

NIOBIAN TITANITE FROM THE HURON CLAIM PEGMATITE, SOUTHEASTERN MANITOBA*

B.J. PAUL†, P. ČERNÝ AND R. CHAPMAN

Department of Earth Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

J.R. HINTHORNE

Department of Geology, Central Washington University, Ellensburg, Washington 98926, U.S.A.

ABSTRACT

Niobian titanite occurs in the Be,Nb-Ta,Ti, REE,Y,Zr,Th,U-bearing Huron Claim pegmatite, in the Winnipeg River pegmatite district of southeastern Manitoba. The titanite is found in vuggy albite and quartz, separate from other Nb,Ta-bearing minerals. The Nb₂O₅ content is the highest ever found in this species (6.5 wt. %), and the combined (Nb,Ta)₂O₅ content (10.2 wt. %) is second only to that of the tantalian titanite from Craveggia (Clark 1974). Normalization to $\Sigma(R^{IV}+R^{VI}) = 8$ yields reasonable formulae for both Huron Claim and Craveggia titanites but with slight Al substitution for Si, which may improve local charge distribution at Nb,Ta-populated octahedra. Titanite-bearing pegmatites are usually low in Nb and Ta, and complex Nb,Ta,Ti-bearing oxide minerals predominate in pegmatites enriched in these elements, suggesting a scarcity of Nb,Ta-rich titanites.

Keywords: niobium, tantalum, titanite, crystal chemistry, pegmatite, Manitoba.

SOMMAIRE

On trouve une titanite niobifère dans la pegmatite Huron Claim, minéralisée en Be, Nb-Ta, Ti, terres rares, Y, Zr, Th et U. du district de la rivière Winnipeg (Sud-Est du Manitoba). La titanite, qui occupe des cavités dans l'albite et le quartz, se trouve isolée des autres minéraux de Nb et Ta. Sa teneur en Nb₂O₅ (6.5% en poids) est ici la plus élevée que l'on connaisse, et sa teneur en (Nb,Ta)₂O₅ (10.2%) n'est surpassée que par celle de la titanite tantalifère de Craveggia (Clark 1974). Par normalisation $\Sigma(R^{IV} + R^{VI}) = 8$, on obtient des formules raisonnables pour les échantillons de Huron Claim et de Craveggia,

indiquant toutefois une légère substitution d'Al à Si, qui améliore probablement la distribution locale des charges sur les octaèdres à Nb-Ta. Les pegmatites à titanite sont généralement pauvres en Nb et Ta; par contre, c'est dans les pegmatites enrichies en ces éléments que prédominent les oxydes de (Nb, Ta, Ti), ce qui expliquerait la rareté des titanites riches en Nb et Ta.

(Traduit par la Rédaction)

Mots-clés: niobium, tantale, titanite, chimie cristalline, pegmatite, Manitoba.

INTRODUCTION

The possibility of appreciable substitution of Nb and Ta for Ti in the structure of titanite, frequently advocated on crystallochemical grounds, has been documented only recently when Clark (1974) described a tantalian titanite from Craveggia, Italy. The present note reports an occurrence of niobian titanite that is second only to the Craveggia mineral in the combined (Nb,Ta) content.

OCCURRENCE

The Huron Claim pegmatite is a member of the Shatford Lake pegmatite group in the Winnipeg River pegmatite district of southeastern Manitoba (Černý *et al.* 1981). The pegmatite is low in Li, Rb and Cs but contains a diversified assemblage of Be, Nb-Ta, Ti, REE, Y, Zr, Th and U minerals (Walker 1931, Ellsworth 1932, Černý & Bristol 1972, B.J. Paul, in prep.). Minerals with substantial Nb and Ta contents include partly disordered columbite-tantalite, microlite, fersmite, niobian rutile, a metamict euxenite-like phase and the titanite described here.

The titanite occurs in vuggy coarse grained (3-8 mm) albite with minor quartz; the vugs are partly filled with clay minerals. Neither the Nb,Ta-rich phases abundant elsewhere in

*Centre for Precambrian Studies, University of Manitoba, Publication No. 56.

†Present address: CCH Resources Ltd., 355 Burrard Street, Vancouver, British Columbia V6C 2G6.

the pegmatite nor any minerals occasionally occurring with them (such as monazite, zircon, uraninite or thorite) are associated with the titanite.

