summary, it is clear that pyrochlore from different samples exhibits wide differences in composition. In general, a high niobium content is related to a low titanium content and low

radioactivity. Variations in niobium content, however, could not be related to variations in colour or physical properties.

## 2. Perovskite

Perovskite normally has a composition expressed by the formula  $\text{CaTiO}_3$ , although extensive substitution by other elements may take place. Experience has shown that perovskite from the Oka area contains appreciable amounts of niobium in substitution for titanium.

The perovskite occurs as disseminated grains, ranging in size from about 0.1 to 1 millimetre in diameter. It is black in colour, with a sub-metallic lustre. The perovskite can be distinguished from other black minerals in the ore, including magnetite and garnet, by its tendency to occur as roughly cubic crystals. Under the microscope, many of the crystals are seen to contain inclusions of gangue minerals (see Figs. 6 and 7) and, more rarely, of sulphides (Fig. 7). Some of the perovskite crystals are partially rimmed by a light coloured, translucent pyrochlore (Fig. 8). The outer margins of this pyrochlore are extensions of the crystal outlines of the perovskite, whereas the contact between the two is highly irregular. This is interpreted as indicating that the pyrochlore has formed at the expense of perovskite, perhaps as an alteration product.



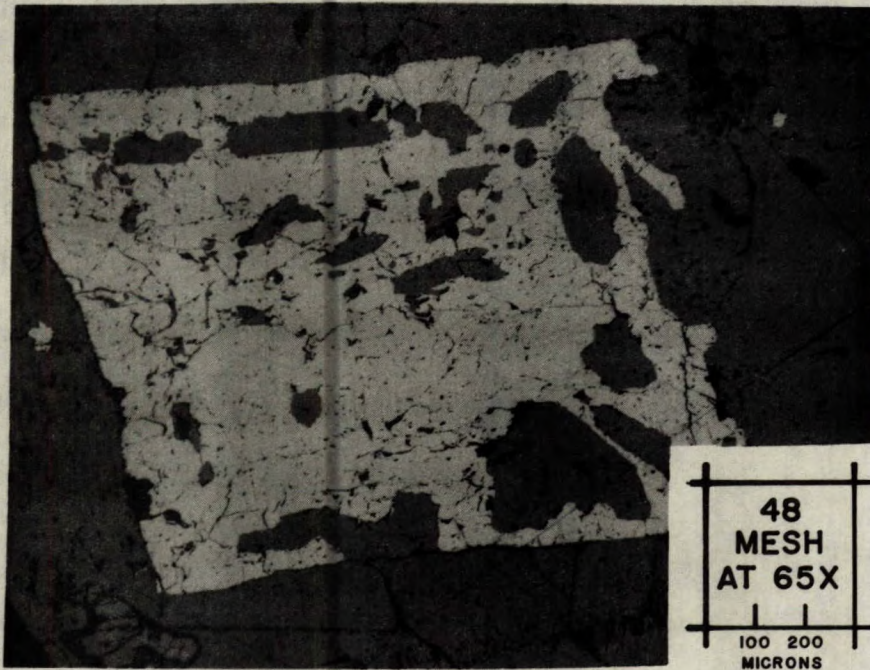


Figure 6 - Photomicrograph of polished section of sample No. 400, showing a relatively large crystal of perovskite (light grey) in calcite (dark grey). The perovskite crystal contains numerous large calcite inclusions.

