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OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 61-146

A MINERALOGICAL INVESTIGATION OF NIOBIUM ORE FROM COLUMBIUM MINING PRODUCTS LIMITED, OKA, QUEBEC

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Ministère des Richesses Naturelles, Québec
SERVICE DES GITES MINÉRAUX
No GM- 14448

by

E. H. NICKEL

MINERAL SCIENCES DIVISION

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Mines Branch Investigation Report IR 61-146

A MINERALOGICAL INVESTIGATION OF NIOBIUM ORE FROM COLUMBIUM MINING PRODUCTS LIMITED, OKA, QUEBEC

by

E.H. Nickel*

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SUMMARY OF RESULTS

The ore from the Columbium 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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CONTENTS

	Page
Summary of Results	i
Introduction	1
Procedure	2
Results of Investigation	4
General Mineralogy	4
Niobium Mineralization	5
1. Pyrochlore	7
2. Perovskite	21
3. Pyrochlore-Perovskite Relationships	30
Other Minerals	32
Conclusions	37
Acknowledgments	39
Reference	39
Appendix	40

- - -

INTRODUCTION

One of the niobium deposits in the Oka area of Quebec has been under development by Columbium Mining Products Limited for several years. During the course of development work, which included extensive diamond drilling and experimental ore dressing, it was realized that not enough was known about the compositional variations of the niobium minerals in the deposit. A meeting was held at the Mines Branch on Nov. 25, 1960 to discuss the problem and exchange relevant background information. The discussion was attended by E.P. McDonough, Secretary of Columbium Mining Products Limited, H.L. Noblitt, metallurgical consultant, D.W. Sullivan, geological consultant, together with M.H. Haycock, Head of the Mineralogy Section and the writer, both of the Mineral Sciences Division of the Mines Branch. It was decided that a mineralogical study should be made of the ore with particular emphasis on determining variations in the niobium content of the pyrochlore, believed to be the principal niobium-bearing mineral in the ore. It was agreed that Mr. McDonough would send a number of samples from different parts of the deposit for the investigation.

As a result, 14 samples of ore were received at the Mines Branch on November 29, 1960. These were stated to be diamond drill core assay rejects, and consisted of material crushed to about minus $\frac{1}{4}$ inch. They had been selected to represent a

diversity of rock types and to span a wide range of niobium contents. At the writer's request a further shipment of 7 samples to supplement those already being studied was received on Feb. 21, 1961. All the samples were accompanied by logging data which included sample locations, descriptions of rock type and niobium contents (see Appendix).

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 and feldspar were found in only a few samples. The minerals are discussed in detail in subsequent sections.

Niobium Mineralization

Nb_2O_5 analyses of the samples as shown in Table 1 were provided by officials of Columbium 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_2O_5 (%)*	TiO_2 (%)**	Gamma-radioactivity*** (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 Columbium 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 $A_{16-x}B_{16}(O,OH)_{48}(F,OH)_8$ [1]. 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 (see Appendix). Hogarth[1] 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 Columbium 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.

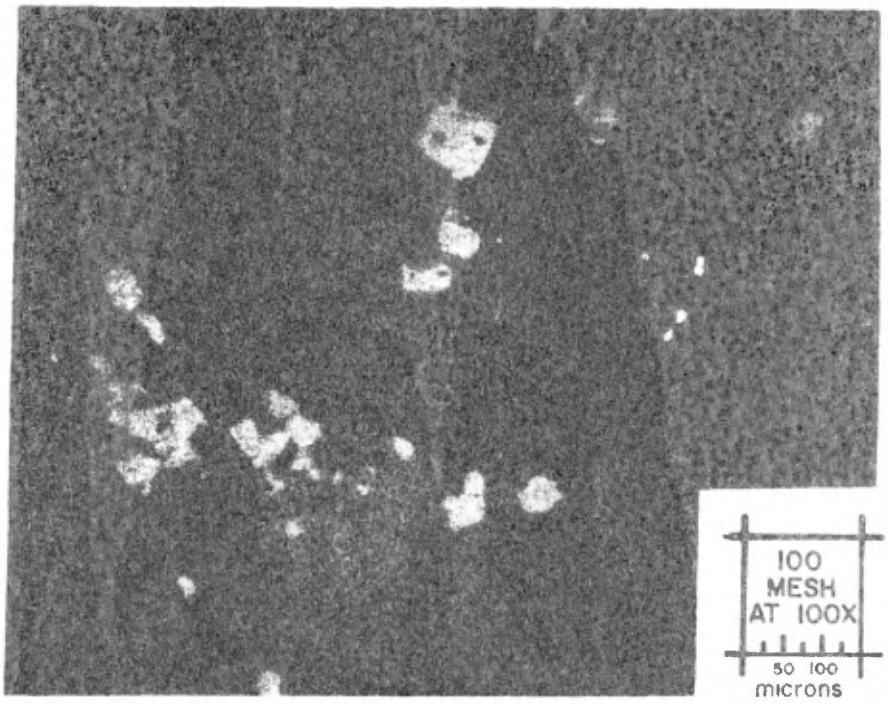


Figure 1 - Photomicrograph of polished section of sample No. 396, showing small disseminated grains of pyrochlore (white) in a matrix of calcite and dolomite (grey). Pits are black.