PHYSICAL PROPERTIES

The titanite occurs as dark brown crystals, 1 to 3 mm in length, which are poorly formed but have the letter-envelope habit typical of the species. Crystals are generally skeletal and partly intergrown with albite. In thin section they are pale brownish, occasionally with darker concentric zones that are faintly pleochroic. The high indices of refraction (> 1.8), birefringence and the optical orientation (optic axial plane // 010, $+2V$ intermediate) correspond qualitatively to those characteristic of normal titanite. Density, measured on a Berman balance using toluene as the buoyant medium, is 3.55 g/cm^3 .

The titanite produces a good X-ray-diffraction pattern; the β value (Table 1) falls slightly below the range given by Higgins & Ribbe (1976). After heating in air at 800°C for 3 hours, slight shifts in b and β are the only statistically significant changes (Table 1).

CHEMICAL COMPOSITION

Electron-microprobe analysis was done in the wavelength-dispersion mode on a MAC-5 instrument, using the following standards: titanite (Ca, Ti, Si), olivine (Fe), manganotantalite (Ta), stibiotantalite (Nb), spinel (Al) and cassiterite (Sn). The specimen current was 0.04 mA at 20 kV. The data were reduced using the EMPADR VII program of Rucklidge & Gasparini (1969).

TABLE 1. PHYSICAL PROPERTIES OF THE HURON CLAIM TITANITE

	natural	$800^\circ/3 \text{ hrs. in air}$
\underline{a} (Å)	7.047(2)	7.045(2)
\underline{b} (Å)	8.665(4)	8.693(5)
\underline{c} (Å)	6.545(2)	6.556(4)
β	113.63(3)	114.02(5)
V (Å ³)	336.1(2)	336.8(2)
D (22°C)	3.55 g/cm^3	

refined from CaF_2 ($\underline{a} = 5.6402 \text{ Å}$) calibrated X-ray powder diffractograms recorded at $0.25^\circ/2\theta/1 \text{ min.}/0.25 \text{ inch}$, CuK alpha radiation

One crystal was examined using an ARL ion-microprobe mass analyzer to quantify the fluorine content and to search for other elements. The operating conditions were similar to those used by Hinthorne & Andersen (1975), with a beam diameter of $15 \mu\text{m}$. The fluorine content was derived from the working curve given in Hinthorne & Andersen (1975), and the value reported in Table 2 has an estimated uncertainty of $\pm 20\%$.

Table 2 gives the results of the electron- and ion-microprobe analyses. The Nb_2O_5 content of the titanite is the highest recorded for this species, and the combined Nb+Ta pentoxides are second only to those of the tantalian titanite from Craveggia, Italy (Clark 1974). The alumina content is also appreciable in both specimens.

DISCUSSION

Crystal chemistry

Using a series of precisely analyzed titanites, Higgins & Ribbe (1976) found that most cationic substitutions affect the octahedral sites, and that the tetrahedral positions are populated exclusively by Si. The $\text{Ca} \leftrightarrow \text{REE}$ and $\text{Ti} \leftrightarrow (\text{Al}, \text{Fe})$ substitutions were the only appreciable variations in their samples, and normalization of the atomic formulae to 1.00 Si led to very good overall site-populations and charge balance. Normalizing the Nb,Ta-rich titanites from Huron Claim and Craveggia to stoichiometric Si, however, yields excess cations in the Ca and Ti sites and totals of positive charges in excess of 40.00 (Table 2, columns 3 and 4). This excess is particularly high for the octahedral cations, and is beyond the limits of possible analytical error.

Normalization to eight octahedral and tetrahedral cations gives formulae with reasonable site-populations and charge balance (Table 2, columns 5 and 6). However, these formulae require slight to moderate tetrahedral substitution of Al for Si. This substitution, absent in Nb,Ta-poor titanites, probably takes place in tetrahedra linked to Nb,Ta-populated octahedra to satisfy the bond-valence requirements of the local oxygens. This explanation seems to be supported by a rough correlation between the $(\text{Nb,Ta})^{\text{VI}}$ and Al^{IV} contents.

