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TANTALIAN NIOBIAN TITANITE FROM THE IRGON CLAIM, SOUTHEASTERN MANITOBA

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ABSTRACT

Tantalian niobian titanite occurs in the IRA pegmatites on the Irgon claim, in the Winnipeg River pegmatite field of southeastern Manitoba. This titanite is a rare early component of a secondary mineral assemblage in miarolitic cavities in the albite. It occurs as dull brown fan-shaped (< 1 mm) aggregates of prismatic crystals. Subsequent crystallization of marcasite and pyrite was followed by an episode of alteration that coated the crystal faces of titanite with iron oxides and produced partial pseudomorphs of yellow-brown oxide after marcasite and pyrite. The titanite is chemically fairly inhomogeneous; the analyses confirm previous work (Clark 1974, Paul *et al.* 1981) in that the principal substitutions in (Nb,Ta)-bearing titanite are: (i) $(Nb,Ta) + (Al,Fe^{3+}) \rightleftharpoons 2Ti^{4+}$, (ii) $(Al, Fe^{3+}) + (OH)^- \rightleftharpoons Ti^{4+} + O^{2-}$.

Keywords: tantalian niobian titanite, pegmatite, chemical composition, Manitoba.

SOMMAIRE

De la titanite à teneurs de tantale et de niobium se présente dans les pegmatites IRA du claim Irgon, dans le champ de pegmatites du fleuve Winnipeg au Manitoba du sud-est. Cette titanite est un rare composant précoce d'un assemblage secondaire de minéraux qui occupe des cavités miarolitiques de l'albite. Elle se trouve en agrégats de cristaux prismatiques, d'un brun sombre et en forme d'éventail (< 1 mm). Une cristallisation postérieure de marcasite et de pyrite fut suivie d'un épisode d'altération au cours duquel les faces des cristaux de titanite se recouvrirent d'oxydes de fer, tandis que marcasite et pyrite produisirent des pseudomorphes partiels d'oxyde brun-jaune. Chimiquement la titanite est plutôt non-homogène; les analyses confirment les travaux antérieurs (Clark 1974, Paul *et al.* 1981), pour autant que les substitutions principales dans les titanites à teneur de (Nb,Ta) soient: (i) $(Nb,Ta) + (Al,Fe^{3+}) \rightleftharpoons 2Ti^{4+}$, (ii) $(Al,Fe^{3+}) + (OH)^- \rightleftharpoons Ti^{4+} + O^{2-}$.

(Traduit par la Rédaction)

Mots-clés: titanite tantalifère et niobifère, pegmatite, composition chimique, Manitoba.

INTRODUCTION

Considerable homo- and heterovalent substitutions occur for Ti^{4+}, O^{2-} and Ca in the structure of titanite, and detailed discussions of such chemical variations are given by Sahama (1946) and Higgins & Ribbe (1976). Clark (1974), Paul *et al.* (1981) and Semenov (1959) described Ta- and (Nb,Ta)-rich varieties, respectively, and showed that the pentavalent cations are accommodated into the structure primarily by the coupled substitution $(Ta,Nb) + (Al,Fe^{3+}) \rightleftharpoons 2Ti^{4+}$ at the octahedral site in the titanite structure. Here we report the occurrence of a (Ta,Nb)-bearing titanite, intermediate in composition between the previously reported occurrences.

OCCURRENCE

The Irgon group of pegmatites occurs just north of Cat Lake in the Winnipeg River district of southeastern Manitoba (Černý *et al.* 1981, Fig. 81). The main Irgon pegmatite strikes west-northwest, and has a maximum width of some 15 metres; close to this spodumene-bearing body are small ptygmatically folded veins, the IRA pegmatites. They consist of distinctly platy albite, flesh-pink to salmon-red in color, with subordinate quartz and accessory beryl. Small miarolitic cavities are widespread, and are commonly stained bright yellow; the (Ta,Nb)-bearing titanite was found as a rare species in a cavity in one of the IRA veins.

EXPERIMENTAL

The titanite was initially identified by powder X-ray diffraction, using a 114-mm Gandolfi camera and Ni-filtered Cu$K\alpha$ radiation. The refined cell-dimensions (Table 1) are close to those reported by Paul *et al.* (1981). The diffraction maxima observed are compatible with the space group $A2/a$, but no single-crystal work was done.

Electron-microprobe analyses were done in the energy-dispersion mode on a MAC-5 instrument, using a Kevex Micro-X 7000 analytical spectrometer with a Si(Li) detector and a 1024-multichannel analyzer operating at 10 eV per channel. The specimen current, as measured on fayalite, was 10 na at 15 kV excitation voltage, and the sample collection time was 200 live seconds. The following standards were used: pyrope (Al,Si), titanite (Ca,Ti), fayalite (Fe), $CoNb_2O_6$ (Nb) and manganotantalite (Ta). Data reduction was done using the Magic V program, written by J.W. Colby. The overlap involving

TABLE 1. CELL DIMENSIONS OF (Ta,Nb)-BEARING TITANITE

	Irgon Claim	Huron Claim*
a(Å)	7.055(4)	7.047(2)
b(Å)	8.652(4)	8.665(4)
c(Å)	6.528(3)	6.545(2)
β^{o}	113.80(4)	113.63(3)
V(Å^3)	364.6(2)	366.1(2)

*Paul et al. (1981).