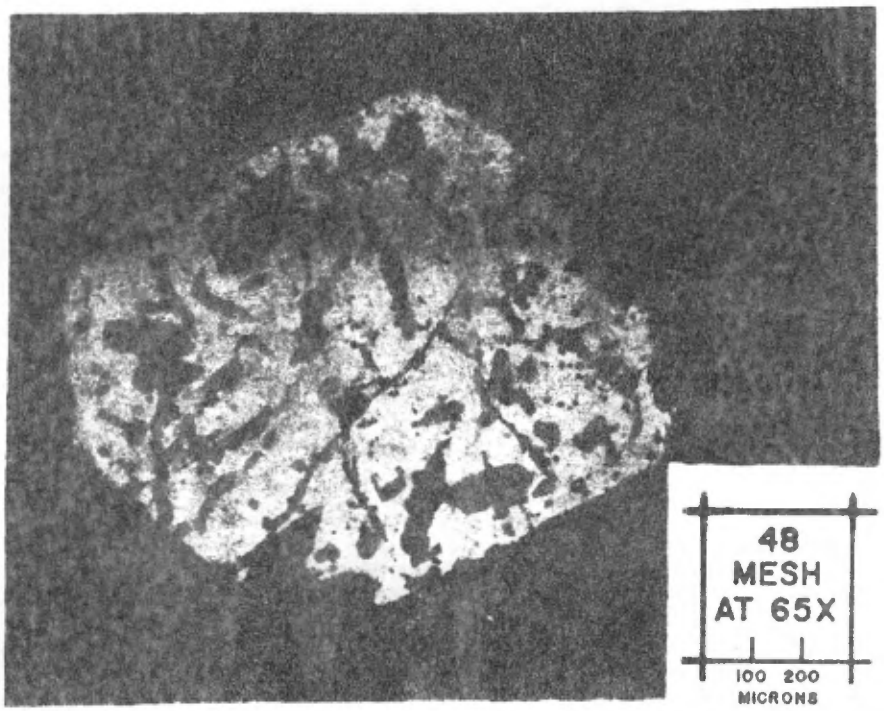


Figure 2 - Photomicrograph of polished section of sample No. 393, showing a relatively large crystal of pyrochlore (white) in calcite (grey). The pyrochlore crystal contains abundant inclusions of calcite. Pits are black.

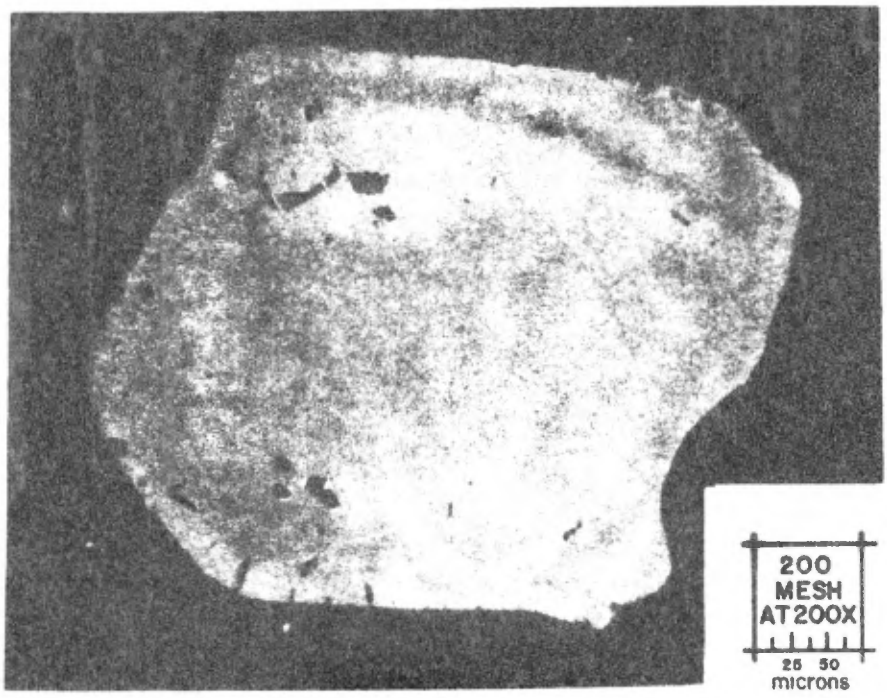


Figure 3 - Photomicrograph (oil immersion) of polished section of a zoned pyrochlore crystal from sample No. 447. The zones are roughly parallel to the external faces of the crystal.

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% Nb_2O_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 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 Contents of Ore Samples and Pyrochlore Concentrates

Sample No.	Nb_2O_5 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_2O_5.