The anionic part of the unit-cell contents shown in Table 2, columns 5 and 6, is only an approximation. It is coincidental that the analyzed F_2 alone fits the charge balance of the

TABLE 2. CHEMICAL COMPOSITION OF THE HURON CLAIM AND CRAVEGGIA TITANITES

	1.	2.		3.	4.		5.	6.
SiO ₂	29.0	26.9	Si	4.00	4.00	Si	3.92	3.84
Al ₂ O ₃	4.7	5.1	Al	0.76	0.90	Al	0.08	0.16
Fe ₂ O ₃	0.5	1.0	Fe ³⁺	0.05	0.11	Σ	4.00	4.00
TiO ₂	26.5	22.2	Ti	2.74	2.48	Al	0.67	0.70
SnO ₂	0.9	0.1	Sn	0.05	0.01	Fe ³⁺	0.05	0.11
Nb ₂ O ₅	6.5	2.9	Nb	0.41	0.19	Ti	2.69	2.38
Ta ₂ O ₅	3.7	16.0	Ta	0.14	0.65	Sn	0.05	0.01
CaO	27.3	25.6	Σ	4.15	4.34	Nb	0.40	0.18
MnO	-	0.05	Ca	4.03	4.07	Ta	0.14	0.62
Na ₂ O	-	0.3	Mn	-	0.01	Σ	4.00	4.00
F ₂	0.8	-	Na	-	0.08	Ca	3.95	3.91
-O=F ₂	-0.3	100.1	Σ	4.03	4.16	Mn	-	0.01
	99.6		Σ cation charge			Na	-	0.08
				+40.40	+41.43	Σ	3.95	4.00
						(F,OH)	0.35	0.25
						O	19.65	19.75
						Σ	20.00	20.00

1. Niobian titanite, Huron Claim; electron-microprobe analysis by R. Chapman 1980, ion-microprobe analysis of F₂ by J.R. Hinthorne 1981.
Mg, Mn, V, P, K and Na detected on ion microprobe within approximately 50-1000 ppm; Li, B, Cr (all <1 ppm), Be, Zr (both <10 ppm), and Ce, La, Pr, Cl (all <50 ppm) not detected on ion microprobe (detection limits estimated).
2. Tantalian titanite, Craveggia (Clark 1974).
3. Niobian titanite Huron Claim; unit cell content normalized to 4.00 Si.
4. Tantalian titanite Craveggia; unit cell content normalized to 4.00 Si.
5. Niobian titanite Huron Claim; unit cell content normalized to (R^{VI} + R^{IV}) = 8.00, anions adjusted to fit cation charge.
6. Tantalian titanite Craveggia; unit cell content normalized to (R^{VI} + R^{IV}) = 8.00, anions adjusted to fit cation charge.

Huron Claim titanite. The lack of accurate data for H₂, Na and REE (*cf.*, low Ca-site total) indicates that the cation and (O,OH,F) contents can stand further refinement. No data are available for F₂ and H₂ in the Craveggia mineral, but the sum of cation charges (<40.00) suggests that (F,OH) substitution in the O(5) position is a distinct possibility. Despite these minor uncertainties, it is beyond doubt that 33% of the Ti sites in the Huron Claim titanite and 41% of them in the Craveggia specimen are occupied by Nb, Ta, Al, Fe and Sn. Four mechanisms appear to facilitate incorporation of these cations:

- (i) $^{VI}Ti^{4+} \leftrightarrow ^{VI}Sn^{4+}$
- (ii) $^{VI}2Ti^{4+} \leftrightarrow ^{VI}(Nb, Ta)^{5+} + ^{VI}(Al, Fe)^{3+}$
- (iii) $^{VI}Ti^{4+} + ^{IV}Si^{4+} \leftrightarrow ^{VI}(Nb, Ta)^{5+} + ^{IV}Al^{3+}$
- (iv) $^{VI}Ti^{4+} + O^{2-} \leftrightarrow ^{VI}(Al, Fe)^{3+} + (F, OH)^{-}$.

The second substitution is evidently the predominant one, compensating internally for most of the potential charge-imbalance generated by heterovalent substitution for Ti⁴⁺.

Expanding the Higgins & Ribbe (1976) for-

mula for the calculation of effective octahedral cation radius (EOCR) in titanite to accommodate Nb, Ta and Sn [EOCR = 0.605 - (0.075 Al/Si) + (0.04 Fe³⁺/Si) + (0.035 Nb/Si) + (0.035 Ta/Si) + (0.085 Sn/Si)] gives 0.597 Å for the Huron Claim specimen. A reasonable comparison with the regression lines of Higgins & Ribbe (1976) should be possible, as the extent of tetrahedral substitution in the Huron Claim titanite is negligible. However, only the *b* dimension falls within the range given by the above authors; *a* is lower and *c* is higher than the predicted values.

