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Barian-titanian micas from Ilha da Trindade, South Atlantic

J. C. GREENWOOD

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, UK

ABSTRACT

Extremely high abundances of TiO_2 (up to 12.57 wt.%) and BaO (up to 7.11 wt.%) are reported from dark reddish-brown phlogopite-biotite rims around paler phlogopite cores in a lamprophyric dyke from Ilha da Trindade, South Atlantic. Both TiO_2 and BaO contents increase towards the rims of the micas and in groundmass crystals. This is accompanied by corresponding increases in FeO*, MnO and Mg number; whereas SiO_2, Al_2O_3, Cr_2O_3, MgO and K_2O abundances all decrease. The substitution of Ba into the biotite structure can be explained by the scheme Ba + Al = K + Si. Ti-substitution schemes however are much more complex, as no general equation can account for all the Ti incorporated into the structure and therefore several schemes are proposed.

KEYWORDS: mica, titanium, barium, Ilha da Trindade.

Introduction

OCCURRENCES of minerals that combine extreme composition variants with strong zoning can provide valuable information for understanding the nature of solid solutions in that phase. Experimental studies (e.g. Foley, 1990) have shown that mica compositions vary with pressure, temperature, f_{O_2}, fluid and whole rock compositions and the crystallising phases present. Separating the influence of these different factors is difficult. Nevertheless, Ti-content can be seen to increase with increasing f_{O_2}, increasing temperature, decreasing pressure and decreasing water content of the system (Foley, 1990). These concepts are illustrated below by electron microprobe analyses of micas in an alkaline lamprophyre dyke, petrographically similar to sannaite (Rock, 1991), from the volcanic island of Trindade, South Atlantic. The composition of these micas can be used to provide information both about the mechanisms by which elements such as Ti and Ba enter the biotite structure, and to further understanding of magma chamber processes.

Ilha da Trindade is situated 1140 km east of the Brazilian coast at 20°30′S and 29°19′W. Its highly silica-undersaturated volcanic products include picritic to phonolitic lavas and associated tuffs (Mitchell-Thomé, 1970). The micas that are the subject of this report occur as phenocrysts and groundmass phases in a dyke which cuts phonolites belonging to the Trindade formation, the oldest volcanism observed on the island. This sample, I70, was collected by U.G. Cordani, Universidade de São Paulo. The micas are associated with diopside, kaersutite, olivine and titanomagnetite phenocrysts. These are set in a groundmass of the same minerals (without olivine), together with sanidine, anorthoclase, nepheline, analcime and accessory apatite and titanite. The whole-rock chemistry has not been analysed, due to the heterogeneity and small size of sample available. Little information about possible melts could be inferred from the data as the large proportion of xenocrysts and zoned crystals suggest that it would not represent a magmatic composition.

The mica phenocrysts are generally euhedral and range in size up to 2 cm. A sharp boundary between the rounded, moderately pleochroic, pale-brown cores and the strongly pleochroic, dark reddish-brown rims reflects significant compositional variation within individual phenocrysts. Reverse pleochroism has not been observed. The phenocryst cores may be classified as phlogopite on the basis of Mg/Fe = <2 (Deer *et al.*, 1963), whereas the rims are transitional between phlogopite and biotite. The phenocrysts show strong zoning from phlogopite cores to phlogopite-biotite rims that are exceptionally rich in Ba (up to 7.11 wt.%) and Ti (up to 12.57 wt.%). Groundmass micas show very similar optical and chemical characteristics to the phenocryst rims.

Analytical technique

Analyses of mica chemistry were performed on a CAMECA SX-50, CAMEBAX, MICROEPMA at the Department of Earth Sciences, University of Cambridge. Analytical conditions were: accelerating voltage = 20 kV and beam current = 15 nA. Major elements and Ba were analysed by wavelength-dispersive methods and F by energy-dispersive spectrometry. Data analyses were carried out using LINK analytical technique and ZAF correction programme. Twelve points were analysed by both wavelength- and energy-dispersive techniques, in order to cross-check the interference between Ba and Ti peaks. The values obtain by these two methods agreed well and did not suggest that Ba-Ti interference was affecting the results.

