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TITANIAN BERTHIERINE: A Ti-RICH SERPENTINE-GROUP MINERAL FROM THE PICTON ULTRAMAFIC DYKE, ONTARIO

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ABSTRACT

A serpentine-group mineral, titanian berthierine, occurs in the groundmass of the Picton ultramafic dyke, near Picton, southeastern Ontario. X-ray diffraction shows that it is isostructural with members of the serpentine group. It occurs as a cryptocrystalline aggregate of apparently fibrous, reddish brown crystals. Electron-microprobe analyses show high TiO_2 (18.5–20.5%), FeO_T(23.7–26.2%), and Al_2O_3 (8.6–16.1%) and low SiO_2 (21.8–26.5%) and MgO (4.9–6.8%) contents. The chemical formula of titanian berthierine $[M_{3-(2x+y+2z)}Ti_{y+z}\square_zAl_{2x}]Al_{2(x+y)}Si_{2-2(x+y)}O_5(OH)_4$($M$ divalent cations, $\square$ octahedral vacancies, x 0.10– 0.015, y 0.39–0.185, z 0.54–0.43), suggests that this phase is a trioctahedral–dioctahedral sheet silicate, and that Ti is incorporated by the combination of the substitutions $2^{VI}M = {}^{VI}Ti + {}^{VI}\square$ and ${}^{VI}M + 2^{IV}Si = {}^{VI}Ti + 2^{IV}Al$. Titanian berthierine is spatially associated with titanian magnesioferrite and ferroan spinel. Textural relations suggest a replacement origin after titanian magnesioferrite. Titanian berthierine is the most Ti-rich serpentine-group mineral reported to date.

Keywords: titanian berthierine, ultramafic dyke, titanian magnesioferrite, ferroan spinel, electron microprobe analyses, Picton, Ontario.

SOMMAIRE

On trouve une berthierine titanifère dans la pâte d'un dyke ultramafique, près de Picton (Sud-Est de l'Ontario). Les données obtenues par diffraction X montrent qu'elle est isotype des structures du groupe de la serpentine. Elle forme des agrégats cryptocristallins brun rougeâtre, apparemment composés de fibres. Les données à la microsonde électronique révèlent de hautes teneurs en titane (18.5–20.5% TiO_2), fer total (23.7–26.2% FeO) et aluminium (8.6 - 16.1% Al_2O_3) et de faibles teneurs en silicium (21.8 - 26.5% SiO_2) et magnésium (4.9 - 6.8%) MgO. La formule chimique, $[M_{3-(2x+y+2z)}Ti_{y+z}\square_zAl_{2x}]Al_{2(x+y)}Si_{2-2(x+y)}O_5(OH)_4$($M$ cations divalent, $\square$ lacune octaédrique, x de 0.10 à 0.015, y de 0.39 à 0.185, z de 0.54 à 0.43) fait penser qu'il s'agit d'un phyllosilicate trioctaédrique - dioctaédrique et que le Ti y est présent grâce à la combinaison des substitutions $2^{VI}M = {}^{VI}Ti + {}^{VI}\square$ et ${}^{VI}M + 2^{IV}Si = {}^{VI}Ti + 2^{IV}Al$. La berthierine est associée à magnésioferrite titanifère et spinelle ferrifère. D'après les textures, la berthierine serait produite par remplacement de la magnésioferrite. Elle constitue, à ce jour, le minéral le plus riche en Ti de la famille des serpentines.

(Traduit par la Rédaction)

Mots-clés: berthierine titanifère, dyke ultramafique, magnésioferrite titanifère, spinelle ferrifère, analyses à la microsonde électronique, Picton, Ontario.

INTRODUCTION

The Picton ultramafic dyke, of Jurassic age, intrudes Ordovician limestone of the Trenton Group in the vicinity of Picton, southeastern Ontario. In the context of geochemical and petrological studies on this dyke, an unidentified silicate mineral was found and referred to as a "Ti–Al–Mg–Fe unidentified phase" (Barnett *et al.* 1984).

In the present paper, we identify this phase as a serpentine-group mineral, report on its occurrence, paragenesis and chemical composition, and present X-ray-diffraction data. This new variety of serpentine is titanian berthierine.

OCCURRENCE AND PARAGENESIS

The Picton dyke consists of a volatile-rich ultramafic igneous rock chemically and mineralogically similar to kimberlite (Barnett *et al.* 1984). The dyke is heterogeneous and consists of a coarse-grained central zone with an inequigranular texture and an aphanitic marginal zone. The central zone consists of olivine, now serpentine, and phlogopite phenocrysts set in a groundmass of serpentine, calcite, chlorite, apatite, perovskite, ilmenite, and several varieties of spinel phases (ferroan spinel, magnesiochromite and titanian magnesioferrite). The detailed petrography, mineralogy and geochemistry of the dyke have been described by Barnett *et al.* (1984).

