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ARTICLE

Geochemistry and petrology of the Búzios Island alkaline massif, SE, Brazil

Geoquímica e petrologia do maciço alcalino da Ilha dos Búzios, SE, Brasil

Celso de Barros Gomes[1]*, Francisco Rubens Alves[1], Rogério Guitarrari Azzone[1], Gaston Eduardo Enrich Rojas[1], Excelso Ruberti[1]

ABSTRACT: The Late Cretaceous Búzios Island alkaline massif intrudes Precambrian charnockites and consists dominantly of syenitic rocks that are cut by a large number of dikes, mostly NE-trending, and representing two distinct suites, a felsic one and a mafic-ultramafic one. Alkali feldspar is the most abundant mineral; other constituents are clinopyroxene, commonly replaced by amphibole/biotite, and opaques. Accessory minerals include occasionally rare phases bearing Zr, Ti, Nb and Rare Earth Elements (REE). The felsic dikes may also have nepheline (sodalite). The mafic-ultramafic suite, in particular the lamprophyres, shows a primary mineral assemblage with olivine, clinopyroxene and amphibole in addition to a groundmass having glassy material and carbonates (*ocelli*). The Búzios rocks are chemically evolved, mostly of potassic affinity and mainly belong to the miaskitic series. Variation diagrams for major and trace elements show a bimodal distribution, suggesting an origin from different magmatic pulses. The rocks are interpreted as having been derived by fractional crystallization processes from a basanitic parental magma. The SiO_2-undersaturated and SiO_2-oversaturated associations present in the massif are apparently not linked to a single magmatic source, and in the petrogeny residual system two trends are evident: the first one towards the phonolitic minimum and the second one towards the rhyolitic minimum, possibly pointing to amphibole fractionation.

KEYWORDS: Igneous petrology; Alkaline rocks; Geochemistry.

RESUMO: *O maciço alcalino da Ilha dos Búzios, do Cretáceo Superior, é intrusivo em charnockitos precambrianos e consiste predominantemente de rochas sieníticas cortadas por grande número de diques, orientados preferencialmente para NE, representando duas suítes distintas: félsica e máfica-ultramáfica. Feldspato alcalino é o mineral mais abundante; outros constituintes são clinopiroxênio, comumente substituído por anfibólio/biotita, e opacos. Minerais acessórios incluem ocasionalmente fases raras contendo Zr, Ti, Nb e elementos terras raras (ETR). Os diques félsicos podem possuir também nefelina (sodalita). A suíte máfica-ultramáfica, particularmente os lamprófiros, apresenta uma assembleia mineralógica primária com olivina, clinopiroxênio e anfibólio, além de massa fundamental com material vítreo e carbonatos (ocelli). As rochas de Búzios são quimicamente evoluídas, de filiação claramente potássica e pertencem sobretudo à série miaskítica. Diagramas de variação para elementos maiores e traços mostram distribuição bimodal, sugerindo a origem a partir de diferentes pulsos magmáticos. As rochas são interpretadas como derivadas por cristalização fracionada a partir de magma parental de composição basanítica. As associações insaturadas e supersaturadas em* SiO_2 *presentes no maciço não estão aparentemente ligadas a uma fonte magmática única, sendo evidentes duas tendências distintas no sistema petrogenético residual: a primeira no sentido do mínimo fonolítico, e a segunda no do mínimo riolítico, possivelmente indicando fracionamento de anfibólio.*

PALAVRAS-CHAVE: *Petrologia ígnea; Rochas alcalinas; Geoquímica.*

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INTRODUCTION

Coastal islands composed mainly of alkaline rocks are found along the shoreline of the state of São Paulo, in Southeastern Brazil, forming stocks and a great number of dikes of variable compositions and dimensions. The well-known occurrences are São Sebastião (the largest island encompassing three syenitic bodies: São Sebastião, Serraria, and Mirante), Búzios, Vitória, and Monte de Trigo (Fig. 1), all aligned along a NE trend parallel to the regional structure represented by the Santos fault and related tectonically to the Southeastern Brazilian Continental Rifting (Riccomini *et al.* 2005). These alkaline centers are included in the Serra do Mar Province (cf. Almeida 1983) or, specifically, in the northern sector of the Serra do Mar Province (cf. Riccomini *et al.* 2005), and were emplaced into the Precambrian crystalline basement (Ribeira belt, 790-510 Ma, cf. Heilbron *et al.* 2008).

