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BARIUM- AND TITANIUM-RICH BIOTITE AND PHLOGOPITE FROM THE WESTERN AND EASTERN GABBRO, COLDWELL ALKALINE COMPLEX, NORTHWESTERN ONTARIO

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ABSTRACT

Barium- and titanium-enriched phlogopite and biotite are found in the subalkaline Eastern and Western Gabbro intrusions that are cut by syenite and syenite pegmatite in the Coldwell alkaline complex, northwestern Ontario. The micas contain up to 6.1 wt% BaO and 8.1 wt% TiO_2. Mica occurs as a fringe on Fe–Ti oxides, an overgrowth on cumulus and intercumulus clinopyroxene, and coarse grains that enclose earlier-formed minerals. Ba–Ti-rich micas are normally found in potassic igneous rocks like lamproites, whereas the samples in this study occur in subalkaline gabbro. In the Western Gabbro, the mica is richer in Ba. This suite shows a trend of increasing Ba with decreasing mineral Mg#, not present in the less Ba-rich samples of the Eastern Gabbro. Most of the grains analyzed have apparent deficiencies in their tetrahedral, octahedral and interlayer sites. Deficiencies in the octahedral sites are due to a combination of Ti-vacancy and Ti-Tschermak substitution. The interlayer-site deficiencies are due to the replacement of K by Ba. Coupled substitutions such as ${}^{XII}Ba + {}^{IV}Al = {}^{XII}K + {}^{IV}Si$ also account for the accommodation of Ba in the structure. Moderately Ba-enriched micas in the Eastern and Western Gabbro are a result of crystallization of Ba-enriched residual liquids trapped in the cumulus framework of the gabbros. In addition, the latest Ba–Ti-rich mica in the Western Gabbro formed in response to infiltration of fluids derived from adjacent bodies of Ba-rich syenite pegmatite.

Keywords: phlogopite, biotite, gabbro, barium, Coldwell alkaline complex, Ontario.

SOMMAIRE

Nous documentons la présence de phlogopite et de biotite enrichies en Ba (jusqu'à 6.1% de BaO, poids) et Ti (jusqu'à 8.1% de TiO_2) dans les unités intrusives subalcalines appelées Eastern et Western Gabbro, du complexe alcalin de Coldwell, en Ontario. Des venues de syénite, localement pegmatitique, recoupent ces unités. Le mica se présente en bordure de grains d'oxydes de Fe–Ti, en surcroissance sur les cristaux de clinopyroxène, soit d'origine cumulative ou en intercumulats, et en grains grossiers qui englobent les minéraux précoces. De telles compositions de mica sont typiques des roches ignées potassiques, par exemple les lamproïtes, tandis que dans ce cas, il s'agit de roches gabbroïques subalcalines. Dans l'unité dite Western Gabbro, le mica est enrichi en Ba. Dans cette suite, le mica fait preuve d'un enrichissement en Ba à mesure que diminue son paramètre Mg#, tandis que ce n'est pas le cas dans l'unité Eastern Gabbro, dont le mica est moins enrichi en Ba. La plupart des cristaux analysés auraient des lacunes dans les sites tétraédriques, octaédriques, et inter-feuillets. Dans les sites octaédriques, les lacunes seraient dues à une combinaison d'une déficience en Ti et de la substitution Ti-Tschermak. Dans les sites inter-feuillets, les lacunes seraient dues au remplacement de K par Ba. Des schémas de substitution couplée comme ${}^{XII}Ba + {}^{IV}Al = {}^{XII}K + {}^{IV}Si$ expliquent aussi la présence de Ba dans la structure. La formation de mica enrichi en Ba résulterait de la cristallisation de liquide résiduel piégé dans les interstices des cumulats de ces massifs gabbroïques. Nous attribuons la génération tardive de mica enrichi en Ba et en Ti dans le Western Gabbro à l'infiltration de fluide dérivé des venues de pegmatite syénitique adjacentes.

(Traduit par la Rédaction)

Mots-clés: phlogopite, biotite, gabbro, baryum, complexe alcalin de Coldwell, Ontario.

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INTRODUCTION

The Coldwell alkaline complex in northwestern Ontario (Fig. 1) is an unmetamorphosed intrusive complex consisting of subalkaline and alkaline gabbro as well as a variety of syenites (Walker *et al.* 1993, Mitchell & Platt 1994). The complex was emplaced early in the magmatic evolution of the middle Proterozoic mid-continent rift at 1108 Ma (Heaman & Machado 1992). It consists of three intrusive centers (Fig. 1; Mitchell & Platt 1994). The oldest center, Center 1, consists of a partial ring dyke of layered to massive gabbroic rocks (Eastern Gabbro) intruded by iron-rich augite syenite (Mitchell & Platt 1978). A small body of layered and heterogeneous gabbro (Western Gabbro) occurs in the western part of the complex and also is associated with iron-rich and locally pegmatitic and Ba-enriched augite syenite (Wilkinson 1983, Penczak 1992), indicating that it also belongs to center 1.

