NIOBIUM-TANTALUM MINERALS FROM GRANITIC PEGMATITES AT GREER LAKE, SOUTHEASTERN MANITOBA

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ABSTRACT

In a group of zoned beryl-bearing pegmatites in the Precambrian of the Winnipeg River area, in southeastern Manitoba, pseudo-ixiolite and microlite are the most widespread Nb-Ta minerals; niobian rutile and cassiterite are less frequent, fersmite and ilmenite are rare.

Pseudo-ixiolite is rarely partly ordered, and has mostly high Mn/Fe and intermediate Ta/Nb ratios. Considerable deviations from the ideal (Mn,Fe)/(Ta,Nb) and cation/oxygen ratios are observed, particularly in specimens rich in Ti and Sn. Niobian rutile shows advanced exsolution of columbite and large unit cell dimensions. Fersmite replaces pseudo-ixiolite in the Huron Claim pegmatite. Cassiterite contains numerous columbite inclusions.

A positive correlation exists between the Mn-content of pseudo-ixiolite and the Li-content of its parent pegmatite; pseudo-ixiolite from Li-bearing pegmatites is also enriched in Ta. Fe-rich pseudo-ixiolite occurs in the exceptional *RE*-rich Huron Claim pegmatite, and in another body rich in titanium oxides. Microlite occurs as a replacement of Mn-rich pseudo-ixiolite, but coexists with Fe-enriched oxides. Cassiterite occurs mainly but not exclusively in the lithium-rich pegmatites.

INTRODUCTION

A group of beryl-bearing pegmatites at Greer Lake, southeastern Manitoba, was discovered 40 years ago (summary by Davies 1957). They were last examined by Dalhart Minerals Corporation in 1957. The surface trenching work offers a good opportunity to study a group of closely related pegmatites and to correlate their mineralogy, geochemistry, and petrological characteristics. This paper is based on laboratory examination of material collected in the field in the fall of 1968 and the summer of 1969.

LOCATION AND GEOLOGICAL SETTING

Greer Lake is located 84 miles ENE of Winnipeg in the northernmost part of the Whiteshell Provincial Park (latitude 50°20′30″, longitude 95°19′). The rocks of the area are gneissic and batholithic granitic rocks with belts of metavolcanic and metasedimentary rocks of the Archean

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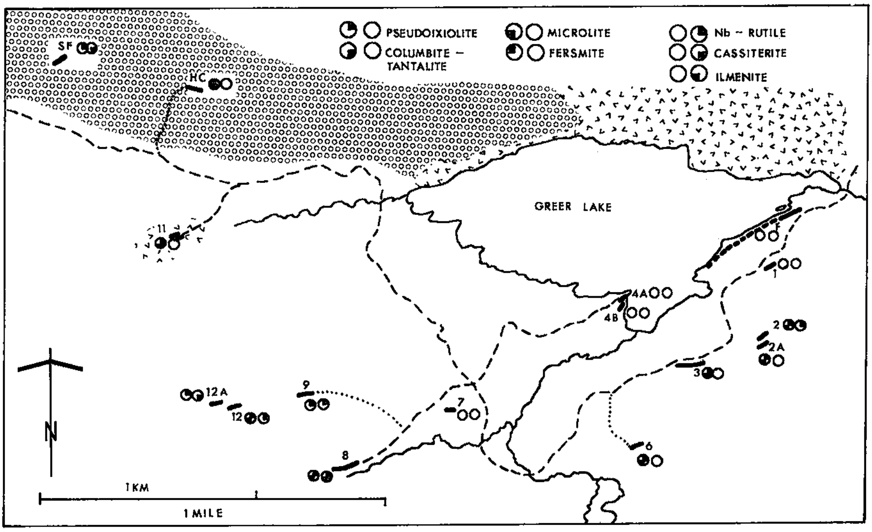

Fig. 1. Topographical and geological situation in the Greer Lake area, uncorrected from aerial photographs. Old truck roads and pegmatite bodies are shown, and diagrams indicating the assemblage of Nb, Ta-minerals in each body. Checks–pegmatitic granite; circles–greenstone; unmarked–granitic and gneissic area.

(Springer 1950; Davies 1957). The rocks south of Greer Lake are intimately mixed with gneissic and granitic rocks. A metavolcanic belt stretches west from the north-western end of the lake, and a pegmatitic beryl-bearing granite crops out north of it (Fig. 1). This latter is possibly the parent rock of the numerous pegmatite bodies south and west of Greer Lake.

Within the area covered by Fig. 1 at least 80 pegmatite bodies crop out; Fig. 1 shows only those opened by prospectors and studied here. Most of these, as well as most of all the pegmatites present, are in the gneissic-granitic area south of the lake. Pegmatites HC (Huron Claim) and SF (Silverleaf lithium pegmatite) are intrusive into metavolcanic amphibolites, and No. 11 lies in a small isolated outcrop of the pegmatitic granite, off the main body of this rock in the north.

Most of the examined pegmatites are well zoned, and carry a simple assemblage of accessory minerals. Beryl and garnet are most abundant, Nb-Ta-oxides and monazite are less frequent; altered cordierite is a characteristic constituent. Two exceptions from this prevalent type are the pegmatites located in metavolcanics; the Silverleaf pegmatite is a lithium-rich body with much lepidolite and spodumene + quartz pseudomorphs after petalite, and the Huron Claim pegmatite is famous for its Nb,U,*RE*,Be,Zr,Th mineralization.

The most detailed reports on the petrology of the area are those by Wright (1932) and Davies (1957); the latter author also lists earlier papers. The only original paper dealing with Nb-Ta-oxides from the Greer Lake pegmatites is an analysis of a Huron Claim columbite by Walker (1931).

MINERALOGY

The Nb-Ta-oxides studied here have been examined in polished sections and, exceptionally, also in transmitted light. *X*-ray powder diffraction records, obtained on a Norelco-Philips diffractometer, using glass slide mounts and an internal standard (CaF_2 annealed at 800°C), were used to collect data for least-squares refinement of unit cell dimensions. This was performed by aid of a computer program written by Evans *et al.* (1963) and later modified by Stewart and Appleman. Specific gravity was determined with a Berman balance, using toluene as suspension medium. Specimens available in sufficient quantity have been analyzed chemically by X-ray fluorescence against standards of mixed metal oxides, in special sample holders adjusted for samples of about 0.2 g.