Geological information on such alkaline occurrences dates back to the last century — as *São Sebastião* (Freitas 1947; Hennies & Hasui 1968, 1977; Bellieni *et al.* 1990; Garda 1995; Lima & Schorscher 1999), *Búzios* (Björnberg & Ellert 1955; Alves 1997), *Vitória* (Motoki & Gomes 1984; Motoki 1986; Motoki *et al.* 1987), and Monte de Trigo (Coutinho & Melcher 1973) —, but more recently these islands, especiallly Monte de Trigo, have become the subject of systematic works dealing mainly with their mineralogy, geochemistry and petrology, like São Sebastião (Augusto & Vlach 2004; Enrich *et al.* 2005), Búzios (Alves & Gomes 2001), Vitória (Motoki *et al.* 2015), and Monte de Trigo (Enrich 2005; Enrich *et al.* 2009, 2016).

K/Ar determinations on mineral concentrates (biotite and amphibole) and whole rocks allowed Alves (1997) to suggest for the Búzios syenitic rocks an average age of 81.4±2.6 Ma (Late Cretaceous) and a younger value of 79.0±2.4 Ma for the associated dikes. The author also reported a Rb/Sr isochron (errochron) including various petrographic types of the massif that indicated an age of 78.0±2.2 Ma, with R_o=0.70500. Several available ages given by different analytical methods for the neighbouring alkaline intrusions range from 90 to 80 Ma, lying mostly in the 86-81 Ma interval (Amaral *et al.* 1967; Sonoki & Garda 1988; Bellieni *et al.* 1990; Montes-Lauar *et al.* 1995; Alves & Gomes 2002; Enrich *et al.* 2005, 2009; Sato *et al.* 2008). Age values in this range also characterize other alkaline occurrences present in the southern part of the São Paulo state, such as Cananeia (83.6 Ma, Spinelli & Gomes 2008), Ponte Nova (87.6 Ma, Azzone *et al.* 2009) and Tunas (84.7±1.2 Ma, Siga Jr. *et al.* 2007).

This paper provides a general picture of the alkaline magmatism of Búzios Island, emphasizing the geochemistry and mineral chemistry of the rocks and contributing to a better understanding of the formation and evolution of the alkaline massif.