In this work, we describe the composition, mechanisms of substitution and possible parageneses of Ba- and Ti-bearing phlogopite and biotite from the Eastern Gabbro and the Western Gabbro.

GEOLOGY AND PETROGRAPHY

The Eastern Gabbro (Fig. 1) consists of three discrete intrusions (Shaw 1994), the largest of which is the Ba-mica-bearing Layered Gabbro Intrusion. This intrusion consists of variably massive to layered gabbroic cumulates ranging in composition from wehrlite to anorthosite. The Western Gabbro is an isolated body of layered and heterogeneous gabbro intruded and locally altered by younger syenites. It has been divided into a massive and a layered series (Penczak 1992) that vary in composition from olivine gabbro to anorthosite. Similarities in rock types and compositions indicate that the Western Gabbro is likely equivalent to the Layered Gabbro.

The gabbroic rocks are unmetamorphosed, layered to massive cumulates with plagioclase, olivine and clinopyroxene ± apatite ± Fe–Ti oxide as the main cumulus phases. Clinopyroxene also occurs as poikilitic intercumulus grains, together with orthopyroxene, biotite, phlogopite, Fe–Ti oxides and, locally, hornblende and traces of granophyric intergrowth of quartz and K-feldspar, which is Ba-bearing in the rocks of the Eastern Gabbro (Shaw 1994).

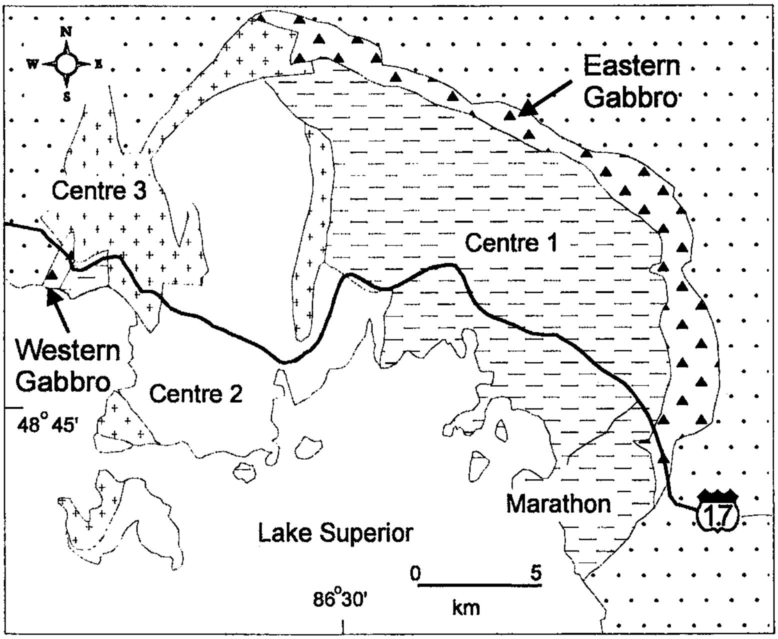

FIG. 1. General geology of the Coldwell alkaline complex, showing the distribution of the intrusive centers and the location of the Eastern Gabbro and the Western Gabbro (after Walker *et al.* 1993).

Both the Eastern Gabbro and the Western Gabbro were intruded by iron-rich augite syenite and by large, irregular bodies of green syenite pegmatite. The contact between gabbro and syenite pegmatite is sharp; macroscopic alteration is restricted to an aureole a few cm wide, but saussuritization of feldspar, serpentinization of olivine and uralitization of clinopyroxene can be traced for up to 20 cm from the contact with the pegmatites.

The gabbroic rocks are evolved (Shaw 1994), with whole-rock Mg# [100 Mg/(Mg + 0.9Fe_{tot}), molar] of 13 to 60; they are enriched in Rb (on average, 26 ppm), Ba (1267 ppm), Sr (1234 ppm), Zr (156 ppm) and rare-earth elements (*REE*; 91 ppm La). Systematic changes in bulk-rock and mineral composition, indicative of simple fractionation, are absent from the gabbros.

Petrographic and mineral chemical criteria indicate that the parent magma was subalkaline in composition (Shaw 1994; in prep.). This makes the occurrence of Ba–Ti-enriched micas unusual, as they are generally confined to potassic igneous rocks (*e.g.*, Mitchell & Bergman 1991, Zhang *et al.* 1993).

PETROGRAPHY

Biotite and phlogopite occur in the gabbros as intercumulus crystals. Mostly, the mica forms ragged grains 0.1–0.25 mm across that fringe earlier-formed Fe–Ti oxides and overgrow cumulus clinopyroxene. Large, poikilitic plates of mica enclosing olivine, clinopyroxene, Fe–Ti oxides and apatite also are present. The grains show variable pleochroism from black-brown or red-brown to pale yellow or yellow-brown. Mica abundances vary from trace to more than 12%, being most abundant in orthocumulate layers.

