



Contents lists available at SciVerse ScienceDirect

Journal of South American Earth Sciences

journal homepage: www.elsevier.com/locate/jsames

Decoupling of paired elements, crossover REE patterns, and mirrored spider diagrams: Fingerprinting liquid immiscibility in the Tapira alkaline–carbonatite complex, SE Brazil

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ARTICLE INFO

Article history:

Received 27 December 2011

Accepted 9 April 2012

Keywords:

Nb–Ta decoupling

Zr–Hf decoupling

Crossover REE patterns

Liquid immiscibility

Alto Paranaíba

Carbonatite

Bebedourite

ABSTRACT

Tapira is an alkaline silicate–carbonatite complex belonging to the kamafugite–carbonatite association in the Late-Cretaceous Alto Paranaíba Igneous Province (APIP). It is dominated by coarse-grained plutonic rocks (bebedourite – a phlogopite-, apatite-, and perovskite-rich clinopyroxenite – with subordinated dunites, wehrlites, carbonatites and phoscorites). The plutonic rocks are crosscut by fine-grained ultramafic alkaline rocks (phlogopite picrites, bebedouritic dikes) and fine-grained carbonatites. Both types of dike-rocks show petrographic evidence of the coexistence of immiscible silicate and carbonatite liquids, such as carbonate ocelli present in the silicate rocks and, more rarely, silicate ocelli within carbonatites. A detailed geochemical study of the rock types in the complex, with emphasis on the fine-grained varieties, showed that whilst some rocks may be related to each other through crystal fractionation (e.g. phlogopite picrites and bebedouritic dikes), others display anomalous trace-element behaviour that cannot be readily explained by the fractionation of a particular phase or combination of phases. We interpret such anomalous geochemical signatures as produced by silicate–carbonate liquid immiscibility, on the basis of available experimental data on partition coefficients between coexisting immiscible liquids. The immiscibility signatures comprise: (a) decoupling of geochemical pairs, such as Nb–Ta and Zr–Hf; (b) rotation of REE patterns, which cross over the patterns of the primitive liquids; and (c) matching and opposite enrichment–depletion trace elements relationships in spider diagrams of conjugate immiscible liquids. We suggest that, once established, such geochemical signatures are very difficult to erase during the subsequent petrogenetic evolution processes, which may result in superimposed conflicting signatures.

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1. Introduction

Along with partial melting, crystal fractionation, and degassing/metamorphism, liquid immiscibility is regarded as a most important differentiation mechanism in alkaline and carbonatitic magmas. Compelling evidence to support carbonate–silicate liquid immiscibility comes from both natural (Dawson and Hawthorne,

1973; Bogoch and Magaritz, 1983; Dawson et al., 1994; Church and Jones, 1995; Kogarko, 1997; Ivanikov et al., 1998; Veksler et al., 1998a; Chalot-Prat and Arnold, 1999; Ray et al., 2000; Frezzotti et al., 2002; Thompson et al., 2002; Bühn and Trumbull, 2003; Chazot et al., 2003; Halama et al., 2005; Solovova et al., 2005; Stoppa et al., 2005; Vichil et al., 2005) and experimental systems (Wendlandt and Harrison, 1979; Hamilton et al., 1989; Jones et al., 1995; Lee and Wyllie, 1997a,b; 1998a,b; Veksler et al., 1998b, 2012; Brooker, 1998; Kjarsgaard, 1998; Brooker et al., 2001a,b). Alternative ways of producing carbonatite magmas are argued by other authors (e.g. Kurszlaukis et al., 1999; Harmer and Gittins, 1998; Nielsen and Veksler, 2002; Chakhmouradian, 2006), who favour either a primary origin in the mantle, or a residual character from crystal fractionation.

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In the case where a parental carbonated silicate magma undergoes carbonate–silicate liquid immiscibility, many chemical elements may enter preferentially one of the conjugate liquids or the other, according to their respective partition coefficients. This should generate geochemical “fingerprints” on each side of the immiscible pair, which can be used to pinpoint possible immiscibility events during magma evolution for a given rock suite.

Interestingly, only relatively few and recent works have recognized such geochemical signatures (e.g. Brod, 1999 and this work; Ivanikov et al., 1998; Thompson et al., 2002; Bühn and Trumbull, 2003; Stoppa et al., 2005), probably due to increased accuracy in modern measurement techniques for some trace elements such as Th, Ta, Hf, and the heavy rare earths (HREE).

In this paper we present petrographic and chemical evidence for liquid immiscibility from the Tapira Alkaline–Carbonatite Complex, SE Brazil, and discuss the possibilities of immiscibility-related signatures in carbonatite and associated silicate rocks.

2. Geological setting

Voluminous magmatism occurred in Central and Southern Brazil, and in Paraguay, Argentina and Uruguay, from the Early Cretaceous to the Eocene. This includes the extensive Early Cretaceous Paraná continental flood basalts (CFB) and the alkaline provinces that surround the Paraná Basin (Morbidei et al., 1995; Bizzi et al., 1995; Gibson et al., 1995a,b; 1997a; Comin-Chiaromonte and Gomes, 1996, 2005; Comin-Chiaromonte et al., 1997; Carlson et al., 1996; Thompson et al., 1998).

These magmatic events have been often associated with the thermal and/or chemical influence of mantle-plumes impacting the base of the continental lithosphere (e.g. Herz, 1977; Toyoda et al., 1994; Gibson et al., 1995a,b; 1997a; VanDecar et al., 1995; Thompson et al., 1998). Contemporaneous CFB and alkaline rocks in western Africa have also been linked with plume impact (e.g. Milner et al., 1995b; Milner and Le Roex, 1996; Lanyon and Le Roex, 1995; Le Roex and Lanyon, 1998). The Early Cretaceous alkaline magmatism in SE and Central Brazil is thought to be associated with the impact of the Tristan mantle plume (Gibson et al., 1997a), which is also considered to be responsible for the Paraná-Etendeka CFB, and contemporaneous alkaline magmatism in western Africa (Milner et al., 1995a,b; Milner and Le Roex, 1996; Le Roex and Lanyon, 1998). The Late Cretaceous and Eocene magmatism in the north and northeast margins of the Paraná Basin is thought to be related to the Trindade mantle-plume (Crough et al., 1980; Gibson et al., 1995b, 1997b; Thompson et al., 1998). The Alto Paranaíba and Goiás provinces, respectively at the northeast and north borders of the Paraná Basin, are two of the largest areas of kamafugite occurrence in the world (Gibson et al., 1995b; Araujo et al., 2001; Junqueira-Brod et al., 2002).

The Alto Paranaíba Igneous Province (APIP), comprises a kamafugite-carbonatite association (Brod et al., 2000), with subordinate kimberlites and lamproites (Gibson et al., 1995b). The ultrapotassic magmas are emplaced into the Neoproterozoic metasedimentary rocks of the Brasília Mobile Belt, located between the southwest border of the Archean São Francisco Craton and the northeast border of the Phanerozoic Paraná Basin. Kamafugites occur as numerous, small hypabyssal plugs and diatremes, but also as the extensive Mata da Corda lavas and pyroclastics (Araujo et al., 2001; Sgarbi et al., 2000). The large (up to 65 km²) intrusive carbonatite-bearing complexes of Catalão, Serra Negra, Salitre, Araxá and Tapira are composed of ultramafic rocks, mainly dunites and bebedourites (diopside–phlogopite–, perovskite–, and apatite-rich rocks, Barbosa et al., 2012) variably transformed into phlogopitites by carbonatite

metassomatism, phlogopite-picrite dikes, carbonatites and phoscorites (Brod et al., 2004). K–Ar dating of phlogopite separates from the Patos de Minas – Carmo do Paranaíba region yielded an age of 83.6 ± 1.4 Ma. (Gibson et al., 1995b). Perovskite ²⁰⁶Pb/²³⁸U ages from the Mata da Corda rocks cluster at 80–81, and 75–76 Ma (Sgarbi et al., 2004).

3. Analytical techniques

A detailed geochemical study of major and trace elements was carried out on the various lithological units of the Tapira complex. All samples were ground with an agate mill to avoid Nb and Ta contamination from carbide. Whole-rock chemical analyses were carried out at the University of Durham, UK. Major elements were determined by X-Ray Fluorescence on fused samples, using a Philips PW1400 Spectrometer, fitted with a PW1500/10 automatic sample changer, Rh tube X-Ray source, operating at 80 kV and 35 mA for all elements. Loss-on-ignition was obtained by weight loss of samples ignited in a Carbolite LMF furnace at 900 °C for 2 h and allowed to cool in a desiccator to minimize moisture absorption, which can be a major source of error in carbonatite LOI determination (Brod, 1999). Trace elements were obtained by a combination of XRF analysis on pressed pellets and ICP-MS analysis on dissolved (HF + HNO₃) sample using a Perkin–Elmer Sciex Elan 6000 ICP Mass Spectrometer, equipped with a cross-flow nebuliser set at 1 ml/min. The plasma was operated at 1100–1300 W. In all cases, analytical quality was controlled with the use of blanks, international reference materials and replicates.

Total carbon, expressed as CO₂, and sulphur were determined for selected samples at the University of Brasília. Carbon and sulphur were analysed by infrared absorption using LECO CR-12 (carbon) and SC-132 (sulphur) furnaces. Oxygen (99.99%) was the carrier gas. Analytical results for selected representative samples are given in Table 1.

4. The Tapira complex

Tapira is the southernmost (19°53'S; 46°50'W) of the APIP alkaline–carbonatite complexes, located approximately 30 km south-southeast of the city of Araxá, Minas Gerais State. It intrudes Neoproterozoic metasedimentary rocks of the Brasília Belt, which are deformed into a dome structure, as well as slightly fenitized and thermally affected near the contact. K–Ar dating of mica yielded ages of 85.6 and 87.2 Ma (Sonoki and Garda, 1988).

The complex is roughly elliptical, 35 km² in area, and consists dominantly of bebedourite, with subordinate serpentinized dunite, carbonatite, syenite, melilitolite (uncompahgrite), ultramafic potassic dikes, and metasomatic phlogopite. The complex is currently mined for phosphate, but also contains important deposits of titanium, niobium, rare earths and vermiculite, formed by residual concentration in the weathering mantle. Recent developments in the phosphate mining area revealed the existence of still unmapped phoscorite towards the central part of the complex, (C.C. Ribeiro, personal communication), although it is still unclear whether these rocks represent the product of crystallization of phoscorite magmas or apatite-rich cumulates from a bebedourite magma.

A geological sketch of the rock distribution in the complex is presented in Fig. 1, mostly based on information gathered from short segments of fresh rock at the bottom of drill cores. The general characteristics of each lithologic unit are described below, a more detailed petrographic account of each unit can be found in Brod (1999) and Brod et al. (2005).

Table 1
Representative analyses of the main Tapira rock types. Oxides expressed in wt. % and trace elements expressed in ppm.