** 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 Nb_2O_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 Nb_2O_5 content, and vice versa, as shown in Figure 5.

TABLE 3

Nb_2O_5 Content of Pyrochlore as Related to Radioactivity of the Pyrochlore and that of the Ore Samples

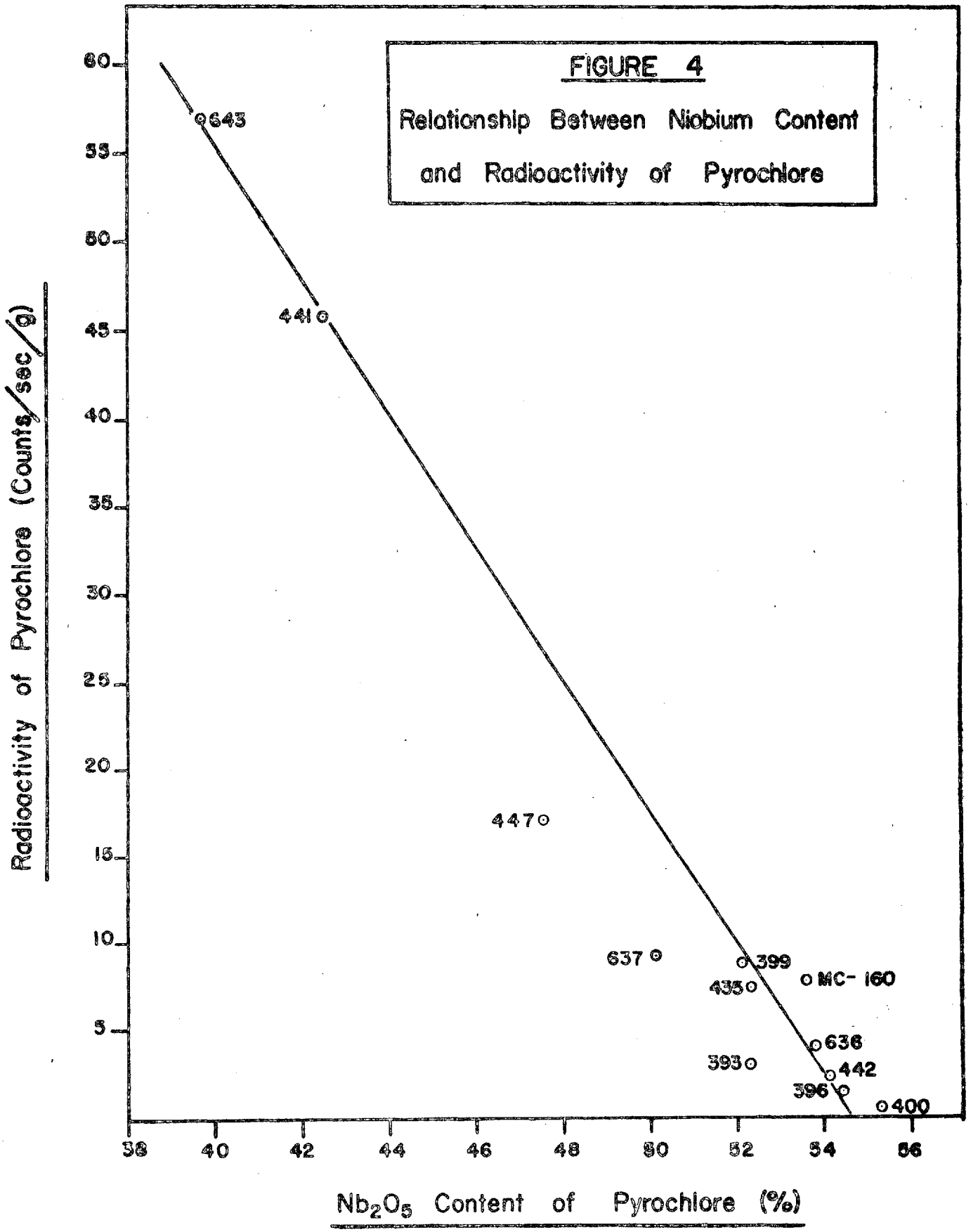
Sample No.	Nb_2O_5 Content* of Pyrochlore (%)	Gamma-Radioactivity	
		Pyrochlore** (counts/sec/g)	Ore Sample*** (counts/sec/100 g)
400	55.2	0.51	0.20
396	54.4	1.34	0.98
442	54.0	2.20	2.56
636	53.7	4.09	3.91
MC-160	53.5	7.69	8.93
393	52.2	2.92	1.40
435	52.2	7.35	4.44
399	52.0	8.75	3.35
637	50.0	9.09	38.79
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_2O_5 content.

** Radiometric analyses by C.M. McMahon, Physics and Radiotracer 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, which explains the rather poor correlation between the Nb_2O_5 content of the pyrochlore and the radioactivity of the ore.