There is minor optical zonation in some of the grains observed; however, zonation is rare. Many of the samples containing Ba-rich mica, particularly those in the Western Gabbro, show a pattern of alteration similar to that observed in gabbros close to syenite pegmatites (see above). In these samples, intercumulus mica is partly altered to chlorite. Secondary, subhedral biotite with red to straw-yellow pleochroism commonly overgrows the altered minerals.

TABLE 1. SELECTED ELECTRON-MICROPROBE DATA ON Ba-Ti-BEARING MICAS, COLDWELL COMPLEX

Sample	RP68	91-267	91-259	91-272	91-265	91-283	91-272	91-259	RP56	91-272	92-276	RP22	RP73	RP64	RP28	RP29	RP29	RP29
Location	WG	EG	EG	EG	EG	EG	EG	EG	WG	EG	EG	WG	WG	WG	WG	WG	WG	WG
SiO_2	39.37	36.98	35.49	37.69	37.38	36.48	37.46	35.05	33.56	33.58	35.14	34.58	34.35	34.89	33.79	33.91	33.09	32.46
TiO_2	0.91	3.33	4.36	3.46	4.81	2.87	4.89	4.73	3.99	4.09	4.28	6.00	5.39	5.25	6.24	6.86	6.93	7.02
Al_2O_3	13.79	12.43	12.31	12.90	13.59	16.33	12.83	11.95	15.94	12.87	15.63	14.27	14.71	15.36	13.82	13.96	13.87	14.14
Cr_2O_3	0.00	0.00	0.05	0.00	0.00	0.03	0.02	0.06	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
MnO	0.00	0.21	0.24	0.06	0.06	0.03	0.12	0.16	0.05	0.11	0.11	0.09	0.08	0.02	0.04	0.09	0.13	0.15
FeO	11.98	18.53	27.82	15.01	15.61	15.43	17.90	26.88	19.18	27.78	13.15	19.69	18.45	14.24	19.00	18.19	17.42	20.27
MgO	18.99	12.63	6.21	16.00	14.37	15.06	12.45	6.87	13.40	5.32	16.06	9.78	11.50	14.42	9.74	9.44	9.84	8.29
CaO	0.03	0.02	0.03	0.00	0.00	0.03	0.00	0.07	0.03	0.00	0.00	0.04	0.02	0.00	0.03	0.02	0.04	0.02
BaO	0.11	0.33	0.45	0.68	0.75	0.89	0.99	1.00	1.16	1.49	1.80	2.26	2.60	3.04	3.67	4.33	5.04	6.07
K_2O	7.76	9.19	8.43	9.18	8.52	8.89	9.09	8.06	6.29	8.67	8.74	8.66	8.50	7.63	7.46	7.47	7.00	7.04
Na_2O	1.44	0.17	0.14	0.15	0.44	0.40	0.11	0.14	0.55	0.08	0.33	0.09	0.17	0.74	0.34	0.47	0.52	0.35
F	0.75	1.66	0.33	1.24	0.84	0.77	1.15	0.40	0.21	0.45	1.26	0.55	0.43	0.56	0.90	0.91	0.99	0.91
Cl	0.06	0.11	0.78	0.36	0.08	0.02	0.37	0.44	0.02	1.92	0.03	0.05	0.04	0.02	0.07	0.06	0.07	0.08
-O=F+Cl	0.33	0.72	0.31	0.60	0.37	0.33	0.57	0.27	0.09	0.62	0.54	0.24	0.19	0.24	0.39	0.40	0.43	0.40
Total	94.86	94.87	96.33	96.13	96.08	96.90	96.81	95.54	94.29	95.74	95.99	95.83	96.05	95.93	94.71	95.31	94.51	96.40
Si	5.756	5.636	5.617	5.588	5.553	5.378	5.605	5.587	5.172	5.438	5.223	5.357	5.292	5.260	5.314	5.306	5.234	5.150
Al	2.244	2.232	2.296	2.254	2.379	2.622	2.262	2.245	2.828	2.456	2.738	2.605	2.671	2.729	2.561	2.574	2.585	2.644
Fe^{3+}	0.000	0.132	0.087	0.158	0.068	0.000	0.133	0.168	0.000	0.106	0.039	0.038	0.037	0.011	0.125	0.120	0.181	0.206
Σ-tet	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Al	0.132	0.000	0.000	0.000	0.000	0.214	0.000	0.000	0.067	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ti^{4+}	0.100	0.382	0.519	0.386	0.537	0.318	0.550	0.567	0.462	0.498	0.478	0.699	0.624	0.595	0.738	0.807	0.824	0.838
Cr	0.000	0.000	0.006	0.000	0.000	0.003	0.002	0.008	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.000	0.027	0.032	0.008	0.008	0.004	0.015	0.022	0.007	0.015	0.014	0.012	0.010	0.003	0.005	0.012	0.017	0.020
Fe^{2+}	1.465	2.330	3.595	1.703	1.871	1.902	2.107	3.415	2.472	3.656	1.596	2.513	2.340	1.784	2.374	2.260	2.123	2.484
Mg	4.138	2.869	1.465	3.536	3.182	3.309	2.776	1.632	3.078	1.284	3.558	2.258	2.641	3.240	2.283	2.201	2.320	1.961
Σ-Oct	5.835	5.608	5.617	5.633	5.598	5.750	5.450	5.644	6.086	5.453	5.646	5.483	5.615	5.622	5.400	5.280	5.284	5.303
Ca	0.005	0.003	0.005	0.000	0.000	0.005	0.000	0.012	0.005	0.000	0.000	0.007	0.003	0.000	0.005	0.003	0.007	0.003
Ba	0.006	0.020	0.028	0.040	0.044	0.051	0.058	0.062	0.070	0.095	0.105	0.137	0.157	0.180	0.226	0.265	0.312	0.377
K	1.447	1.787	1.702	1.736	1.614	1.672	1.735	1.639	1.236	1.791	1.657	1.711	1.670	1.467	1.496	1.491	1.412	1.425
Na	0.408	0.050	0.043	0.043	0.127	0.114	0.032	0.043	0.164	0.025	0.095	0.027	0.051	0.216	0.104	0.143	0.159	0.108
Σ-Int	1.866	1.860	1.778	1.819	1.785	1.842	1.825	1.756	1.475	1.911	1.857	1.882	1.881	1.863	1.831	1.902	1.890	1.913
F	0.347	0.800	0.165	0.581	0.395	0.359	0.544	0.202	0.102	0.230	0.592	0.269	0.210	0.267	0.448	0.450	0.495	0.457
Cl	0.015	0.028	0.209	0.090	0.020	0.005	0.094	0.119	0.005	0.527	0.008	0.013	0.010	0.005	0.019	0.016	0.019	0.022
Charge	44.155	44.739	44.846	44.493	44.872	44.422	45.130	44.819	43.617	44.998	44.520	45.386	45.012	44.939	45.476	45.890	45.821	45.799
Mg#	73.90	53.80	28.50	65.50	62.10	63.50	55.30	31.30	55.50	25.40	68.50	47.00	52.60	64.30	47.70	48.00	50.20	42.20