Chemistry

Representative analyses are given in Table 1. The phlogopite cores (122 analyses) show only limited chemical variations, with TiO_2 = 6.79–9.53 wt.%, BaO = 0.33–1.48 wt.%, SiO_2 = 34.29–38.99 wt.%, Al_2O_3 = 13.45–17.47 wt.%, K_2O = 7.53–9.28 wt.% and Mg number [Mg/(Mg+Fe)] = 0.68–0.77. In contrast, the phenocryst rims and groundmass crystals (62 analyses) show a much greater range of compositions. Extremely high TiO_2 contents of up to 12.57 wt.% occur in the phenocryst rims and groundmass crystals. These approach the highest values yet recorded in the literature; TiO_2 = 14.1 wt.% in biotites from Hawaiian nephelinites (Mansker *et al.*, 1979). BaO contents are also high (up to 7.11 wt.%). Both TiO_2 and BaO contents increase

TABLE 1. Representative analyses of micas from I70 and BM 87171(920)

	Phenocryst cores I70			Phenocryst rims I70			G-mass	920
	bi17	di03	diii08	bi48	bii06	dvi05	dv01	d11
SiO_2	36.49	36.36	36.87	32.28	35.69	36.07	32.85	36.22
TiO_2	8.27	7.70	7.87	12.57	10.05	11.31	12.19	4.60
Al_2O_3	16.08	15.63	15.83	15.27	15.92	14.31	14.95	14.29
Cr_2O_3	0.13	0.03	0.05	0.20	0.12	0.06	0.02	0.09
FeO*	10.49	10.61	10.66	11.15	10.05	10.38	11.05	17.88
MnO	0.07	0.10	0.10	0.11	0.11	0.14	0.11	0.22
MgO	16.90	16.92	16.98	12.96	15.85	15.03	13.33	13.67
BaO	0.34	0.73	0.65	6.26	2.22	1.76	5.74	0.17
CaO	0.08	0.00	0.02	0.04	0.02	0.00	0.09	0.05
Na_2O	0.90	1.01	0.99	0.96	0.89	1.11	1.04	0.80
K_2O	9.17	8.61	8.58	6.51	8.19	7.92	6.66	9.13
F	0.34	1.43	0.99	0.49	0.82	0.84	0.74	0.29
Total	99.26	99.12	99.58	98.80	99.93	98.93	98.80	97.41
Si	5.42	5.47	5.48	5.05	5.33	5.44	5.13	5.67
Al	2.81	2.77	2.77	2.81	2.80	2.54	2.75	2.63
Ti	0.92	0.87	0.88	1.48	1.13	1.28	1.43	0.54
Fe	1.30	1.34	1.33	1.46	1.26	1.31	1.44	2.34
Cr	0.02	0.00	0.01	0.02	0.01	0.01	0.00	0.01
Mn	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.03
Mg	3.74	3.79	3.76	3.02	3.53	3.38	3.10	3.19
Ba	0.02	0.04	0.04	0.38	0.13	0.10	0.35	0.01
Ca	0.01	0.00	0.00	0.01	0.00	0.00	0.02	0.01
Na	0.26	0.29	0.29	0.29	0.26	0.32	0.32	0.24
K	1.74	1.65	1.63	1.30	1.56	1.52	1.33	1.82
Cations	16.24	16.24	16.20	15.84	16.03	15.93	15.88	16.50
Mg #	0.74	0.74	0.74	0.67	0.74	0.72	0.68	0.58