Titanian berthierine is associated with type-2 and type-3 spinel occurrences in the Picton dyke (Barnett *et al.* 1984). Type-1 spinel occurs as euhedral grains of magnesiochromite included within serpentinized olivine phenocrysts. Type-2 spinel defines aggregates of euhedral to subhedral grains scattered throughout the groundmass, and compositionally zoned; a magnesiochromite core is mantled by ferroan spinel and rimmed by titanian magnesioferrite. In some parts of the dyke a definite atoll texture is developed, with a zone of titanian berthierine present between the inner ferroan spinel and the outer titanian magnesioferrite rim (Fig. 1, 2). The central grain of each atoll is commonly euhedral, but grains comprising the outer margin of titanian magnesioferrite are ragged and discontinuous (Figs. 1, 2). Type-3 spinel occurs as euhedral and subhedral grains of titanian magnesioferrite and, rarely, ferroan spinel, forming a discontinuous ring around serpentinized olivine (Fig. 3). In spite of different textural variations (Types 2, 3), titanian magnesioferrite and ferroan spinel show only narrow ranges of compositional variation (Barnett *et al.* 1984). Representative compositions of these spinel phases are given in Table 1.

Titanian berthierine occurs as an apparent product of the pseudomorphous replacement of the titanian magnesioferrite only (Figs. 1–6). The ferroan spinel and the magnesiochromite are apparently not involved in the reaction. Original grains of titanian magnesioferrite exhibit all stages of replacement: incipient, extensive and complete. Original outlines of euhedral and granular grains are well preserved (Fig. 4).

Certain grains of titanian magnesioferrite are also replaced by a cryptocrystalline aggregate of fine-grained crystals with extremely high reflectivity under reflected light. Electron-microprobe analysis indicates an extremely high Ti content (up to 67.0 wt.% TiO_2), suggesting that this aggregate is a mixture of anatase or perovskite with a silicate phase.

In thin section, Ti-serpentine occurs as translucent cryptocrystalline aggregates of apparently fibrous grains. In type-2 spinel aggregates, the apparently fibrous grains of titanian berthierine are oriented normal to the {111} faces of spinel, giving the appearance of sector zoning (Fig. 1). Titanian berthierine is light to dark reddish brown in color. It is optically anisotropic, with a weak birefringence,

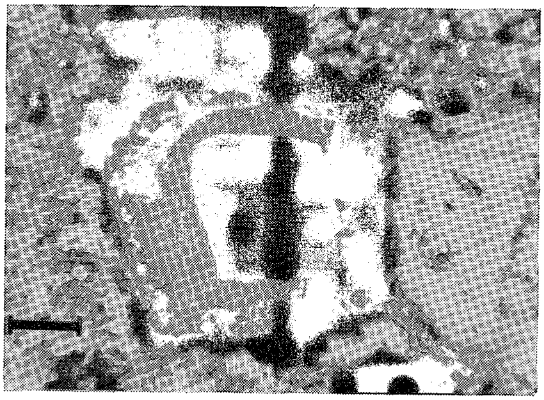

FIG. 1. Titanian berthierine associated with type-2 spinel showing atoll texture. Intermediate "lagoon" region of titanian berthierine consists of apparently fibrous crystals oriented normal to {111} of central spinel grain with euhedral morphology. Scale bar: 50 μm. Transmitted light, plane polarized.

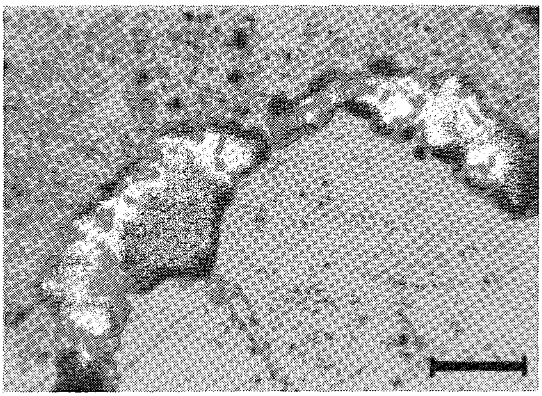

FIG. 3. Titanian berthierine with type-3 spinel that surrounds serpentinized phenocrysts at lower right. A few grains of titanian magnesioferrite (black) are partly replaced by titanian berthierine. Scale bar: 70 μm. Transmitted light, plane polarized.