TABLE 2. CHEMICAL COMPOSITIONS* (wt.%) OF TANTALIAN NIOBIAN TITANITE FROM IRGON CLAIM

	1	2	3	4
SiO_2	29.21	30.16	29.54	30.19
Al_2O_3	3.70	5.73	4.89	4.78
TiO_2	26.33	27.59	27.44	28.43
Fe_2O_3	1.21	0.54	0.67	1.05
Ta_2O_5	6.01	4.11	5.47	4.42
Nb_2O_5	5.43	2.17	3.46	3.13
CaO	27.37	28.12	27.82	27.33
	99.25	98.42	99.30	99.32
Si	0.999	1.002	0.992	1.008
Al	0.001	-	0.008	-
Σ(IV)	1.000	1.002	1.000	1.008
Al	0.148	0.244	0.186	0.188
Fe	0.031	0.014	0.017	0.026
Ti	0.677	0.689	0.693	0.714
Ta	0.056	0.037	0.050	0.040
Nb	0.084	0.033	0.053	0.047
Σ(VI)	0.996	0.997	0.999	1.015
Ca	1.003	1.001	1.001	0.997
Al+Fe^{3+}	0.179	0.238	0.203	0.214
Nb+Ta	0.140	0.070	0.103	0.087

*derived from electron-microprobe data.

Ta*M*α,β and Si*K*α,β in the analytical region of interest for Si (1.65–1.77 KeV) was resolved by stripping the Ta*M* lines of a reference spectrum, $FeTaO_4$, from the region. The reference spectrum was scaled to each titanite spectrum by normalizing on energy in the region of the Ta*L*α line, the line used for Ta analysis. Typical compositions representing individual determinations are shown in Table 2; because of the probable presence of OH and F, the compositions were normalized to 3 cations.

CRYSTAL CHEMISTRY

There is considerable inhomogeneity in all the components of the octahedral site in this particular titanite. Nevertheless, the principal substitutions whereby Nb, Ta, Al and Fe^{3+} are incorporated into the titanite structure are immediately apparent:

$$(Nb,Ta) + (Al,Fe^{3+}) \rightleftharpoons 2Ti^{4+}$$
$$(Al,Fe^{3+}) + (OH,F)^- \rightleftharpoons Ti^{4+} + O^{2-}$$

the substitution of hydroxyl and fluorine for oxygen presumably occurring at the formally underbonded O(1) site. It is apparent from Table 2 that there is a considerable range in the relative proportion of these two substitutions.

PARAGENESIS

The miarolitic cavities are generally bounded by crystal faces of albite. Occasionally, additional minerals of the matrix bound or project into the cavities, particularly needles of black tourmaline; these needles penetrate both albite and beryl, suggesting contemporaneity. Prior to any secondary mineralization, the acicular crystals were subject to a fairly intense shattering event, and resulting debris adheres to the albite walls.

The first secondary minerals to appear in the cavities were bityite, $CaLiAl_2(AlBeSi_2)O_{10}(OH)_2$, and (Ta,Nb)-bearing titanite, but these do not occur together. Bityite is common, whereas the titanite is rare, being observed in only one of the 125 cavities examined. The titanite is dull brown, and occurs in fan-shaped radiating aggregates of prismatic crystals, the aggregates being less than 1 mm in largest dimension. Following the crystallization of titanite, there was minor sulfide mineralization in the form of both marcasite and pyrite. Marcasite occurs both as tiny prisms and as wedge-shaped crystals, the latter often producing cockscomb twins. Pyrite occurs as simple cubes, generally smaller than the marcasite crystals. This was followed by an episode of alteration that produced a fairly intense yellow staining of the cavity walls and replaced most of the sulfides by iron oxides and hydroxides, producing yellow-brown pseudomorphs.

This paragenesis is similar to that of the niobian titanite reported by Paul *et al.* (1981). Both occur in miarolitic cavities in coarse-grained albite, as the earliest phase of the assemblage of secondary minerals. There are also similarities with the tantalian titanite reported by Clark (1974). The latter occurs as inclusions in tantalian rutile; the pegmatites of the Irgon claim also contain niobian tantalian rutile (Černý *et al.* 1981). The niobian titanite from the Huron claim is not closely associated with any other (Ta,Nb)-rich phases, but niobian rutile is a common primary oxide phase in the pegmatite.

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