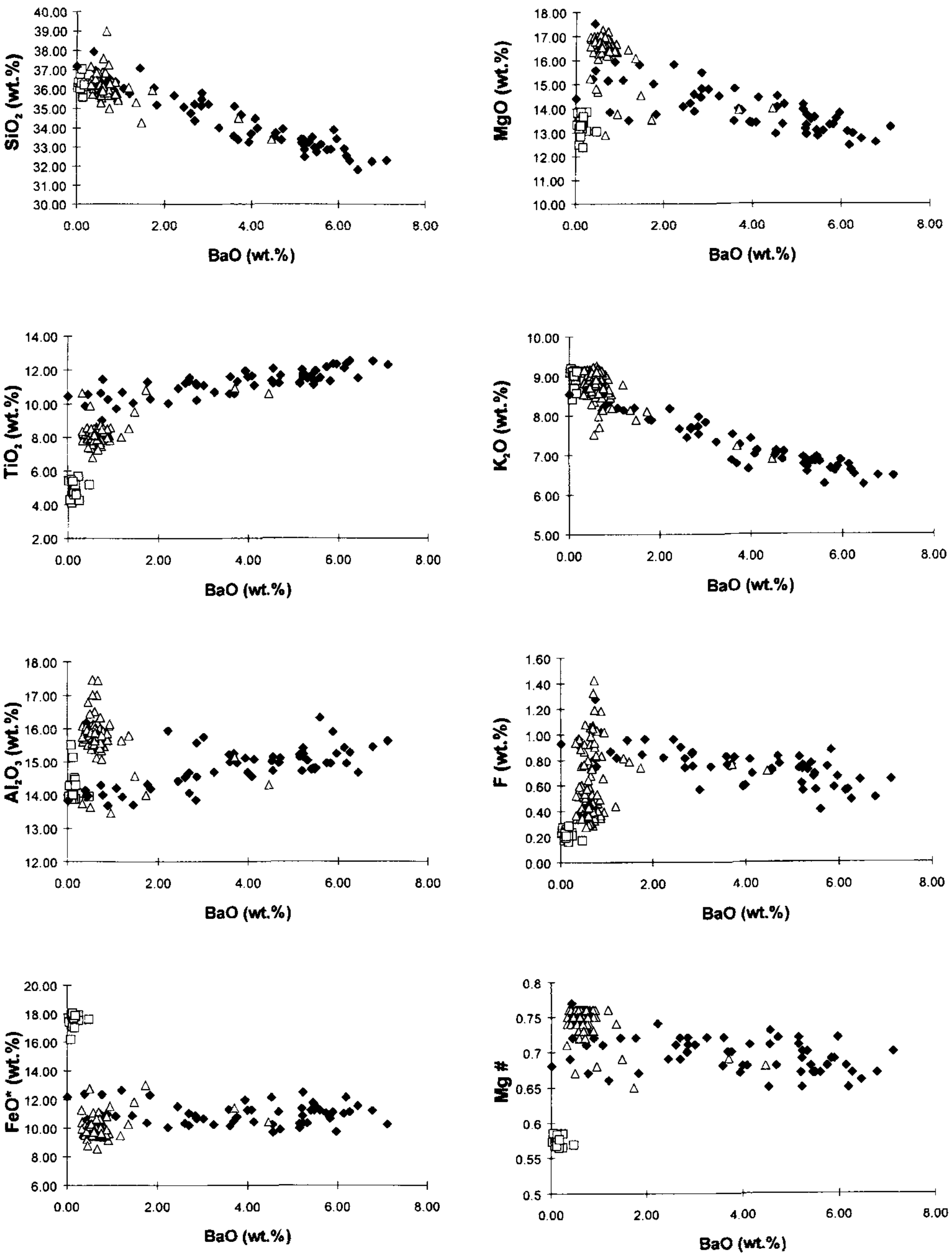

FIG. 1. Variation of selected elements with BaO for micas from I70 and biotites from a xenolith (BM 87171(920)), also from Ilha da Trindade. I70 phlogopite-biotite phenocryst rims and groundmass crystals are represented by filled diamonds, I70 phlogopite phenocryst cores by open triangles and biotites from BM 87171(920) by open squares.

towards the rims of the phenocrysts, along with FeO*, MnO and Mg number (0.59–0.74). Abundances of SiO_2 (31.83–39.56 wt.%), Al_2O_3 (13.63–16.32 wt.%), Cr_2O_3 (0–0.25 wt.%), MgO (11.79–15.95 wt.%) and K_2O (6.25–8.76 wt.%) all decrease (Fig. 1).