	Phlogopite	picrite	Bebedouritic dike	Bebedouritic dike	Bebedourite B1	Bebedourite B2	Bebedourite B2	Syenite	Carbonatite C1	Carbonatite C2	Carbonatite C3	Carbonatite C4	Carbonatite C5
SiO ₂	29.88	27.62	36.70	36.70	29.80	38.01	31.98	53.73	0.60	2.12	7.66	0.92	2.20
TiO ₂	3.80	4.65	3.98	3.98	5.60	2.94	6.05	17.14	0.14	0.08	0.54	0.02	0.06
Al ₂ O ₃	3.48	3.61	7.41	7.41	4.96	4.91	4.90	4.25	0.41	0.06	2.16	0.40	0.60
Fe ₂ O ₃ (T)	12.98	14.02	15.95	15.95	12.31	11.63	14.90	1.08	1.08	1.22	3.21	0.50	3.18
MnO	0.20	0.27	0.25	0.25	0.11	0.23	0.21	0.11	0.34	0.31	0.11	0.07	0.58
MgO	18.87	7.40	6.04	6.04	12.46	9.92	8.79	3.12	5.93	3.89	3.62	0.66	16.92
CaO	13.30	18.21	19.38	19.38	20.63	20.72	21.95	2.71	36.89	45.21	42.98	49.74	26.26
Na ₂ O	0.55	0.46	0.66	0.66	0.55	1.15	0.57	0.42	0.40	0.41	0.42	0.33	0.31
K ₂ O	3.27	5.68	4.27	4.27	3.31	3.02	3.31	13.38	0.02	0.05	1.90	0.01	0.02
P ₂ O ₅	2.18	3.69	2.04	2.04	7.30	4.92	4.76	0.39	0.36	0.27	3.47	0.07	0.27
LOI	10.84	12.34	1.98	1.98	1.96	2.80	1.31	2.32	37.20	42.09	31.26	42.87	41.65
BaO	0.34	0.53	0.27	0.27	0.17	0.23	0.19	0.91	12.83	0.80	0.25	0.28	4.98
SrO	0.41	0.49	0.23	0.23	0.19	0.29	0.18	0.18	2.99	2.30	1.61	1.96	1.58
Total	100.09	98.97	99.16	99.16	99.31	100.77	99.10	99.08	99.18	98.81	99.19	97.83	98.60
CO ₂	9.39	12.05	1.07	1.07	1.83	1.55	0.66	1.88	38.37	42.14	32.83	44.96	43.72
S	0.05	0.26	0.17	0.17	0.03	0.02	0.02	0.15	0.00	0.15	0.15	0.04	0.35
Cr	835.2	36.4	27.0	27.0	3.7	1.5	3.1	22.4	24.1	0.1	9.2	0.1	15.1
Ni	704.0	24.5	12.5	12.5	47.0	33.4	23.2	19.7	18.4	16.8	18.5	10.2	6.4
Sc	23.57	23.31	16.08	16.08	54.64	42.85	72.36	3.53	13.79	12.5	3.79	0	17.14
Ba	3000.3	4725.4	2394.1	2394.1	1512.2	2031.6	1660.2	8160.3	114871.4	7133.9	2218.9	2476.8	44581.5
Rb	106.8	129.0	76.5	76.5	112.5	66.4	95.5	133.2	0.5	1.2	38.0	0.8	2.5
Sr	3441.1	4157.1	1980.4	1980.4	1591.6	2449.4	1518.9	1523.1	25249.7	19450.2	13655	16564.6	13336.4
Zr	680.5	1229.1	2757.9	2757.9	141.7	1005.5	6052.5	2942.3	0.9	2.8	223.5	7.5	5.4
Hf	15.428	25.897	64.571	64.571	5.174	27.585	142.611	39.912	0.118	0.089	4.429	0.145	0.224
Nb	229.1	428.4	303.5	303.5	189.1	222.8	332.3	359.3	108.5	41.6	144.9	10.7	515.4
Ta	12.203	21.342	4.422	4.422	12.678	7.499	6.418	7.074	0.202	0.319	12.54	0.756	0.209
Th	37.83	41.29	2.63	2.63	10.27	18.99	2.29	25.18	13.18	20.64	24.84	2.32	91.14
Y	44.73	83.31	98.74	98.74	49.19	65.75	208.98	11.65	71.55	77.71	72.55	61.63	58.23
La	320.93	540.5	121	121	367.5	416.8	144	120.3	1575.9	1530.9	508.7	333.3	947.9
Ce	637.06	1095.2	203.8	203.8	662.3	791.2	202.3	260.2	2491.6	2689.6	1150.4	697.2	1443.6
Pr	69.95	118	23.8	23.8	69.8	83.6	22.9	29.7	218.9	270.3	128	68.7	125.7
Nd	256.17	430.5	94.3	94.3	256.5	304	96.6	102.7	658.9	920.9	480.8	247.3	376.8
Sm	35.8	58.5	19.5	19.5	40.6	45	26.6	13.5	63.3	103.1	63.6	34.1	38.3
Eu	9.18	15.05	6.58	6.58	11.28	12.41	10.39	3.23	17.2	23.32	16.11	9.45	10.13
Gd	20.87	34.67	20.25	20.25	28.1	30.63	34.04	6.48	30.67	45.84	37.2	23.3	19.24
Tb	2.52	4.16	2.91	2.91	3.16	3.59	5.94	0.74	3.88	5.14	4.19	2.8	2.79
Dy	10.55	18.28	15.96	15.96	12.72	15.2	33.56	2.87	16.07	19.86	17.45	12.25	12.62
Ho	1.62	2.92	3	3	1.82	2.35	6.62	0.47	2.59	2.99	2.64	1.97	2.14
Er	3.39	6.48	7.83	7.83	3.42	4.94	17.06	1.1	6.07	6.64	5.75	4.33	5.27
Tm	0.413	0.822	1.11	1.11	0.354	0.572	2.517	0.161	0.814	0.858	0.675	0.565	0.669
Yb	2.167	4.397	6.327	6.327	1.678	3.057	13.942	1.139	4.736	4.759	3.531	2.991	3.009
Lu	0.276	0.564	0.835	0.835	0.194	0.4	1.894	0.154	0.651	0.658	0.438	0.423	0.314

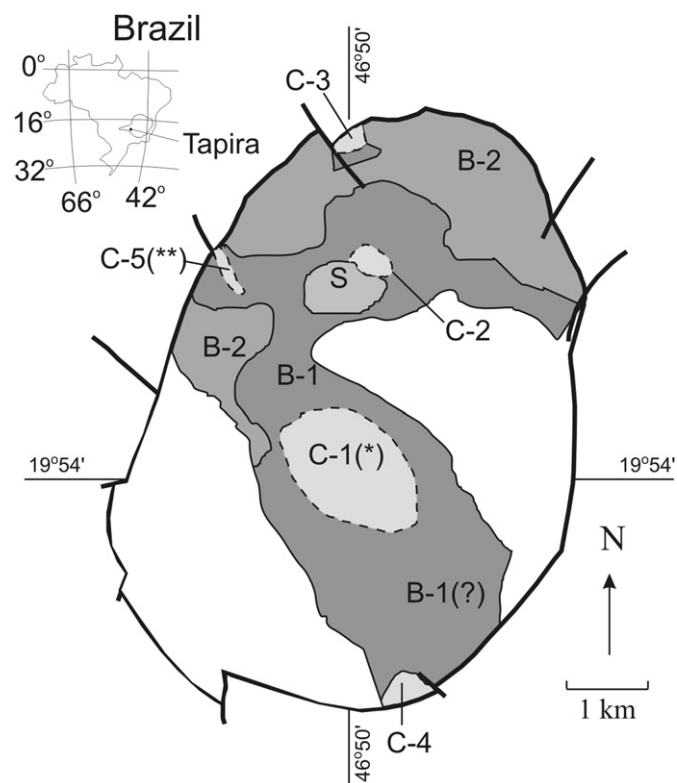


Fig. 1. Geological sketch of the Tapira complex. Units represented are Bebedourites (B1, B2), Carbonatites (C1 to C5), Syenite and Syenite–carbonatite breccia (S). Drill core information in the central and southern portion of the complex is scarce. No drill-core information available in the white areas. (*) C1 includes newly discovered phoscorite occurrences. (**) C5 rocks also occur as scattered dikes and veins throughout the complex.

4.1. The Silicate Plutonic Series

In this work, coarse-grained silicate rocks (dunites, wehrlites, bebedourites and syenites) are referred to collectively as the Silicate Plutonic Series (SPS). The ultramafic rocks consist dominantly of bebedourite, sub-divided into the B1 and B2 units (Fig. 1). Because of their restricted occurrence, dunites, wehrlites, and modal variations in the proportions of perovskite, magnetite and/or apatite are not individualized within B1 and B2 in Fig. 1.

Bebedourites vary from fine to coarse grained, locally pegmatitic, may have a strongly oriented fabric, and consist mainly of diopside with variable amounts of phlogopite, perovskite, apatite, magnetite, melanite, and titanite. Modal variations can produce facies rich in olivine (dunites, wehrlites), perovskite-magnetite or apatite. Whilst this is primarily the result of magmatic layering, some of the apatite- or perovskite-magnetite-rich rocks may occur as discordant bodies cutting the igneous layering or even penetrating the country rock. Such features suggest the remobilisation of pockets of crystal-mush and, in conjunction with the scarcity of fenitisation effects, may indicate that the intrusion was partially consolidated during emplacement. Rare, coarse-grained to pegmatoidal melilitites (uncompahgrites) were described from the northeastern border of the complex (Guimarães et al., 1980), consisting dominantly of melilite-group minerals with subordinate phlogopite, apatite, titanomagnetite, diopside, perovskite, and wollastonite. The ultramafic rocks of the SPS are intruded by syenites, carbonatites, and ultramafic dikes.

B2 rocks typically formed under higher SiO_2 activity than B1, which is supported by: a) the presence of primary Ti-rich

(melanite) garnet and titanite in B2 wehrlites and bebedourites; b) absence or very low modal content of perovskite throughout B2; c) disequilibrium features of the existing perovskite, which is invariably replaced by Ti-rich silicate minerals, d) intercumulus K-feldspar in the B2 most evolved, perovskite-free bebedourites (Brod et al., 2005).

Syenites occur as small independent intrusions or as fragments in carbonatite–syenite breccias. Besides K-feldspar, they may contain significant phlogopite and/or aegerine pyroxene, with accessory amounts of zircon and titanite. Carbonate globules and irregular patches are locally present (Fig. 2), indicating the coexistence with immiscible carbonatite liquid.

4.2. Carbonatites

A number of carbonatite bodies intrude, brecciate and metasomatize the SPS rocks. They were sub-divided (Brod, 1999) into units C1 to C5, according to location (Fig. 1) and petrographic or compositional characteristics. The intrusive bodies range from massive carbonatite plugs through dikes to small veinlets.

Carbonatite intrusion in the ultramafic rocks often results in the development of a metasomatic phlogopitite (phlogopite + magnetite + dolomite), whose best examples are found at the contact of the C1 carbonatite with the B1 bebedourites and wehrlites (Fig. 1).

Brecciation of SPS rocks by intrusive carbonatite is also a common feature. In the northwest portion of the complex, C2 carbonatites intrude both the B1 bebedourites and the syenites. In the area marked “S” in Fig. 1, carbonatites percolate fractures in the syenitic rock to form monomitic breccias, indicating intrusion by magmatic stoping. The detached angular fragments of syenite are usually surrounded by phlogopite-rich reaction rims. In the Tapira mine area, a more explosive style of C2 carbonatite intrusion resulted in the local development of small diatremes filled with polymitic breccias, containing angular blocks of several petrographic varieties of SPS rocks, in addition to less frequent xenoliths of country rock.

Some fine-grained carbonatite dikes may contain silicate globules (Fig. 2), indicating coexistence with immiscible silicate magmas.

Three compositional types of carbonatite were recognized. Calciocarbonatites occur in the C1, C3 and C4 bodies, dolomite-bearing calciocarbonatites in C1 and C2, and magnesiocarbonatites in C5. The former two types occur as massive bodies and dikes, whereas magnesiocarbonatites occur as a dike swarm in the area marked C5 (Fig. 1) and also as late-stage dikes and veinlets scattered throughout the complex. Pyrochlore (in calciocarbonatites and dolomite calciocarbonatites), apatite, phlogopite, magnetite, pyrite and barite are the main accessory minerals.