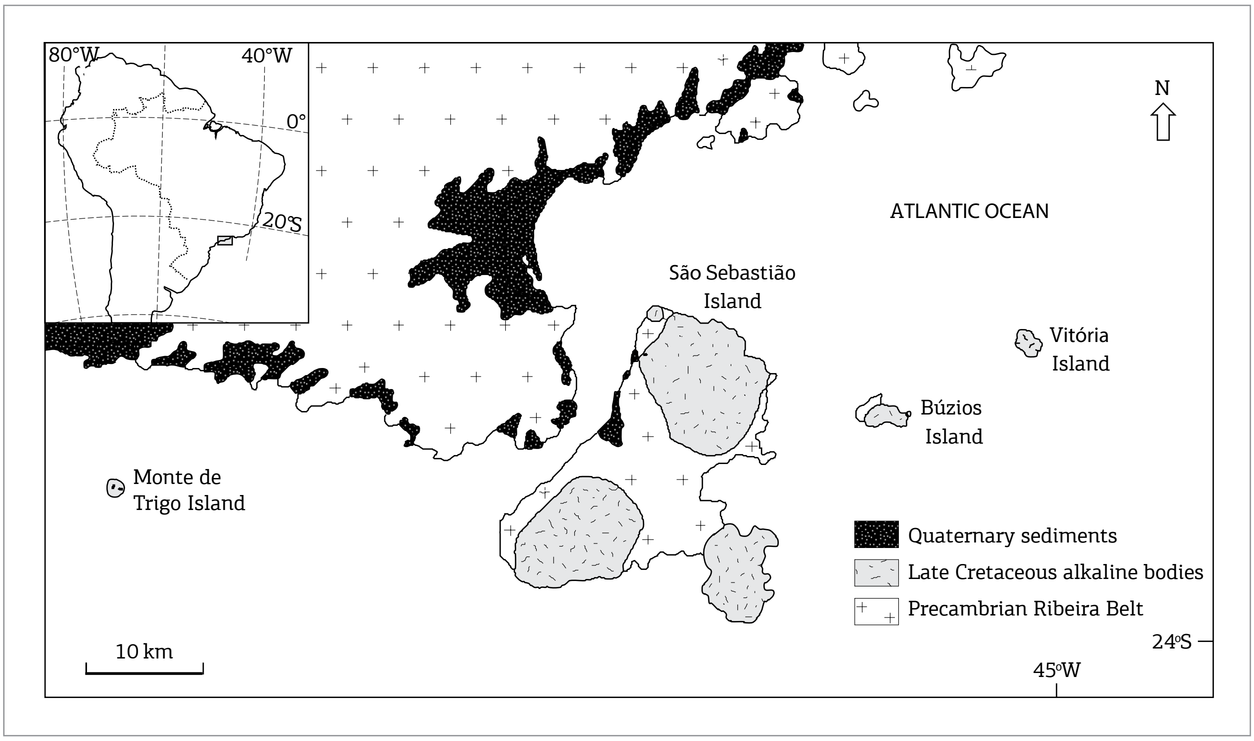

Figure 1. Geological map of the northern sector of the Serra do Mar Province (after Alves and Gomes 2001, simplified).

GEOLOGICAL ASPECTS

The Búzios alkaline massif, which includes Búzios Island and a very small nearby island named Somítica, is irregular and extends more than 3 km N-S and 5 km E-W (Fig. 2). The main island covers an area of approximately 7.5 km^2 and lies approximately 30 km from the continent. It is composed mostly of syenites totalling more than 90% of the entire area, with coarse-grained Precambrian charnockites with dark green colour and oriented feldspars occurring as country rocks in its NW and SW sections. Other basement rocks (gneisses and amphibolites) crop out locally as small intercalations and xenoliths or form banded structures.

Dikes are widespread, intruding either country rocks or syenites, and can be assembled into two distinct suites, felsic one and mafic-ultramafic one. They are predominantly NE-trending, subvertical, around 10 centimeters to a few meters wide, and sometimes extend more than 100 meters in length. Cross-cutting bodies with different compositions that form multiple intrusions are also noted. The many dikes seem to indicate the presence of various magmatic stages, although the field relationships involving the different types and the syenitic rocks are not clear.

Xenoliths are usually found in the contact zone between the syenites and country rocks, with the most common type represented by charnockites and mafic lithologies. In addition, quartz-filled, irregular, miarolitic cavities with dimensions of centimeters are present in many places, frequently in association with syenitic rocks.

The syenites and associated microsyenitic rocks can be grouped into the following suites: the first one bears only trace amounts of quartz, and the second one is more enriched in the mineral (up to 5%). These latter petrographic types occur commonly in the NW and SW parts of the island associated with charnockites. Scarce lithologies having higher quartz content (granophyric varieties) are also recognized. In Le Maitre's (1989) quartz, alkali feldspar, plagioclase, feldspathoid (QAPF) classification diagram, the syenites