FIGURE 4
Relationship Between Niobium Content and Radioactivity of Pyrochlore
Radioactivity of Pyrochlore (Counts/sec/g)
60
55
50
45
40
35
30
25
20
15
10
5
643
441
447
637
399
435
MC-160
636
393
442
396
400
38
40
42
44
46
48
50
52
54
56
Nb2O5 Content of Pyrochlore (%)

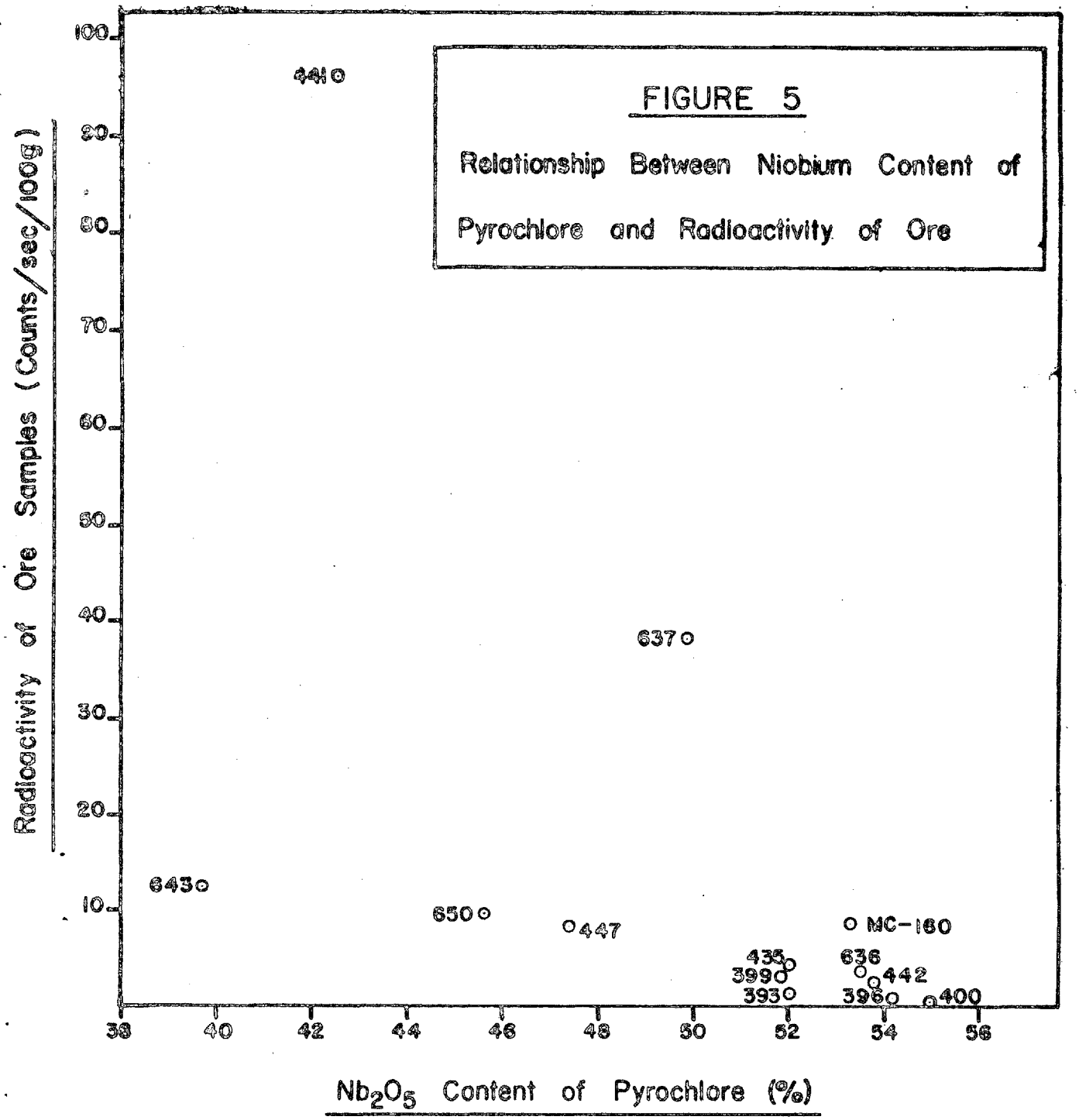


FIGURE 5

Relationship Between Niobium Content of Pyrochlore and Radioactivity of Ore

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_2 (%)*	Nb_2O_5 (%)**	U + Th (%)***
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 Nb_2O_5: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 Nb_2O_5 content of the pyrochlore. Table 6, however, shows that there is no consistent relationship between the Nb_2O_5:TiO_2 ratio in the ore and the Nb_2O_5 content of the pyrochlore. Any relationship that might have existed has probably been obscured by the presence of perovskite since it contains major amounts of both niobium and titanium.

TABLE 6

Relationship Between the Nb_2O_5:TiO_2 Ratio in the Ore and the Nb_2O_5 Content of the Pyrochlore

Sample No.	Nb_2O_5:TiO_2* in Ore	Nb_2O_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_2O_5 (%)**
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 10.38A, 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 $CaTiO_3$, 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.