4.3. Ultramafic dikes

The plutonic rocks of the Tapira complex are crosscut by numerous ultramafic dikes, usually a few centimetres or tens of centimetres thick, rarely reaching thickness over 1 m. Some of these dikes represent the mineralogically least-evolved silicate rocks found in Tapira and in all other carbonatite complexes of the APIP (e.g. Gibson et al., 1995a, b; Brod et al., 2000, 2004). They are often porphyritic, containing euhedral olivine (less frequently phlogopite, apatite, clinopyroxene or perovskite) phenocrysts set in a carbonate- and phlogopite-rich fine-grained to aphanitic groundmass with subordinate apatite and opaque minerals (chromite to Ti-rich magnetite). Despite their ultramafic and porphyritic character, these rocks do not fit the available classification schemes for lamprophyre-like rocks (e.g. Streckeisen, 1978; Rock, 1986, 1991;

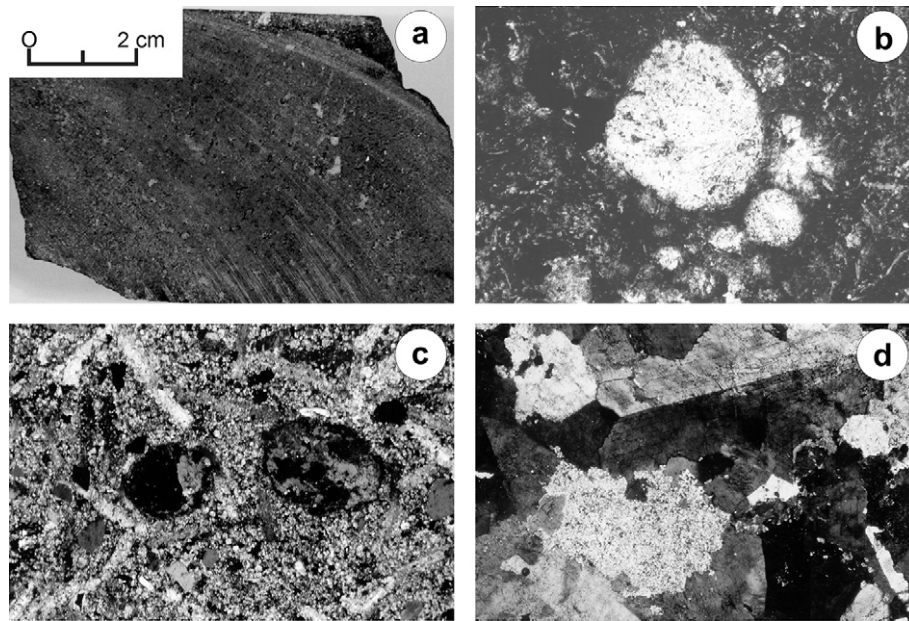


Fig. 2. Textural features of carbonate-silicate liquid immiscibility in Tapira rocks. (a) Phlogopite picrite showing small white carbonate globules. (b) Photomicrograph of rounded carbonate globules in fine-grained bebedouritic dike, plane-polarised light. Field of view = 2×1.3 mm. (c) Photomicrograph of feldspathic globules in carbonatite. Note the rounded shapes and the lack of alteration. Cross-polarised light, Field of view = 3×1.9 mm. (d) Photomicrograph of irregularly-shaped carbonate patch in syenite. Note the absence of alteration in the adjacent orthoclase. Cross-polarised light. Field of view = 3×1.9 mm.

Le Maitre, 2002; Tappe et al., 2005). In this work we follow the suggestion of Gibson et al. (1995b), and refer to these dikes as phlogopite picrites, on the basis of their high content of olivine and phlogopite, and very high MgO content (up to 21 wt. %). Flow textures are marked by the orientation of olivine and phlogopite phenocrysts as well as of groundmass phlogopite. Locally, the concentration of olivine phenocrysts towards the centre of the dikes indicates some degree of flow-differentiation in these magmas. Globules or irregularly-shaped pockets of carbonate (Fig. 2) in the phlogopite picrites suggest the onset of liquid immiscibility at a very early stage during the petrological evolution of the Tapira complex.

A second type of ultramafic dike occurs at Tapira. This variety is mineralogically and chemically similar to bebedourites, but is individualized here as bebedouritic dikes because of its very fine-grained character and its emplacement in fractures. Bebedouritic dikes contain rare phenocrysts of phlogopite, clinopyroxene, and/or apatite, set in a groundmass of the same phases plus magnetite and carbonate. They are characterized by the absence of olivine and chromite, and interpreted as a more evolved counterpart of the phlogopite picrites. Immiscible carbonate globules or irregular patches are locally present. The abundance of carbonate in the groundmass increases with differentiation, in some cases leading to the formation of a silicocarbonatite.

Both types of ultramafic dikes are mostly restricted to the interior of the complex, but occasionally occur in the country rock, both in the vicinity and away from the intrusion, in which case chilled margins may develop.

Although the mineralogy of these rocks does not warrant their classification as kamafugites in a petrographic sense, as they do not contain kalsilite, Brod et al. (2000) demonstrated that these ultramafic dikes are chemically related to the APIP kamafugites, both in terms of major and trace elements, thus establishing a kamafugite-carbonatite association in the province.

The presence of carbonatite globules in several silicate rock-types (phlogopite-picrites, bebedouritic dikes, syenites) and the

concurrent, but rarer, presence of silicate globules in carbonatites (Fig. 2) indicate that liquid immiscibility was a recurring process, spreading from very early (phlogopite picrites) to late (syenites) stages in the evolution to the Tapira complex.

5. Whole-rock geochemistry

Any attempts towards a geochemical study of complex rock associations such as the one in Tapira must be preceded by an assessment as to which of the rock-types present are likely to represent or approximate to liquids. In particular, coarse-grained plutonic rocks may either be the product of *in situ* crystallisation, in which case their bulk-rock chemistry would reflect that of the original magma, or they may be formed by accumulation of one or more mineral phases, in which case the chemical composition will depart significantly from that of the liquid.

In the case of the Tapira coarse-grained ultramafic rock-types, common and substantial modal variations imply that textures and structures produced by igneous layering and changes in cumulus-intercumulus phase relations are more easily recognisable. In fact, many of the rocks in the SPS represent cumulates, rather than just liquids, which poses difficulties for the interpretation of their chemical composition, particularly the major-element oxides. In addition, both syenites and carbonatites can also be generated by crystal accumulation processes, but recognizing cumulates in coarse-grained varieties of these rocks may be difficult by petrographic means alone.

Coherent volcanic rocks or, in the Tapira case, fine-grained dikes provide the best estimate of the composition of original magmatic liquids. Therefore, phlogopite-picrites, bebedouritic dikes and some fine-grained carbonatitic dikes occurring in Tapira are likely to represent, or at least approximate, the composition of some of the magmatic liquids involved in the evolution of the complex. The ultramafic dikes are of particular interest, since they can provide insights into the chemical aspects of primitive liquids.

Although some isolated occurrences of phlogopite-picrites are found throughout the APIP, these rocks seem to be particularly associated with the carbonatite-bearing intrusions in the province (Gibson et al., 1995b; Brod et al., 2000). Field, petrographic, and mineralogical evidence suggest that phlogopite-picrites represent the least evolved magmas from Tapira and other APIP carbonatite complexes. Therefore, it seems logical to investigate whether they can be regarded as: a) primary magmas derived from the mantle; and b) parental magmas to the other rocks in the complex.

For the reasons above, the dike rocks are investigated first, to lay out the basis in which the chemical characteristics of the other rocks can be examined. In order to allow direct comparison with data from the carbonatites, major-element analysis of the phlogopite-picrites and other Tapira silicate rocks are reported here on a “wet” basis (i.e. not recalculated to 100 wt.%), since LOI values are mostly related to the presence of primary phlogopite, primary groundmass carbonate and carbonate ocelli (Brod et al., 2000).

5.1. Phlogopite-picrite dikes

Phlogopite-picrites are extremely silica-undersaturated ($\text{SiO}_2 = 24.30\text{--}33.40$ wt. %), carbonate-rich ($\text{CO}_2 = 3.29\text{--}21.9$ wt. %) and strongly potassic ($\text{K}_2\text{O} = 2.68\text{--}5.87$ wt. %). They also contain high CaO (9.31–19.41 wt. %) and TiO_2 (3.24–5.37 wt. %), and typically low Al_2O_3 (1.63–4.69 wt. %). $\text{K}_2\text{O}/\text{Na}_2\text{O}$ varies from 2.14 to 14.86. The high MgO contents (8.73–21.34 wt. %) positively correlate with high Cr and Ni, testifying to their unevolved character.

The high Cr (134–1012 ppm) and Ni (82–932 ppm) contents are consistent with the ultramafic character of these rocks, suggesting that the least evolved members of the phlogopite-picrite series can be considered as mantle-derived primary magmas. Scandium is moderately high (22–37 ppm). Phlogopite-picrites are strongly enriched in incompatible elements, particularly Ba, Sr and the sum of the rare-earth elements, which can all reach a few tenths of a percent. High field-strength element (HFSE) concentrations are high (Nb: 160–360 ppm; Ta: 10–22 ppm; Zr: 470–1000 ppm and Hf: 10–23 ppm). All samples behave coherently in spider diagrams (Fig. 3a) forming a pattern that peaks at La (up to 1600 times chondritic abundance) with negative anomalies at Rb, K, Sr and, to a lesser extent, Ti. Chondrite-normalized ratios of “paired elements” (i.e. elements with similar geochemical behaviour) such as $\text{Zr}_{(\text{N})}/\text{Hf}_{(\text{N})}$, $\text{Y}_{(\text{N})}/\text{Ho}_{(\text{N})}$ and $\text{Nb}_{(\text{N})}/\text{Ta}_{(\text{N})}$ show little variation, in the ranges 1.16–1.52, 8.6–9.9 and 0.58–1.34, respectively.

The rare-earth element (REE) patterns (Fig. 3b) of phlogopite-picrites are smooth and steep, showing strong enrichment of the lighter (LREE) relatively to the heavier rare earths (HREE). Chondrite-normalized $\text{La}_{(\text{N})}/\text{Lu}_{(\text{N})}$ ratios range from 69 to 210, but most values are concentrated between 90 and 160.

5.2. Bebedouritic dikes

This group comprises fine-grained rocks that, although still ultramafic, are mineralogically more evolved than the phlogopite-picrites. Their chemical composition is also more variable, and it is possible that rocks within this group had more than one origin or evolved along different paths.

Chemically, the bebedouritic dikes can be distinguished from phlogopite-picrites by their lower MgO (2.99–12.48 wt. %), higher CaO (15.93–26.03 wt. %), P_2O_5 (2.04–6.02 wt. %) and, in some cases, higher CO_2 (1.07–22.27 wt. %). These characteristics reflect the absence of olivine and the increase in the proportion of clinopyroxene, apatite and groundmass carbonate. Like the phlogopite-picrites, they are extremely silica-undersaturated (18.4–36.7 wt. % SiO_2) and have low Al_2O_3 contents (2.04–7.41 wt. %). They are

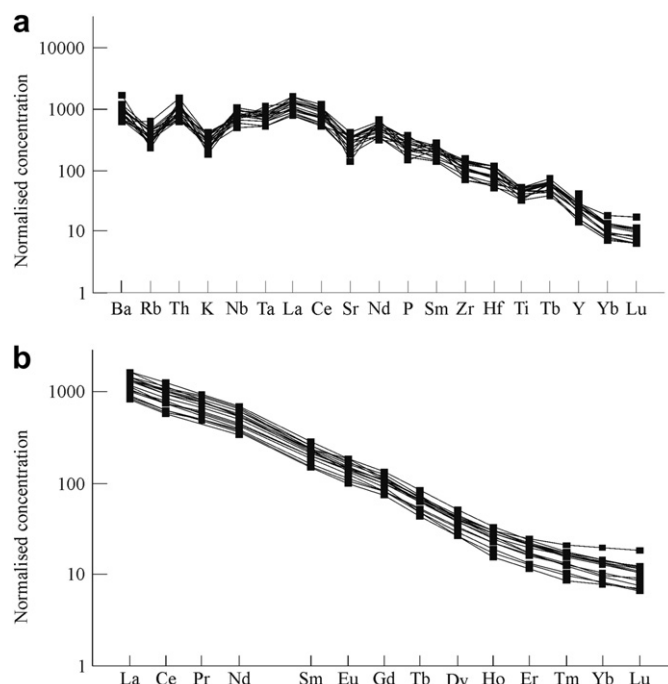


Fig. 3. (a) Trace-element spider diagram showing the composition of phlogopite picrites, normalized to chondrite (except Rb, K and P), with normalisation values from Thompson et al. (1984). (b) Chondrite-normalized REE patterns of phlogopite-picrites. Normalisation factors from Boynton (1984).

also strongly potassic (2.56–5.95 wt. % K_2O), with variable $\text{K}_2\text{O}/\text{Na}_2\text{O}$ (1.2–13.2).