Paragenetic and geochemical considerations

The apparent scarcity of Nb, Ta-rich titanites may be due partly to a restricted number of modern analyses of this mineral and to a lack of analyzed titanites from pegmatites with a diversified assemblage of more exotic species. However, considering the paragenetic types of pegmatites containing titanite, some geochemical constraints become apparent. Titanite-bearing pegmatites are usually poor in Nb and Ta (*e.g.*, Heinrich 1959). Ti-rich pegmatites are usually

also enriched in REE, U and Th; complex oxides of Na, Ca, Nb, Ta, Ti and REE (e.g., minerals of the pyrochlore, euxenite, polycrase, and fergusonite groups: Ellsworth 1932, Satterly & Hewitt 1955) are the more frequent species that incorporate Nb and Ta. Nevertheless, it is this type of pegmatite in which new occurrences of Nb,Ta-rich titanite may be found. By analogy with the Huron Claim pegmatite, the following conditions seem necessary: (i) a relatively high Nb,Ta concentration, (ii) a high Ca content (Ca-fermite, microlite, clinzoisite-epidote), (iii) the REE content bound mainly in phosphates (monazite) and U,Th predominantly in simple oxides and silicates (uraninite, thorite, zircon) and (iv) a limited number and abundance of complex Nb,Ta,Ti-oxide minerals (a euxenite-like phase and niobian rutile).

The paragenesis of the Craveggia pegmatite is not known in sufficient detail to contribute to the above speculation (Prior & Zambonini 1908). However, the mode of occurrence of tantalian titanite in this pegmatite provides an interesting contrast to that of the Huron Claim mineral. In Craveggia, tantalian titanite is found as inclusions in Ta,Nb-rich rutile (strüverite); the Nb,Ta contents of titanite and rutile may be indicative of Ta,Nb partitioning between these minerals in a Ta,Nb-rich environment. On the other hand, the Huron Claim titanite seems to be separated from other Nb,Ta-bearing species that occur elsewhere in the pegmatite in spectacular local concentrations; yet the titanite also contains considerable Nb and Ta.

ACKNOWLEDGEMENTS

This study was supported by the Canada-Manitoba Subsidiary Agreement on Mineral Exploration and Development in Manitoba, and by an N.S.E.R.C. Operating Research Grant to the second author. Particular thanks are due to Dr. F.C. Hawthorne for his contributions to the electron-microprobe analysis and for his critical reading of the manuscript.

REFERENCES

- ČERNÝ, P. & BRISTOL, N.A. (1972): New mineral occurrences in pegmatites of southeastern Manitoba. *Can. Mineral.* 11, 560-563.
- , TRUEMAN, D.L., ZIEHLKE, D.V., GOAD, B.E. & PAUL, B.J. (1981): The Cat Lake-Winnipeg River and the Wekusko Lake pegmatite fields, Manitoba. *Man. Mineral Res. Div. Econ. Geol. Rep.* ER80-1.
- CLARK, A.M. (1974): A tantalum-rich variety of sphene. *Mineral. Mag.* 39, 605-607.
- ELLSWORTH, H.V. (1932): Rare-element minerals of Canada. *Can. Dep. Mines, Geol. Surv. Econ. Geol. Ser.* 11.
- HEINRICH, E.W. (1959): Sphene-allanite pegmatites of Griffith Township, Renfrew County, Ontario. *Can. Mineral.* 6, 339-347.
- HIGGINS, J.B. & RIBBE, P.H. (1976): The crystal chemistry and space groups of natural and synthetic titanites. *Amer. Mineral.* 61, 878-888.
- HINTHORNE, J.R. & ANDERSEN, C.A. (1975): Micro-analysis for fluorine and hydrogen in silicates with the ion microprobe mass analyzer. *Amer. Mineral.* 60, 143-147.
- PRIOR, G.T. & ZAMBONINI, F. (1908): On strüverite and its relation to ilmenorutile. *Mineral. Mag.* 15, 78-89.
- RUCKLIDGE, J. & GASPARRINI, E. (1969): EMPADR VII. Specifications of a computer program for processing electron microprobe analytical data. *Dep. Geol., Univ. Toronto.*
- SATTERLY, J. & HEWITT, D.F. (1955): Some radioactive mineral occurrences in the Bancroft area. *Ont. Dep. Mines, Geol. Circ.* 2.
- WALKER, T.L. (1931): Rare minerals in pegmatite, Pointe du Bois, Manitoba. *Univ. Toronto Stud., Geol. Ser.* 30, 9-13.

Received June 1981, revised manuscript accepted July 1981.