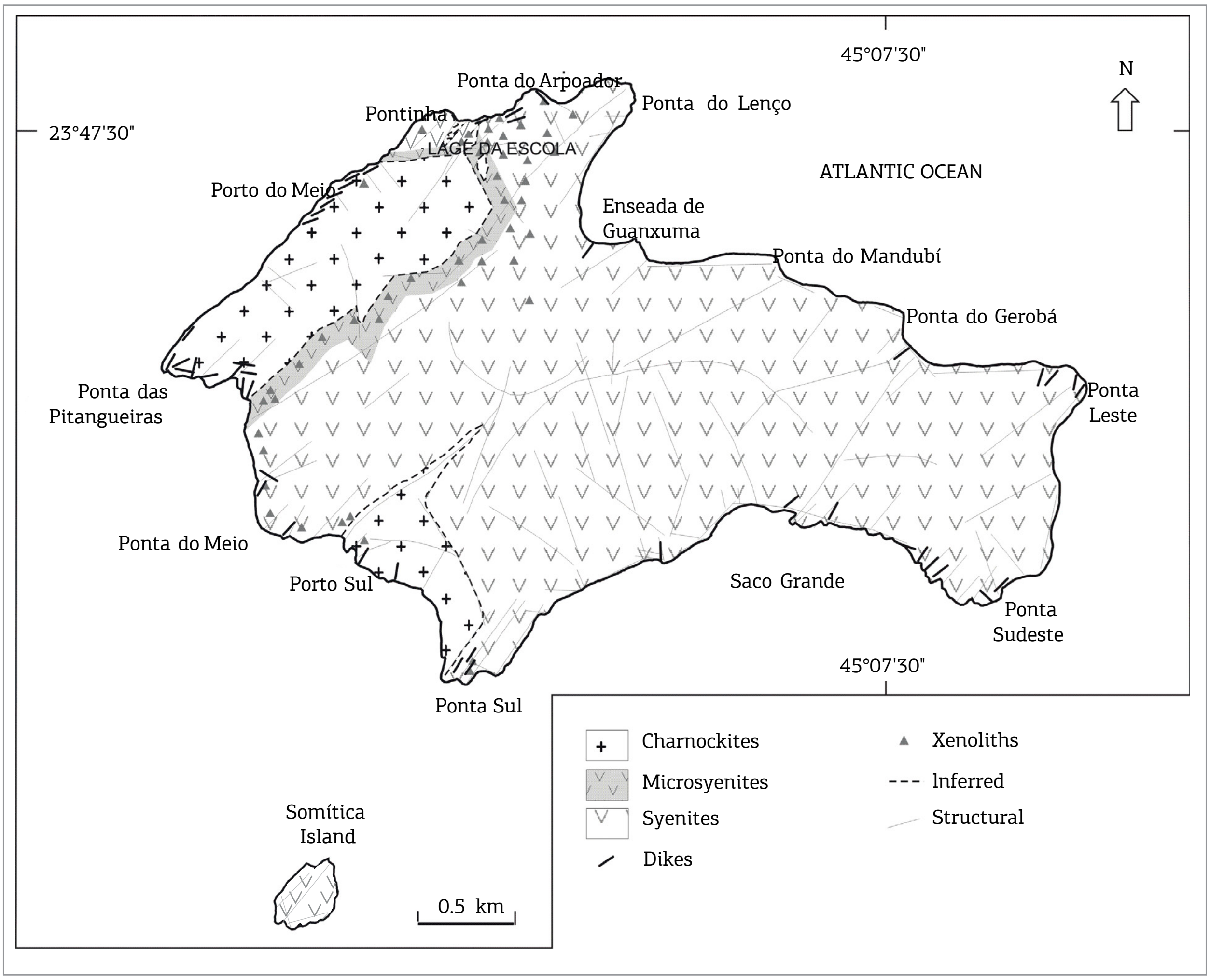

Figure 2. Geological map of the Búzios Island (after Alves 1997, simplified).

generally plot in the alkali feldspar syenite and quartz-alkali feldspar syenite fields, with a clear prevalence of the former rocks. The syenites are dominantly coarse-grained, with a massive aspect, light to dark gray in color, and equigranular to inequigranular in texture. Fine-grained varieties are also classified as alkali feldspar microsyenites or quartz-alkali feldspar microsyenites. More rarely, they lie in the alkali feldspar (micro) granite field. These rocks show light color and equigranular to seriate texture, are occasionally porphyritic and are of light color; in a few cases, they can be typically aplitic in texture.