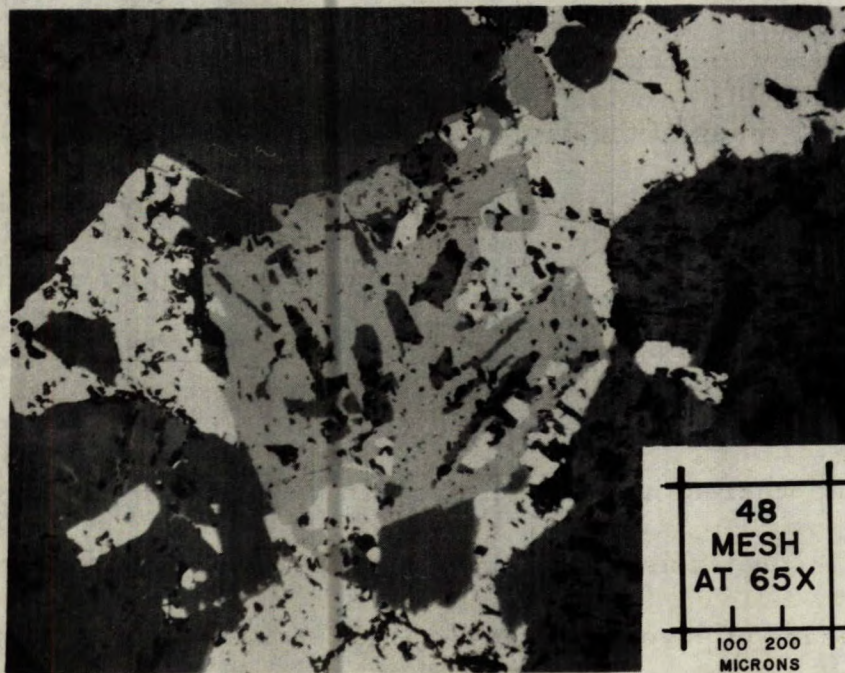
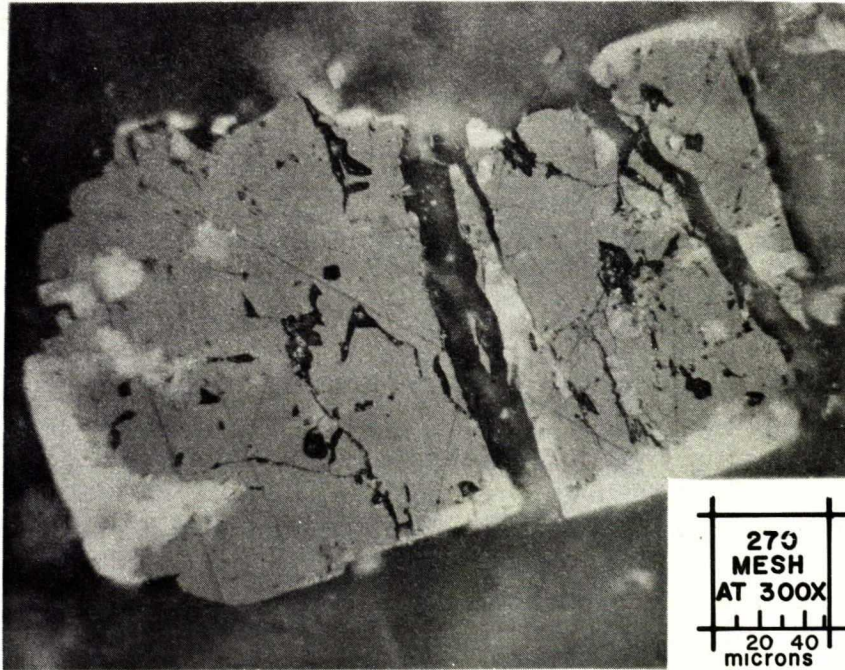


Figure 7 - Photomicrograph of polished section of sample No. 396, showing a perovskite crystal (light grey) partially surrounded by pyrrhotite (white), and containing inclusions of calcite (dark grey) and pyrrhotite. The surrounding gangue minerals are calcite and pyroxene.





**Figure 8 -** Photomicrograph of polished section of sample No. 396 in oil immersion and nicols partly crossed. This shows a perovskite crystal (light grey) with some intimately associated pyrochlore (white). The tendency of the pyrochlore to occur along the margins of the perovskite indicates pseudomorphous replacement of the perovskite by pyrochlore.

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Although the crystals have the outward appearance of cubes, X-ray diffraction patterns of the perovskite reveal that the mineral is not truly cubic. According to single crystal X-ray diffraction analysis by J.F. Rowland of the Physical Chemistry Section, the mineral is orthorhombic. Powder X-ray diffraction patterns exhibit a slight deviation from a cubic pattern, but can be used to calculate a pseudo-cubic unit cell that bears a close

geometrical relationship to the true unit cell. Variations of cell dimensions with composition will be discussed later.

To obtain enough pure perovskite for a complete chemical analysis, a perovskite concentrate produced by H.L. Noblitt during the course of beneficiation tests was further up-graded by repeated heavy liquid and magnetic separations. X-ray diffraction patterns of the final perovskite concentrate exhibited only perovskite lines, indicating a relatively low level of contamination by other minerals. A polished section of the concentrate, however, revealed the presence of a small amount of pyrite, which is probably responsible for the sulphur reported in the analysis. The results of chemical and semi-quantitative spectrographic analyses of the perovskite are shown in Tables 8 and 9, respectively.