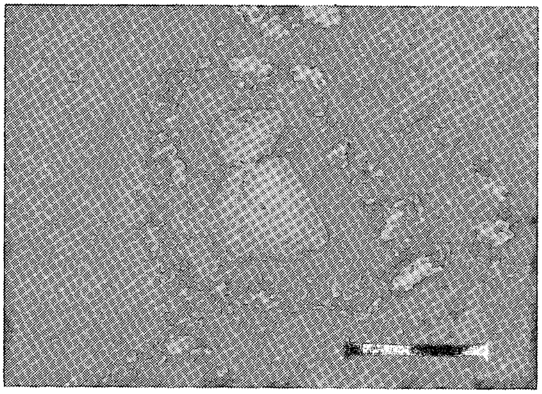

FIG. 2. Atoll spinel with a wide "lagoon" of titanian berthierine. Outer rim of titanian magnesioferrite (white) is partly replaced by titanian berthierine. Central grains with euhedral morphology consist of magnesiochromite core (light grey) and ferroan spinel margin (dark grey) and are not involved in the replacement. Scale bar: 100 μm. Reflected light, plane polarized.

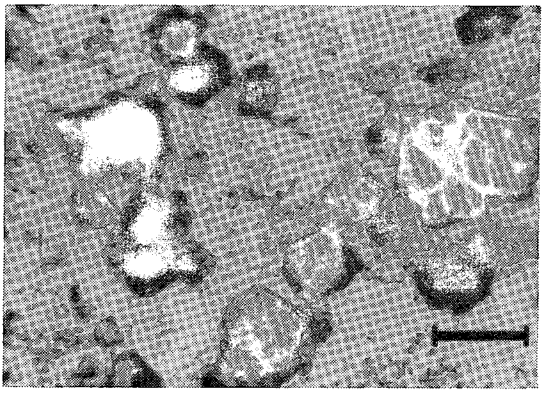

FIG. 4. Titanian berthierine occurring as pseudomorphous replacement products of titanian magnesioferrite. Original outline of spinel grain is well preserved. Some grains show an incipient stage of replacement, in which central part of grain (black) is titanian magnesioferrite and marginal area is titanian berthierine. Scale bar: 70 μm. Transmitted light, plane polarized.

similar to that of serpentinized phenocrysts. Representative microprobe data for the serpentinized phenocrysts, which apparently were olivine, are given in Table 3. Based on the criteria of Wicks & Whittaker (1977), the pseudomorphous serpentine probably is lizardite.

X-RAY-DIFFRACTION ANALYSIS

Individual pseudomorphous masses of titanian berthierine (0.1–0.3 mm in diameter) were removed from uncovered thin sections and thick sections and mounted as single or aggregate "grains" on glass fibres. Samples were taken of pseudomorphs within and around grains of serpentinized olivine and of pseudomorphs isolated within the altered groundmass. All attached serpentine and altered groundmass was carefully trimmed from the pseudomorphs before mounting, although it was not possible in all cases to remove included grains of spinel. Four separate mounts were prepared and examined by Gandolfi camera (57.3 mm diameter, Cr*Kα*, Fe*Kα* radiation), Debye–Scherrer camera (114.6 mm diameter, Cr*Kα*, Fe*Kα* radiation) and, in one case, precession camera (Mo*Kα* radiation) methods.

Precession-camera analysis of a single pseudomorph mount with no visible spinel inclusions revealed only powder rings, with no indication of preferred orientation of the crystallites. The Debye–Scherrer reflections of titanian berthierine also occur as uniform powder-rings. This confirms the petrographic observation of the fine grain-size. Some thin sections do suggest a preferred (possibly radial) alignment of titanian berthierine fibres (*e.g.*, Fig. 1), but this was not manifest in our somewhat limited X-ray-diffraction study.

The X-ray powder data for titanian berthierine presented in Table 2 are average data for the various Gandolfi and Debye–Scherrer patterns obtained with Cr*Kα* radiation. The limited amount of material available prevented documentation of a more complete powder-pattern. Several of the recorded lines have the appearance of diffraction bands, but this effect may result from the coalescence of several adjacent diffuse lines. A number of lines were barely discernible from background and were not recorded. Line 8 is a spinel diffraction and line 11 is a composite titanian berthierine – spinel diffraction. Spinel inclusions yield single-crystal reflections on the Debye–Scherrer patterns.