Calculated structural formulae on the basis of 22 oxygens for the phenocryst cores show that they are close to stoichiometric, with the tetrahedral sites completely filled by Si and Al cations (average = 8.00 p.f.u.). The octahedral sites display slightly more variability (5.56–6.37 p.f.u.), with an average of 6.18 cations p.f.u.. The 12-fold co-ordination sites are also close to stoichiometric, with an average of 1.99 cations p.f.u.. The phenocryst rims and groundmass crystals are calculated to have a total of 15.92 cations p.f.u., compared with 16.18 cations p.f.u. for the cores. The calculated structural formulae for the rims and groundmass crystals indicate that there are vacancies in the tetrahedral sites (average = 7.96 cations p.f.u.), although both the octahedral (average = 5.98 p.f.u.) and 12-fold (average = 1.98 p.f.u.) co-ordination sites are again generally stoichiometric. The deficiency in the tetrahedral sites is likely to be filled by either Fe, Ti or Mg, thus creating an octahedral site vacancy.

Possible substitution mechanisms

Considerable debate still exists over the exact substitution schemes which may occur in phlogopite-biotite micas (e.g. Zhang *et al.*, 1993; Thompson *et al.*, 1997; Edgar, 1992; Mansker *et al.*, 1979). In the case of Ti in particular, this is exacerbated by a lack of agreement about its possible valency and site occupancy. The micas analysed here appear to display different substitution trends for the phenocryst cores, on the one hand, and rims and groundmass crystals on the other (Fig. 2). A further trend is observed in biotites contained in a mafic xenolith from Ilha da Trindade (BM 87171(920)), consisting of coarse-grained diopside, biotite, kaersutite, anorthoclase, apatite and titanite. This xenolith was collected by the Discovery Expedition, 1901, and forms part of

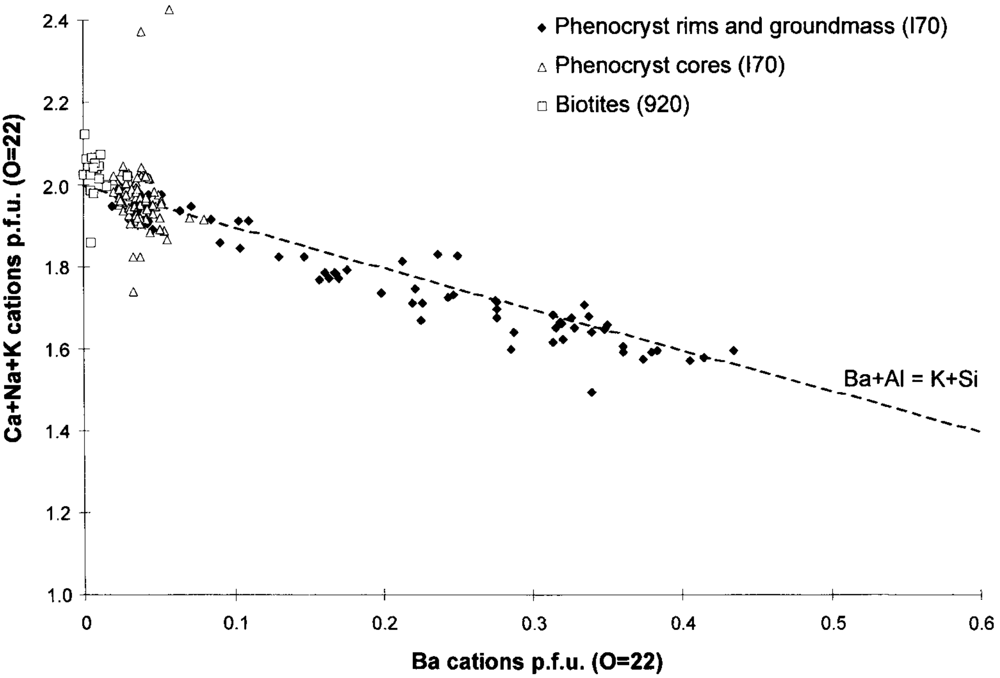

FIG. 2. Plot of (Ca+Na+K) against Ba for Trindade micas, showing the proposed substitution scheme for Ba in phenocryst rims and groundmass crystals.

the collection of the Natural History Museum, London.