The more evolved character of the bebedouritic dikes leads to a more significant control of trace-element concentration by processes such as fractional crystallisation or liquid immiscibility. The most striking difference in trace-element content between phlogopite-picrites and bebedouritic dikes is the extreme depletion of the latter in some compatible elements, such as Cr and Ni, both usually below 40 ppm, signalling previous extensive fractionation of olivine and Cr-rich spinel.

Not all compatible elements are depleted in the bebedouritic dikes. For instance, Sc may reach even higher concentrations (up to 68 ppm) than those observed in the phlogopite-picrites. Among a number of Tapira mineral separates analysed for trace elements by ICP-MS (Brod, 1999), diopside yielded significant Sc contents (111 ppm), whereas other calcium-rich minerals, such as apatite, perovskite and calcite, contain negligible amounts of Sc. Therefore, the enrichment of the bebedouritic dikes in this element mostly indicates clinopyroxene contribution.

Bebedouritic dikes are generally enriched in incompatible elements, showing very high Sr (up to 11000 ppm in a high-carbonate sample, but generally between 2000 and 6000 ppm) and Ba (up to 5600 ppm). Zr and Hf contents are variable reaching up to 4000 ppm and 64 ppm, respectively. Niobium reaches higher concentrations (230–520 ppm) than in the phlogopite-picrites, but Ta can be relatively depleted (1–22 ppm) in some samples. This disparate behaviour induces wide variations in chondrite-normalized $\text{Nb}_{(\text{N})}/\text{Ta}_{(\text{N})}$ ratios, which will be discussed in greater detail later in this paper.

Fig. 4 illustrates the trace-element relationships in bebedouritic dikes, along with a shaded field representing the composition range of phlogopite-picrites. Patterns for the majority of samples (only representative analyses plotted in Fig. 4a) show good approximation to the phlogopite-picrites, apart from slightly

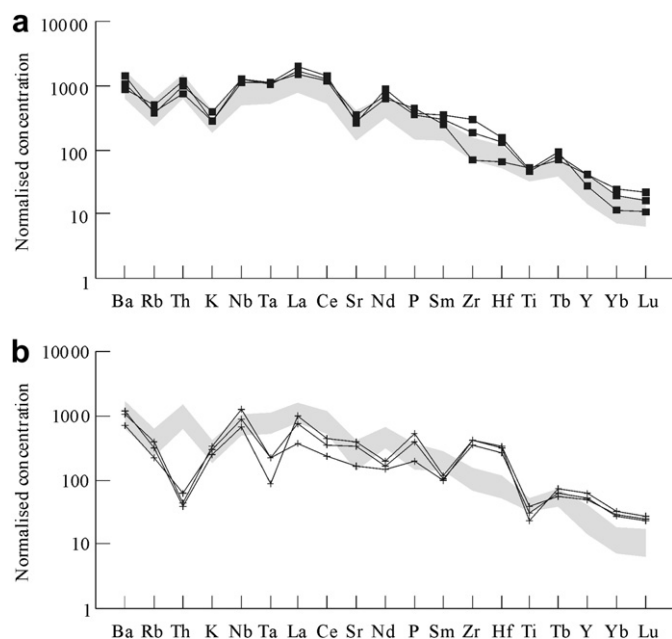


Fig. 4. Normalized trace-element diagrams for bebedouritic dikes, compared with the range of phlogopite picrites (shaded field). The bebedouritic dikes can be divided in two groups, represented in (a) and (b), according to their trace-element relationships (see text). Concentrations normalized to chondrite (except Rb, K and P) according to Thompson et al. (1984).

higher REE, Zr, and Hf contents, which can all be readily explained by residual concentration during crystal fractionation. However, for a small group of samples (Fig. 4b) trace-elements depart significantly from the primitive pattern. Although their major-element contents are similar to those of the first group, these rocks have much higher Zr and Hf, strong Th depletion, no Sr anomaly and a positive P anomaly. Another striking feature is their much higher chondrite-normalized $Nb_{(N)}/Ta_{(N)}$. It should also be noted that this group also has lower LREE and higher HREE than the phlogopite-picrites and the remainder of the bebedouritic dikes.

The REE patterns of bebedouritic dikes are illustrated in Fig. 5. The first diagram shows chondrite-normalized REE patterns and the second diagram shows the same samples normalized to a primitive phlogopite-picrite, together with the range of phlogopite-picrite compositions (shaded field). The two groups of bebedouritic dikes identified in Fig. 4 have contrasting REE behaviour. The first group produces normalized REE patterns that are parallel to those of phlogopite-picrites, albeit at generally higher values for all REE. As with other trace elements, this results from a natural progression of the phlogopite-picrites to bebedouritic dikes via crystal fractionation.

On the other hand, the anomalous bebedouritic dikes with positive Zr–Hf and negative Th anomalies in spider diagrams are also depleted in LREE and enriched in HREE, relative to the phlogopite-picrites. Fig. 5 shows that their REE patterns “cross over” those of the first group at Dy. The anomalous REE patterns are difficult to reconcile with crystal fractionation of REE-bearing phases present in the Tapira ultramafic rocks, such as apatite and perovskite. Tapira apatite preferentially concentrates REE from Ce to Sm, relative to the primitive phlogopite-picrite composition (Brod, 1999) but its removal from the liquid is inconsistent with the positive P anomaly in Fig. 4. Furthermore, Tapira and other APIP perovskites (Brod, 1999; Gravina et al., 2002) show flat, steep LREE to HREE slopes, and the enrichment factors in Tapira perovskite relatively to the primitive phlogopite picrite are similar or marginally lower for Ce to Sm than for La and Eu (Brod, 1999). Thus,

if any Ce to Sm pattern was produced by perovskite removal from the primitive phlogopite-picrite magma, it would be opposite to that observed in Fig. 5.

It is clear from the trace-element features described above that, although the phlogopite picrites may evolve to the bebedouritic dikes through crystal fractionation, the latter group encompasses rocks with more than one origin, or which underwent distinct differentiation processes.

The interpretation of the chemical properties of the SPS rocks is less straightforward than that of the dikes, due to the effect of extensive crystal accumulation. Nevertheless, some general chemical features and differences between the B1 and B2 units are pointed out in the following paragraphs.

5.3. Wehrlites and olivine-bearing cumulates

The chemical composition of the olivine-bearing rocks is highly variable, both in terms of major and trace elements, depending upon which mineral phases accompany olivine in the rock. For example, TiO_2 may reach up to 15.6 wt. % in perovskite-rich rocks, and P_2O_5 may be as high as 10.5 wt. % in apatite-rich rocks. They have generally low SiO_2 (12–33 wt. %) and high, but variable MgO (11–30 wt. %), $Fe_2O_{3(T)}$ (12–27 wt. %) and CaO (8–26 wt. %).

The olivine-rich rocks also usually contain significant amounts of Cr (up to 1200 ppm) and Ni (up to 1100 ppm), which distinguishes them from the generally Cr- and Ni- poor bebedourites. However, it should be stressed that exceptions to this rule do occur, and some olivine-bearing cumulates may be Cr- and Ni-poor, whereas rare bebedourites may contain high amounts of these elements. In particular, some Cr- and Ni-poor, olivine-bearing

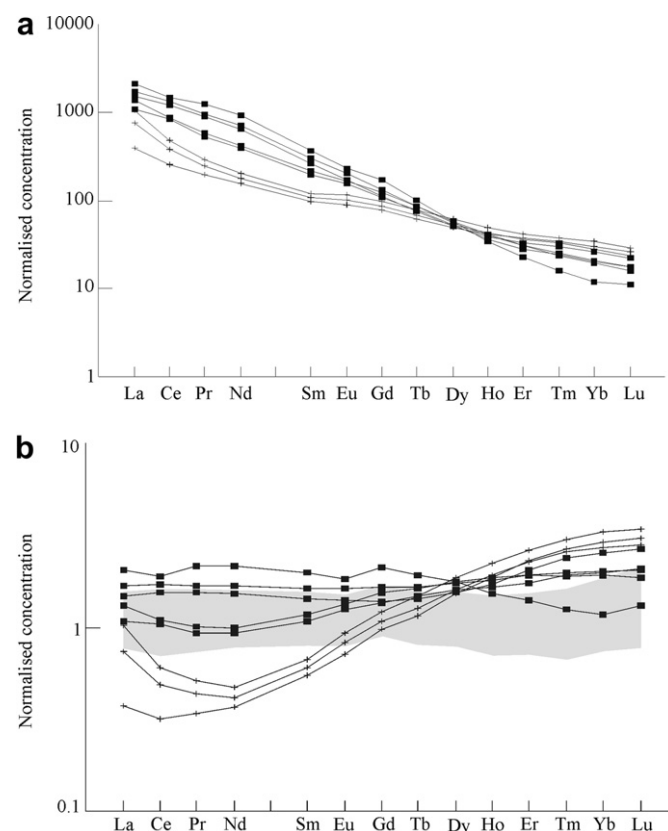


Fig. 5. REE patterns of bebedouritic dikes normalized to: (a) chondritic values of Boynton (1984) and (b) primitive phlogopite-picrite. The shaded field in diagram (b) covers the range of Tapira phlogopite picrites.

(wehrlitic) cumulates may have formed from carbonatitic or phoscoritic magmas, as suggested by the mineral chemistry of olivine and spinel (Brod et al., 2005; and our unpublished data).

5.4. Bebedourites

The absence of both olivine and Cr-rich spinel, and the increased amounts of clinopyroxene, in comparison with the olivine-bearing rocks, are reflected in the chemical composition of most bebedourites by higher SiO₂ (13–47 wt. %), Na₂O (0–1.2 wt. %) and CaO (18–27 wt. %), and lower Fe₂O_{3(T)} (6–20 wt. %), MnO (0.11–0.31 wt. %), and MgO (5.5–16.5 wt. %). The very low Cr (usually below 20 ppm) and Ni (usually below 50 ppm), and the high Sc (up to 145 ppm), which are typical of both B1 and B2 bebedourites, can be explained by the same mineralogical changes.

Although the chemical composition of the bebedourites is variable and, in many cases, there are extensive compositional overlaps between B1 and B2, some broad chemical distinctions between the two units can be outlined. In terms of major elements, B1 bebedourites have higher TiO₂ and tend to have slightly higher MgO, whilst bebedourites from B2 have higher SiO₂, MnO and to a lesser extent CaO. Regarding the trace elements, B2 rocks have notably higher Zr, Hf, Th and LREE than B1, for the same SiO₂ content. Spider diagrams for representative analyses of bebedourites from the two units are presented in Fig. 6.