Preliminary analysis by microprobe suggested that

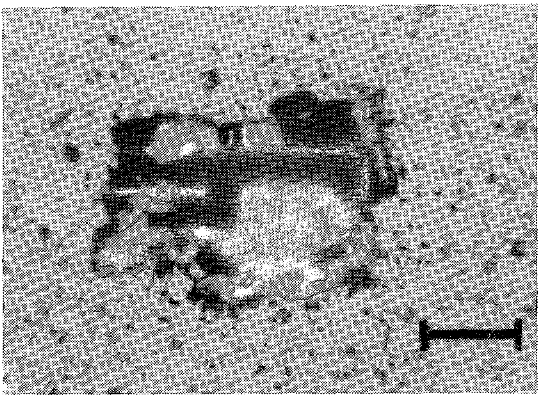

FIG. 5. Type-2 spinel showing a zoned central grain with a magnesiochromite core (black) mantled by ferroan spinel marginal area (dark grey). Outer rim consists of titanian magnesioferrite (black) and titanian berthierine (light grey). Titanian magnesioferrite directly mantles central grains of ferroan spinel and is partly replaced by titanian berthierine. Scale bar: 70 μm. Transmitted light, plane polarized.

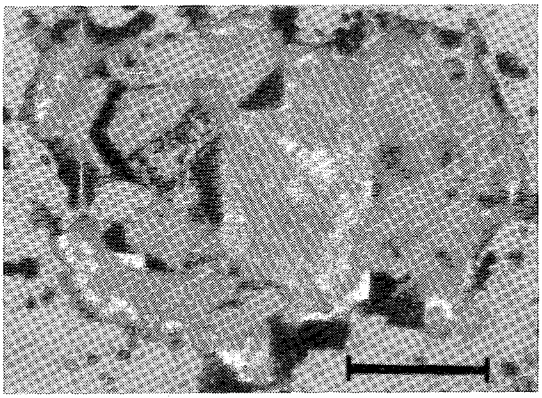

FIG. 6. Titanian berthierine mantling but not replacing a ferroan spinel central grain (dark grey). Original spinel morphology is preserved and marked by small grains of titanian magnesioferrite (black). Scale bar: 40 μm. Transmitted light, plane polarized.

TABLE 1. REPRESENTATIVE COMPOSITION OF SPINEL PHASES

	1	2	3
wt. %			
TiO_2	12.21	2.50	2.38
Al_2O_3	16.31	48.95	10.59
Cr_2O_3	0.18	0.50	48.32
Fe_2O_3*	34.23	16.54	9.81
FeO*	22.33	12.66	16.50
MnO	0.31	0.20	0.19
MgO	14.76	18.97	12.51
Total	100.33	100.32	100.30
	Formulae based on 4 oxygen atoms		
Ti	0.289	0.051	0.058
Al	0.605	1.553	0.405
Cr	0.005	0.011	1.239
Fe^{3+}	0.811	0.335	0.240
Fe^{2+}	0.588	0.285	0.447
Mn	0.008	0.005	0.005
Mg	0.693	0.761	0.605
	2.999	3.001	2.999

1 titanian magnesioferrite, 2 ferroan spinel, 3 magnesiochromite. Compositions determined by electron microprobe. * Calculated on a magnetite-ulvöspinel basis (Carmichael 1967).

the unknown is either serpentine-like or chlorite-like, and this is immediately confirmed by the X-ray powder pattern. Moreover, the characteristic 14.1 to 14.3 Å chlorite line (001) is not present on the 114.6-mm-diameter Debye–Scherrer films, and the 4.65 Å chlorite line (003) is also absent. Therefore, the unknown mineral appears to be a 1:1 layer silicate of the serpentine group and is appropriately identified as titanian berthierine. Precise comparison with existing powder-data for serpentine-group minerals is hampered by its unusual chemistry and uncertainty in the nature of the polytype. However, our data for titanian berthierine are quite similar to the patterns of berthierine (PDF 31-618, Brindley & Youell 1953) and brindleyite (PDF 31-892A, Maksimovic & Bish 1978). Furthermore, there is good agreement with the calculated powder-pattern for $2H_1$ $Mg_3Si_2O_5(OH)_4$ (Bailey 1969) and fair agreement with the *1M* (-*3T*) polytype (Table 2). The titanian berthierine pattern has been indexed provisionally with the $2H_1$ unit-cell. The 6-layer orthohexagonal unit-cell used in PDF 13-4 to index the type *F* aluminian serpentine of Bailey & Tyler (1960) gives a more complete description of the pattern. However, Jahanbagloo & Zoltai (1968) reported that an aluminian serpentine that gives the same powder-pattern as the type *F* specimen has a 9-layer or 18-layer structure.

