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A MINERALOGICAL EXAMINATION OF NIOBIUM-BEARING SAMPLES FROM ST. ANDRÉ, QUEBEC, SUBMITTED BY SOQUEM

by

E. H. NICKEL AND D. R. OWENS

MINERAL SCIENCES DIVISION

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ABSTRACT

A mineralogical examination has been made of three sets of samples of niobium-bearing rock from St. André, Quebec. Most of the samples consist predominantly of carbonate minerals, chiefly dolomite and calcite, but also contain appreciable amounts of apatite and pyrite. Several of the samples are heavily indurated by iron oxides and hydroxides. Two niobium-bearing minerals were found -- pyrochlore and a niobian rutile, with pyrochlore predominating. The pyrochlore has a variable composition, with Nb_2O_5 contents ranging between 55% and 67%. Some of the pyrochlore also contains relatively large amounts of Ta_2O_5, BaO, SrO and FeO. The niobian rutile has a variable niobium content, variations between about 4% and 24% Nb_2O_5 having been detected. The presence of the niobian rutile can be expected to complicate the recovery of niobium from the ore.

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Direction des mines

Rapport d'investigation IR 70-36

ÉTUDE MINÉRALOGIQUE D'ÉCHANTILLONS NIOBIUMIFÈRES PROVENANT DE SAINT-ANDRÉ, AU QUÉBEC, SOUMIS PAR SOQUEM

par

E. H. Nickel* et D. R. Owens**

RESUMÉ

Trois séries d'échantillons de roche niobiumifère prélevés à Saint-André, au Québec, ont fait l'objet d'une étude minéralogique. La plupart des échantillons renferment une forte proportion de minéraux carbonatés, principalement de la dolomite et de la calcite, mais contiennent aussi des quantités appréciables d'apatite et de pyrite. Plusieurs d'entre eux sont fortement indurés par des oxydes et des hydroxydes de fer. On a découvert deux minéraux niobiumifères, le pyrochlore et un rutile niobique, mais le pyrochlore demeure l'élément prédominant, étant de composition variable, avec des teneurs en Nb_2O_5 allant de 55 à 67 p. 100. Quelques pyrochlores contiennent aussi des quantités relativement importantes de Ta_2O_5, de BaO, de SrO et de FeO. Le rutile niobique contient du niobium en quantité variable; on a relevé des teneurs allant de 4 à 24 p. 100 en Nb_2O_5. On peut s'attendre à ce que la présence du rutile niobique rende plus difficile la récupération du niobium contenu dans le minerai.

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INTRODUCTION

On April 24, 1970, a small shipment of samples was received from Mr. Marcel Vallée, project manager of SOQUEM, 2382 Ste. Foy Road, Ste. Foy, Quebec. In an accompanying letter to Mr. H.M. Woodrooffe, Chief of the Mineral Processing Division, Mr. Vallée reported that the samples were obtained from three columbium-bearing zones of a carbonatite complex at St. André, Argenteuil County, Quebec. The samples, and accompanying details, are as follows:

Lot 1: Drill hole 709-02, 47 ft. to 187.6 ft. : 0.71% Nb_2O_5.
Samples at 77 ft. and 112 ft.

Lot 2: Drill hole 709-02, 340 ft. to 400 ft. : 0.71% Nb_2O_5.
Samples at 342 ft., 357 ft., 373.5 ft., 385 ft. and 396 ft.

Lot 3: Drill hole 709-03, 16 ft. to 100 ft. : 0.49% Nb_2O_5.
Samples at 29 ft., 46 ft., 64 ft., 78 ft. and 90 ft.

In the text of this report, samples will be identified by lot number and footage, as for example, 2-373.5 (this means lot 2, at 373.5 ft.).

Mr. Vallée requested that the niobium-bearing minerals, and associated minerals, be identified, that estimates be made of the granulometry of the pyrochlore, and that the Nb_2O_5 content of the pyrochlore be determined.

PROCEDURE

A polished section was made from each of the samples received. These polished sections were examined under an ore microscope, and most of them were also examined by an electron microprobe analyzer. Thin sections and heavy-liquid separations were made from several of the samples to assist in identifying and characterizing some of the minerals.