Most B1 bebedourites are characterized by relatively small, or non-existent, negative Rb and K anomalies (Fig. 6a), although such features do appear in a small number of samples (e.g. dashed line in Fig. 6a). Phosphorus and titanium highs are conspicuous, associated with increased modal contents of perovskite and apatite.

Representative trace-element patterns of B2 bebedourites are shown in Fig. 6b. While most diagrams are not too dissimilar to those of B1, other samples produce more “spiky” patterns. Many B2 samples show a negative Ti anomaly, consistent with the

extensive perovskite fractionation during earlier (B1) stages. High modal percentages of apatite are represented by phosphorus highs. The higher Zr and Hf contents of these rocks, when compared with B1, support the more evolved character of B2. However, one sample with extreme Zr and Hf enrichment also shows a negative Th anomaly, a positive P spike, and strong relative enrichment in heavy REE, forming a pattern remarkably similar to some of the bebedouritic dikes (Fig. 4b). Another prominent feature in Fig. 6b is the wide variation in the Nb/Ta ratios. This sudden change in the behaviour of Nb and Ta seems to be a conspicuous geochemical signature of relatively evolved ultramafic rocks from Tapira (i.e. some bebedouritic dikes, and some B2 bebedourites).

The rare-earth element patterns for bebedourites of B1 and B2 are shown in Figs. 7 and 8. B1 and most B2 bebedourites have chondrite-normalized La_(N)/Lu_(N) ratios similar to those of the phlogopite-picrites, but B2 span a much wider range of REE concentrations. The dashed line in Fig. 7 is the high-Zr, low-Th B2 sample discussed previously (see Fig. 6b). The REE crossover pattern resembles that of some of the bebedouritic dikes. Note that the crossover REE patterns observed in some bebedouritic dikes and B2 rocks are not present in B1 bebedourites.

5.5. Syenites

Tapira syenites vary from alkaline to peralkaline. The peralkalinity index (P.I.), calculated as the molecular ratio (K₂O + Na₂O)/Al₂O₃, ranges from 0.81 to 1.12, but most samples are concentrated between 0.85 and 0.95. These values are significantly lower than those observed in Tapira ultramafic dikes (mostly

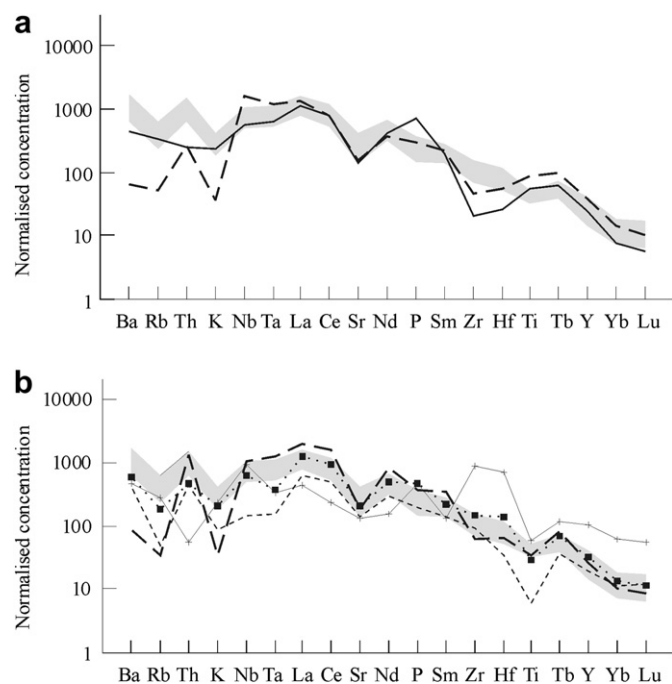


Fig. 6. (a) Trace-element variation of selected analyses of B1 bebedourites compared with the range of phlogopite-picrites (shaded field). (b) Normalized trace-element diagram of representative analyses of B2 bebedourites. Shaded field is the range of phlogopite-picrite compositions. Concentrations normalized to chondrite (except Rb, K and P) according to Thompson et al. (1984).

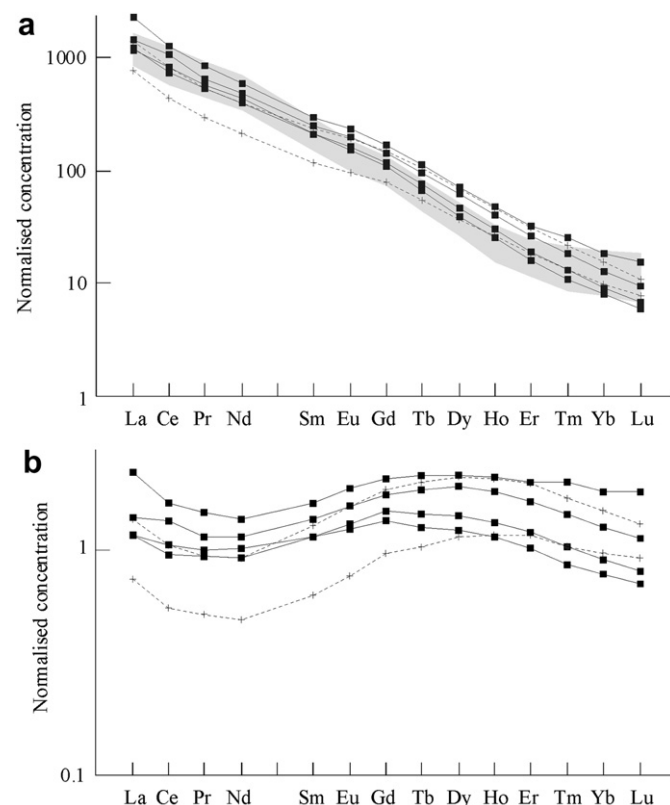


Fig. 7. REE composition of B1 bebedourites normalized to: (a) chondritic values of Boynton (1984) and (b) primitive phlogopite-picrite. Shaded field in diagram (a) is the range of phlogopite-picrites from Tapira.

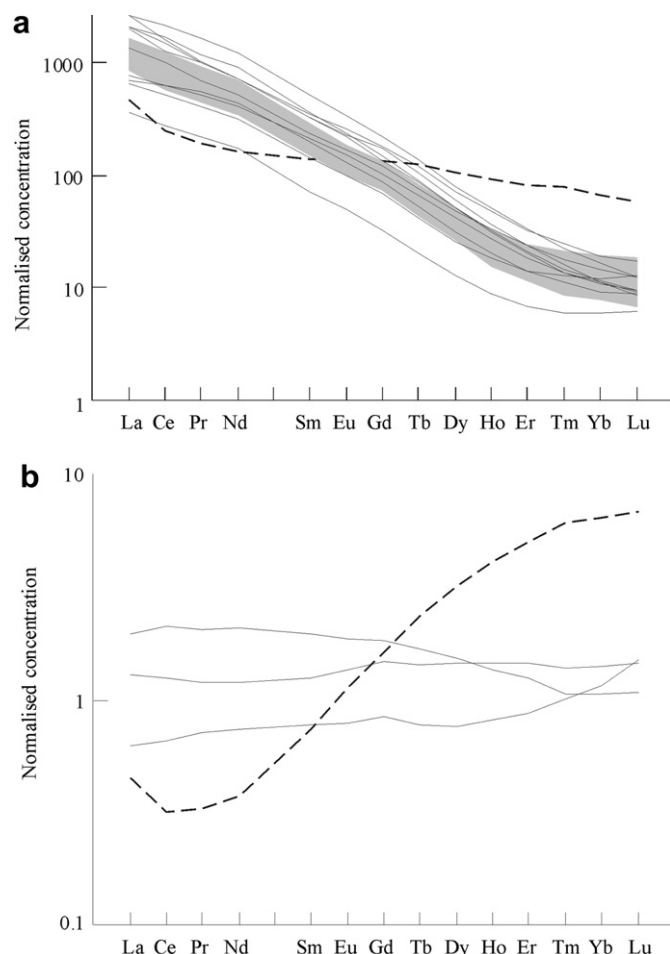


Fig. 8. REE patterns of B2 bebedourites, normalized to: (a) the chondritic values of Boynton (1984) and (b) primitive phlogopite-picrite. Dashed line is a high-Zr, low-Th bebedourite (see text).

between 1.0 and 3.0), underlining the fact that the syenites are not as Al-deficient as the more mafic rocks.

The potassic to ultrapotassic character of Tapira syenites is clearly indicated by their K_2O/Na_2O ratios (wt. % basis), which vary from 5.8 to 34.6, but are usually higher than 20.

With regard to major-element oxides, Tapira syenites are characterized by SiO_2 varying from 53 to 55 wt. %, Al_2O_3 from 15.8 to 18.9 wt. %, very high K_2O (12.9–14 wt. %) and low Na_2O (0.38–0.65 wt. %). CaO contents vary greatly (from 1.62 to 9.16 wt. %), but correlate positively with CO_2 , suggesting that a significant part of the calcium is hosted by interstitial and/or secondary carbonate, rather than by silicate minerals. P_2O_5 varies from 0.02 to 0.78 wt. %, $Fe_2O_3(T)$ from 2.71 to 5.66 wt. % and CO_2 from 1.55 to 4.67 wt. %.

As expected for evolved felsic rocks, all compatible elements are present in very low concentration. One remarkable exception is Sc, which may reach up to 30 ppm, but is only significant in the clinopyroxene-rich syenites, confirming the previous observations that Sc distribution is strongly controlled by the pyroxene.

The distribution of other trace elements is illustrated in Fig. 9a. The most prominent feature is the positive anomaly of Zr and Hf, flanked by troughs at P and Ti. Also noteworthy is the relatively low ΣREE and the variable Nb/Ta ratios when compared with those of the phlogopite-picrites. Chondrite-normalized REE diagrams for representative samples of Tapira syenites are shown in Fig. 9b. It can be seen from the diagram that the syenites have lower REE

contents than the phlogopite-picrites. The middle REE are particularly depleted, resulting in a concave-upward pattern.

5.6. Carbonatites

With the exception of some dikes and breccias associated with the C2 unit, all other carbonatites have less than 10 wt. % SiO_2 , and the majority of samples have less than 5 wt. % SiO_2 . The concentrations of TiO_2 and Al_2O_3 are usually below 1 wt. %. Alkalis are present in low concentrations, with Na_2O varying from 0 to 0.8 wt. % and K_2O reaching up to 2.6 wt. %, depending on the amount of phlogopite present in the sample. P_2O_5 may reach up to 7.7 wt. %. $Fe_2O_3(T)$ and MgO are usually below 10 wt. %, except for matrix of the breccias, where $Fe_2O_3(T)$ may reach up to 19 wt. %, and the dolomite-carbonatites, which have MgO varying from 17 to 20 wt. %.

Tapira carbonatites show extreme concentration and wide variation in the abundance of several trace elements. Compatible trace-element concentrations are usually very low and, on average, the lowest contents are found in rocks of C1 and C5. Most samples of Tapira carbonatites have Cr below 25 ppm, Ni below 15 ppm, and Sc below 20 ppm. Notable exceptions are carbonatite dikes from the C2 unit, where all compatible trace elements are present in higher amounts than in the coarser grained carbonatites. These rocks may have up to 65 ppm Cr, 22 ppm Ni, 380 ppm V and 40 ppm Sc.