The Nb-Ta-oxide most common in the investigated pegmatites is pseudo-ixiolite. Microlite is also widespread, whereas niobian rutile and cassiterite are restricted to a few localities; fersmite and ilmenite have been found each in only one pegmatite.

Pseudo-ixiolite and columbite-tantalite

Pseudo-ixiolite, $(Fe,Mn,Ta,Nb,Sr, etc.)_4O_8$, as defined by Nickel *et al.* (1963), is a complex Nb-Ta-oxide similar to ixiolite but with the difference that its structure may be inverted by heating (by ordering of the cations probably) to give an XRD pattern similar to columbite. This mineral has been identified in all the Greer Lake pegmatites that have Nb-Ta-oxides (see Fig. 1), and the XRD patterns of these specimens showed the development of the columbite-cell 7 Å peak after heating (800°C, 16 hours, atmosphere $CO/CO_2 = 2.5$).

In the Huron Claim pegmatite (HC in Fig. 1) it forms flat lath-shaped crystals up to 10 cm long. It is imbedded in coarse-grained albite, associated with beryl, monazite, zircon, and thorite, and frequently replaced by fersmite. Davies (1957) reports that about 500 pounds of columbite have been taken from the pegmatite.

The Silverleaf lithium pegmatite has two types of pseudo-ixiolite, in brickshaped rectangular crystals up to 3 cm long, and in wedge-shaped rods of the same size. The first type occurs in fractures and on intergranular surfaces of the blocky K-feldspar zone; the other is associated with lithium micas and spodumene + quartz aggregates.

In all other pegmatites, pseudo-ixiolite forms either tabular grains in a medium-grained albite + quartz + muscovite + garnet assemblage in the internal parts of the pegmatite bodies, or radiating bunches of fibrous laths in cleavelandite between the blocky K-feldspar and central quartz core.

In pegmatites 2, 11 and HC, there were, in addition to pseudo-ixiolites, a few crystals which were distinguished by a small 7 Å peak in the XRD powder pattern. These peaks were enlarged by heating (temperature and atmosphere as above). These crystals are therefore partially disordered columbite or partially ordered pseudo-ixiolite, and they are marked in Fig. 1 as columbite-tantalite.

Cell dimensions of natural and heated specimens are compared in Fig. 2. The dimensions of HC specimens fall between those of the other natural pseudo-ixiolites and the position of the heated, well ordered specimens. The numerical values of unit cell dimensions are given in Table 1 for the chemically analyzed samples.

TABLE 1. UNIT CELL DIMENSIONS OF CHEMICALLY ANALYSED PSEUDO-IXIOLITE

Specimen	*State*	a_0	b_0	c_0	V
GL-2A-17	nat.*	4.749 ± .006	5.739 ± .003	5.147 ± .007	420.84 ± .39**
	heat.***	14.349 ± .004	5.742 ± .002	5.083 ± .002	418.84 ± .15
GL-9-19	nat.	4.726 ± .001	5.716 ± .001	5.114 ± .002	414.42 ± .15
	heat.	14.271 ± .006	5.724 ± .002	5.063 ± .002	413.55 ± .22
GL-9-20	nat.	4.729 ± .001	5.723 ± .001	5.135 ± .001	416.88 ± .09
	heat.	14.285 ± .008	5.722 ± .003	5.061 ± .003	413.75 ± .30
HC-2	nat.	4.741 ± .002	5.725 ± .002	5.093 ± .003	414.75 ± .24
	heat.	14.287 ± .005	5.735 ± .002	5.058 ± .002	414.46 ± .19
GL-12A-1	nat.	4.749 ± .001	5.741 ± .002	5.151 ± .002	421.35 ± .15
	heat.	14.380 ± .004	5.746 ± .001	5.084 ± .002	420.10 ± .16
SF-17	nat.	4.762 ± .001	5.747 ± .001	5.150 ± .001	422.79 ± .09
	heat.	14.426 ± .004	5.765 ± .001	5.081 ± .001	421.95 ± .13
SF-21	nat.	4.756 ± .001	5.744 ± .002	5.150 ± .002	422.13 ± .15
	heat.	14.415 ± .004	5.755 ± .001	5.088 ± .002	422.09 ± .16
SF-22	nat.	4.759 ± .002	5.748 ± .002	5.150 ± .003	422.67 ± .24
	heat.	14.417 ± .004	5.756 ± .002	5.084 ± .002	421.89 ± .16

* Natural specimen, disordered pseudo-ixiolite structure.

** True volume multiplied by 3.

*** Heated at 1,000°C. for 16 hrs. in $CO/CO_2 = 2.5/1$ atmosphere; ordered columbite structure.

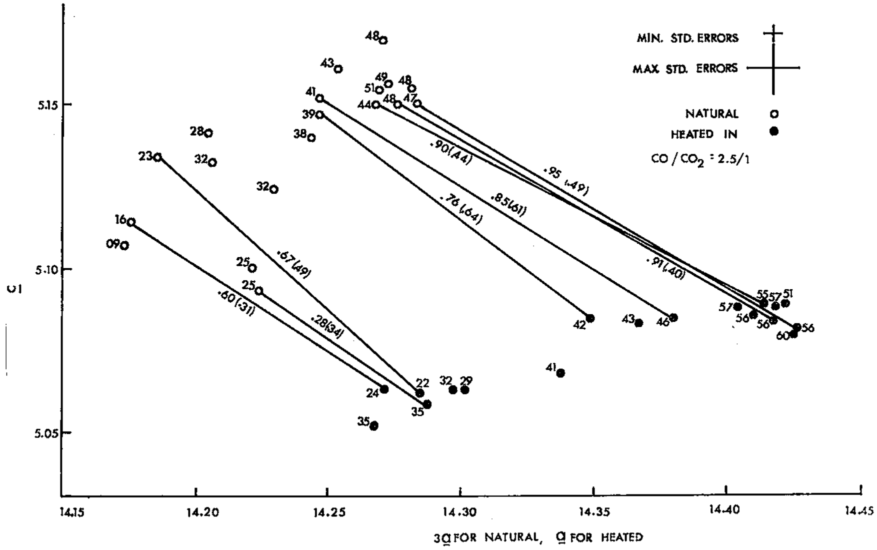

Fig. 2. Plot of cell dimensions of natural and heated pseudo-ixiolites. The figure at each point indicates the second and third decimal place of the *b* parameter (*e.g.* 16 reads 5.716Å). Thin lines connect u.c.d. plots of analyzed specimens; other joins are omitted to avoid confusion. The first figure on a join indicates the Mn/(Mn+Fe) ratio, the second (in brackets) denotes the Ta/(Ta+Nb) ratio. Note the positive correlation of all three unit cell dimensions, particularly in heated specimens, and their positive correlation with most Mn/(Mn+Fe) ratios.