Barium substitution

As mentioned above, the micas analysed from I70 have almost stoichiometric interlayer occupancy, irrespective of the positioning of the analysis point within the crystal. A plot of Ba against (K+Na+Ca) gives a 1:1 linear array (Fig. 2), suggesting that Ba replaces K in the interlayer site. This is coupled with the replacement of Si by Al, to offset the charge imbalance (Mansker *et al.*, 1979; Edgar, 1992), giving an overall substitution as follows:

$$^{[12]}\mathrm{Ba} + {}^{[4]}\mathrm{Al} = {}^{[12]}\mathrm{K} + {}^{[4]}\mathrm{Si}.$$

Ti substitutions

A fall in the number of tetrahedral + octahedral cations is observed with increasing Ti content. Where (Si+Al) < 8, a further cation is required to fill the tetrahedral site. The possible candidates are Fe, Ti and Mg. The presence of substantial amounts of Fe^{3+} (>0.1 cations p.f.u.) in the tetrahedral site can be ruled out as this would lead to reverse pleochroism (Wendlandt, 1977). Farmer and Boettcher (1981) have suggested that where (Si+Al+Ti) $\geqslant$ 8 the order of preferential incorporation into the tetrahedral site is Si^{4+} > Al^{3+} > Ti^{4+} > Fe^{3+}. Further support for the presence of what is traditionally regarded as an 'octahedral' cation in a tetrahedral site is provided by Fig. 3 which shows that, as the number of tetrahedral deficiencies increase, so the number of octahedral cations tends to rise, often to above stoichiometric levels. These excess 'octahedral' cations can therefore be used to fill the vacancies in the tetrahedral site. This figure also suggests that excess tetrahedral Al may be incorporated into vacancies in the octahedral site in phenocryst cores. The trend displayed for these phenocryst cores is much better defined than that for the rims and groundmass crystals. This difference may be attributed to the variety of substitution mechan-

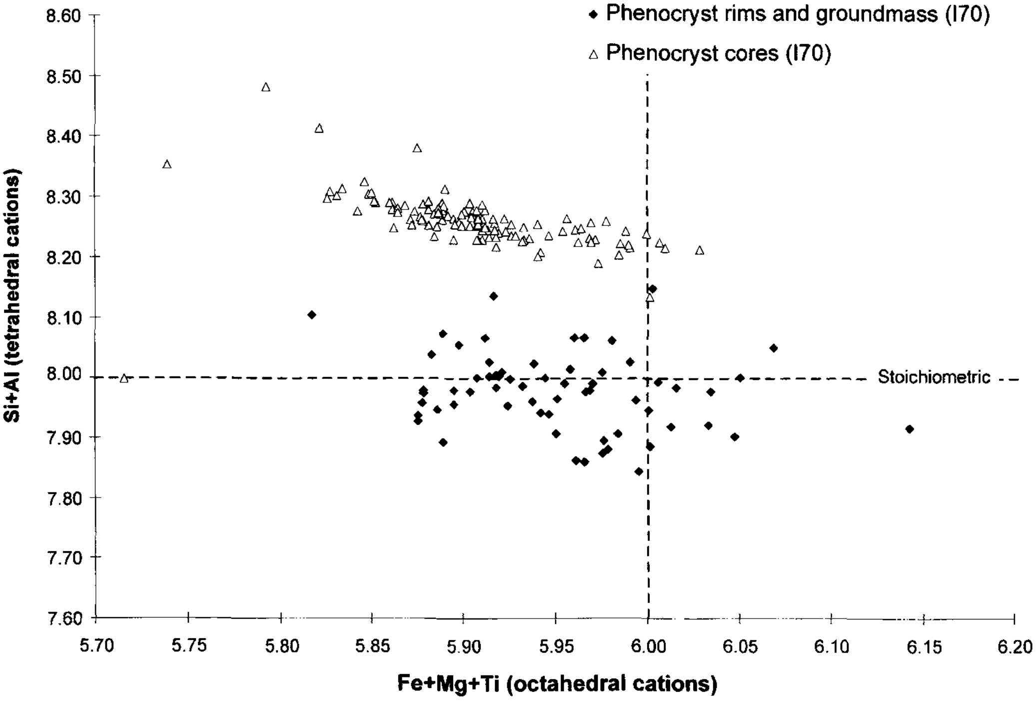

FIG. 3. Plot of traditional octahedral cations (Fe+Mg+Ti) against tetrahedral cations (Si+Al), showing an increase in the number of tetrahedral vacancies in phenocryst rims and groundmass crystals compared with the cores. This suggests the presence of tetrahedral Fe, Mg or Ti in the biotite structure.