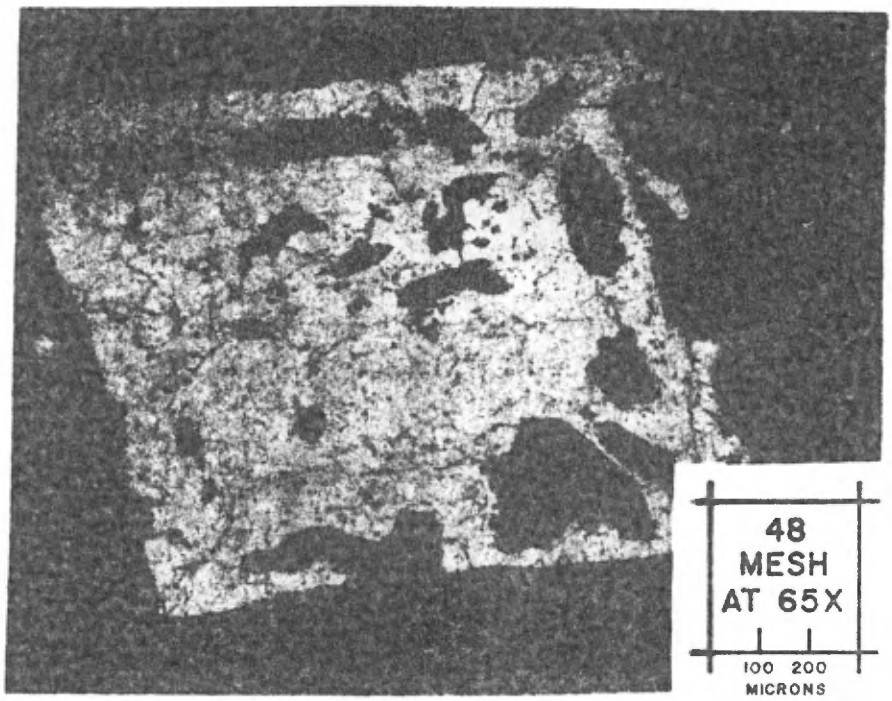


Figure 6 - Photomicrograph of polished section of sample No. 400, showing a relatively large crystal of perovskite (light grey) in calcite (dark grey). The perovskite crystal contains numerous large calcite inclusions.

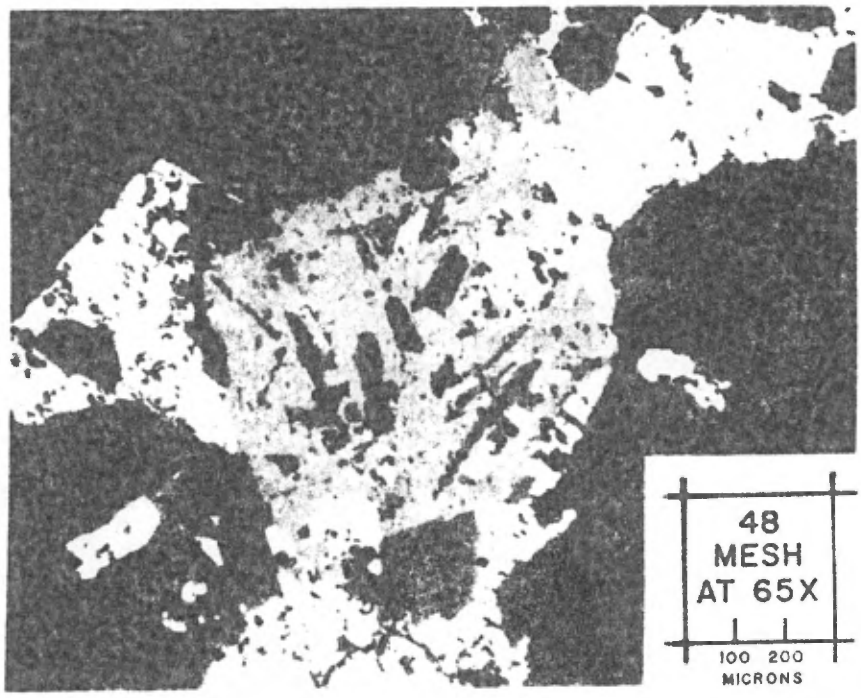


Figure 7 - Photomicrograph of polished section of sample No. 396, showing a perovskite crystal (light grey) partially surrounded by pyrrhotite (white), and containing inclusions of calcite (dark grey) and pyrrhotite. The surrounding gangue minerals are calcite and pyroxene.