Chemical analyses of eight pseudo-ixiolite samples are presented in Table 2. Three specimens that could be separated free of any visible admixtures gave totals between 99 and 101%, and those contaminated by silicates will add up to close to 100% if the impurities are added to the analysis in the estimated amounts given at the bottom of Table 2. The impurities are mostly quartz and feldspar, some mica (not biotite), so there is no ambiguity in the analyses of the amounts of heavy metals of the oxide minerals.

As shown in Table 2, for a unit cell content based on 8 oxygens, (Mn+Fe) is mostly higher than 1.33, (Ta+Nb+Ti+Sn) lower than 2.67, and the sum of metals higher than 4. The compositions of these pseudo-ixiolites, plus those listed by Schröcke (1966, Table 2), show a weak general correlation between an excess of (Mn+Fe) and enrichment in Sn and Ti.

The cationic non-stoichiometry with (Ta+Nb+Sn+Ti) / (Mn+Fe) <2, particularly in GL–9–19 and 20, resembles true ixiolites (of analyses in

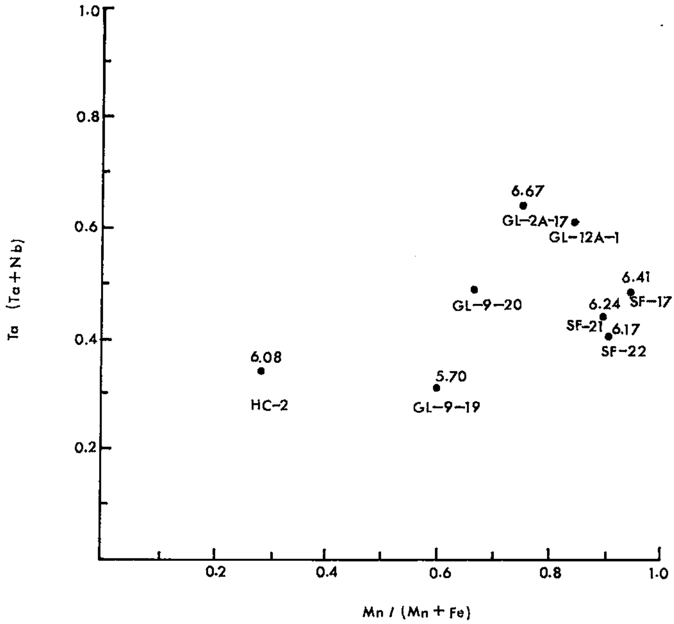

FIG. 3. The Ta/(Ta+Nb) *vs.* Mn/(Mn+Fe) plot of the analyzed pseudo-ixiolites. Each point numbered as in Tables 1 and 2, and specific gravity stated when measured on the analyzed sample. Note the positive correlation of specific gravity with the tantalum content.

Table 2

Analyst, K. Ramlal 1970; sample location as shown in Fig. 1.

SF-17	large wedge-shaped crystal in purple Li-mica; contaminated by about 5 vol.% albite and quartz.
SF-21	radial aggregate of tabular crystals in potassium feldspar.
SF-22	radial aggregate of tabular crystals in potassium feldspar.
HC-2	flat lath-shaped crystals in albite.
GL-9-19	bunch of radiating fibrous crystals in cleavelandite; contaminated by about 5 vol.% albite, quartz and mica.
GL-9-20	radiating fibrous crystals in cleavelandite; contaminated by about 30 vol.% albite and mica.
GL-2A-17	large bunch of radiating fibers in cleavelandite, partly metamict; contaminated by about 3 vol.% albite and mica.
GL-12A-1	fine lath-shaped radiating crystals in albite and quartz; contaminated by about 30 vol.% of these minerals.

TABLE 2. CHEMICAL ANALYSES OF PSEUDO-IXIOLITE

	SF-17	SF-21	SF-22	HC-2	GL-9-19	GL-9-20	GL-2A-17	GL-12A-1
Chemical analyses								
FeO	1.0	1.8	1.8	16.4	8.4	7.1	3.9	2.2
MnO	19.8	16.5	18.4	4.5	12.6	14.6	12.6	12.4
Nb_2O_5	29.9	34.9	37.4	42.5	38.0	25.3	20.25	18.7
Ta_2O_5	47.4	45.4	42.0	37.3	20.0	39.6	61.0	49.4
TiO_2	0.0	0.21	0.0	0.18	4.55	1.4	2.1	1.05
SnO_2	0.1	1.5	0.3	0.0	1.5	0.9	0.0	1.0
	98.2	100.31	99.9	100.88	94.05	88.9	99.85	84.75
Recalculated to 100%								
FeO	1.0	1.8	1.8	16.2	8.9	8.0	3.9	2.6
MnO	20.1	16.5	18.4	4.5	13.4	16.4	12.6	14.6
Nb_2O_5	30.5	34.8	37.4	42.1	40.4	28.4	20.3	22.1
Ta_2O_5	48.3	45.2	42.1	37.0	30.9	44.6	61.1	58.3
TiO_2	0.0	0.2	0.0	0.2	4.8	1.6	2.1	1.2
SnO_2	0.1	1.5	0.3	0.0	1.6	1.0	0.0	1.2
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Atomic proportions based on 8 oxygens								
Fe	0.08	0.13	0.13	1.20	0.62	0.61	0.32	0.21
Mn	1.57	1.28	1.41	0.33	0.96	1.28	1.04	1.20
Nb	1.29	1.44	1.53	1.68	1.56	1.20	0.89	0.97
Ta	1.24	1.13	1.16	0.89	0.72	1.12	1.63	1.55
Ti	0.00	0.01	0.00	0.01	0.30	0.11	0.16	0.09
Sn	0.003	0.06	0.01	0.00	0.06	0.04	0.00	0.04
Total	4.18	4.05	4.24	4.11	4.22	4.36	4.04	4.06
Mn/(Mn+Fe)	0.95	0.90	0.91	0.28	0.60	0.67	0.76	0.85
Ta/(Ta+Nb)	0.49	0.44	0.40	0.34	0.31	0.49	0.64	0.61
$\frac{(Ta+Nb+Sn+Ti)}{(Mn+Fe)}$	1.53	1.87	1.67	1.69	1.67	1.30	1.97	1.88
Sp.gr.	6.41	6.24	6.17	6.08	5.70	n.d.	6.67	n.d.