Felsic dikes are variable in composition and consist of rocks SiO_2-undersaturated (nepheline/sodalite mycrosyenites and sodalite phonolites) to SiO_2-saturated (microsyenites and trachytes) and SiO_2-oversaturated (rhyolites). The saturated types are especially widespread over the whole island. The SiO_2-rich varieties mostly occur intruding the charnockites, whereas the SiO_2-poor types commonly have syenites as country rocks. On the other hand, the mafic-ultramafic dikes are represented by alkaline rock types such as alkali basalts, basanites, tephrites, trachybasalts, and lamprophyres (dominantly camptonites following Le Maitre 1989). In rocks of this assemblage, the texture is usually holocrystalline, fine-grained to aphanitic, and microporphyritic to porphyritic; and the color varies from light gray to black. Diabase dikes with tholeiitic affinity predate the alkaline activities and were also found in the island cutting the charnockites and presenting textural re-equilibration probably due to the intrusion of the alkaline magmas.

A detailed and complete mineralogical and petrographic description of the Búzios alkaline rocks is given in Alves (1997), with a more concise version published by Alves and Gomes (2001).

MINERALOGY

Chemical analyses of feldspars, clinopyroxenes, amphiboles, micas, and opaques and diagrams relating cationic concentrations and ratios of distinct elements in some minerals are listed in Alves (1997) (for the data source and analytical conditions, access the site: http://www.teses.usp.br/teses/disponiveis/44/44135/tde-18092015-174733/pt-br.php). Analyses of rare minerals (see Table 1) were

Table 1. Representative WDS analyses of Zr-, Ti-, Nb-, and REE-rich silicate minerals of agpaitic dikes from Búzios Island.

Mineral	**Wöhlerite**	**Låvenite**	**Mosandrite**	**Rosenbuschite**	**Eudialyte**	**Astrophyllite**
Rock-type	**Nepheline microsyenite**	**Phonolite**	**Phonolite**	**Nepheline microsyenite**	**Phonolite**	**Phonolite**
wt%						
SiO_2	29.19	28.36	29.57	31.08	47.60	33.65
TiO_2	1.25	2.94	6.10	6.79	0.09	9.68
ZrO_2	14.56	27.23	2.44	13.27	12.21	0.90
HfO_2	0.21	0.29	n.a.	<0.11	0.28	<0.11
Nb_2O_5	13.43	5.22	3.41	2.84	2.38	1.62
Al_2O_3	<0.02	<0.02	0.07	<0.02	0.30	1.36
Y_2O_3	0.42	0.33	1.25	0.67	0.51	<0.04
La_2O_3	<0.05	<0.05	4.86	0.10	1.20	n.a.
Ce_2O_3	0.25	<0.09	10.44	0.38	1.71	<0.08
Nd_2O_3	n.a.	n.a.	2.55	0.23	0.34	n.a.
FeO	0.95	4.55	<0.06	0.83	5.09	26.79
MnO	1.39	5.66	0.09	2.12	4.97	8.28
MgO	0.07	0.05	<0.02	0.05	<0.02	0.24
SrO	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
CaO	25.91	8.09	22.16	25.91	8.17	1.56
Na_2O	7.40	10.93	8.57	9.34	8.11	2.21
K_2O	<0.02	0.03	0.05	0.04	0.29	6.34
F	3.29	2.97	7.02	5.04	0.46	0.84
Cl	<0.03	<0.03	<0.03	<0.03	1.33	<0.03
-O≈F,Cl	1.39	1.25	2.96	2.12	0.49	0.35
Sum	96.92	95.40	95.61	96.56	94.53	93.11

n.a.: not analyzed

performed in a Jeol JXA-8600 electron microprobe at the Geoanalítica, at University of Sao Paulo (USP) facility, using an accelerating voltage of 15 kV, a beam current of 20 nA and a combination of well-analyzed natural and synthetic standards.