TABLE 8

Chemical Analysis of Niobian Perovskite

CaO	25.95%
Na <sub>2</sub> O	4.03
R.E. Oxides	2.03
K <sub>2</sub> O	0.03
Nb <sub>2</sub> O <sub>5</sub>	43.90
TiO <sub>2</sub>	10.05
Fe <sub>2</sub> O <sub>3</sub>	8.74
MgO	2.20
MnO	0.77
SiO <sub>2</sub>	0.45
Loss on ign.*	<u>1.55</u>
	<u>99.70</u>

\* Includes 0.90% S and 0.36% H<sub>2</sub>O.

Analyst: R.C. McAdam, Analytical Chemistry  
Subdivision.

TABLE 9

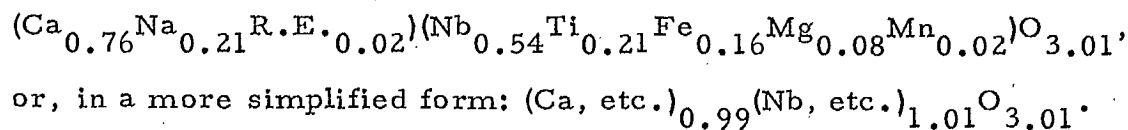
Semi-Quantitative Spectrographic Analysis for  
Minor Elements in Niobian Perovskite

Ce	1.5 %
La	0.3
Zr	0.3
Sr	0.2
Y	0.1
Al	0.09
Ni	0.04
Gd	0.03
V	0.03
Dy	0.01
Yb	0.01

Analyst: Miss E.M. Kranck, Analytical Chemistry  
Subdivision.

Recalculation of the chemical analysis to conform to the generalized perovskite formula  $ABO_3$  is shown in Table 10. The recalculated composition was obtained from the analysis, shown in Table 8, in the following manner: The  $SiO_2$  is most likely due to contamination by a silicate mineral, probably pyroxene. Assuming this to be the case,  $SiO_2$  was excluded and the amounts of CaO and MgO in pyroxene (diopside) corresponding to the 0.45%  $SiO_2$  were subtracted from the analytical values. Since the sulphur appears to be due to contamination by pyrite, the amount of iron in pyrite corresponding to the 0.90% sulphur was subtracted from the analyzed  $Fe_2O_3$  value. The remainder of the loss of ignition (composed of water and possibly carbon dioxide) was also excluded from the calculations. The weights of the remaining oxides were then recalculated to 100.00%.

When the elements are divided into two groups with large (A) and small (B) ionic radii, respectively, it is found that the total atomic proportions of these two groups are close to the 1:1 ratio required by the generalized perovskite formula  $ABO_3$ . The complete empirical formula of the niobian perovskite can be written as:



The molecular (formula) weight is 158.2. If the unit cell is assumed to contain 8 formula units, then the calculated specific gravity is 4.48. This is in good agreement with the measured specific gravity of 4.40.

TABLE 10

Calculation of Atomic Proportions in Niobian Perovskite

Constituent	Recalculated Wt %*	Element	Wt %	At. Props	At. Props x 1.5847**
CaO	26.75	Ca	19.12	0.4770	0.76
Na <sub>2</sub> O	4.19	Na	3.11	0.1353	0.21
R.E. Oxides	2.11	Ce	1.72	0.0123	0.02
K <sub>2</sub> O	0.03	K	0.02	0.0005	--
Nb <sub>2</sub> O <sub>5</sub>	45.62	Nb	31.89	0.3432	0.54
TiO <sub>2</sub>	10.45	Ti	6.26	0.1307	0.21
Fe <sub>2</sub> O <sub>3</sub>	7.92	Fe	5.54	0.0992	0.16
MgO	2.13	Mg	1.28	0.0526	0.08
MnO	0.80	Mn	0.62	0.0113	0.02
	<u>100.00</u>				
		O	<u>30.44</u>	<u>1.9025</u>	<u>3.01</u>
			<u>100.00</u>	<u>3.1646</u>	<u>5.01</u>

\* See text (page 26).