EG- Eastern Gabbro, WG - Western Gabbro. Formulae calculated on the basis of 22 atoms of oxygen. Charge calculated with tet + oct = 14 apfu

$Fe3^+$ calculated as the amount required to fill tetrahedral site, remainder as Fe^{2+}

ANALYTICAL METHODS

All samples were analyzed by wavelength-dispersion spectrometry (WDS) on a JEOL JXA–8600 electron microprobe at the University of Western Ontario. An accelerating voltage of 15 kV and a beam current of 10 nA were used. Most samples were analyzed with a defocused, 5-μm electron beam to minimize the migration of potassium.

Benitoite ($BaTiSi_3O_9$) was analyzed to assess the overlap between the $BaL\alpha_1$ and $TiK\alpha_1$ lines. The benitoite gave values within ±0.15% absolute of the expected value of 37.08% BaO; the amount of Ti was found to be within ±0.17% of the known value of 19.32% TiO_2, indicating that error due to overlap of Ba and Ti peaks is minimal.

RESULTS

This study is based on results of about 140 analyses of biotite and phlogopite from the Eastern Gabbro and the Western Gabbro (Table 1). Micas were classified as biotite (88%) or phlogopite (12%) according to the criteria of Deer *et al.* (1966). Structural formulae are based on 22 atoms of oxygen, and the cation charge was calculated with octahedrally and tetrahedrally coordinated cations made equal to 14 (Table 1). None of the samples was analyzed for Fe^{3+}.

All of the grains analyzed lie within the eastonite – siderophyllite – phlogopite – annite field (Fig. 2). Mica compositions from the Western Gabbro define a trend from phlogopite toward the siderophyllite end-member, whereas those from the Eastern Gabbro lie parallel to the phlogopite – annite join (Fig. 2).

Ba-rich mica (>1 wt% BaO) is more common in the Western Gabbro. The grains show a trend of increasing Ti and decreasing Mg# with increasing Ba (Fig. 3). The mica from the Eastern Gabbro is only moderately enriched in Ba; only 27% of the grains analyzed have more than 1 wt% BaO. Mica in the Eastern Gabbro is Ti-rich (Fig. 3a), but does not show the distinct trend that characterizes mica from the Western Gabbro. The same is true of Mg# (Fig. 3b). Ba contents vary within individual samples; for example, sample RP29 contains mica with Ba contents ranging from 1.66 to 6.07 wt% BaO. In this sample, Ti increases with increasing Ba, and Mg# decreases as Ba increases.

Structural formulae

Structural formulae calculated on the basis of 22 atoms of oxygen (Table 1) show that most of the mica grains analyzed are apparently deficient in their tetrahedral site ($^{IV}Si + {}^{IV}Al < 8.00$). They also show deficiency in the octahedral sites, with cation totals between 5.4 and 5.9 atoms per formula unit (*apfu*), which is less than the 6.00 cations in an ideal trioctahedral mica. The interlayer ($^{XII}Ca + {}^{XII}Ba + {}^{XII}Na + {}^{XII}K$) site in most of the grains also is deficient (<2.00), varying from 1.7 to 1.95 *apfu.*

Calculation of structural formulae on the basis of a constant number of cations in the tetrahedral and octahedral site (6.00 + 8.00) results in excess charges for the cations, suggesting either substitutions involving vacancies or cations of variable valence state.