Feldspars

Alkali feldspar, mainly represented by micro- to mesoperthite of distinct and complex textural patterns, is the most important constituent of the Búzios rocks. The mineral is abundant in all of the lithologies, except for the mafic and lamprophyric rocks, in which it occurs interstitially or within the *ocelli* as a very pure potassic phase. Alkali feldspar usually shows a low anorthite (An) content and a heterogeneous composition that grades continuously along the orthoclase (Or)-albite (Ab) side of the Or-Ab-An ternary diagram or is grouped mainly at its Ab corner (Figs. 3A and 3B). In dikes, the mineral is found as microcrysts to phenocrysts of either albite or sanidine, or even as exsolution lamellae. Plagioclase is almost restricted to the mafic-ultramafic dikes, forming crystals widely variable in composition (An_{75-30}), with the matrix phases generally more enriched in Ab compared to the larger grains (Fig. 3C).

Clinopyroxenes

These minerals are present as large crystals in medium- to coarse-grained rocks, as microcrysts to phenocrysts in fine-grained varieties, or as groundmass phases in some felsic to mafic-ultramafic dikes. The composition is highly variable,

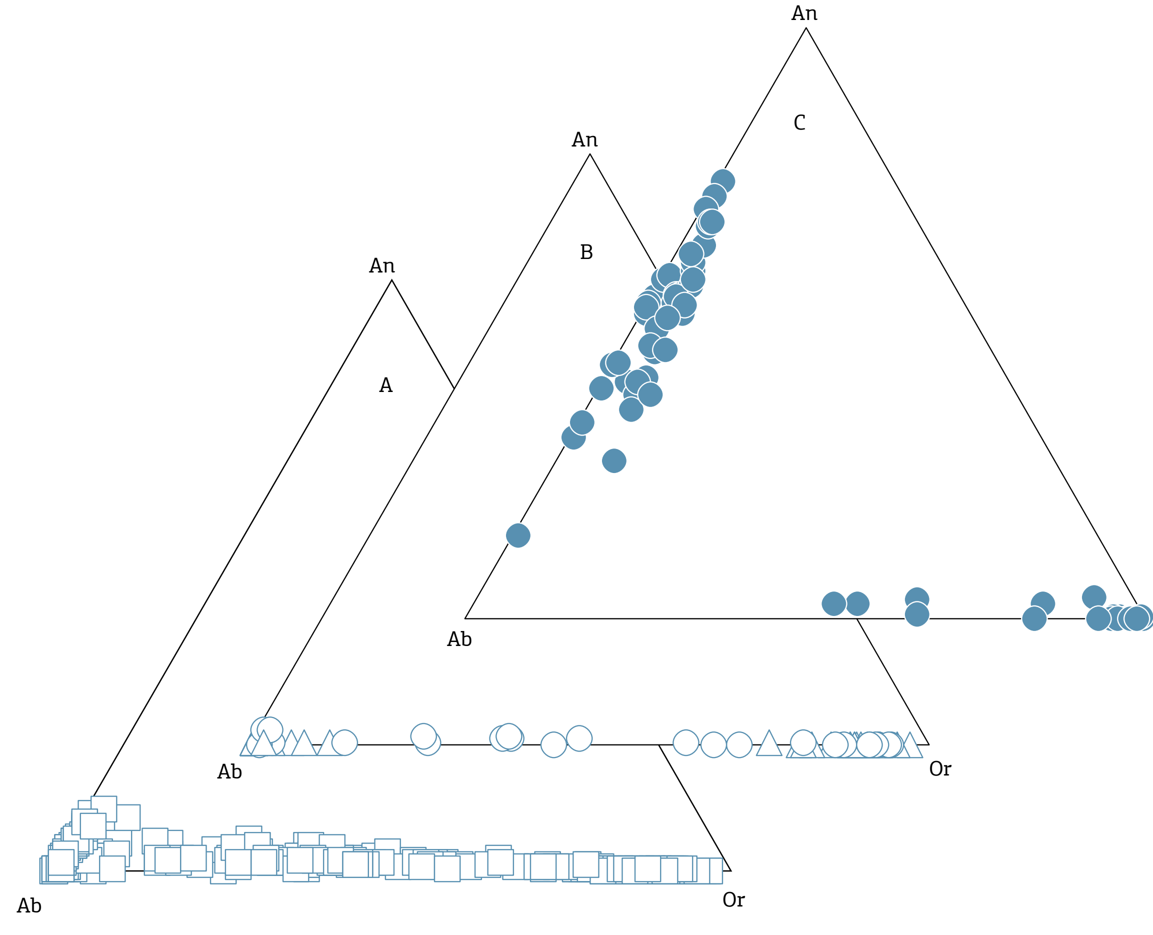

Figure 3. Chemical analyses of Búzios feldspars in the Ab-Or-An diagram (after Alves 1997). *Symbols*: (A) open square, syenite; (B) open circle, trachyte; open triangle, nepheline (sodalite) microsyenite and phonolite; (C) full circle, mafic-ultramafic rocks.