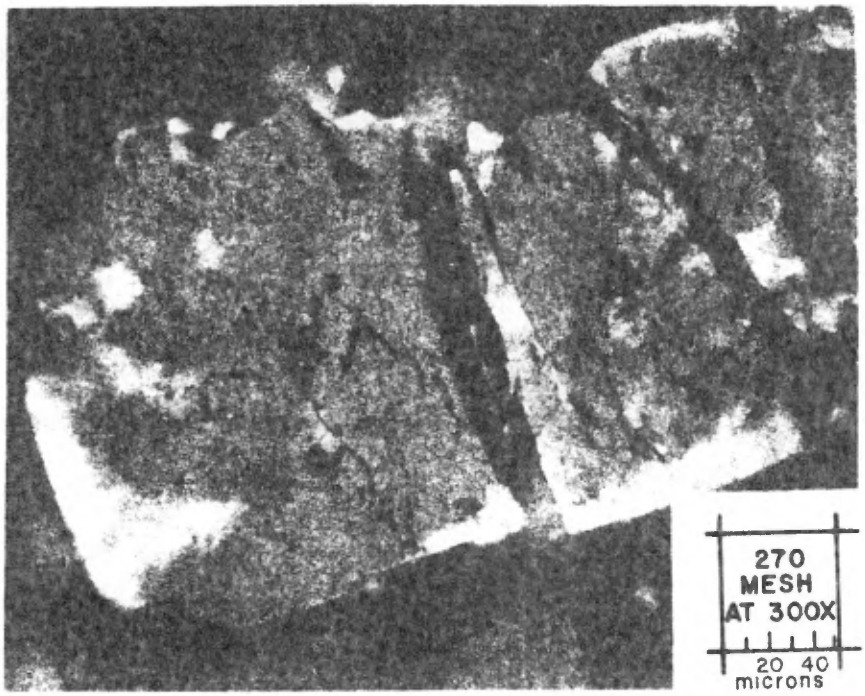


Figure 8 - Photomicrograph of polished section of sample No. 396 in oil immersion and Nicols partly crossed. This shows a perovskite crystal (light grey) with some intimately associated pyrochlore (white). The tendency of the pyrochlore to occur along the margins of the perovskite indicates pseudomorphous 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. Its cell dimensions may, however, be expressed in terms of a pseudo-cubic unit cell with a unit cell

parameter, in the case of sample MC-233 of 7.724A. According to powder diffraction photographs, the value for this sample is 7.739A. It will be shown later that the cell parameters of the perovskite vary appreciably.

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_2O	4.03
R.E. Oxides	2.03
K_2O	0.03
Nb_2O_5	43.90
TiO_2	10.05
Fe_2O_3	8.74
MgO	2.20
MnO	0.77
SiO_2	0.45
Loss on ign.*	1.55
	99.70

* Includes 0.90% S and 0.36% H_2O.

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 amount 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: $(Ca_{0.76}Na_{0.21}R.E._{0.02})(Nb_{0.54}Ti_{0.21}Fe_{0.16}Mg_{0.08}Mn_{0.02})O_{3.01}$, or, in a more simplified form: $(Ca, etc.)_{0.99}(Nb, etc.)_{1.01}O_{3.01}$. 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_2O	4.19	Na	3.11	0.1353	0.21	0.99 = A
R.E. Oxides	2.11	Ce	1.72	0.0123	0.02	
K_2O	0.03	K	0.02	0.0005	--	
Nb_2O_5	45.62	Nb	31.89	0.3432	0.54	
TiO_2	10.45	Ti	6.26	0.1307	0.21	
Fe_2O_3	7.92	Fe	5.54	0.0992	0.16	1.01 = B
MgO	2.13	Mg	1.28	0.0526	0.08	
MnO	0.80	Mn	0.62	0.0113	0.02	
	100.00	O	30.44	1.9025	3.01	
			100.00	3.1646	5.01	

* See text

** 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 Nb_2O_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 Nb_2O_5 content of the perovskite varies over a wide range, values from 14.5% to 47.5% Nb_2O_5 having been obtained.

TABLE 11

The Niobium Content of Perovskites from Different Samples

Sample No.	Nb_2O_5 (%)**
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 Nb_2O_5 content of the perovskite is compared with the Nb_2O_5: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_2O_5 Content of Perovskite to its Cell Parameter and the Nb_2O_5:TiO_2 Ratio of the Ore

Sample No.	Nb_2O_5 (%)*	Cell Parameter** (A)	Nb_2O_5:TiO_2*** 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_o, calculated from X-ray powder patterns.

*** Calculated from values shown in Table 1.

Table 12 also shows that the pseudo-cubic cell edge a_o, as measured from X-ray powder diffraction patterns, decreases with decreasing Nb_2O_5 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 Nb_2O_5 content. Perovskite, on the other hand, predominates in samples with a low Nb_2O_5 content.

All the samples from which pyrochlore and/or perovskite were concentrated in sufficient amounts for analysis are shown in Table 11, 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_2O_5 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 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 Nb_2O_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.

Other Minerals

A variety of carbonate minerals has been found in the ore. Calcite greatly preponderates over the other carbonates, and is the most abundant mineral in the ore. It is white in colour, and varies from transparent to translucent. A spectrographic analysis of calcite concentrated from sample No. 400 is shown in Table 14. The strontium, magnesium and manganese shown are probably in chemical combination with the calcite; the other elements shown are probably due largely to contamination by other minerals.