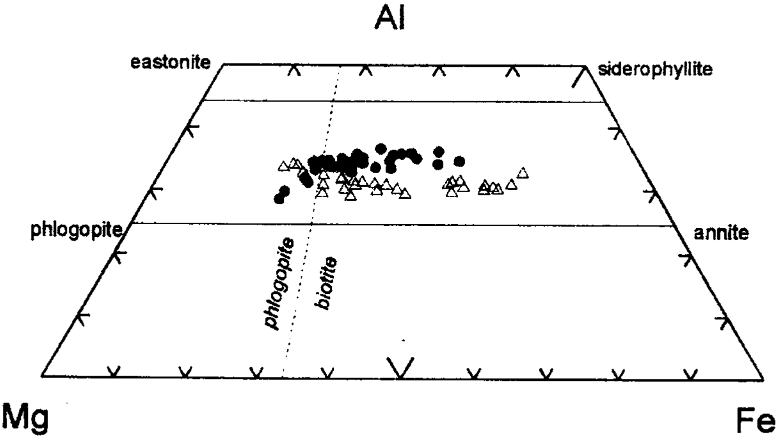

FIG. 2. Mg–Al–Fe plot of Eastern Gabbro (Δ) and Western Gabbro (●) micas. Fields from Mitchell (1995).

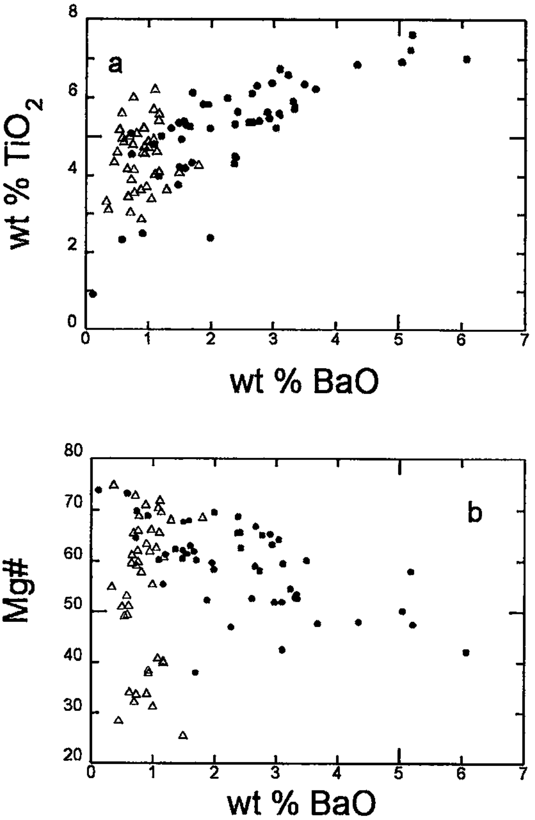

FIG. 3. BaO *versus* (a) TiO_2 and (b) Mg# for mica samples of the Eastern Gabbro and Western Gabbro (symbols as in Figure 2).

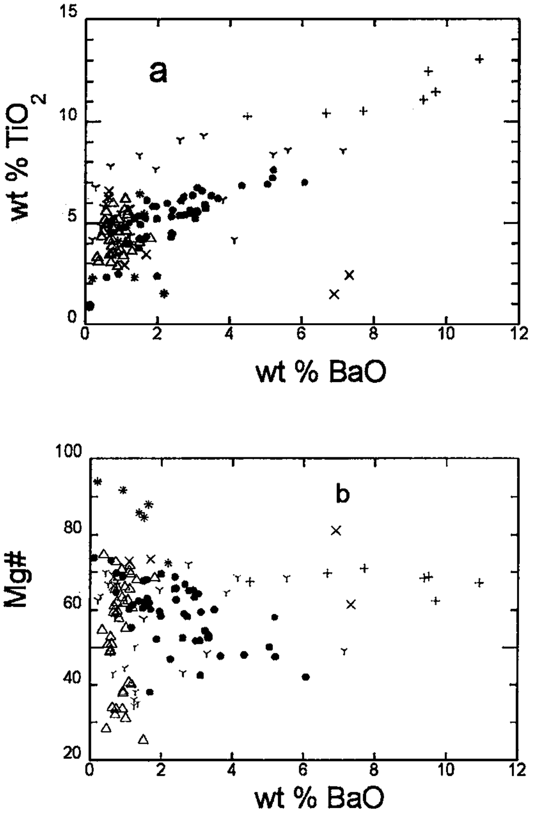

FIG. 4. Comparison of mica compositions from the Eastern Gabbro (Δ) and Western Gabbro (●) with those from leucitites from China (+), Ti-poor mica from lamproites (*), Roman Province potassic rocks (×) and lower crustal gabbro, Italy (Y). These data are compiled from Mitchell & Bergman (1991), Holm (1982), Thompson (1977), Zhang *et al.* (1993), and Bigi *et al.* (1993).