ranging from more calcic to calcic-sodic to sodic types in the WEF (wollastonite, entatite, ferrossilite) — Jd (jadeite, $NaAlSi_2O_6$) — Ae (aegirine, $NaFe^{3+}Si_2O_6$) (cf. Morimoto *et al.* 1988) triangular diagram (Fig. 4A). In the classical Wo (wollastonite, $Ca_2Si_2O_6$) — En (enstatite, $Mg_2Si_2O_6$) — Fs (ferrossilite, $Fe_2Si_2O_6$) diagram (Fig. 4B), they are represented exclusively by diopside in mafic-ultramafic dikes and by diopside-hedenbergite grading to aegirine-augite in mostly syenitic rocks. An aegirinic composition characterizes the felsic dikes (Fig. 4A). Zoning is a common feature of the clinopyroxenes, as indicated by chemical changes and variable pleochroism. A decrease in Mg and a concomitant increase in Fe and Na contents is noticed from cores to rims of crystals. This negative correlation is also a characteristic feature of clinopyroxenes from the three Búzios rock suites, whereas a negative correlation between Mg and Ti is particularly common in minerals from the mafic-ultramafic suite (Alves 1997). On the whole, these chemical variations reflect the transition of clinopyroxenes of diopsidic composition to minerals more enriched in the acmite molecule. Regarding the pleochroism, a lighter green color is a common feature of the nuclei of zoned crystals, whereas a darker green is typical of its margins.