isms operating in these micas, leading to heterogeneities in the crystal structure at higher-Ti contents. A strong negative correlation between Ti and (Si+Al) suggests that it is Ti cations, rather than Fe or Mg (which show less variation and a poorer correlation with (Si+Al)), that enter the tetrahedral site as shown below:

$$^{[4]}Ti = {}^{[4]}Si$$

However, insufficient tetrahedral vacancies are available to accommodate all the Ti present in these micas and therefore another substitution mechanism must be involved. Data from the high-Ti rims and groundmass crystals can be seen to lie broadly parallel to a line representing a Ti-Tschermak's substitution (Fig. 4).

$$^{[6]}Ti + 2^{[4]}(Al,Fe^{3+}) = {}^{[6]}(Mg,Fe^{2+}) + 2^{[4]}Si$$

Again, this substitution alone cannot account for all the Ti present in the structure, but may occur in combination with the other schemes mentioned. As Ti increases, the total number of cations is seen to fall, to below 16 p.f.u., which suggests that a Ti-vacancy substitution of the type shown below may also occur:

$$^{[6]}Ti + {}^{[6]}\square = 2^{[6]}(Mg,Fe^{2+})$$

Other occurrences of high-Ti micas

High-Ti micas are found in a variety of igneous rock types, such as lamprophyres, lamproites and other potassic and sodic alkaline rocks (Bachinski and Simpson, 1984). Selected data are presented in Fig. 5. Micas from Ilha da Trindade are seen to lie on a trend parallel to that for phlogopites in potassic lavas from the Wudalianchi, Erkeshan and Kekuo (WEK) volcanic fields of NE China (Zhang *et al.*, 1993). They also overlap the field for micas from Mongolian leucite basanites (Ryabchikov *et al.*, 1982). When compared with micas from other oceanic islands, only Hawaiian nephelinite micas are seen to have slightly higher Al_2O_3 contents (Mansker *et al.*, 1979); these could even be interpreted as lying further along the trend defined by the Ilha da Trindade phenocryst rims and groundmass crystals. Samples from Gough (Le Roex, 1985) and a Cape Verde lamprophyre (Furnes and Stillman, 1987) also plot close to some of the Trindade micas. Biotites from an Ilha da Trindade xenolith (BM 87171(920)) have much lower abundances of TiO_2, similar to those observed in metasomatic phlogopites from Canary Island xenoliths (Wulff-Pedersen *et al.*, 1996).