COMPARISON WITH Ba–Ti-RICH MICA FROM OTHER LOCALITIES

Ba–Ti-rich mica is common in potassic igneous rocks (Mitchell & Bergman 1991, Edgar 1992, Zhang *et al.* 1993), but is rare in gabbroic rocks. Ba–Ti-rich mica is known from only one other gabbroic suite, that of lower crust origin exposed in the Ivrea zone, Italy (Bigi *et al.* 1993).

The mica compositions described here are similar to Ba–Ti phlogopite from the Ivrea zone (Bigi *et al.* 1993), the Roman Province (Thompson 1977, Holm 1982) and Montana (Wendlandt 1977) in terms of their Ba, Ti, Fe and Mg contents (Fig. 4). They show some similarities with low-Ti mica from lamproites (Mitchell & Bergman 1991), but have much lower Mg# (Fig. 4).

SUBSTITUTIONS

As noted by Zhang *et al.* (1993), it is difficult to assign unique substitutions to micas because (1) the complexity of the potential substitutions, (2) the problems in determining valency of Fe and Ti, and (3) the possibility that Ti, Fe and Mg might occur in tetrahedral coordination (Foley 1990).

Incorporation of Ba

Ba substitutes for interlayer cations in the 12-fold site in micas. Replacement of K by Ba in the mica structure involves a charge compensation that can either be achieved by vacancies in the structure:

$$^{XII}Ba + \square = 2\,^{XII}K \quad (1)$$

(Mitchell 1981, Wagner & Velde 1986), or by complex coupled substitutions involving cations from both the octahedral and interlayer site, such as

$$^{XII}\mathrm{Ba} + {}^{IV}\mathrm{Al} = {}^{XII}\mathrm{K} + {}^{IV}\mathrm{Si} \qquad (2)$$

(Wendlandt 1977, Mansker *et al.* 1979). Most of the mica compositions from the Eastern Gabbro and the Western Gabbro have low interlayer-site occupancies (Fig. 5a), suggesting the presence of vacancies; however, this substitution does not explain all of the compositional variation (Mitchell & Bergman 1991), and a more complex coupled substitution is likely. The most likely substitution (2) is shown in Figure 5b. It has been suggested as the main substitution involving the transition from phlogopite–biotite to kinoshitalite (Dasgupta *et al.* 1989, Brigatti & Poppi 1993). However, this substitution does not account for deficiencies in the 12-fold site, so that the simple substitution (1) also must be important. More complex substitutions, such as the "tetraferriphlogopite" – phlogopite solid solutions (Mitchell & Bergman 1991), cannot be tested without information on the proportion of Fe^{3+}.

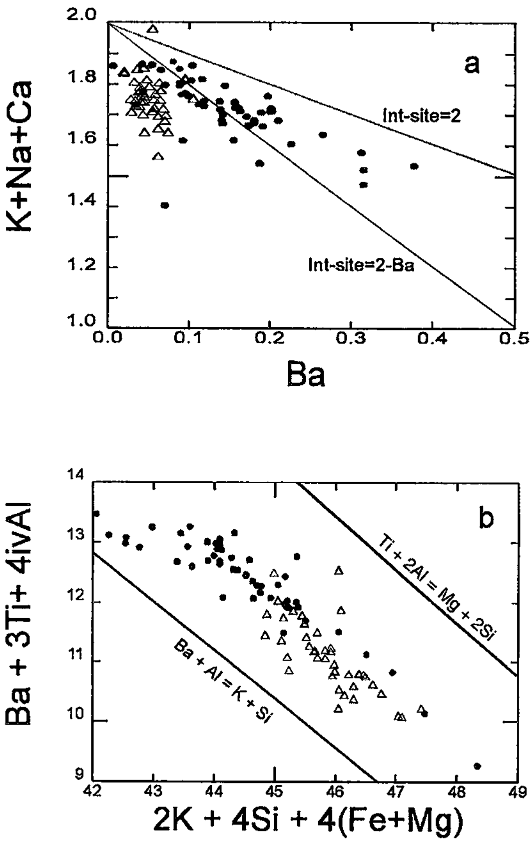

FIG. 5. a) Proportion of Ba *versus* interlayer cations in mica samples of the Eastern Gabbro and Western Gabbro showing Interlayer site = 2 and Interlayer site = 2 – Ba trends. b) 2K + 4Si + 4(Fe,Mg) *versus* Ba + 3Ti + 4Al (after Guo & Green 1990), showing trend of coupled substitution Ba + Al = K + Si. Symbols as in Figure 2.