All analyses were made with the electron microprobe analyzer, using appropriate standards and making the usual corrections. The quantitative analyses are restricted to very small areas and should not be taken for average compositions. X-ray scanning photographs were made of one zoned pyrochlore crystal to illustrate the compositional variations.

RESULTS OF INVESTIGATION

General Descriptions of Samples

Lot 1: Both samples (77 ft. and 112 ft.) are porous and friable, and heavily indurated by iron oxides. The principal mineral appears to be dolomite, which is veined and coated by goethite. Apatite and hematite are moderately abundant. Small amounts of a mineral high in manganese was found by the electron microprobe. This mineral did not give an X-ray diffraction pattern, and it can be concluded that the mineral is probably an amorphous manganese oxide. Pyrochlore occurs as disseminated grains through a wide size range, with the majority coarser than 325 mesh. The largest grains observed were about 200 microns in size.

Niobian rutile could not be positively identified in the samples because of its similarity to the abundant goethite and hematite. However, some qualitative electron microprobe traverses across the polished sections showed some mineral grains that are compositionally similar to niobian rutile, hence the presence of this mineral can therefore be assumed.

Lot 2: These samples consist largely of white rock, mottled with grey and yellow patches. Carbonate minerals predominate in all the samples. There is a variety of carbonate minerals, including calcite, dolomite, ankerite and siderite. Dolomite appears to be the most abundant of the carbonate minerals; it, like the calcite, is generally white in colour. The yellowish-brown carbonates appear to be predominantly ankerite, with some siderite. Both the ankerite and siderite contain appreciable amounts of manganese.

Pyrite is present in all the samples, and apatite in most. The pyrite is generally in the form of coarse grains, but in one of the samples (396 ft.) it also occurs as fine filigree veinlets in the carbonate. Relatively minor amounts of feldspar, hematite and quartz were also observed.

Pyrochlore was observed in all the samples. It is irregularly distributed, as disseminated grains in the carbonate minerals. The pyrochlore varies greatly in grain size. In the sample from 373.5 ft., most of the pyrochlore is finer than 325 mesh. In contrast, the pyrochlore at 385 ft. is relatively coarse, with most of the grains larger than 65 mesh; the largest grains are up to about 0.5 mm in size. Other samples exhibit a wide size range. In general, however, the majority of the pyrochlore appears to be coarser than 325 mesh.

Niobian rutile was found in all the samples from this lot. It is not as abundant as the pyrochlore, and is generally finer-grained, rarely exceeding 75 microns (about 200 mesh) in size.

Lot 3: These samples are similar in appearance to those in Lot 2, and the mineralogical compositions of the samples, with the exception of the sample at 29 ft. are also similar to the samples in Lot 2. The sample at 29 ft. is exceptional in that it contains only very minor amounts of carbonate minerals, and a high percentage of apatite. Hematite is also abundant in this sample both as coarse grains and as fine disseminations. Some barite was also identified. This sample (29 ft.) contains more pyrochlore than any of the other samples in the shipment. The pyrochlore in the samples of Lot 3, like that in Lot 2, occurs as disseminated grains, through a wide range of sizes, but the majority appears to be coarser than 325 mesh.

Niobian rutile does not appear to be as common in the samples of Lot 3 as in Lot 2, and was found in only about half of the samples.

Compositional and Textural Features of the Niobium Minerals

a) Pyrochlore

The pyrochlore exhibits pronounced variations in composition, within, as well as between samples. No attempt was made to arrive at an average composition because the samples submitted were spot samples and are not necessarily representative of the entire body. However, several grains from different samples were analyzed by the electron microprobe analyzer to illustrate the variations in composition. The results are shown in Table 1.

TABLE 1

Results of Electron Microprobe Analyses of Several Pyrochlores

		1-77: Zoned Crystal		1-77: Composite Crystal	
	2-385	Core	Edge	a	b
Nb_2O_5	67.3	65.9	58.4	65.5	55.5
Ta_2O_5	-	0.2	3.3	2.0	5.2
TiO_2	2.9	1.9	1.7	2.0	2.0
FeO	0.1	-	0.4	0.2	0.8
CaO	15.2	17.0	0.9	17.1	1.5
Na_2O	5.9	n.d.	n.d.	n.d.	n.d.
BaO	4.9	-	7.5	0.1	8.0
SrO	1.3	1.3	11.7	0.3	12.2
Totals	97.6	86.2	83.9	87.2	85.2

(n.d. = not determined).