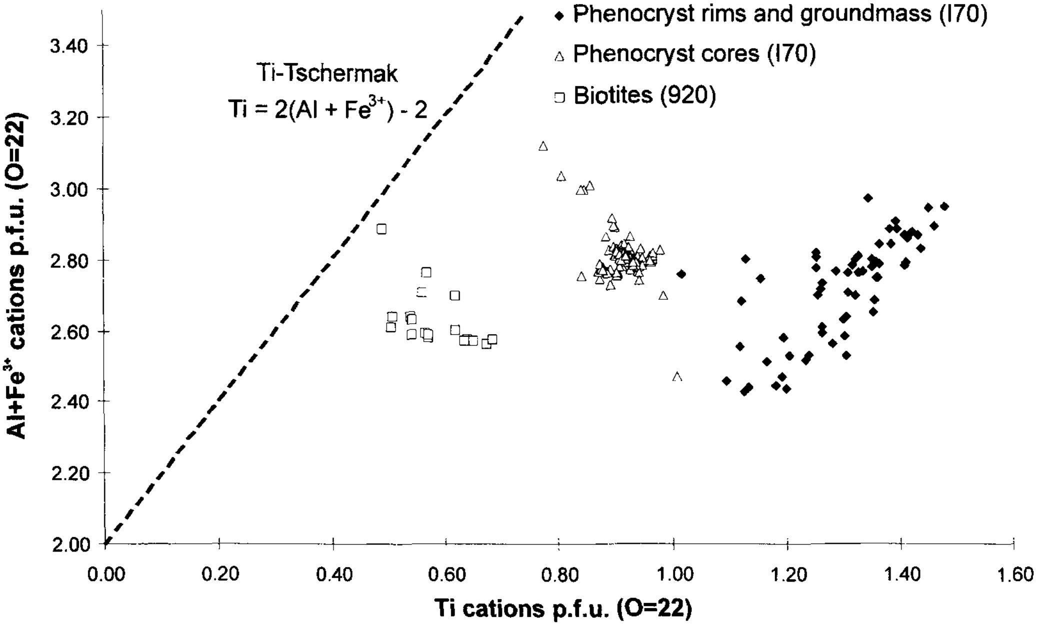

FIG. 4. Plot of ($Al+Fe^{3+}$) against Ti for Trindade micas, with a line representing a Ti-Tschermak's substitution. Phenocryst rims and groundmass crystals form a trend approximately parallel to this line.

Elevated TiO_2 contents in micas are also found across SE Brazil, in magmatism thought to be associated with the Trindade mantle plume. The Alto Paranaíba and Iporá igneous provinces are postulated by Gibson *et al.* (1995) to be associated with the initial impact of the Trindade mantle plume under central Brazil ~85 Ma. Micas from Iporá minettes (Gibson *et al.* unpublished data) in particular show compositions similar to those described here from Ilha da Trindade (I70) (Fig. 5). The Alto Paranaíba mafic and ultramafic intrusions (Meyer *et al.*, 1994), and the associated Mata da Corda lavas, SE Brazil (Leonardos *et al.*, 1991), do not show the same degree of Ti-enrichment. However, the TiO_2 and Al_2O_3 contents of micas from the Mata da Corda lavas