In summary, the X-ray powder-diffraction data identify the unknown as a serpentine-group mineral (titanian berthierine). This is consistent with its chemical composition and its apparent fibrous habit.

CHEMICAL COMPOSITION

Chemical analyses were done using the MAC-400 electron microprobe at the University of Western Ontario (wavelength dispersion, 15 kV and sample current 0.025 μA). Data were corrected using the MAGIC computer program of Colby (1971). The following standard materials were used: bronzite for Si, Mg and Fe, kaersutite for Al and Ti, diopside for Ca, orthoclase for K, albite for Na, chromite for Cr, and rhodonite for Mn. Repesentative compositions are reported in Table 3. Estimated errors are ± 3% for major elements and ± 5% for minor elements. The analyses were done on 25 separate grains in sections cut from the same rock chip used for the X-ray-diffraction study.

Titanian berthierine is characterized by high Ti (18.5–20.5 wt.% TiO_2), Fe (23.7–26.2 wt.% FeO_T) and Al (8.6–16.09 wt.% Al_2O_3) contents and low Si (21.8–26.5 wt.% SiO_2) and Mg (4.9–6.8 wt.% MgO) contents. It exhibits significant variations in Ti, Al, Mg, Fe and Si, which do not appear to be related to the textural details of its occurrence. Although H_2O and other volatile components were not determined, the oxide totals of probe analyses are generally lower than 90 wt.%, suggesting the presence of H_2O or other components.

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR TITANIAN BERTHIERINE, WITH COMPARATIVE DATA FOR $Mg_3Si_2O_5(OH)_4$ POLYTYPES†

	titanian berthierine			1M-3T			$2H_1$		
line	hkl	d(Å)	I/Io	hkl	d(Å)	I/Io	hkl	d(Å)	I/Io
1	002	7.27	100	001	7.100	88	002	7.100	100
				020	4.625	14			
2	100	4.56	50b	110	4.519	27	100	4.625	45
				$11\bar{1}$	4.242	22			
3	102	3.86	5	021	3.875	17	102	3.875	55
4	-	3.62	3						
5	004	3.524	50	002	3.550	60	004	3.550	68
				111	3.492	12			
6	-	3.33	5						
7	-	3.15	2						
8		(3.024)*	(30)						
9	104	2.901	2	022	2.816	6	104	2.816	19
10	110,111	2.623	15	$20\bar{1}$	2.649	26	110	2.670	3
							111	2.624	12
11	112	2.483**	50b		?		112	2.499	98
12	006,113	2.370	10	$20\bar{2}$	2.387	100	006	2.367	7
							113	2.326	35
13	-	2.286	3	201	2.263	6			
				$20\bar{3}$	2.007	25	115	1.945	35
14	115,204	1.907	25b	042	1.938	2	204	1.938	5
				202	1.886	6			
				$31\bar{2}$	1.697	2	122	1.697	9
15	122,108, 206,117	1.677	20b	$20\bar{4}$	1.665	32	108	1.657	2
				151	1.661	2	206	1.654	5
							117	1.615	20
				$3\bar{1}3$,203	1.568	14	124	1.568	5
16	124,300, 302	1.542	30b	060	1.542	29	300	1.542	33
				061	1.506	13	302	1.506	14

Data obtained using CrKα radiation. † Bailey (1969). * Spinel reflection, b band, ** interference due to spinel reflection.

Discussion

Structural formula and cation substitutions

As titanian berthierine has been identified from the X-ray powder-diffraction data to be a serpentine-group mineral, it is reasonable to assume that the low total of oxides in the probe analyses largely reflects the presence of H_2O bound in the crystal structure. However, the presence of absorbed water could not be ruled out; hence we calculated cation proportions and chemical formula on the basis of anhydrous serpentine with 7 oxygen atoms (*e.g.*, Wicks 1979). The calculated chemical formulae (Table 3) show significant amounts of octahedral vacancies and a predominance of tetrahedral Al cations (^{IV}Al) over octahedral Al cations (^{VI}Al). Ti occupies approximately ¼ of the octahedral sites. The assignment of Al to both tetrahedral and octahedral sites is based on an analogy with the structural formulae of berthierine (Brindley & Youell 1953), brindleyite (Maksimovic & Bish 1978) and Al-rich multilayer lizardite (Wicks & Plant 1979). It is also supported by the clear negative correlation between the proportions of Si and Al cations in the chemical formulae (Fig. 7).