Several comments should be made on the results shown in Table 1. The analysis of sample 2-385 is the most complete of the analyses. It does not total 100% because fluorine and water, common constituents of pyrochlore, could not be determined by the electron microprobe. The other analyses are less complete because Na_2O was not determined.

In spite of the analyses being incomplete, the results nevertheless demonstrate the major compositional variations. The apparent substitution of CaO by SrO and BaO in two of the analyses of pyrochlore from sample 1-77 is particluarly striking. Such barium-strontium pyrochlores have been referred to as "pandaite" in the literature. It is interesting to note such extreme compositional differences within one crystal, and this is illustrated by the electron-microprobe scanning photographs made from the analyzed zoned crystal in sample no. 1-77 (Figure 1). The analyzed pyrochlore from sample 2-385 shows only moderate amounts of BaO and SrO, which indicates that all degrees of substitution of CaO by BaO and SrO may be present in the pyrochlores from this deposit.

Figure 1(a). Electron back-scatter image: Lighter areas indicate elements with higher atomic numbers than the darker areas.

Figure 1. (continued).

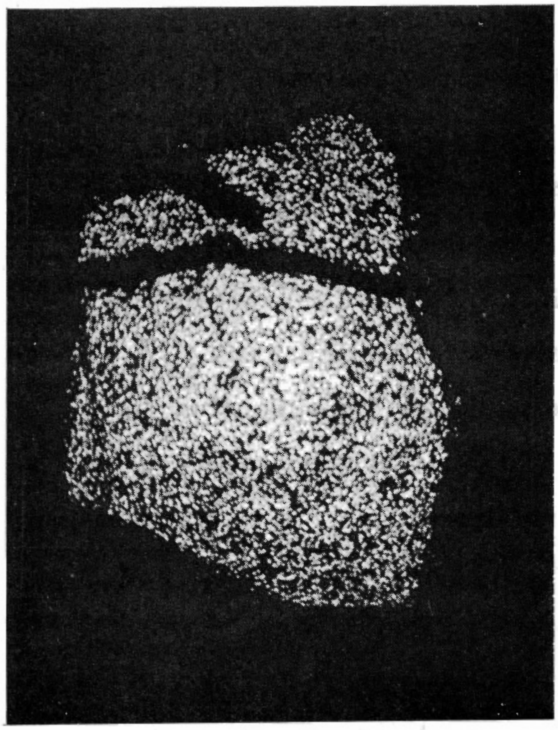

Figure 1(b). X-ray image for Nb Lα.

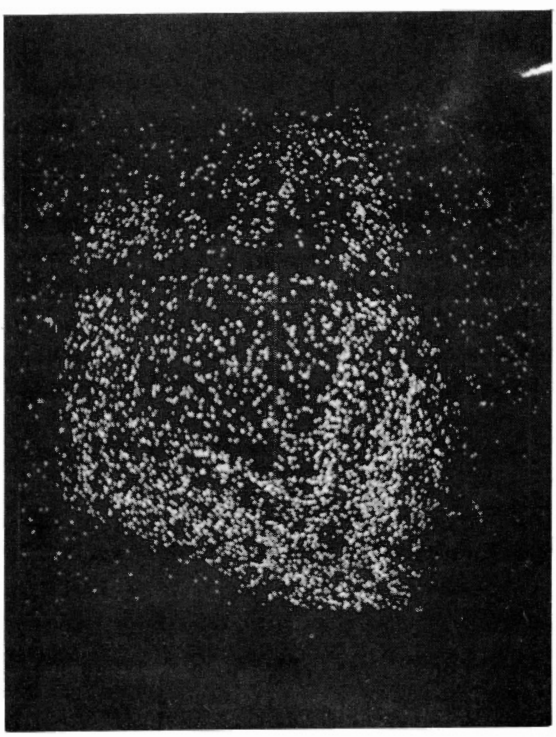

Figure 1(c). X-ray image for Ta Lα.

Figure 1. (continued).

Figure 1(d). X-ray image for Ca Kα.