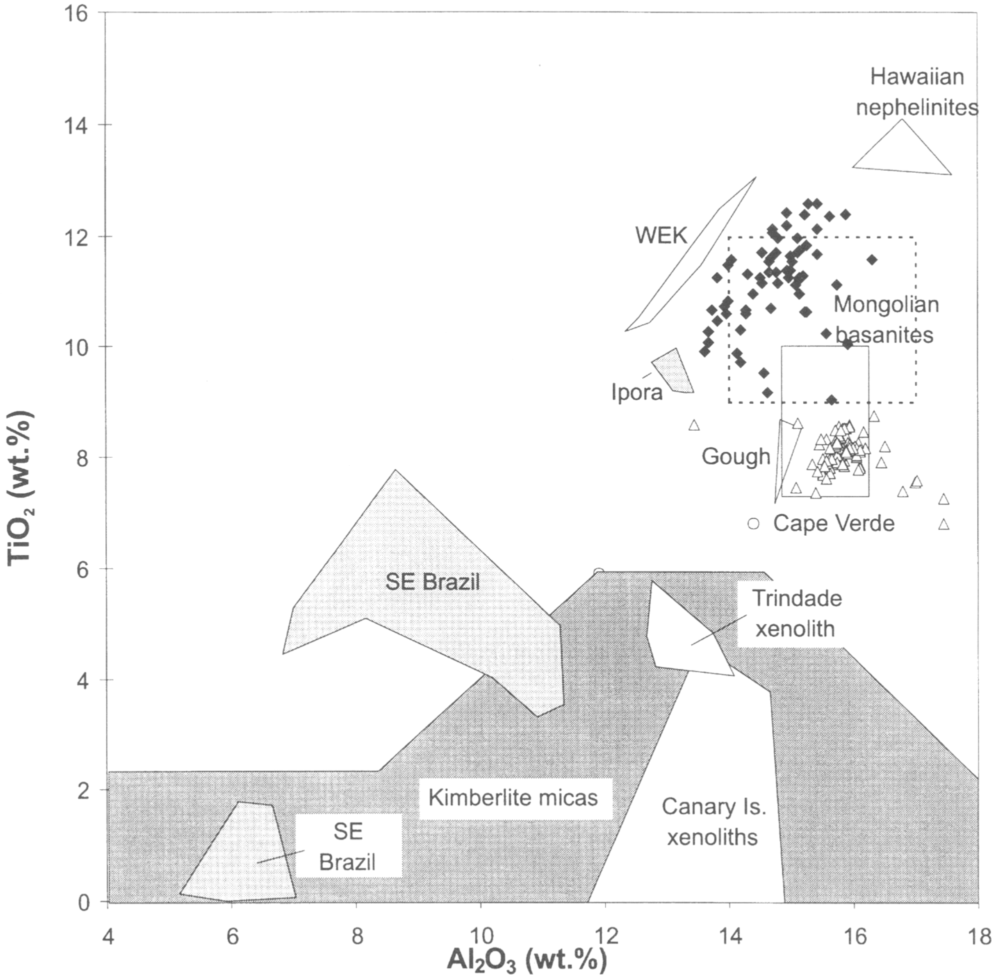

FIG. 5. Variations of Al_2O_3 and TiO_2 contents in micas from I70 (triangles = phenocryst cores, diamonds = phenocryst rims and groundmass), compared with biotites from a Trindade mafic xenolith (BM 87171(920)); other oceanic islands; Hawaii (Mansker *et al.*, 1979), Gough (Le Roex, 1985), Cape Verde (Furnes and Stillman, 1987) and the Canary Islands (Wulff-Pedersen *et al.*, 1996); Brazilian magmatism; Iporá minettes (Gibson *et al.*, unpublished data), SE Brazil: the Alto Paranaíba intrusions (Meyer *et al.*, 1994) and the associated Mata da Corda volcanics (Leonardos *et al.*, 1991) and Abrolhos Platform basalts (Fodor *et al.*, 1989) (open circles); and from Mongolian basanites (Ryabchikov *et al.*, 1982), the WEK olivine leucitites, NE China (Zhang *et al.*, 1993) and kimberlites (Mitchell, 1986).

plot along a trend roughly parallel to that defined by the phenocryst rims from I70. Biotites from the Abrolhos Platform, off the SE Brazilian coast (Fodor *et al.*, 1989), show compositions intermediate between these and the Ilha da Trindade samples.

Discussion

The high-Ti, late crystallising phenocryst rims and groundmass crystals described here approach the most extreme compositions reported for magmatic micas. The abrupt change in composition from phenocryst cores to rims may be due to magma mixing, related to injections of new magma into the chamber. These new melts may either have been of a slightly different composition, or they may have been injected at lower pressures, or both. This magma mixing scenario is also supported by the presence of similar compositional zoning in co-existing phases. Clinopyroxenes, in particular, have bright green, pleochroic diopside cores, surrounded by purplish Ti-rich rims. Titanomagnetite and kaersutite phenocrysts are also strongly zoned. although these compositional variations are less optically apparent.

The information acquired from these micas can be used to further our understanding of the processes which formed Ilha da Trindade. Figure 5 demonstrates that the highest Ti contents are found either in micas from oceanic islands, or from continental rift zones. This is consistent with the observations mentioned above (Foley, 1990), suggesting that Ti contents are seen to increase with decreasing pressure and increasing temperature. However, the presence of kaersutite in I70 suggests that the melt from which the Trindade micas crystallised was Al-saturated, whereas the starting compositions used by Foley are extremely deficient in Al. Nevertheless, the data reported here appear to support the general hypotheses proposed by Foley, despite the differences in both the starting compositions and the values of TiO_2 which have been obtained experimentally and in nature.

The islands of Hawaii, Cape Verde and Gough are all postulated to have been formed by relatively thin, oceanic lithosphere passing over a hot mantle plume, i.e. at elevated mantle temperatures and low pressures, similar to the conditions postulated to be involved in the formation of Ilha da Trindade (Gibson *et al.,* 1995). However, xenoliths from both Ilha da Trindade and the Canary Islands appear to contain micas with significantly lower Ti contents. These micas are thought to have been formed by mantle metasomatism. This suggests that the high-Ti micas described above are unlikely to be metasomatically derived and can thus be regarded as a primary, rather than secondary, phase in these rocks.

High-Ti and Ba contents in micas appear to be restricted to highly silica-undersaturated, basaltic igneous rocks, implying that they formed at relatively high temperatures and low pressures. A variety of mechanisms have been proposed for the incorporation of Ti and Ba into the biotite structure. These reflect the influence of many factors, but the most important appears to be the bulk composition of the residual liquid.

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