TABLE 3. COMPOSITION OF TITANIAN BERTHIERINE AND SERPENTINE AFTER OLIVINE

	1	2	3	4	5	6	7
wt. %							
SiO_2	22.73	23.40	22.29	25.50	26.19	23.87	42.75
TiO_2	20.48	19.09	19.82	20.13	18.58	19.03	0.00
Al_2O_3	15.74	12.99	13.97	12.64	9.84	12.99	0.40
Cr_2O_3	0.29	0.02	0.25	0.36	0.66	0.24	0.00
FeO*	24.04	26.18	25.64	24.72	24.06	24.63	16.66
MnO	0.27	0.06	0.00	0.01	0.07	0.04	0.00
MgO	4.87	5.81	5.34	4.90	6.80	5.69	24.71
CaO	0.73	0.50	0.63	0.66	0.58	0.61	0.16
Na_2O	0.00	0.03	0.07	0.01	0.29	0.11	0.00
K_2O	0.04	0.09	0.11	0.18	0.16	0.13	0.04
Total	89.19	88.17	88.12	89.11	87.23	87.33	84.72
Formulae based on 7 oxygen atoms							
Si	1.198	1.263	1.204	1.344	1.412	1.290	2.181
Al^{IV}	0.802	0.737	0.796	0.656	0.588	0.710	0.000
	2.000	2.000	2.000	2.000	2.000	2.000	2.181
Al^{VI}	0.176	0.089	0.093	0.128	0.037	0.117	0.024
Ti	0.812	0.775	0.805	0.798	0.753	0.773	0.000
Cr	0.012	0.001	0.011	0.015	0.028	0.010	0.000
Fe	1.060	1.181	1.158	1.089	1.085	1.113	0.711
Mn	0.012	0.003	0.000	0.000	0.003	0.002	0.000
Mg	0.383	0.467	0.430	0.385	0.547	0.458	1.880
Ca	0.041	0.029	0.037	0.037	0.037	0.035	0.008
Na	0.000	0.003	0.007	0.001	0.030	0.011	0.000
K	0.003	0.006	0.008	0.012	0.011	0.008	0.002
	2.499	2.554	2.548	2.465	2.531	2.527	2.625
$\square^{VI}$	0.50	0.45	0.45	0.53	0.47	0.47	
H_2O**	1.9	2.1	2.1	1.9	2.3	2.3	

1-5 composition of individual grains, 6 average composition, based on 25 analyses (electron microprobe), 7 serpentine pseudomorph after olivine phenocryst (composition is the average of four analyses). * Total iron as FeO. ** Calculated mole proportion of H_2O relative to anhydrous formula (see text).

Octahedral vacancies amount to about 0.5 cations sites per formula unit. Titanian berthierine is clearly a trioctahedral–dioctahedral sheet silicate. The nature of the cation substitutions and the eventual classification of this mineral can best be understood by examining the formula in terms of ideal end-member compositions. Thus brindleyite, with an ideal formula of $M_{1.75}\,\mathrm{Al}_{1.0}\,\square_{0.25}(\mathrm{Si}_{1.5}\mathrm{Al}_{0.5})\mathrm{O}_5(\mathrm{OH})_4$ (Maksimovic & Bish 1978), where M represents the

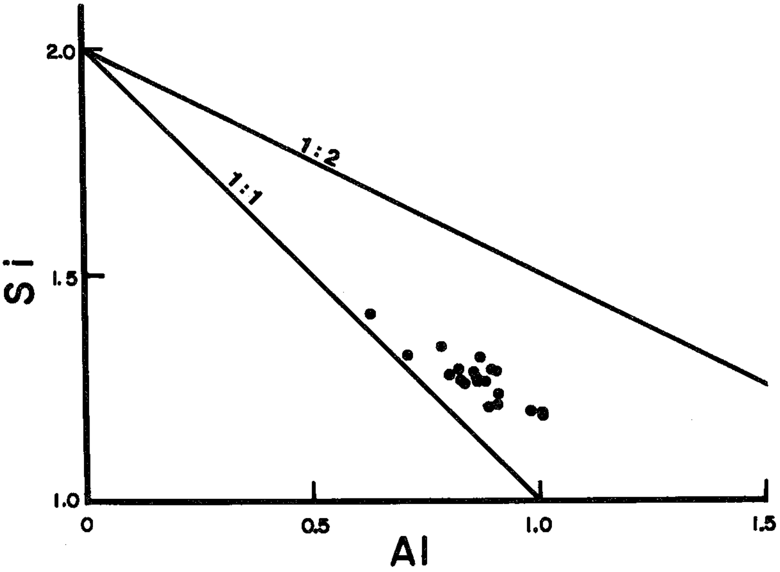

FIG. 7. Relation between the proportions of Si and Al cations in the chemical formula of titanian berthierine. Numbers of Si and Al cations were calculated on the basis of an anhydrous serpentine formula (7 oxygen atoms). Titanian berthierine compositions plot between lines 1:1 and 2:1, indicating ^{IV}Al predominant over ^{VI}Al.