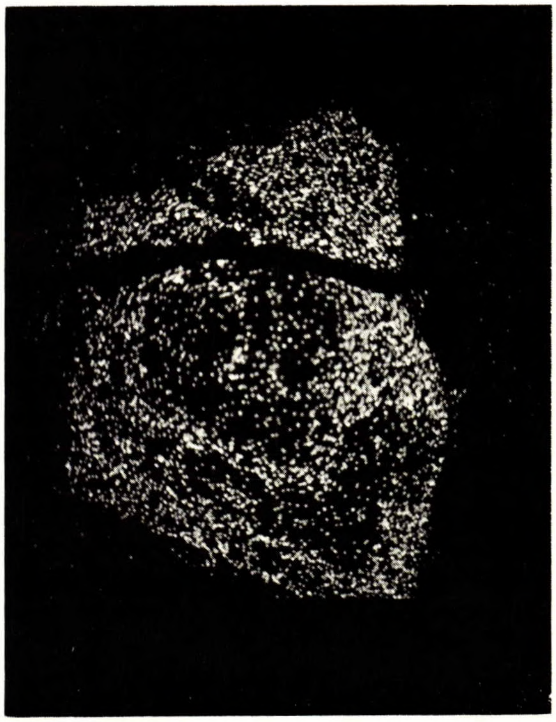

Figure 1(e). X-ray image for Sr Lα.

Figure 1. (continued).

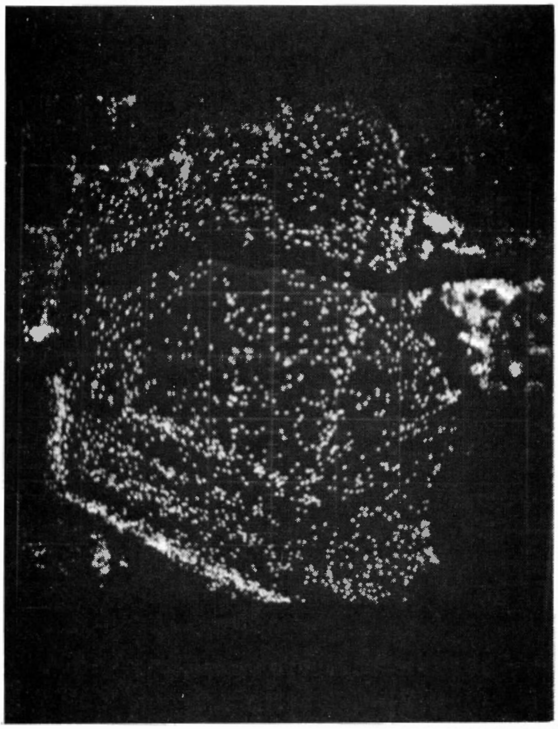

Figure 1(f). X-ray image for Fe Kα.

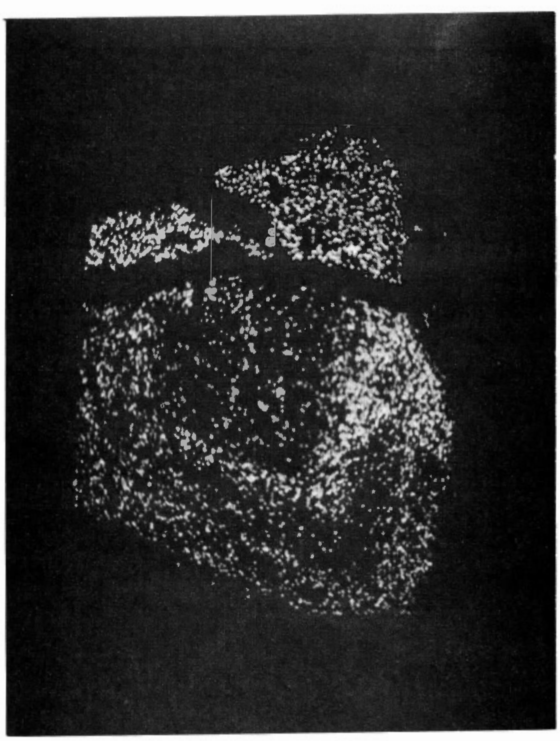

Figure 1(g). X-ray image for Ba Kα.