The LREE/HREE fractionation in carbonatites is the largest among Tapira rocks. La/Yb ratios vary in the range 95–635 for the C1 unit, 95–321 (but most samples below 180) for C2, 125–144 for C3, 111–185 for C4 and 150–1130 for the late-stage dolomite carbonatites of C5. The La/Yb ratio of Tapira carbonatites is plotted

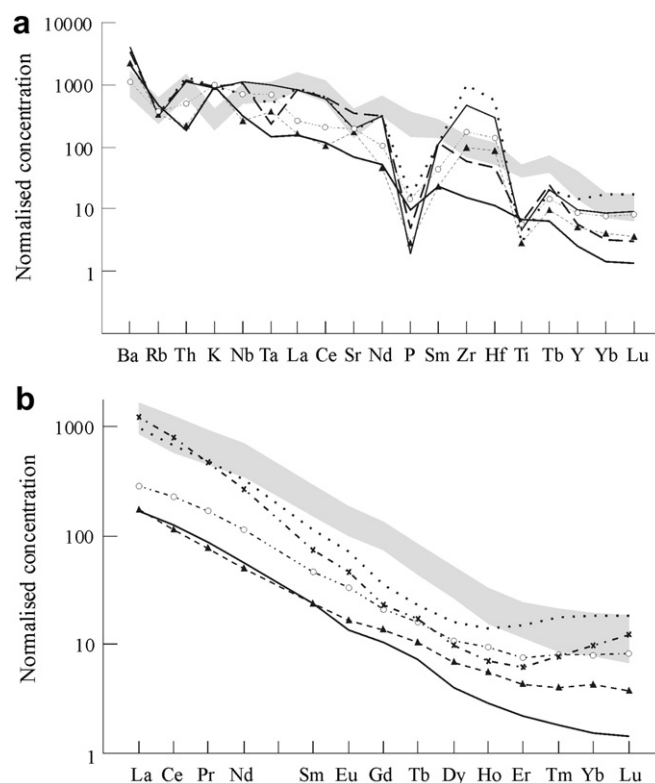


Fig. 9. (a) Chondrite-normalized trace-element diagram for Tapira syenites. Concentrations normalized to chondrite (except Rb, K and P) according to Thompson et al. (1984). Shaded field is the range of phlogopite-picrites. (b) REE patterns of Tapira Syenites, normalized to the chondritic values of Boynton (1984).

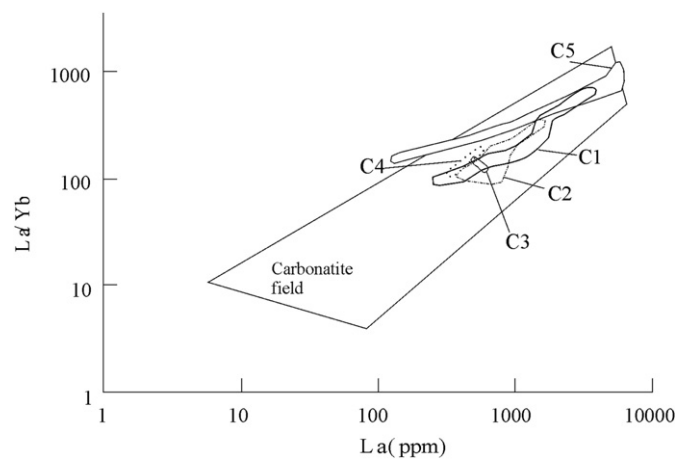


Fig. 10. La/Yb vs. La diagram, showing the composition of Tapira carbonatites, grouped into units C1 to C5. Carbonatite field is from Andersen (1987).

against La in Fig. 10. All the samples plot in the upper half of the carbonatites field, demonstrating their strong LREE/HREE fractionation. Spider diagrams for carbonatites from the various units are shown in Figs. 11 and 12. Tapira carbonatites are strongly enriched in Ba (up to 115000 ppm), Nb (up to 2450 ppm) and REE (Σ REE up to 19180 ppm), and depleted in Rb, K, Ta, Zr, Hf and Ti, with respect to the phlogopite-picrite field.

The most striking feature of C1, C2 and C5 carbonatites is the “spiky” nature of the trace-element patterns, with alternate enrichment and depletion of several elements, including decoupling of the geochemical pairs Nb–Ta and Zr–Hf. Niobium and tantalum are extremely fractionated from each other (compare

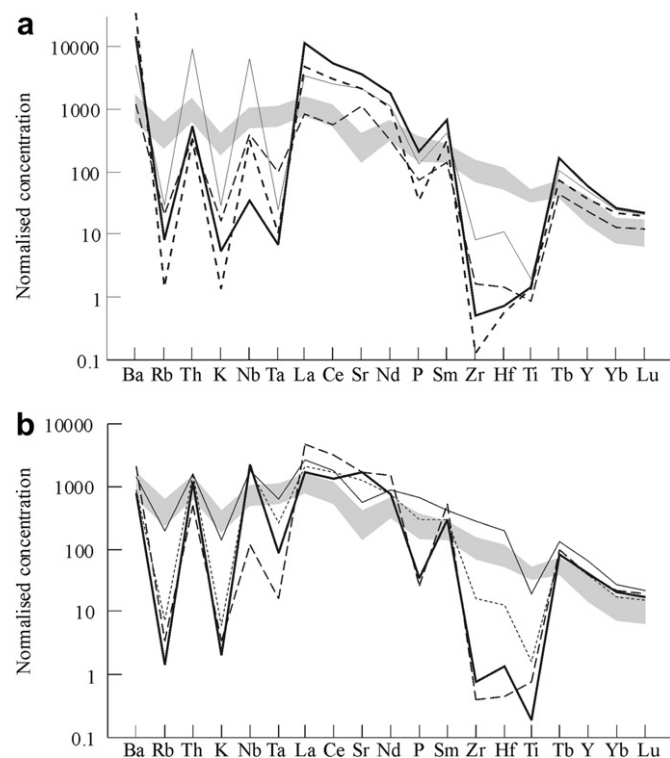


Fig. 11. Spider diagrams for selected samples of carbonatites from C1 (a) and C2 (b), compared with the range of phlogopite-picrites (shaded field). Concentrations normalized to chondrite (except Rb, K and P) according to Thompson et al. (1984).

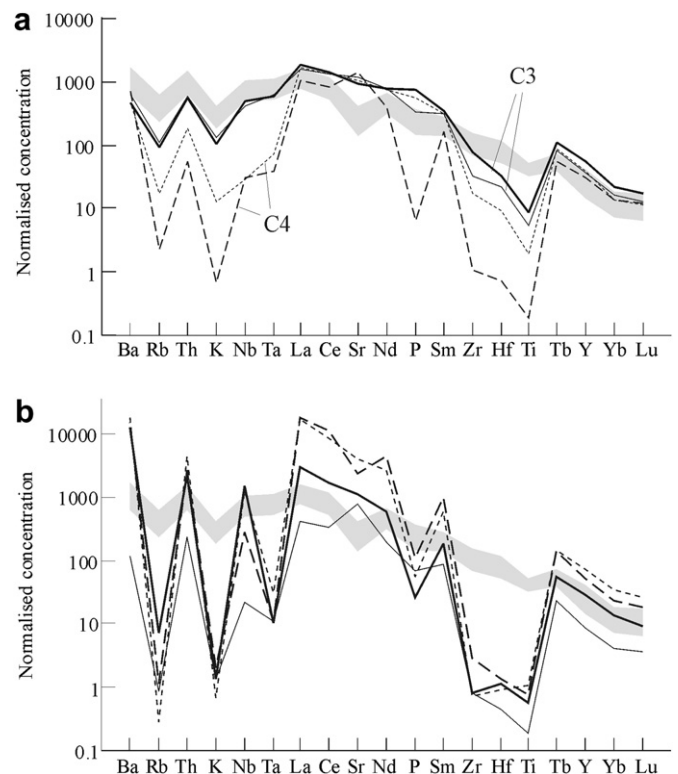


Fig. 12. Normalized trace-element diagrams for carbonatites from: (a) C3 and C4; (b) C5. Shaded field is the range of phlogopite-picrites. Concentrations normalized to chondrite (except Rb, K and P) according to Thompson et al. (1984).

with the Nb/Ta ratio of the phlogopite-picrites - shaded field), with Nb showing some enrichment and Ta showing an extreme depletion relative to their contents in primitive Tapira magmas. Both Zr and Hf are strongly depleted. The Zr/Hf ratio is variable, and apparently decreases with increasing degree of Zr + Hf depletion, changing from >1 in the least depleted rocks to <1 in the most depleted, which suggests that Hf is slightly less incompatible than Zr in the carbonatite system.

Rocks from the C3 and C4 units have some of the features observed in the spider diagrams for previously discussed carbonatite units, but the magnitude of the anomalies is smaller. C3 carbonatites, in particular, show the closest approximation to the phlogopite-picrite primitive pattern. A significant difference is observed in the behaviour of Nb and Ta between the carbonatites from C1 + C2 + C5 units and those from C3 + C4. Whilst carbonatites from the former group show a conspicuous negative Ta anomaly, the latter have Nb/Ta ratios that are similar to those of the phlogopite-picrites, although in C4 the absolute concentrations of both Nb and Ta are significantly lower. Furthermore, the Zr–Hf section of the C3 and C4 spider diagrams does not show the slope inversion observed in C1, C2, and C5. Finally, it should be noted that the likeness observed in key chemical features between C3 and C4 is consistent with the similarities noted in the petrography and mineral chemistry of these rocks (Brod, 1999).

6. Discussion

Taken together, fine-grained dike rocks such as phlogopite picrites, bebedouritic dikes and some carbonatites provide the best (yet incomplete) available approximation of the range of alkaline magmas involved in the generation and evolution of the Tapira complex.

The chemical (e.g. high MgO, Cr and Ni contents, undifferentiated REE patterns) and petrographic evidence of the least evolved Tapira rocks (phlogopite-picrites) indicate that they are primary, mantle-derived carbonated (up to 20 wt. % CO₂) silicate liquids. This is further supported by high Sr contents and mantle-like carbon and oxygen stable isotopes of the groundmass carbonate (our unpublished data). Tapira rocks are also compositionally similar to phlogopite-picrites associated with other APIP carbonatite complexes (e.g. Gibson et al., 1995b), and have strong geochemical affinities with the kamafugitic magmatism in the province (Brod et al., 2000). It has been argued (Bizzi et al. 1995) that APIP kamafugites do not represent primitive magmas but are relatively evolved. Although this is true of pyroxene-rich typical kamafugites and also of Tapira bebedouritic dikes, the evidence presented here indicates that the phlogopite-picrites are high-MgO rocks, clearly capable of fractionating olivine and chromite, and should therefore be considered primitive. The common presence of phenocrysts in the fine-grained dikes suggests that these magmas may have been affected by crystal fractionation processes, to an unknown extent. However, because the phenocryst assemblage consists largely of olivine, their influence on whole-rock chemistry should not affect extensively the trace-element contents (other than Ni), which is in good agreement with the very consistent REE- and trace-element patterns displayed by all analysed phlogopite-picrites.

Other varieties of fine-grained dikes (i.e. bebedouritic, carbonatitic) are likely to represent evolved liquids or near-liquid compositions. For instance, it is obvious from petrography and major-element chemistry that the bebedouritic dikes are incapable of producing olivine- and/or chromite-rich cumulates. In fact, the extremely low concentrations of Cr and Ni in these rocks suggest that they were derived from a more primitive liquid (e.g. a phlogopite-picrite) after extensive olivine + chromite fractionation. On the other hand, the composition of the bebedouritic dikes is appropriate for the fractionation of clinopyroxene, apatite, and perovskite, which makes them an attractive alternative of parental liquids to the coarse-grained bebedourite cumulates. Both the high Sc and CaO, and the phenocryst assemblage of the bebedouritic dikes are consistent with this interpretation.

However, some bebedouritic dikes described here, especially the more evolved ones, show anomalous geochemical behaviour (e.g. crossover REE patterns and dramatic changes in the relative abundances of Th, Nb, Ta, Zr and Hf), which are difficult to explain simply by fractionation of a particular phase or combination of phases. These variations may indicate the involvement of liquid immiscibility processes in the origin of these rocks, in addition to crystal fractionation. The presence of carbonate globules (ocelli) or carbonate patches in phlogopite picrites, bebedouritic dikes, and syenites, together with the occurrence of silicate globules within fine-grained carbonatite dikes further supports the involvement of liquid immiscibility as an important petrogenetic process at Tapira.