divalent octahedral cations and □ the octahedral vacancies, becomes:

0.5	$M_3(Si_2)O_5(OH)_4$	trioctahedral
0.25	$MAl_2(Al_2)O_5(OH)_4$	trioctahedral
0.25	$Al_2\square(Si_2)O_5(OH)_4$	dioctahedral

Likewise, Ti-serpentine becomes:

w	$M_3(Si_2)O_5(OH)_4$	trioctahedral	(1)
x	$MAl_2(Al_2)O_5(OH)_4$	trioctahedral	(2)
y	$M_2Ti(Al_2)O_5(OH)_4$	trioctahedral	(3)
z	$MTi\square(Si_2)O_5(OH)_4$	dioctahedral	(4)

End member (2) results from the familiar "tschermakite" substitution and, combined with end member (1), yields the berthierine formula (Brindley & Youell 1953). However, this end member is relatively unimportant in titanian berthierine (Table 3, Fig. 7). The important substitutions appear to be $^{VI}Mg + 2^{IV}Si = {}^{VI}Ti + 2^{IV}Al$ and $2\ {}^{VI}Mg = {}^{VI}Ti + {}^{VI}\square$, which are represented by end members (3) and (4), respectively. These two types of substitutions have been suggested to be the common mechanism for Ti incorporation in phlogopite (Forbes & Flower 1974, Robert 1976, Arima & Edgar 1981). Their relevance to titanian berthierine may be demonstrated by analyzing the mineral compositions with the following reasoning:

from end member (3) $y\ Ti = ½\ ({}^{IV}Al - {}^{VI}Al)$
and, from end member (4), $2Ti = {}^{VI}\square$

Therefore, the proposed complex substitution requires $\Sigma Ti = (y+z) = ½({}^{IV}Al - {}^{VI}Al) + {}^{VI}\square$. A plot of Ti *versus* $½({}^{IV}Al - {}^{VI}Al) + {}^{VI}\square$ (Fig. 8) is in good agreement with this requirement.

In the present scheme for reducing the microprobe data to mineral formulae, Fe is assumed to be Fe^{2+}. Our calculations show that the Fe^{3+} content must be fairly low. Assuming that the low totals of the probe analyses represent a H_2O content bound in the crystal structure, the molecular proportion of H_2O relative to anhydrous total cations was calculated. The results are in good agreement with the theoretically deduced H_2O content in the serpentine structure (Table 3).