\*\* This factor brings the total of the cationic constituents (A + B) to 2.00.

The most notable feature of the niobian perovskite is its high niobium content - much higher, in fact, than that of any naturally-occurring perovskite reported heretofore. Since the niobium content of the perovskite is comparable to that of some of the pyrochlore, the perovskite must be regarded as an ore mineral of niobium in this deposit.



To determine whether or not the niobium content of the perovskite is uniform, a number of perovskites from different samples were analyzed for  $\text{Nb}_2\text{O}_5$ . To reduce, to a minimum, contamination by other minerals, particularly pyrochlore, the perovskite concentrates were purified by hand-picking under a stereomicroscope. The results of the analyses (Table 11) show that the  $\text{Nb}_2\text{O}_5$  content of the perovskite varies over a wide range, values from 14.5% to 47.5%  $\text{Nb}_2\text{O}_5$  having been obtained.

TABLE 11

The Niobium Content of Perovskites from Different Samples

<u>Sample No.</u>	<u><math>\text{Nb}_2\text{O}_5</math> (%)</u> **
393	44.9
396	43.0
447	32.8
650	36.8
MC-233	14.5
MC-249	32.0
MC-254	25.3
Crystals *	47.5

\* Large crystals from a mill sample provided by H.L. Noblitt.

\*\* Analyses by R.C. McAdam, Analytical Chemistry Subdivision.

When the  $\text{Nb}_2\text{O}_5$  content of the perovskite is compared with the  $\text{Nb}_2\text{O}_5:\text{TiO}_2$  ratios of the corresponding ore samples (Table 12), a direct relationship is evident. This indicates that the perovskite is compositionally sensitive to variations in the niobium and titanium content of the ore.

TABLE 12

Relationships of the Nb<sub>2</sub>O<sub>5</sub> Content of Perovskite to its Cell Parameter and the Nb<sub>2</sub>O<sub>5</sub>:TiO<sub>2</sub> Ratio of the Ore

Sample No.	Nb <sub>2</sub> O <sub>5</sub> (%) <sup>*</sup>	Cell Parameter <sup>**</sup> (A)	Nb <sub>2</sub> O <sub>5</sub> :TiO <sub>2</sub> <sup>***</sup> Ratio in Ore
393	44.9	--	1.18
396	43.0	--	1.12
650	36.8	7.787	0.59
447	32.8	7.760	0.66
MC-249	32.0	--	0.31
MC-254	25.3	7.748	0.40
MC-233	14.5	7.739	0.22

\* From Table 11, arranged in decreasing order.

\*\* Pseudo-cubic cell edge a<sub>o</sub>, calculated from X-ray powder patterns.

\*\*\* Calculated from values shown in Table I.

Table 12 also shows that the pseudo-cubic cell edge a<sub>o</sub>, as measured from X-ray powder diffraction patterns, decreases with decreasing Nb<sub>2</sub>O<sub>5</sub> content. The perovskites for which no cell parameters are given in Table 12 produced X-ray patterns that were too diffuse to permit accurate measurement.

### 3. Pyrochlore-Perovskite Relationships

Both the pyrochlore and perovskite contain high percentages of niobium, and must therefore both be considered as ore minerals of niobium. As stated earlier, there is a great variation in the pyrochlore:perovskite ratio in the different samples, although, on the whole, pyrochlore appears to predominate, particularly in those samples with a high  $\text{Nb}_2\text{O}_5$  content. Perovskite, on the other hand, predominates in samples with a low  $\text{Nb}_2\text{O}_5$  content.

All the samples from which pyrochlore and/or perovskite were concentrated in sufficient amounts for analysis are shown in Table 13, arranged in order of decreasing niobium content.

TABLE 13

Relationship Between Niobium Contents of the Ore Samples and those of the Contained Pyrochlore and Perovskite

Sample No.	Nb <sub>2</sub> O <sub>5</sub> Content, %*		
	Ore Samples	Pyrochlore	Perovskite
441	1.11	42.5	
MC-160	0.99	53.5	
400	0.88	55.2	
636	0.68	53.7	
393	0.60	52.2	44.9
396	0.55	54.4	43.0
435	0.54	52.2	
643	0.51	39.7	
637	0.47	50.0	
442	0.43	54.0	
650	0.39	45.7	36.8
447	0.37	47.5	32.8
399	0.33	52.0	
MC-254	0.19		25.3
MC-249	0.16		32.0
MC-233	0.16		14.5

\* Data are compiled from Tables 1, 2 and 11 and arranged in order of decreasing niobium content of ore samples.