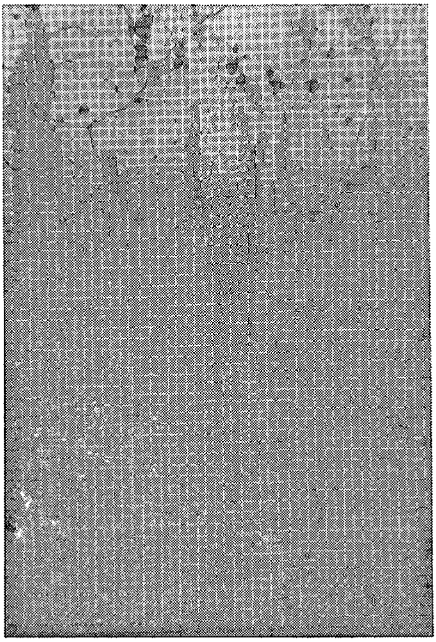

FIG. 4. Niobian rutile-like phase (light grey) intergrown with pseudo-ixiolite, resembling an exsolution product; pseudo-ixiolite penetrated by microlite (darker strips in the pseudo-ixiolite matrix). Specimen GL-2-1, crossed nicols, linear magnification 50x.

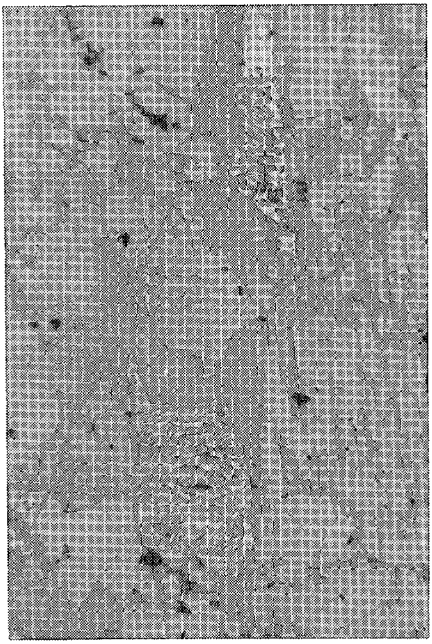

FIG. 5. Vermicular ovoids of the same niobian rutile-like phase as in Fig. 4. (light grey), with the immediately adjacent pseudo-ixiolite host (grey) replaced by microlite (dark grey). Specimen GL-2-1, crossed nicols, linear magnification 50x.

Nickel *et al.* 1963, Knorring *et al.* 1969) but all the minerals studied here develop a true columbite cell after heating, without any other phases detectable by *x*-ray powder study.

The presence of $Fe_2^{3+}(Nb, Ta)_2O_8$ as a component in solid solution in pseudo-ixiolite is a possibility. It would explain the high contents of (Fe+Mn) and the low contents of (Nb+Ta) that are described above, but would not account for the deviations from the metal:oxygen ratio of 1:2. There is no direct evidence of the presence of Fe^{3+} in our samples, since the contents of iron were determined by *x*-ray fluorescence, and in the list of analyses in Table 2 the amount of total iron is presented as FeO. This assumption, that iron is mostly bivalent, is based on a presumed similarity with natural and synthetic columbite-tantalites (*c.f.* Vlasov *et al.* 1964; Schröcke 1966; Turnock 1966*a* and *b*); there is no data on Fe^{+2}/Fe^{+3} for pseudo-ixiolites.

Deviations from the metal:oxygen ratio of 1:2 may be explained by an oxygen deficiency, as suggested also for niobian and tantalian rutiles (Černý *et al.* 1964).

Generally, all the deviations from the classic columbite-type formula should not be surprising in pseudo-ixiolite, whose disordered state does not impose any requirements on cationic stoichiometry, and whose structure could contain defects.

For most specimens—both natural and heated—the unit cell dimensions increase with the Mn/(Mn+Fe) ratio, as expected from syntheses and other natural occurrences (Fig. 2; Brandt 1943, Kumskova 1962, Schröcke 1966); exceptions are the GL–9 specimens mentioned above. The Ta/(Ta+Nb) ratio has no detectable influence on the cell parameters but shows the well-known positive correlation with specific gravity (Fig. 3); the GL–9–19 specimen is again exceptional, showing much lower specific gravity than expected; no data could be obtained for the GL–9–20 sample.

TABLE 3. PARTIAL CHEMICAL ANALYSES OF NIOBIAN RUTILE, MICROLITE, AND PSEUDO-IXIOLITE PARTLY REPLACED BY FERSMITE

	GL-8(W)-28	GL-11-15	HC-1	Walker (1931)
FeO	14.2	1.8	13.0	14.77
MnO	2.6	2.7	3.8	2.17
CaO	n.d.	n.d.	1.42	2.66
MgO	n.d.	n.d.	n.d.	0.45
Nb_2O_5	33.2	17.9	47.5	52.26
Ta_2O_5	20.9	60.5	29.5	26.41
TiO_2	22.8	2.0	0.2	0.49
SnO_2	6.3	0.8	0.0	n.d.
ZrO_2	n.d.	n.d.	n.d.	0.65
H_2O	n.d.	n.d.	n.d.	0.21
	100.0	(85.7)	95.42	100.20
Sp.gr.	5.04	n.d.	5.82	5.87

Analyst, K. Ramlal, 1970.

GL-8(W)-28, niobian rutile recalculated to 100% from the analyzed total 93.3%; sample was slightly contaminated by albite, quartz and mica; specific gravity calculated.

GL-11-15, microlite slightly contaminated by albite and quartz; remainder to 100% adequate to CaO and Na_2O of microlite.

HC-1, pseudo-ixiolite from Huron Claim, partly replaced by fersmite; remainder to 100% compares well with *RE*-oxides of fersmite.