The substitutions suggested here are the same as those proposed for micas in lamproites (Mitchell & Bergman 1991). The mica found in lamproites commonly has as little as 1.8 *apfu* in the interlayer site, which compares with the average interlayer occupancy of 1.84 observed in our samples. Other incidences of Ba-bearing trioctahedral mica generally have interlayer cations close to the ideal occupancy (2.00); however, mica compositions in gabbro from the lower crust (Bigi *et al.* 1993) also show deficiencies in the interlayer site.

Deficiencies in the tetrahedral site

More than 70% of the grains analyzed have deficiencies in their tetrahedral site, *i.e.*, $^{IV}Si + {}^{IV}Al < 8.00$, suggesting that another cation is present in this site. Farmer & Boettcher (1981) have suggested that both Ti^{4+} and Fe^{3+} can occur there. Bol *et al.* (1989) suggested that incorporation of Ti^{4+} at the tetrahedral site is possible but unlikely, because of the electrostatic repulsion of Ba^{2+} and Ti^{4+}, which would increase the lattice energy of the crystal. Octahedrally coordinated Ti is much more likely to occur, as the tetrahedral sites are closer to the interlayer than the octahedral sites.

The presence of an excess charge on the basis of 14 tetrahedral + octahedral cations (Table 1) might be due to the presence of tetrahedrally coordinated Fe^{3+}, although this has not been proven. Zhang *et al.* (1993) have suggested that Fe^{3+} might be capable of residing in the tetrahedral site in Ba-rich micas in potassic lavas from northeastern China. However, Fe^{3+} is not tetrahedrally coordinated in Ba-rich mica from gabbros in the Ivrea Zone, Italy (Bigi *et al.* 1993), which is similar in composition to the suite described here. In the present study, tetrahedral sites have been filled to 8 cations using Fe^{3+} (Table 1); the rest of the iron is assumed to be Fe^{2+} in the octahedral site.

Deficiencies in the octahedral site

Ti- and Ba-rich micas are commonly deficient in the octahedral site (Mitchell & Bergman 1991, Bigi *et al.* 1993, Zhang *et al.* 1993). Several schemes of substitution have been proposed [Mitchell & Bergman (1991) and references therein]. In the mica from the Eastern Gabbro and the Western Gabbro, the most likely substitutions are:

$$2^{VI}\mathrm{Mg} = {}^{VI}\mathrm{Ti} + \square \qquad (3)$$

(Forbes & Flower 1974), and

$$^{VI}Mg + 2\,^{IV}Si = {}^{VI}Ti + 2\,^{IV}Al \qquad (4)$$

(Robert 1976).

Substitution (4) recalls the Ti-Tschermak substitution:

$$^{VI}(Mg,Fe^{2+}) + 2\,^{IV}Si = {}^{VI}Ti^{4+} + 2\,^{VI}(Al,Fe^{3+}) \qquad (5)$$

(Zhang *et al.* 1993).

However, this scheme of substitution cannot be fully assessed owing to the lack of data on the oxidation state of iron.

The mica samples define trends intermediate between those for substitutions (3) and (4) (Figs. 6a, b). Further evidence for a Ti–vacancy substitution is shown by the correlation of Ti *versus* Mg + Fe^{2+}_{calc} (Fig. 6c). Other substitutions, such as the Ti–oxy substitution (Arima & Edgar 1983), cannot be tested, as the H_2O contents of the micas are not known.

For their Ba-bearing micas from the gabbroic suite in the Ivrea Zone, Bigi *et al.* (1993) reported the data with all Fe expressed as Fe^{2+}, as well as analyzed proportions of Fe^{2+} and Fe^{3+}. The analyses with all Fe as Fe^{2+} show deficiencies in the octahedral site similar to those described here; however, such deficiencies are not present in samples where the proportion of Fe^{2+} and Fe^{3+} is known. This finding suggests that the calculated site-deficiencies might be due in part to the lack of analytical data for Fe^{3+}.

ORIGIN OF Ba–Ti-RICH MICAS IN THE COLDWELL SUITE

Although micas from the Eastern Gabbro and the Western Gabbro show the same pattern of substitution, it is likely that they have different parageneses, on the basis of their distinct compositional trends (Figs. 2, 3).

The Eastern Gabbro micas are only moderately enriched in Ba, and could have crystallized from an evolved intercumulus liquid trapped during the accumulation of the Layered Gabbro Intrusion. In most of these cases, the mica is found in fresh gabbro, *i.e.*, where alteration is minimal.

Moderately Ba-enriched micas in the Western Gabbro have compositions similar to those in the Eastern Gabbro and likely formed by the same mechanism of early incorporation of Ba into intercumulus mica. This mechanism does not, however, explain the origin of late-formed (low-Mg#) Ba-rich mica, which overgrows secondary minerals in the gabbro. Ba is strongly compatible in mica (Henderson 1982) and should enter the structure during the earliest stage of crystallization. The observation that early-formed (high-Mg#) micas are less enriched in Ba than later-formed (low-Mg#) micas suggests that Ba was added to the Western Gabbro during the mica's crystallization.