The occurrence of carbonate globules (ocelli) in silicate alkaline rocks is considered evidence of silicate–carbonate liquid immiscibility (e.g. Morbidelli et al., 1995; Ivanikov et al., 1998; Vichil et al., 2005). On the other hand, Chakhmouradian (2006) argues that vesiculation features may be mistaken by bona fide immiscible globular structures, particularly if the globules are composed of low-Sr calcite, together with other mineral atypical of carbonatites, such as zeolite. High Sr contents in carbonate have been widely accepted as a criterion for igneous origin (e.g. Wall et al., 1993; Rosatelli et al., 2010). At Tapira, the carbonate globules, as well as the groundmass carbonate in phlogopite picrites and bebedouritic dikes are dominantly of Sr-, Ba- and Mn-rich calcite (up to 2.8 wt. % SrO, 1.6 wt. % BaO and 0.5 wt. % MnO, Brod, 1999), with much rarer dolomite (up to 0.3 wt. % BaO and 0.5 wt. % SrO, Brod, 1999), may occasionally contain typical carbonatite phases, such as

tetra-ferriphlogopite, and have C–O isotopic compositions (our unpublished data) consistent with magmatic carbonate, which leads us to interpret these ocelli and the groundmass carbonate as a primary magmatic component. Although much rarer, the presence of silicate globules in the conjugate fine-grained carbonatites strengthens this interpretation. It is important to note that the presence of immiscible globules in phlogopite picrites, bebedouritic dikes and syenites suggest that liquid immiscibility was recurrent during the evolution of the complex.

6.1. Experimental constraints on liquid immiscibility

The relative preference of a particular element for the carbonate or silicate liquid can be quantified by the distribution coefficient ($k_D^{\text{sil/carb}}$) defined as the concentration of the element in the silicate liquid divided by the concentration of the element in the conjugate carbonatite liquid. Data on the partition of various elements between silicate and carbonatite immiscible liquids have been reported (e.g. Wendlandt and Harrison, 1979; Hamilton et al., 1989; Jones et al., 1995; Veksler et al., 1998b, 2012), but the number of studies is still small, and some variables are still poorly constrained. For instance, the results for a single element may vary significantly between different studies and the partition of some elements between silicate and carbonate liquid may be strongly dependent on temperature, pressure or composition (i.e. mafic or felsic) of the system. By using a centrifuge autoclave, Veksler et al. (1998b) achieved excellent separation of the immiscible silicate and carbonate liquids, and thus were able to overcome some of the technical problems for experimental determination of partition coefficients between immiscible liquids. Recent determination on a range of immiscible liquids (Veksler et al., 2012) confirmed these earlier studies.

The following general observations can be made from the studies mentioned above, and are of particular relevance for the investigation of the Tapira complex:

- Th partitions preferentially into the silicate liquid (Jones et al., 1995; Veksler et al., 2012).
- Sr and Ba partition preferentially into the carbonate liquid (Hamilton et al., 1989; Jones et al., 1995; Veksler et al., 1998b, 2012)
- Both Nb and Ta partition into the silicate liquid (Hamilton et al., 1989; Jones et al., 1995; Veksler et al., 1998b, 2012), but data for both elements under the same experimental conditions are scarce. Veksler et al. (1998b, 2012) pointed out that Ta partitions into the silicate liquid to a much larger degree than Nb (enrichment factor for Ta in the silicate liquid up to 5.6 times greater than that of Nb, in water-free systems and up to 2.5 times greater than Nb in water-bearing systems, Veksler et al., 2012). Consequently, some degree of Nb–Ta decoupling can be expected if liquid immiscibility occurs in the genesis of carbonatite complexes. Hamilton et al. (1989) detected a consistent dependence of Ta behaviour on pressure, temperature and composition. According to their results the partition of Ta into the silicate liquid is enhanced by decreasing temperature, decreasing pressure and increasing polymerisation of the silicate liquid. Unfortunately, the study by Hamilton et al. (1989) did not include Nb. However, based on the Ta variation, there is a (largely unconstrained) possibility that the magnitude of Nb–Ta decoupling during immiscibility may depend on the same variables.
- Zr and Hf partition very strongly into the silicate liquid. The study by Veksler et al. (1998b) has shown an average enrichment factor of 62 for Zr and 107 for Hf, in the silicate liquid, relative to the carbonatite. Veksler et al. (2012) found silicate/

carbonatite partition coefficients of up to 435 for Zr and 667 for Hf, in water-free systems, but up to 18 and 19, respectively, for water-bearing systems. These results are consistent with those of Hamilton et al. (1989) for Hf, but not for Zr, although it should be noted that Hamilton et al. (1989) detected a large scatter in their Zr and Hf data. Veksler et al. (1998b) also suggest that some decoupling of the geochemical pair Zr–Hf may be expected during immiscibility, although this should be of a lesser magnitude than that of the Nb–Ta pair.

e) The REE may show variable behaviour. Although the magnitude of REE partition coefficients between silicate and carbonatite immiscible liquids varies from one experimental work to the other, the results of Hamilton et al. (1989) and Veksler et al. (1998b, 2012) show that there is a consistent internal behaviour within the REE group. Thus, the $K_D^{\text{sil/carb}}$ increases progressively from La to Lu, for a range of experimental conditions, but whether (or which) REE will effectively partition into the silicate or carbonate liquid seems to depend strongly on pressure, temperature and composition of the starting materials. In any case, it is noteworthy that the progressive differences in the partition coefficients are likely to produce LREE/HREE fractionation in the immiscible pair, with La/Lu ratios increasing in the carbonatite liquid and decreasing in the corresponding silicate conjugate, regardless of the intensive variables of the system.

The low-pressure studies (up to 1 kbar) of Veksler et al. (1998b, 2012) suggest that all REE but La show preference for the silicate liquid. The results of Hamilton et al. (1989), for a range of pressures, temperatures and different starting compositions, suggest that the partition of the REE into the silicate liquid is favoured by increasing temperature (at constant $P = 3$ kb) and decreasing pressure (at constant $T = 1150$ °C). The effect of pressure is particularly interesting, since it suggests that all REE partition into the silicate liquid at <2 kb, and all REE partition into the carbonate liquid at 6 kb. At 3 kb Hamilton et al. (1989) obtained $K_D^{\text{sil/carb}} < 1$ for the LREE and $K_D^{\text{sil/carb}} > 1$ for the HREE, with Gd closest to the unity (0.93), which should result in extreme LREE/HREE fractionation between the immiscible liquids in such conditions. These results suggest, as stated by Hamilton et al. (1989), that only carbonatites generated by liquid immiscibility at relatively high pressures will become strongly enriched in REE, relative to the silicate counterpart. The $K_D^{\text{sil/carb}}$ for the LREE seems to be higher in more evolved (phonolitic) than in less evolved (nephelinitic) liquids, but the $K_D^{\text{sil/carb}}$ for the HREE does not vary a great deal with composition. This suggests that the LREE/HREE fractionation between the conjugate liquids (see above) would be enhanced in felsic systems.

6.2. Chemical fingerprints of liquid immiscibility

According to the considerations above, a number of geochemical signatures may be expected to be generated during silicate–carbonate liquid immiscibility, several of which can be detected in chondrite-normalized spider and REE diagrams. These include:

a) Anomalously high Nb/Ta and moderately high-Zr/Hf ratios in the carbonatite immiscible liquid. It is important to note that both Nb and Ta show preference for the silicate liquid, although at different partition coefficients. Therefore, the Nb–Ta decoupling signature will be far more pronounced in the carbonate-rich liquid than in the silicate-rich counterpart. The same reasoning can be applied to Zr–Hf decoupling, since both Zr and Hf also partition strongly to the silicate melt.

b) Anomalously high chondrite-normalized La/Lu in the carbonatite liquid and correspondingly low La/Lu in the silicate conjugate, generating crossover REE patterns. Additionally, if immiscibility occurs at relatively high pressures, the carbonatite should become enriched in the bulk of the REE, with corresponding depletion in the silicate conjugate but the opposite would be expected for a low-pressure immiscibility event.

c) Generally low Th, Ta, Zr, and Hf abundances in the carbonatite liquid. The silicate conjugate should have corresponding, and opposite, anomalies, making this a powerful method to test both immiscibility and consanguinity between carbonatites and associated silicate rocks. This should produce mirrored anomalies in spider diagrams, which may include the REE, depending on pressure, as discussed above. It is important to note that bulk Zr + Hf depletion in the carbonatite is expected to be of greater magnitude than that of Nb + Ta, because of the very large partition coefficients of Zr and Hf into the silicate liquid (e.g. Veksler et al., 1998b).

All such immiscibility-related anomalies are present in Tapira rocks, in some form or another. They occur in bebedouritic dikes (Fig. 4b and Fig. 5), B2 bebedourites (Fig. 6b and Fig. 8), syenites and carbonatites (compare Fig. 9 with Fig. 11 and Fig. 12b), but are absent in the most primitive phlogopite-picrites (Fig. 3). Our ongoing research on other APIP complexes suggests that these features are more common than previously recognized in the Province. Furthermore, the Tapira complex contains both carbonatites generated by liquid immiscibility and carbonatites generated by fractional crystallisation (Brod, 1999), as discussed below.

Fig. 13a shows the composition of Tapira phlogopite-picrites in the Hamilton projection, together with the silicate–carbonate miscibility gap, the silicate–carbonate liquidus boundary (after Lee and Wyllie, 1997b), and a number of possible fractionating mineral phases. Where data is available for Tapira minerals (Brod, 1999), the average composition is plotted. Additional mineral phases are ideal compositions. The shape and size of the miscibility gap and of the silicate–carbonate liquidus boundary can vary significantly, depending on pressure, temperature, composition and CO₂ saturation (e.g. Lee and Wyllie, 1998b; Brooker, 1998; Kjarsgaard, 1998), but their precise location in this diagram is not critical for the purpose of illustrating the behaviour of Tapira rocks.

The predominance of olivine phenocrysts, and progressive variations in MgO and Cr (our unpublished data) of the phlogopite-picrites suggest that olivine and chromite are the main mineral phases fractionating from these rocks. The diagram illustrates that the removal of a mixture of olivine and chromite at first, possibly with some perovskite and pyroxene at a later stage, will drive the residual liquid towards the two-liquid miscibility gap and, consequently, towards the production of conjugate silicate and carbonate liquids. This is significant in the Tapira complex because it indicates that liquid immiscibility may have occurred at a relatively early stage in the magmatic evolution, in good agreement with the presence of carbonate ocelli in some of the phlogopite-picrite dikes.

If, in a slightly more fractionated liquid, the precipitation of olivine is accompanied by clinopyroxene and phlogopite, the composition of the residual liquids will still move away from the SiO₂ + TiO₂ + Al₂O₃ apex and a progressive increase in residual carbonate will occur, since only silicate phases are precipitating. The evolving liquid in this case may or may not hit the miscibility gap, depending on the type and relative proportion of the crystallizing phases.