Walker (1931) "columbite" Huron Claim; most probably pseudo-ixiolite partly replaced by fersmite. Analyst, V. J. Oswald.

In pegmatite No. 2, there are microscopic grains or skeletal patches of niobian rutile in aggregates of pseudo-ixiolite which has been partially replaced by microlite (Figs. 4, 5, 6). The rutile is mostly in microlite, with lesser amounts in pseudo-ixiolite, except for a few aggregates in which the rutile exists exclusively in the pseudo-ixiolite in a fine intergrowth pattern as shown in Fig. 4. An interpretation of these textures is that Nb-rutile exsolved from pseudo-ixiolite, followed by the growth of microlite which replaced pseudo-ixiolite from the crystal boundaries inward, and which engulfed the rutile without reaction (see Fig. 5).

Microlite

Microlite commonly replaces pseudo-ixiolite crystals and penetrates from the partial pseudomorphs into adjacent feldspar and quartz (Fig. 6). In addition, granular intergrowths of pseudo-ixiolite and microlite occur in pegmatites No. 6 and 8; the two minerals appear to have originated simultaneously and to have coexisted without any reaction (Fig. 7). Microlite filling interstices between pseudo-ixiolite blades has been also observed. Isolated grains of pure microlite have been found only in the pegmatite GL–11.

Microlite is grayish-brown to dark brownish-gray, and practically undetectable when intimately intergrown with pseudo-ixiolite. X-ray study has shown that all microlites examined are perfectly crystalline, without noticeable change in intensities and *d*-spacings after heating. For the analyzed GL–11–15 specimen, $a = 10.399 \pm .001$ Å; four other specimens yielded values in the 10.375–10.410 Å range. This suggests that no Sr+Ba rich varieties occur in the pegmatites studied (these would have higher cell parameters). However, no other information about the chemical composition can be derived from structural dimensions (*cf.* Veen, 1963).

Chemical analysis of the GL–11–15 specimen (Table 3) has shown the molecular Nb_2O_5/Ta_2O_5 ratio to be 0.67, which is lower than those of the analyzed pseudo-ixiolites (Table 2). This is, unfortunately, the only information available about the composition of the cubic microlite-pyrochlore-type phases encountered. It is not possible, of course, to extrapolate this single analysis to all other occurrences, but the chance of finding some other member of the pyrochlore-microlite group in these pegmatites seems to be small. Tantalum-rich microlite is quite common in this type of granitic pegmatite, coexisting with or replacing tantalum-poorer columbite-type phases (*e.g.* Ginzburg 1956). The occurrence of true pyrochlore is restricted to more or less alkaline parageneses; other

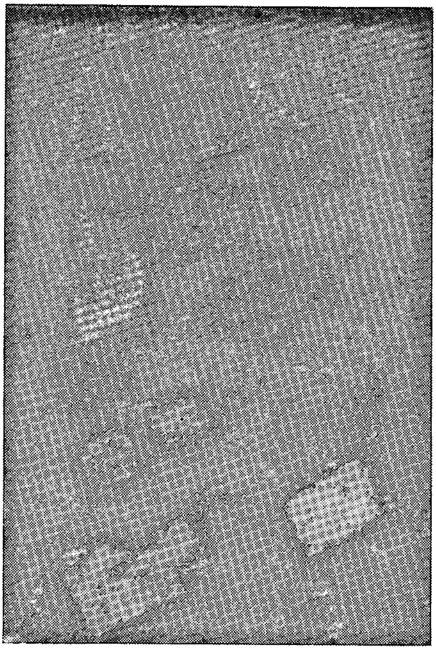

FIG. 6. Section across a bundle of radiating pseudo-ixiolite crystals (light grey) partly replaced by microlite (darker shade). Microlite penetrates also the feldspar matrix (dark grey); some light, high-relief grains in the pseudo-ixiolite crystals are probably niobian rutile. Specimen GL-2-2, crossed nicols, linear magnification 20x.

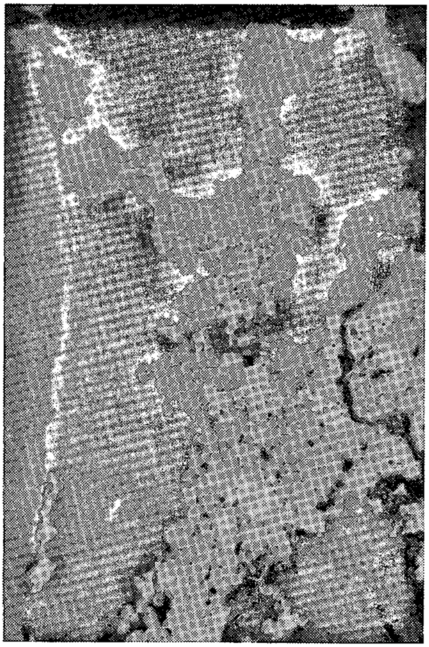

FIG. 7. Coexisting microlite and pseudo-ixiolite; grey microlite forms rounded equidimensional grains in light grey pseudo-ixiolite, both are imbedded in feldspar (dark grey). Specimen GL-6-1, crossed nicols, linear magnification 20x.

niobian varieties that are mostly rich in titanium (hatchettolite, obruchevite, betafite, etc.) occur in Nb,Ti,*RE*,Zr,Th,U rich pegmatites (*cf.* Vlasov *et al.* 1964). The only pegmatite related to this latter type studied here is the Huron Claim body; a possible pyrochlore-microlite phase has been found here only as tiny grains in polished sections.

Thus all cubic 10.4 Å minerals studied here are tentatively classified as microlite. Analysis of their composition would be feasible only by aid of electron microprobe, because they occur intergrown with other oxides on a fine scale.

Fersmite

This mineral—a complicated Ca,Al,Mg,*RE*-bearing member of the columbite group—was found only in the Huron Claim pegmatite. It replaces crystals of pseudo-ixiolite and often forms complete pseudomorphs after them (Fig. 8). Irregular grains without any crystal faces have also been found, closely attached to these pseudomorphs.

Fersmite is black-brown and semi-translucent, displays in transmitted light high birefringence, weak pleochroism (in pale brown and colourless), and is optically positive with medium $2V$. In polished sections fersmite is darker and softer than pseudo-ixiolite, lighter than microlite, and shows strong bireflectivity. Reddish-brown internal reflections can be observed only in oil immersion.