The other carbonate minerals occur as extremely fine-grained irregular aggregates, commonly intergrown with each other and with silicate minerals. As such, they have the appearance of secondary minerals formed by the alteration or decomposition of earlier minerals. Of these carbonate minerals, dolomite is the most common. It exhibits wide colour variations from bluish-green to red. Some of the bluish-green aggregates have cores of hornblende, which suggests that at least some of the dolomite is a secondary alteration product of this mineral. Other carbonate minerals found in the ore include magnesite, siderite and strontianite. These were found in only small amounts, generally as intergrowths with dolomite or calcite.

Apatite was found in almost all of the samples. It is clear and colourless, and occurs in granular aggregates. A semi-quantitative spectrographic analysis of apatite concentrated from sample No. 400 is shown in Table 14. The strontium and arsenic content of the apatite is of particular interest, since these elements are probably in chemical combination with the apatite, the strontium substituting for calcium, and arsenic for phosphorus. The silicon content is unusually high. It is unlikely that this much silicon would be due only to contamination by silicate minerals, since the principal silicates present in the ore also contain major amounts of magnesium and/or iron, both of which are relatively low in the spectrographic analysis. This suggests that there may be some

TABLE 14

Semi-Quantitative Spectrographic Analyses of Calcite, Apatite, and Pyroxene

	Calcite	Apatite	Pyroxene
Ca	pc	pc	pc
Sr	1%	1%	0.1%
Na	nd	nd	0.7
Mg	0.2	0.2	9
Fe	0.03	0.05	6
Mn	0.2	0.1	1
P	0.3	pc	nd
Si	0.2	2	pc
Al	0.01	0.02	0.6
Nb	0.01	0.1	0.1
V	0.003	0.1	0.04
Ti	0.001	0.007	0.15
Ba	0.06	0.02	0.01
As	nd	0.2	0.2
Cr	nd	nd	0.04
Ni	nd	nd	0.01

(nd = not detected; pc = principal constituent)

Analyst: Miss E.M. Kranck, Analytical Chemistry Subdivision, Mineral Sciences Division.

replacement of phosphorus by silicon in the apatite structure, as is the case in silicate-apatites.

The principal ferromagnesian silicates in the ore are pyroxene and biotite, and are primarily responsible for the dark colour exhibited by some of the ore. Pyroxene is one of the principal minerals in the ore, although generally subordinate to calcite. It is green in colour, and occurs both as granular aggregates and as disseminated grains in calcite. Its spectrographic analysis (Table 14) indicates that the principal constituents are calcium, magnesium, iron, and silicon. The pyroxene is therefore most likely an intermediate member of the diopside-hedenbergite series. This is confirmed by refractive index measurements of the pyroxene.

Biotite is common in the ore. It is black in colour, and occurs as disseminated flakes and as relatively coarse aggregates.

Monticellite, a calcium-magnesium silicate, was found in most of the samples. It is light brown to pink in colour, is transparent, and occurs as relatively large disseminated grains.

Hornblende was found in only a few of the samples. It appears to have been largely altered to dolomite.

Small amounts of nepheline were found in some of the samples.

Zeolite minerals identified in the ore are analcite and natrolite. These minerals are white to cream-coloured, and are extremely fine-grained, commonly intergrown with carbonate

minerals. The zeolites are probably secondary alteration products, possibly after nepheline.

Some black garnet has been found in the ore. Its unit cell parameter corresponds to that of andradite, a calcium-iron variety.

Magnetite is the most abundant opaque mineral in the ore. It occurs chiefly as disseminated grains irregularly distributed throughout the samples.

Sulphide minerals, chiefly pyrite and pyrrhotite, with a very small amount of chalcopyrite, occur in the samples in varying proportions, chiefly as disseminated grains. Some of the pyrrhotite exhibits peripheral oxidation to pyrite and magnetite. In some of the samples the pyrrhotite has been largely replaced by a fine-grained intergrowth of pyrite and magnetite. This oxidation may be expressed by the equation $6FeS + 2\ O_2 \longrightarrow 3FeS_2 + Fe_3O_4$. In a few instances, the oxidation has proceeded further, with the partial conversion of magnetite into hematite.

Other minerals found in the ore in small amounts are feldspar, zircon, barite and fluorite. Some samples also contain small amounts of a red radioactive material as thin films around other mineral grains. It could not be identified, but is probably responsible for the anomalously high radioactivity in a few of the samples which cannot be correlated with the radioactive element content of the pyrochlore.

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 Nb_2O_5/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 the most of the pyrochlore has a Nb_2O_5 content of 50% or better. 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.