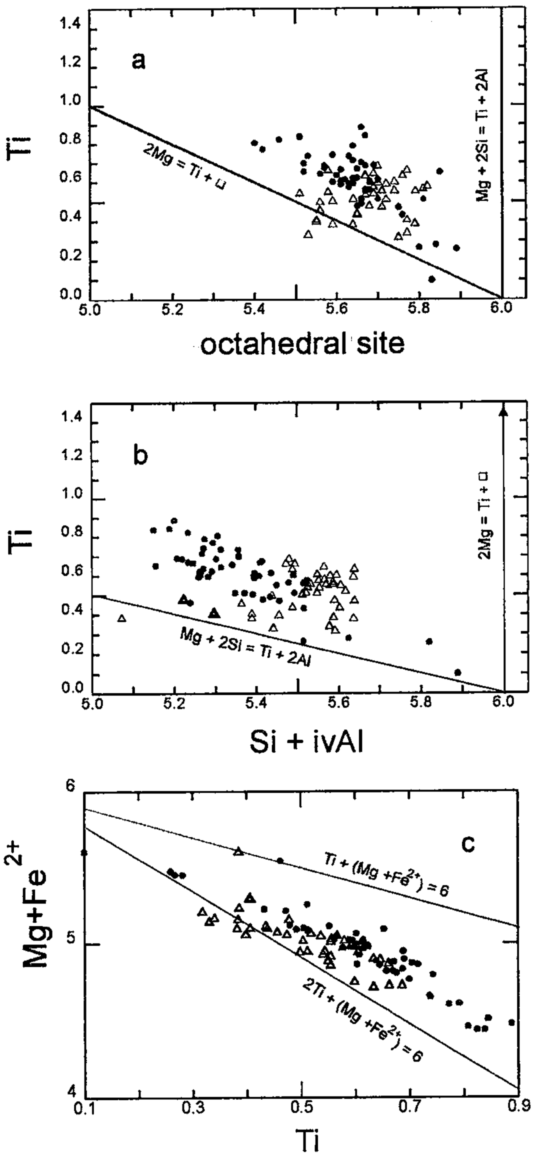

FIG. 6. Extent of substitution in the octahedral site in micas (symbols as in Figure 2). a) Ti *versus* occupancy of the octahedral sites. b) Si + ^{IV}Al *versus* Ti. c) Ti *versus* Mg + Fe^{2+} (Fe^{3+} calculated from Fe_{tot} – Fe^{3+} required to fill tetrahedral sites). Substitutions in a) and b) from Mitchell & Bergman (1991), in c) from Zhang *et al.* (1993).

The mica in the Western Gabbro commonly is found in rocks with intense alteration, similar to that found around syenite pegmatites. These pegmatites have been shown to be at least locally enriched in Ba; some samples contain up to 9761 ppm Ba (Penczak

1992), and might be a source for Ba in the micas. Fluids emanating from the augite syenite pegmatites could have metasomatized the gabbros and enriched them in Ba while conditions were still suitable for the crystallization of Ba–Ti mica. The high density of syenite pegmatites in the Western Gabbro may explain the prevalence of Ba-rich mica in this area.

CONDITIONS OF CRYSTALLIZATION

Titanium-bearing micas are stable over a wide range of pressures and temperatures (Mitchell & Bergman 1991). Most studies have been carried out in potassic systems, and as such, may not be directly relevant to the present study. At moderate pressures, Ti solubility decreases with pressure and increases with increasing temperature (Flower 1971, Arima & Edgar 1983). On this basis, pressure estimates of 2 kbar for the emplacement of the Coldwell alkaline complex (Mitchell & Platt 1978) suggest that pressure conditions were suitable for the formation of titaniferous mica.

An estimate of the temperature of crystallization of the intercumulus Ba–Ti mica is not possible. The range of temperatures over which titaniferous mica can crystallize is large (Mitchell & Bergman 1991), and some of the mica may be subsolidus. This is most likely for the Ba-rich micas in the Western Gabbro, as field relations indicate that the gabbro was solid at the time of pegmatite emplacement. Thus it is likely that both true igneous micas and metasomatic micas are present in the same rocks.

CONCLUSIONS

1) Unusually Ba-rich Ti-bearing biotite and phlogopite occur as intercumulus phases in subalkaline gabbros in the Coldwell alkaline complex. These micas contain up to 6.07 wt% BaO and 8.1 wt% TiO_2 and are similar to micas from lower-crust gabbro and in potassic igneous rocks.

2) Incorporation of Ba into interlayer sites occurred by coupled substitution of Ba + Al for K + Si, with development of interlayer vacancies to explain deficiencies in the 12-fold site.

3) Ti incorporation is explained by a combination of Ti-vacancy and Ti-Tschermak substitutions.

4) Moderately Ba-enriched (1–2 wt% BaO) micas in the Eastern Gabbro and the Western Gabbro seem to have formed from Ba-rich intercumulus liquid during the final stages of crystallization of the gabbro. Strongly Ba-enriched micas in the Western Gabbro seem to have formed by metasomatism due to infiltration of a Ba-rich fluid derived from adjacent bodies of syenite pegmatite.

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