The x-ray powder diffraction pattern is similar to the one reported by Hess & Trumpour (1959). Unit cell dimensions are $a = 15.061 \pm 0.00$ Å, $b = 5.732 \pm 0.004$, $c = 5.216 \pm 0.004$; these are similar to the values found by the above authors and to those determined for the type fersmite by Bondstedt-Kupletskaya & Burova (1946), and for a synthetic analogue by Komkov (1960) (in Strunz 1966). The *RE*-rich, Y-enriched variety of fersmite described by Makarochkin *et al.* (1963) has different parameters.

Walker (1931) published a chemical analysis of alleged columbite from the Huron Claim pegmatite which gave a surprisingly high CaO content of 2.66% (Table 3). The density of the analyzed material was 5.87 and Walker regarded it as adequate for a columbite with the Nb/Ta ratio found by analysis. However, such a composition should have specific gravity of about 6.00, according to Berman's equation (Palache *et al.* 1944). Since fersmite contains 10-15% CaO and its specific gravity is just below 5.00, it is most probable that Walker's "columbite" was actually pseudo-ixiolite contaminated with fersmite. A new analysis of such material, with fersmite admixture proven by x-ray diffraction study, gave analogous results (Table 3).

Lack of material does not allow at present a more detailed study of this rare species, which was found in pegmatites only once (Makaroch-

Table 4. Unit Cell Dimensions of Niobian Rutile

Specimen	a_0	c_0	c_0/a_0
GL-8(W)-28	4.643 ± .004	2.984 ± .007	0.6427
GL-8C-30	4.648 ± .001	2.997 ± .001	0.6449
GL-12-1	4.650 ± .002	2.998 ± .002	0.6447
GL-9-18	4.654 ± .001	3.000 ± .001	0.6450
Rutile *	4.594	2.958	0.6439

* Synthetic TiO_2 (Powder Diffraction File 4-0551).

FIG. 8. Fersmite (darker phase) replaces a large pseudo-ixiolite crystal (lighter material). Specimen HC-3, crossed nicols, linear magnification 15x.

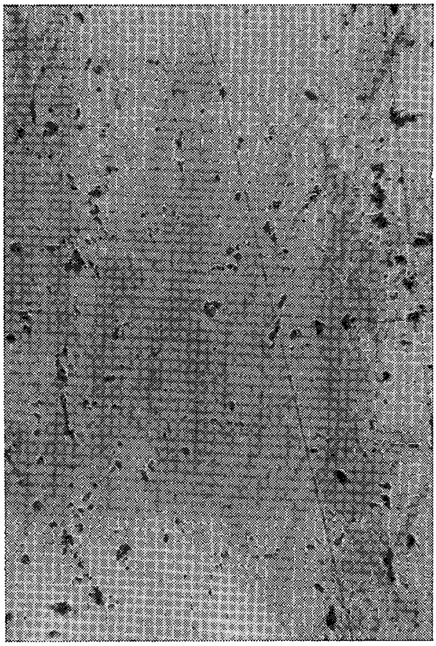

FIG. 9. Flame-like exsolution lamellae of columbite in niobian rutile follow two crystallographic directions in the host mineral. Specimen GL-8(2)-28, crossed nicols, linear magnification 70x.

kin *et al.* 1963). The other findings come from nepheline syenite exocontacts in the U.S.S.R., from carbonatites in Tanganyika, Norway, British Columbia, and U.S.S.R., and from carbonate veins in Montana and Idaho (*cf.* Vlasov *et al.* 1964; Heinrich & Levinson 1961; Veen 1963).

Niobian rutile

This mineral occurs in the No. 2, 8, 9, and 12 pegmatites. Its occurrence as inclusions in pseudo-ixiolite from the No. 2 pegmatite has been described above. In the other localities, Nb-rutile forms irregular grains with dark steel-grey colour and grainy fracture surface, mostly not distinguishable from pseudo-ixiolite in the field.

The crystals from pegmatites 8, 9, and 12 contain abundant, regularly-disseminated inclusions of columbite in exsolution-type patterns such as intersecting sets of flame-like lamellæ (Fig. 9), or irregular evenly disseminated grains. Despite the high percentage of columbite already exsolved, the unit cell dimensions of this rutile are very high (Table 4), comparable to those of homogeneous tantalian rutiles and higher than those of their exsolved niobium-rich counterparts (*cf.* Černý *et al.* 1964, Tab. 5, Fig. 4; Tschuchrov *et al.* 1965, p. 259-265). Only the Mozambique Nb-rutile described by Faria & Quadrado (1966) shows a higher c parameter. This indicates that the amount of $(Fe,Mn)(Nb,Ta)_2O_6$ in solid solution was exceptionally high in the original homogeneous minerals. Only one specimen (GL–8–28) was available in quantity sufficient for chemical analysis, but it confirms this assumption (Table 3). Recalculation leads to the formula $(Ti_{0.65}Fe_{0.45}Mn_{0.08}Nb_{0.58}Ta_{0.22}Sn_{0.09})_{\Sigma 2.07}O_4$. The analyzed specimen shows lower Ti content than the niobian rutile from Ukrainian pegmatite, which contains the lowest Ti percentage known to date (36.24 wt. %, Tschuchrov *et al.* 1965, p. 262). Also, Nb-rutile #GL–9–18 may have an even greater content of $(Fe,Mn)(Nb,Ta)_2O_6$ in solid solution, because its density (S.G. = 5.36) is greater than that of GL–8–28.

Cassiterite

Cassiterite was found only in the Silverleaf, No. 8 and 12A pegmatites. It forms isolated black grains at the first locality but was recognized only by *x*-rays in the latter, mixed with pseudo-ixiolite.