Figure 1. Electron back scatter and X-ray images of zoned pyrochlore grain, sample 1-77.

X-ray diffraction patterns of the zoned pyrochlore confirm the existence of two pyrochlores, since the patterns consist of two sets of lines, one set representing normal pyrochlore and the other set corresponding to a larger unit cell, attributable to the barian-strontian variety.

The relatively high Ta_2O_5 content in several of the samples is also worth noting.

Most of the pyrochlore is creamy white in colour, including the analyzed pyrochlores shown in Table 1. In several samples, however, the pyrochlore is reddish brown, as in sample 2-357, for example. In sample 2-373.5, some of the pyrochlore crystals have a reddish-brown core and a white margin (Figure 2). Electron microprobe analysis showed that the reddish-brown pyrochlore forming the core contains about 5% iron, which is much higher than any of the analyses shown in Table 1. It can be concluded therefore, that the reddish-brown colour can be attributed to iron. The reddish-brown pyrochlore in sample 2-357 contains an abundance of very fine-grained inclusions that could not be positively identified (Figure 3), but which have a high iron content, and are probably some form of iron oxide or hydroxide. This suggests that the iron content of that pyrochlore was so high that not all the iron could be accommodated in the pyrochlore lattice, and that it therefore separated out in the form of iron oxide inclusions.

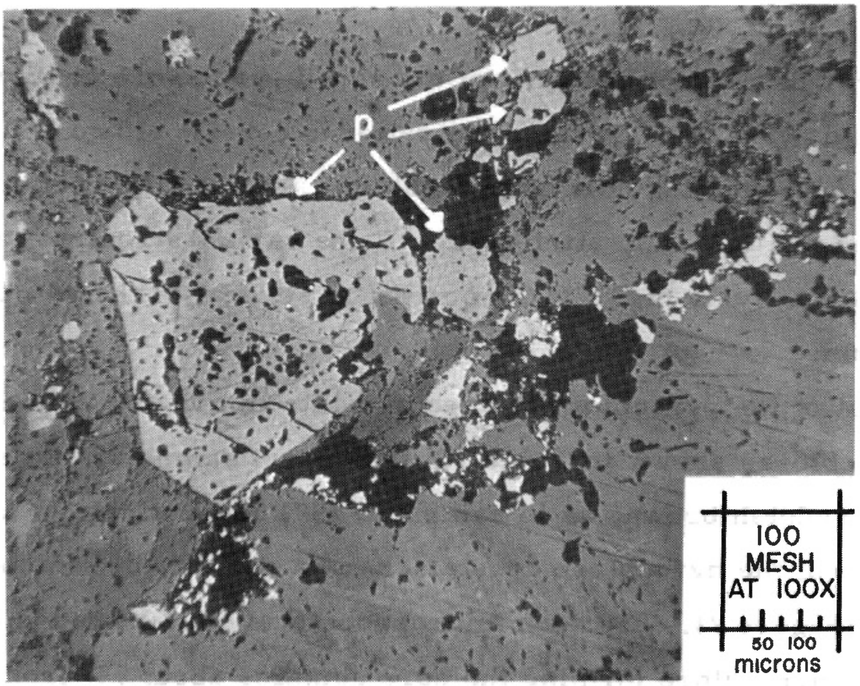

Figure 2. Polished section of sample 2-373.5, showing a large euhedral crystal and some smaller anhedral grains of pyrochlore (light grey, marked by arrows) and many small grains of niobian rutile. The niobian rutile (also light grey) occurs in the irregular band running diagonally across the photograph, and is not readily distinguished from the pyrochlore in this reproduction. Black areas are polishing pits. The large pyrochlore crystal has a darker core, which is reddish brown in oblique illumination.