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APPENDIX

COMPILED FROM DIAMOND DRILL CORE LOGGING DATA SUPPLIED BY COLUMBIUM MINING PRODUCTS LIMITED

Sample No.	Hole No.	From (ft)	To (ft)	% Nb_2O_5	Log
393	71	45	55	.60	Greyish-blue crystalline limestone, 25% access. mins. Some bands in limestone have considerable greenish diopside, blue sodalite, reddish nephelite ? and brownish monticellite. Much dark red pyrochlore and some straw coloured betafite ? and perovskite the darker bands in limestone. Lineation variable from 30° to 50° to core axis. There seems to be more yellowish to cream coloured calcite from 45′ on. Limestone has different overall appearance and mineral content than it has further northwest on strike, towards holes 64, 73.
395	71	62	68.5	.29	Ijolite 95%, dark green, partially biotitized and cut by calcite veinlets. Much apatite in places. Fair to good pyrochlore in the soda pyroxene - calcite - biotite sections.
396	71	68.5	75.5	.55	Grey to bluish limestone, 25% access. mins. as above. Fairly good pyrochlore. One 3 in. long area of completely biotitized limestone.
399	71	95	105	.33	Ijolite 80%, dark green fine-grained. Altered in places to biotite and apatite. Occasional band of limestone and some calcite veinlets. Some very good pyrochlore in some apatite - calcite - biotite rock in the limestone and also within the altered ijolite. Some light grey patches in the ijolite may be nepheline okaite (see 76′ to 80′)

Sample No.	Hole No.	From (ft)	To (ft)	% Nb_2O_5	Log
400	71	105	115	.88	Grey to yellowish limestone. 30 - 40% access. minerals. Much monticellite. Some sodalite, vesuvianite, diopside and fluorite, the latter occurring at contact of a band of ijolite - okaite rock.
435	73	35	45	.54	Ijolite, massive to brecciated and biotitized. Cut by calcite veinlets in the biotitized areas. The ijolite alternates with a dark grey limestone with 25% access. mins. Some pyrochlore within the altered ijolite and limestone and along the contacts of limestone and ijolite. Ijolite to limestone ratio 90:10.
441	73	95	105	1.11	Ijolite, altered, mostly biotitized and minor calcite. Much pyrochlore not only in slightly altered ijolite now but in rich bands of soda pyroxene - calcite - biotite - pyrochlore rock. More pyrochlore in the less altered ijolite than in holes to the southeast.
442	73	105	115	.43	Grey limestone 25% access. mins. Some good pyrochlore in the apatite - calcite - biotite bands in limestone and in the soda pyroxene - calcite - biotite - pyrochlore rock. Good lineation in limestone in places at 45° to 55° to core axis. Some intrusive bands of ijolite slightly altered, some biotitization and occasional 1′ to 2′ zones of good pyroxene - calcite - biotite - pyrochlore rock.

Sample No.	Hole No.	From (ft)	To (ft)	% Nb_2O_5	Log
447	73	150	160	.37	Grey massive crystalline limestone with 25 to 30% access. mins. Several bands of fine apatite - calcite - biotite rock some with good pyrochlore. Good lineation at 40° - 50°.
636	64	19	28	.68	Ijolite brecciated and almost completely altered. Much biotite and altered with limestone. Some very good pyrochlore in ijolite and limestone.
637	64	28	38	.47	Grey crystalline limestone 25% access. mins. Some bands of apatite - calcite - biotite rock rich in pyrochlore.
643	64	90	100	.51	Yellowish-grey limestone 30% access. mins. Fair pyrochlore.
644	64	100	110	.16	Yellowish and grey limestone interbanded. Some pyrochlore in dark bands in apatite rich grey limestone.
650	64	160	171	.39	Grey limestone with several bands apatite - calcite - biotite rock with pyrochlore. Few zones of altered ijolite as 164 to 167. Good pyrochlore both contacts.
MC-137	16	250	265	.34	All crystalline limestone disseminated with magnetite and biotite many brown crystals pyrochlore. Radioactivity more than 2 x normal.
MC-138	16	265	275	.56	Nearly all magnetite and biotite just a little limestone. Radioactivity more than 2 x normal.

Sample No.	Hole No.	From (ft)	To (ft)	% Nb_2O_5	Log
MC-160	16	675	700	.99	Exactly same as (650-675) except more pyrochlore which is quite plentiful but it appears there is betafite associated. Radioactivity 2 x normal.
MC-233	21	50	75	0.16	Crystalline limestone with up to 25% acc. including biotite, magnetite, soda pyroxene and monticellite.
MC-245	21	350	375	0.19	350-352: Limestone. 352-355: Skarn: over 50% magnetite and biotite plus calcite and apatite. Good very radioactive pyro at 354. 355-367.5: Br. ij. with fair biotite. 367.5-375: Massive lim. with 10-15% acc. Radioactivity 2 x normal.
MC-249	21	450	475	0.16	Massive, white, med. to coarse crystalline lim. with 10-15% acc. including some monticellite. Minor pyro at 456.4.
MC-254	21	575	600	0.19	Same as above, more bluish. Minor pyro at 492. Radioactivity 2½ x normal.