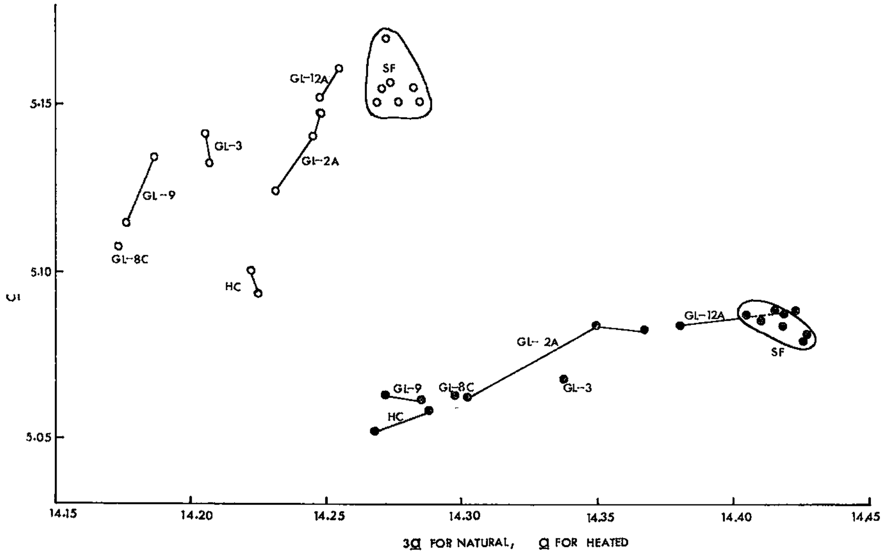

FIG. 10. Plot of cell dimensions of natural and heated pseudo-ixiolites as in Fig. 2. Lines connect (or encircle) specimens from a single pegmatite body.

Polished sections of the Silverleaf cassiterite show that it is fairly homogeneous in central parts of individual grains, but contains numerous tiny grains of columbite at the margins. Maybe this columbite is a segregated product of exsolution, but neither transitions to dusty or lamellar columbite, nor needle-shaped tapiolite exsolutions (*cf.* Ramdohr 1961 for description of characteristic exsolution phenomena) have been seen. Small grains and veinlets of a grey phase darker than cassiterite were also found, mostly closely associated with columbite.

Specific gravity 6.83 measured for one of the Silverleaf grains suggests a relatively high solid solution and/or admixture of lighter phases, as compared to 7.01 calculated for pure SnO_2. Unit cell dimensions of the same specimen did not show any significant departure from those known

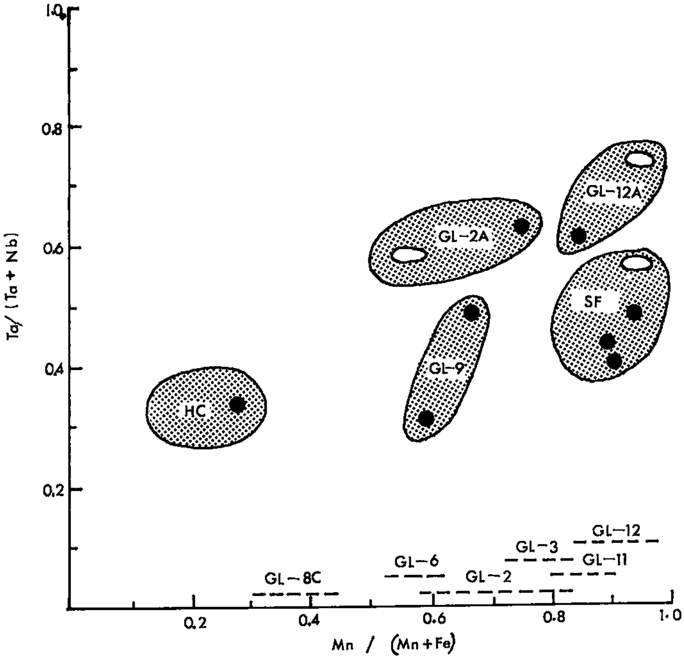

FIG. 11. Plot of Ta/(Ta+Nb) vs. Mn/(Mn+Fe) ratios of pseudo-ixiolites from different pegmatite bodies. Solid circles correspond to the analyzed specimens from Fig. 3; open ovals denote specimens with composition estimated from specific gravity and unit cell dimensions. Dotted areas cover the probable compositional fields for individual pegmatites, based also on partial estimates of other specimens. Dashed lines along the abscissa show the Mn/(Mn+Fe) ratios for pegmatites where no information about the Ta,Nb-contents is available.

for pure SnO_2, as is usual with natural cassiterite of any chemical composition.

Ilmenite

Ilmenite was found only once in the No. 8 pegmatite, and only in an *x*-ray diffraction pattern of a mixture of Nb-rutile and pseudo-ixiolite where four of its most prominent reflections were identified. Subsequent search for this potential Nb, Ta-carrier at the same locality and in other pegmatites was not successful. Maybe this ilmenite is only an exsolution product in niobian rutile, but its *x*-ray reflections seem to be intense: the amount of ilmenite exsolved from niobian rutile is usually very small, if any, and only the strongest reflection (at around 2.73 Å) can be detected (Černý *et al.* 1964).

PARAGENETIC RELATIONS

The Nb-Ta-oxides constitute only a small fraction of their parent pegmatites. Nevertheless their diversity reflects the geochemical character of their parent pegmatites.

1) The greatest contents of Mn in pseudo-ixiolite occur in Li-rich pegmatites, *viz*: the Silverleaf lithium deposit, and in pegmatites 11, 12 and 12A that carry lithium micas. The next greatest content of Mn in pseudo-ixiolite was found in Nos. 2, 2A, 3, 6, and 9 pegmatites, that are located close to lithium-enriched bodies (no. 9 close to Nos. 12 and 12A, the others close to the Li-bearing Captain Claim and Top of the World Claim pegmatites approx. 0.5 mile east of them; (*cf.* Wright 1932, Davies 1957).

2) The greatest contents of Fe in pseudo-ixiolite occur in the Huron Claim pegmatite, which carries also partly ordered columbite, fersmite, and some microlite. The composition of pseudo-ixiolite and columbite, as well as the assemblage of Nb-Ta-minerals and other accessories, is different from that of the other pegmatites (Figs. 1, 11); this corresponds to the generally different character of this pegmatite.

The second greatest Fe-content was found in pseudo-ixiolite from No. 8 pegmatite, and is still distinctly separated from the cluster of Mn-rich phases above $Mn/(Mn+Fe) = 0.5$ (in Fig. 11). The highest concentration of Nb-rutile and the only occurrence of ilmenite is characteristic for this pegmatite; both these phases are iron-rich, too.

3) The content of Ta in pseudo-ixiolite is generally greater in samples from lithium-bearing pegmatites, but not proportionally to the apparent

lithium concentration. Pseudo-ixiolite from the Silverleaf lithium deposit is richer in Nb than that from No. 12A body which carries only negligible amounts of lithium mica.