The following conclusions can be drawn from the data given in Table 13:

- a) The  $\text{Nb}_2\text{O}_5$  content of the pyrochlore, ranging from 39.7% to 55.2%, is higher on the whole than that of the perovskite, which varies from 14.5% to 44.9%.
- b) In those samples from which both pyrochlore and perovskite were obtained for analysis, the pyrochlore invariably has a higher niobium content than the perovskite.
- c) There is no consistent relationship between the niobium content of the ore sample and that of the contained pyrochlore. However, the niobium content of the perovskite appears to decrease with decreasing niobium content in the ore sample.

## CONCLUSIONS

### a. Mineralogy

The ore contains two niobium-bearing minerals--pyrochlore and niobian perovskite. The niobium content of both minerals is quite variable. That of the pyrochlore appears to be related to other compositional features, notably the substitution of titanium and radioactive elements, both of which increase with decreasing niobium content. Attempts have been made to correlate the

niobium content of the pyrochlore with features that might be observed readily, such as colour of the pyrochlore and the mineralogical composition of the ore, but no such direct correlation could be made.

The niobium content of the perovskite, although extremely variable, is generally lower than that of the pyrochlore. It decreases with decreasing niobium content of the ore, and appears to be directly related to the  $\text{Nb}_2\text{O}_5/\text{TiO}_2$  ratio in the ore. Decrease in niobium content of the perovskite is accompanied by a decrease in the unit cell parameter.

b. Ore Dressing

With respect to beneficiation, both pyrochlore and perovskite have higher specific gravities than most of the other minerals in the ore, which suggests the possibility of gravity concentration. The small grain size of some of the pyrochlore and the inclusions of gangue in the larger grains of pyrochlore and perovskite necessitate fine grinding if the niobium minerals are to be effectively liberated from gangue particles.

Complications in beneficiation of the ore can be anticipated, due to two factors: the compositional variations of the pyrochlore, and the presence of niobian perovskite.

The presence of pyrochlore with a relatively low niobium content may be expected to adversely affect the grade of concentrate obtainable. How serious this problem may be depends

on the amount of low-grade pyrochlore in the ore. The proportion of high- to low-grade pyrochlore in the deposit is not known, but if the samples investigated are representative, then most of the pyrochlore has a  $\text{Nb}_2\text{O}_5$  content of 50% or more. The inverse relationship found between niobium content and radioactivity of the pyrochlore might be used as a rough guide to distinguish between high-grade and low-grade pyrochlore.

The presence of niobian perovskite is an important factor because it appears to be sufficiently abundant and its niobium content sufficiently high to cause a significant loss in niobium recovery if the perovskite is not recovered. On the other hand, its niobium content is sufficiently lower than that of the pyrochlore to lower the grade of concentrate. This problem may be minimized if the very low-grade portions of the orebody can be rejected by selective mining, since this investigation has shown that the low-grade material consists predominantly of low-grade perovskite with little pyrochlore.

## ACKNOWLEDGEMENTS

The writer gratefully acknowledges the contributions made to this investigation by other officers of the Mineral Sciences Division of the Mines Branch, without which this investigation would not have been possible. Of particular importance are the chemical analyses provided by chemists of the Analytical Chemistry Subdivision, under the direction of R.C. McAdam. Spectrographic determinations were made by Miss E.M. Kranck, also of the Analytical Chemistry Subdivision. The radiometric determinations were provided by J.L. Horwood and C.M. McMahon of the Physics and Radiotracer Subdivision. J.F. Rowland of the Physical Chemistry Section contributed toward the X-ray diffraction analysis.

## REFERENCES

1. E.H. Nickel. A Mineralogical Investigation of Niobium Ore from Columbian Mining Products Limited, Oka, Quebec, Mines Branch Investigation Report IR 61-146, Department of Mines and Technical Surveys, Ottawa (1961). Industrial Confidential.
2. D.D. Hogarth. A Study of Pyrochlore and Betafite, The Canadian Mineralogist, vol. 6, pt. 5, 610-633 (1961).

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