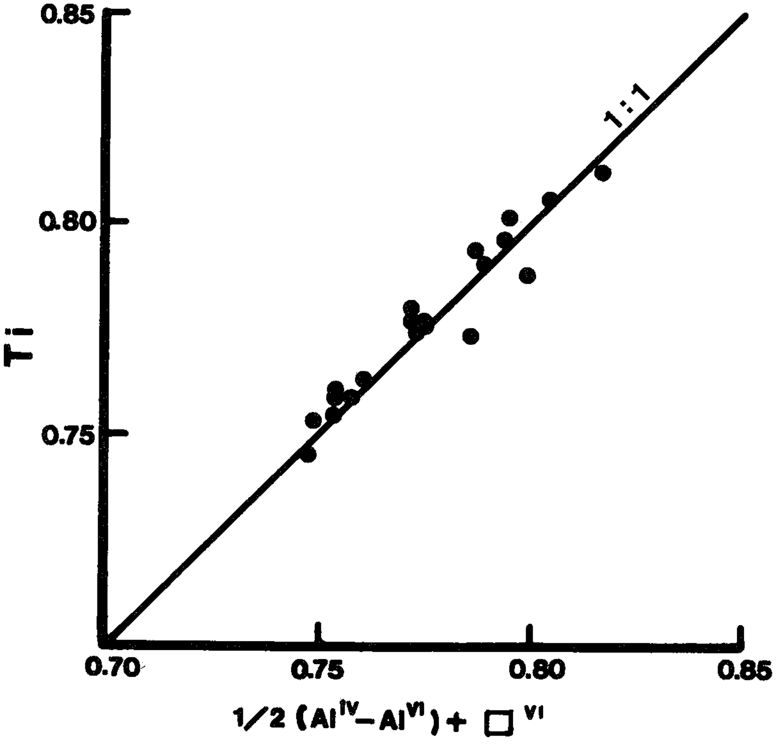

FIG. 8. Relation between Ti and $½({}^{IV}Al - {}^{VI}Al) + {}^{VI}\square$ in the chemical formula of titanian berthierine. Titanian berthierine compositions plot along a line 1:1, suggesting that Ti is incorporated in titanian berthierine by the combination of the substitution schemes $^{VI}Mg + 2^{IV}Si = {}^{VI}Ti + 2^{IV}Al$ and $2^{VI}Mg = {}^{VI}Ti + {}^{VI}\square$.

On the basis of results of microprobe and X-ray-diffraction analyses and the preceding discussion, we suggest the general chemical formula of titanian berthierine is: $[M_{3-(2x+y+2z)}\mathrm{Ti}_{y+z}\square_z\mathrm{Al}_{2x}]$ $[\mathrm{Al}_{2(x+y)}\mathrm{Si}_{2-2(x+y)}]\mathrm{O}_5(\mathrm{OH})_4$ with x 0.10–0.015, y 0.39–0.185 and z 0.54–0.43. The number z of octahedral vacancies is larger than y, the value of the parameter 1/2 (^{IV}Al–^{VI}Al), suggesting the predominant presence of the dioctahedral end-member $(M\mathrm{Ti}\square)(\mathrm{Si}_2)\mathrm{O}_5(\mathrm{OH})_4$ over the trioctahedral $(M_2\mathrm{Ti})(\mathrm{Al}_2)\mathrm{O}_5(\mathrm{OH})_4$ end-member. However, z ranges from 0.43 to 0.54 (average 0.47), and the overall character of titanian berthierine from Picton remains trioctahedral. The total Ti-bearing end members $(y+z)$ make up about 80 mol. % of titanian berthierine.

The extremely high combined Ti and Al contents are unique features of titanian berthierine. High Al contents, comparable to that of titanium berthierine, have been reported for the serpentine-group minerals lizardite (Wicks & Plant 1979), amesite (Steinfink & Brunton 1956), berthierine (Brindley & Youell 1953), brindleyite (Maksimovic & Bish 1978), kellyite (Peacor *et al.* 1974) and zinalsite (Chukhrov & Petrovskaia 1971). However, the Ti content of serpentine-group minerals is usually negligible (Wicks & Plant 1979). To our knowledge, the titanian berthierine from Picton is the most Ti-rich serpentine-group mineral reported to date.

Origin

Elucidation of the physical and chemical conditions for the formation of titanian berthierine are beyond the scope of this study, as no experimental data on the stability of serpentine in the Ti-bearing system are available. However, the textural details of its occurrences in the Picton dyke rock may give some implications of its origin.

Titanian berthierine does appear to be pseudomorphously replacing pre-existing titanian magnesioferrite. For titanian berthierine associated with type-3 spinel, a replacement origin is clearly indicated by the presence of relict titanian magnesioferrite in titanian berthierine grains (Fig. 3) and well-preserved spinel morphology (Figs. 3, 4). This is also marked in type-2 spinel where the titanian magnesioferrite rim is partly or extensively replaced by titanian berthierine (Figs. 5, 6). Based on these textural relations, the atoll texture of type-2 spinel (Figs. 1, 2) is considered to have been formed by preferential selective replacement of titanian magnesioferrite by titanian berthierine. Central grains of ferroan spinel show distinct euhedral forms (Figs. 1, 2), and ferroan spinel was apparently not involved in this reaction.

Titanian berthierine is very fine-grained and apparently fibrous, a habit usually associated with geologically low temperatures. Furthermore, serpentine-group minerals are not considered stable above 550°C at 1 kbar and 600°C at 5 kbar (Caruso & Chernosky 1979). Titanian berthierine probably formed during the period of alteration (serpentinization) of the Picton dyke, which presumably occurred through reaction of late magmatic aqueous fluids with pre-existing titanian magnesioferrite. The surrounding country-rocks are not metamorphosed. The formation of titanian berthierine under these conditions is likely dependent on the particular chemistry of the host spinel phase. Titanian magnesioferrite, with high Mg, Ti and Al contents (Table 1), provided a unique local supply of Fe, Mg, Al and Ti. The late magmatic fluids probably introduced Si and H_2O. To clarify the mode of formation of titanian berthierine, an experimental study of the stability of serpentine in the system MgO–FeO–Al_2O_3–TiO_2–SiO_2–H_2O will be required.

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