4) In most of the pegmatites, pseudo-ixiolite seems to occur only in one unit : either in medium-grained albite + quartz + muscovite + garnet assemblage (No. 8, 11, 12A), or in late cleavelandite (No. 2, 2A, 9). It was found in both units in the No. 3 pegmatite, where no significant difference between the Fe and Mn contents of pseudo-ixiolites from the two units (Figs. 2 and 10) have been found. In the Silverleaf pegmatite, the later varieties associated with lithium minerals are enriched in Mn + Ta as contrasted to earlier pseudo-ixiolite from blocky K-feldspar (Table 1, Fig. 11).

5) Microlite is widespread, replacing pseudo-ixiolite in most localities but coexisting with relatively Fe-rich pseudo-ixiolite in No. 6 and 8 veins.

6) Cassiterite is most common in the Li-rich Silverleaf pegmatite, and occurs also in other veins with lithium minerals but is not restricted to them.

7) No Nb-Ta-minerals were found in the pegmatites F, 1, 4A, 4B, and 7, that are linearly arranged parallel to the country rock foliation in the central and eastern part of the area studied. Maybe this has some geochemical significance, but it should be stressed that (with exception of No. 1) the outcrops of these particular veins are very poor and the amount of dumped rock very small; thus the "absence" of Nb, Ta-phases may be due to insufficient sampling.

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REFERENCES

BRANDT, K. (1943) : X-ray studies on ABO_4 compounds of rutile type and AB_2O_6 compounds of columbite type. *Arkiv Kemi, Miner. Geol.* **17-A,** 1-8.

BONSHTEDT-KUPLETSKAYA, F.M. & BUROVA, T.A. (1946) : Fersmite — a new calcium niobate from the Vishnevye Mts. pegmatites, Central Urals (in Russian). *Doklady Acad. Sci. U.S.S.R.* **52,** 69-72.

Černý, P., Čech, F. & Povondra, P. (1964) : Review of ilmenorutile — strüverite minerals. *N. Jahrb. f. Miner., Abh.* **101,** 142-172.

Davies, J.F. (1957) : Geology of the Winnipeg River area (Shatford Lake — Ryerson Lake), Lac du Bonnet mining division, Manitoba. *Manitoba Dept. Mines and Nat. Res., Mines Branch Publ.* **56-1.**

Evans, H.T., Appleman, D.E. & Handwerker, D.S. (1963) : The least squares refinement of crystal unit cells with powder diffraction data by an automatic computer indexing method (abs.) *Progr. Ann. Meeting Amer. Cryst. Assoc.* 1963, 42-43.

Faria, J. Lima de & Quadrado, R. (1966) : Ilmenorutile and strüverite from Nampoca, Alto Ligonha, Mozambique. *Garcia de Orta (Lisboa)* **14,** 305-310.

Ginzburg, A.I. (1956) : On some characteristics of tantalum geochemistry and on types of tantalum mineralization (in Russian). *Geokhimia* 74-83.

Heinrich, E. Wm. & Levinson, A.A. (1961) : Carbonatic niobium-rare earth deposits, Ravalli County, Montana. *Amer. Mineral.* **46,** 1424-1447.

Hess, H.D. & Trumpour, H.J. (1959) : Second occurrence of fersmite. *Amer. Mineral.* **44,** 1-8.

Knorring, O.V., Sahama, Th.G. & Lehtinein, M. (1969) : Scandian ixiolite from Mozambique and Madagascar. *Bull. Geol. Soc. Finland* **41,** 75-77.

Kumskova, N.M. (1962) : X-ray study of the minerals of the columbite-tantalite group (in Russian). *X-ray Study of Mineral Raw Materials* (Rentgenografia mineralnovo syria) No. 1.

Makarochkin, B.A., Eskova, E.M. & Aleksandrov, V.B. (1963) On a new rare-earth variety of fersmite (in Russian). *Doklady Acad. Sci. U.S.S.R.* **148,** 179-182.

Nickel, E.H., Rowland, J.F. & McAdam, R.C. (1963) : Ixiolite, a columbite substructure. *Amer. Mineral.* **48,** 961-979.

Palache, C., Berman, H. & Frondel, C. (1944) : *Dana's System of Mineralogy,* 7th ed., **1.** Wiley New York.

Ramdohr, P. (1961) : Magnetische Cassiterite. *Bull. Comm. Géol. Finlande* **196,** 473-481.

Schröcke, H. (1966) : Über Festkörpergleichgewichte innerhalb der Columbit-Tapiolitgruppe, sowie Columbit-Tapiolitgruppe mit $YTi(Nb,Ta)O_6$, Euxenit, und mit $FeNbO_4$. *N.Jb. Miner. Abh.* **106,** 1-54.

Springer, G.D. (1950) : Mineral deposits of the Cat Lake-Winnipeg River area, *Manitoba Dept. Mines & Nat. Res. Mines Branch Publ.* **49-7.**

Strunz, H. (1966) : *Mineralogische Tabellen,* 4th ed. Akademie-Verlag Leipzig.

Tschuchrov, F.V. ed. (1965) : *Minerals — a reference book,* Vol. II, pt. 2, Simple Oxides (in Russian). Nauka Moscow.

Turnock, A.C. (1966*a*) : Fe-Nb Oxides: Phase relations at 1180°C. *J. Am. Ceramic Soc.* **49,** 177-180.

Turnock, A.C. (1966*b*) : Synthetic wodginite, tapiolite and tantalite. *Can. Mineral.* **8,** 461-470.

Veen, A.H.v.d. (1963) : A study of pyrochlore. *Verhandelingen v.h. Konink. Nederlands geol. Mijnbouw. genootschap, geol. series No.* **22,** 188pp.

Vlasov, K.A. ed. (1964) : *Geochemistry and Mineralogy of Rare Elements and Genetic Types of their Deposits,* **2** — Mineralogy of rare elements (in Russian). Nauka Moscow. Engl. translation Jerusalem 1966.

Walker, T.L. (1931) : Rare minerals in pegmatite, Pointe du Bois, Manitoba. *Contr. to Canad. Mineralogy 1931, Univ. Toronto Studies, geol. series* **30,** 9-13.

Wright, J.F. (1932) : Geology and Mineral deposits of a part of Southeastern Manitoba. *Canada Dept. Mines and Res., Mines and Geol. Branch Memoir* **169,** 150 pp.

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