The composition of Tapira bebedouritic dikes is illustrated separately, in the diagram of Fig. 13b. Note that these rocks do not contain olivine phenocrysts and are depleted in chromium. Instead,

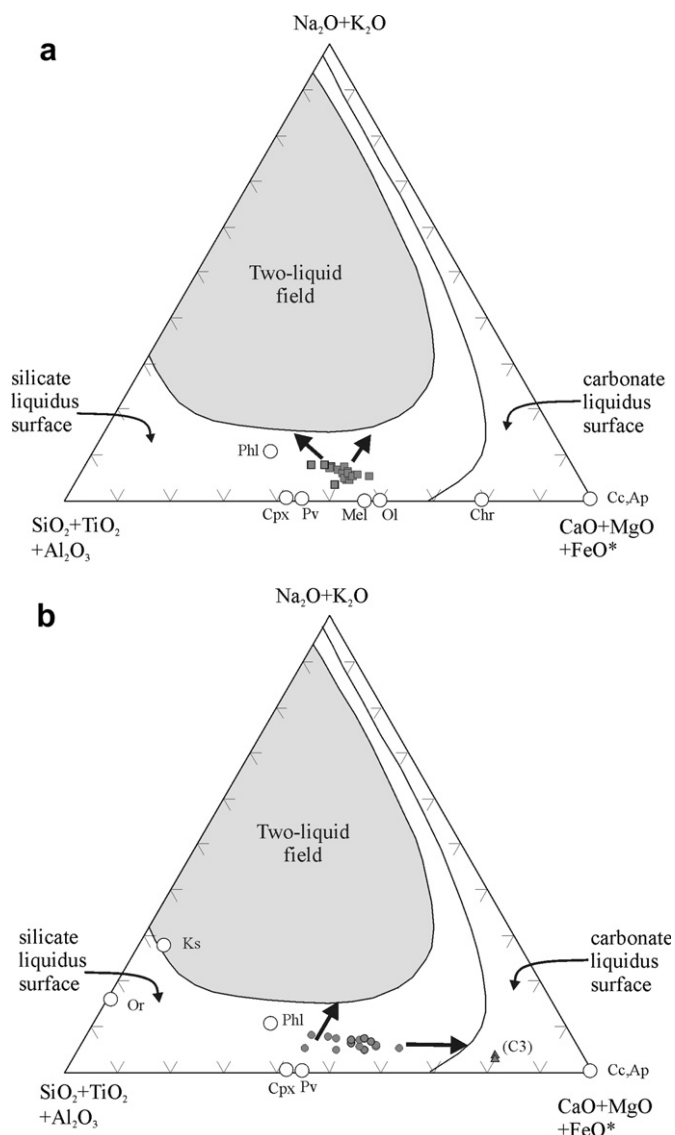


Fig. 13. Representation of the Tapira rocks in the Hamilton Projection (after Lee and Wyllie, 1997b). (a) Phlogopite picrites. (b) bebedouritic dikes and C3 carbonatites (see text). The composition of relevant mineral phases is also plotted: Ol = Olivine; Mel = melilitite, Pv = perovskite, Cpx = clinopyroxene, Chr = chromite, Cc = calcite, Ap = apatite, Phl = phlogopite, Ks = kalsilite, Or = orthoclase.

the petrographic and geochemical evidence indicate that they will fractionate clinopyroxene, phlogopite and perovskite, with variable amounts of apatite. Again, if clinopyroxene and perovskite are the main fractionation phases, it is possible that the evolving magma would intercept the miscibility gap, thus generating immiscible silicate and carbonate liquids.

However, extensive crystallisation of potassic phases such as phlogopite, K-feldspar or kalsilite will substantially change the evolution path of the magma. Phlogopite is a common phenocryst phase in many bebedouritic dikes. K-feldspar is present in small amounts in the groundmass, and as rare inclusions in apatite microphenocrysts from some bebedouritic dikes. Some of the most evolved B2 bebedourites also contain interstitial K-feldspar. This suggests that felsic potassic phases will crystallize from these rocks, in addition to clinopyroxene and phlogopite, during the latest differentiation stages. In Tapira the felsic silicate minerals seem to

be mainly feldspar, but kalsilite has been reported by Sgarbi et al. (1998) in bebedourite-like xenoliths from the Mata da Corda kamafugites. As a consequence of the removal of a potassic mineral assemblage, the composition of the residual liquids will progress away from the $\text{SiO}_2 + \text{TiO}_2 + \text{Al}_2\text{O}_3$ apex, towards the $\text{CaO} + \text{MgO} + \text{FeO}$, and not towards alkali enrichment. This trend is apparently inconsistent with the expected major-element variation in the vast majority of igneous systems (i.e. decrease in MgO , coupled with increase in SiO_2 and alkalis), but considered a plausible alternative in studies of carbonatites and associated rocks (Veksler et al., 1998a; Kjarsgaard, 1998). In the bebedouritic dikes this trend is accompanied by relative enrichment in groundmass carbonate.

As discussed previously, carbonatites formed by liquid immiscibility would show geochemical fingerprints of the immiscibility process, such as Nb–Ta decoupling, high LREE/HREE fractionation and Zr + Hf depletion. These features are present in several samples of Tapira carbonatites, particularly those of the C1 and C2 units. Also, because the evolving liquid intercepts the miscibility gap at a relatively early stage, the carbonatites generated by this process would have relatively high MgO contents. Although some of the C1 and C2 carbonatites probably represent accumulations of calcite crystals their MgO content is generally higher than those from C3 and C4. This is consistent with the crystallisation of primary tetraferriphlogopite (Brod et al., 2001) in C1 carbonatites and with the presence of interstitial or groundmass dolomite in both C1 and C2 carbonatites.

If the magma evolution trend does not intercept the immiscibility gap, carbonatites may still form when the evolving liquid reaches the carbonate–silicate liquidus boundary. It is important to note that carbonatites formed in this way would lack the geochemical signatures of immiscible liquids, discussed above. This seems to be the case of C3 and, maybe, C4.

Among Tapira carbonatites, only the rocks from the C3 and C4 units do not show evidence of strong decoupling between Nb and Ta. In fact, these carbonatites have a chondrite-normalized Nb/Ta ratio similar to the Tapira parental magmas (see Fig. 12), suggesting that they were not formed by an immiscibility process. Furthermore, the composition and textural properties of phlogopite and clinopyroxene from the C3 carbonatite suggest that they are entrained xenocrysts from the SPS (Brod, 1999; Brod et al., 2001). These characteristics, and the spatial association with the B2 bebedourites, suggest that C3 are the final residue of the fractionating magma from which B2 crystallized. The abundance of entrained xenocrysts from B2 suggests that the carbonatites may have separated from the forming pile of B2 cumulates by some physical process such as filter pressing.

The interpretation of the C4 carbonatites is less straightforward, since these rocks have relatively low Nb/Ta ratio, but still show some degree of relative Zr + Hf depletion. If they were originated by a fractionation process similar to the one described above for C3, the studied samples must represent calcite flotation cumulates, in order to explain the stronger Rb, K, P, Zr, Hf, and Ti depletions.

We pointed out earlier that some of the more evolved bebedouritic dikes, as well as some B2 evolved bebedourites share a number of “anomalous” geochemical properties, when compared with the remainder of Tapira silicate rocks. These remarkable differences include: a) anticlockwise rotation of REE patterns, which cross over those of the primitive liquids; b) strong depletion in Th; c) strong enrichment in Zr + Hf and d) Nb–Ta decoupling. At first sight, the crossover REE patterns and the positive anomalies of Zr + Hf suggest that the anomalous B2 bebedourites and the anomalous bebedouritic dikes represent the silicate side of an immiscible silicate–carbonatite pair. On the other hand, Th would be expected to increase, and the Nb/Ta ratio

would be expected to decrease in the silicate-rich immiscible liquid but, surprisingly, the observed Nb/Ta and Th variations in these rocks are exactly the opposite, apparently contradicting the immiscibility hypothesis.

Brod (1999) demonstrated that such contrasting signatures within a single rock are the result of multiple immiscibility events occurring at various depths during the evolution of the complex, combined with degassing-related alkali loss. A full account of the evolution model for Tapira, including mineral chemistry, as well as stable and radiogenic isotope evidence, is beyond the scope of this paper and will be discussed elsewhere. Such intricate evolution is not unique of the Tapira Complex. For instance, Dawson (1998) demonstrated that the apparently unexpected variations in mineral and rock chemistry, and the relationships between the different rock-types from the Oldoinyo Lengai volcano (Tanzania), cannot be explained by a single mechanism, but are the result of a complex interplay of processes such as fractionation, unmixing of silicate and carbonatite liquids and CO₂ degassing.

The geochemical signatures of silicate–carbonate liquid immiscibility described for the Tapira complex may be more common than previously thought, but have been recognized elsewhere.

Nb–Ta and Zr–Hf decoupling by liquid immiscibility were probably overlooked in early carbonatite studies, perhaps due to insufficient analytical accuracy in Ta and Hf determination. Thompson et al. (2002) recognized Nb–Ta decoupling features similar to the ones described above in the Swartbooisdrif carbonatites (Namibia). The same Nb–Ta behaviour can be observed in other published data sets, such as a suite of melilitite–carbonatite–nephelinite dikes from the Turii Peninsula, Russia (Ivanikov et al., 1998). Whilst experimental studies indicate that the Zr/Hf ratio should slightly increase in the carbonatite conjugate, some published whole-rock analyses of immiscible silicates and carbonatites show an opposite effect (e.g. Bühn and Trumbull, 2003; Thompson et al., 2002), similar to the one observed in Tapira, but the reason for this is not yet clear.

Stoppa et al. (2005) identified crossover rare-earth patterns between kamafugite–carbonatite pairs in Italy, interpreting them as a result of liquid immiscibility occurred at high pressures, which is in good agreement with the experimental results of Hamilton et al. (1989), and with the results presented here. It should be stressed that the formation of crossover REE patterns will be maximized for a pressure condition where the silicate–carbonate partition coefficient is higher than 1 for the HREE and lower than 1 for the LREE (e.g. 3 kb, for the system investigated by Hamilton et al. 1989).

Bühn and Trumbull (2003) described mirrored spider diagram anomalies between silicate rocks (nepheline–foitite and nepheline–sienite) and carbonatites from the Kalkfeld complex, Namibia, interpreting them as the result of silicate–carbonate liquid immiscibility. In their case, virtually all elements in the spider diagram show complementary enrichment–depletion relationships relatively to the assumed parental composition, which suggests that the efficiency of immiscibility increases in compositionally evolved (syenitic) systems.

7. Conclusions

Carbonatite–silicate liquid immiscibility processes are likely to produce several types of easily recognizable geochemical fingerprints, such as:

a) decoupling of geochemical pairs like Nb–Ta and Zr–Hf, whereby the Nb/Ta chondrite-normalized ratio will increase, and Zr/Hf will vary in the carbonatite branch, with little or no visible effect on the silicate conjugate.

- b) Anticlockwise rotation of REE patterns in the silicate branch, and clockwise rotation of REE patterns in the carbonatite branch, with La/Lu ratios decreasing in the former and increasing in the latter, comparatively to the primitive liquids. This will typically generate crossover REE patterns.
- c) Bulk enrichment of Zr and Hf in the silicate branch, and a corresponding bulk decrease in these elements in the carbonatite branch, generating mirrored anomalies in spider diagrams. These features may also be present for other elements, such as Th, Rb, K, P, and the REE.
- d) Strong Ta depletion in the carbonatite branch.

It should be noted that the appearance of these geochemical signatures depends on composition, temperature and pressure of the system, as well as they may superimpose one another when liquid immiscibility is recurrent during magma evolution.

The available field, petrographic, chemical, mineralogical, and isotopic evidence indicate that the Tapira complex, similarly to many other alkaline–carbonatite complexes worldwide, resulted of a complex interplay of several different petrogenetic processes, such as liquid immiscibility, crystal fractionation, and degassing/metamorphism. Interestingly, once established, the geochemical signatures of liquid immiscibility are not easily erased by subsequent processes.

Acknowledgements

The Universities of Brasília and Durham are thanked for the access to their analytical facilities. This research was financially supported by Brazilian funding agencies CNPq and CAPES. The first author thanks R. N. Thompson and S. A. Gibson for comments and discussions during the early stages of this work. Suggestions by L. N. Kogarko and an anonymous referee helped improve an earlier version of this manuscript.

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