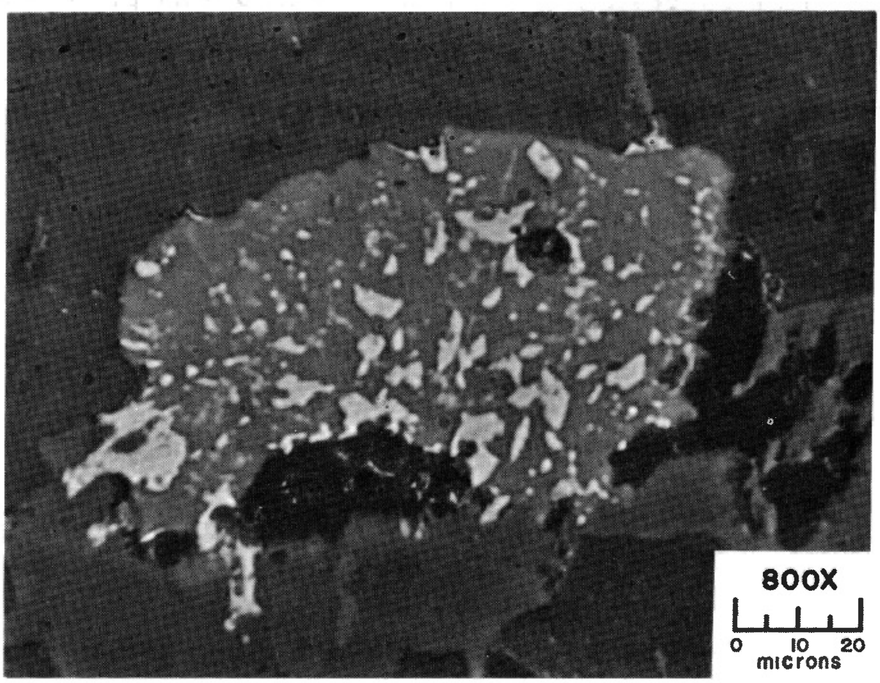

Figure 3. Polished section of sample 2-357 showing an irregular pyrochlore grain (medium grey) with abundant inclusions of iron oxides (light grey).

Some of the pyrochlore (Figure 2, for example) is euhedral, or shows the development of some crystal facets. Most grains, however, do not exhibit crystal facets, and have generally rounded outlines. Although the pyrochlore in one sample contains inclusions of iron oxides (Figure 3), the pyrochlore from the other samples generally does not contain appreciable amounts of inclusions, either of gangue minerals, or of the niobian rutile.

b) Niobian Rutile

This mineral has the rutile structure, but may contain substantial amounts of niobium and tantalum. (Some Norwegian material has been reported to contain 32% Nb_2O_5). The mineral is sometimes also referred to as "ilmenorutile", but the authors prefer to use the more descriptive term, "niobian rutile".

The composition of the niobian rutile does not appear to be uniform, particularly with respect to its niobium content. Several mineral grains from sample 2-373.5 (shown in Figure 2) were analyzed by the electron microprobe, with the results shown in Table 2.

TABLE 2

Electron Microprobe Analysis of Niobian Rutile from Sample 2-373.5

Oxide	Wt.%*	Wt.% (Corr.)**
TiO_2	77.6	77.1
Nb_2O_5	18.1	18.0
FeO	4.9	4.9
CaO	0.4	--
K_2O	0.3	--
	101.3	100.0

*Converted from elemental percentages.

**CaO and K_2O subtracted, and remainder calculated to 100%.

Semi-quantitative analyses of grains of niobian rutile from other samples indicated Nb_2O_5 contents varying between about 4 and 24% Nb_2O_5, and even greater extremes may be present. The average composition of the niobian rutile is not known, but indications are that an appreciable amount of the niobium is represented by this mineral.

The niobian rutile is quite widespread, having been found in most of the samples examined, but it appears to be much less abundant than the pyrochlore.

CONCLUSIONS

Pyrochlore is the predominant niobium-bearing mineral in the samples examined. Most of it appears to be relatively coarse, and no great difficulties should be experienced in achieving a high degree of liberation by grinding the ore to minus 325 mesh. The pyrochlore shows considerable variations in composition, with the niobium content varying between 55% and 67% Nb_2O_5.

Niobian rutile can be expected to present problems in achieving good recoveries and grades because of its appreciable niobium content (up to about 24% Nb_2O_5). If rejected in the milling process, it will probably produce high tailings losses; if concentrated with the pyrochlore it will inevitably reduce the grade. Added to this is the fact that the niobian rutile is generally quite fine-grained, and will probably be difficult to liberate from the gangue minerals.

ACKNOWLEDGEMENTS

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