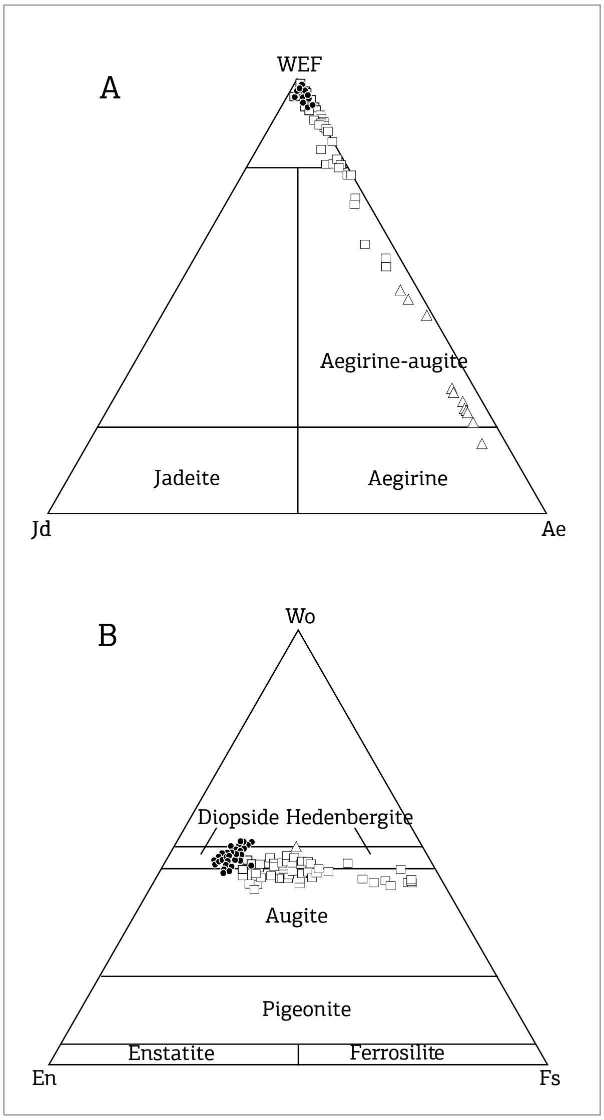

Figure 4. Chemical analyses of Búzios clinopyroxenes (A) in the WEF-Jd-Ae diagram of Morimoto *et al.* (1988) and (B) in the classical Wo-En-Fs system (after Alves 1997). *Symbols*: (A) open square, syenite; (B) open circle, trachyte; open triangle, nepheline (sodalite) microsyenite and phonolite; (C) full circle, mafic-ultramafic rocks.

Figure 5 shows the crystallization trends of clinopyroxenes from Búzios and other alkaline occurrences from Southeastern Brazil. Two distinct trends for the Búzios minerals are distinguished. The first trend exhibits a continuous increase in the Fe* (Fe^{2+}+Mn+Fe^{3+}-Na) concentration, with Na almost constant during the decrease of Mg content, followed by a Na enrichment in low Mg- clinopyroxenes; it is commonly associated with amphibole-bearing rocks (Fig. 5A). The second trend, represented by the rims of zoned crystals from syenitic rocks and by samples from felsic dikes, displays a strong enrichment in Na and minor variations in the Mg/Fe* ratio; it is usually associated with amphibole-free rocks (Fig. 5B). The first trend presents similarities with those of minerals from the São Sebastião Island (Bellieni *et al.* 1990), the Morro Redondo (Brotzu *et al.* 1989) and the Morro de São João (Brotzu *et al.* 2007) alkaline intrusions (Fig. 5C). On the other hand, the second trend approaches the pattern displayed by rocks from the Mantiqueira Mountain complexes of Passa Quatro (Brotzu *et al.* 1992) and Itatiaia (Brotzu *et al.* 1997), as also shown in Figure 5C. Variable oxidizing conditions during crystallization could account for the difference in Fe^{2+} enrichment relative to Fe^{3+} and Na enrichment in clinopyroxenes (Marks *et al.* 2008).

Amphiboles

These minerals are widespread in Búzios rocks and usually formed after the breakdown of clinopyroxenes. In some samples, particularly of mafic and lamprophyric dikes, they constitute a primary phase and represent the principal mafic mineral in these rocks. Generally, the amphiboles are joined by biotite that occurs along the borders of their crystals or occupies the cleavage planes. The evolution of these minerals is similar to that of the clinopyroxenes, grading in syenitic rocks from more magnesian towards more iron-rich compositions, with the amphiboles mostly classified as Mg- and Fe-hornblende, respectively (cf. Leake 1997). The enrichment in Fe is also accompanied by a progressive increase in Na content. In a few samples, the amphiboles are

Fe-barroisite, edenite or hastingsite in composition. In felsic dikes, the mineral corresponds to katophorite (highest Fe contents) and riebeckite in more Na-rich varieties, whereas in mafic-ultramafic ones, it falls dominantly into the kaesurtite field and contains high Ti and Al concentrations.

Micas

Micas are present in all lithologies of the massif, but less frequently in felsic dikes. Except in the lamprophyric rocks, the minerals are of secondary origin and variable color and occur closely associated with clinopyroxenes and amphiboles. The chemical composition shows high Ti and wide variations in Al contents and Fe/Fe+Mg ratios, although in most of the cases the minerals may be called biotite. The more magnesian varieties are related to mafic-ultramafic dikes and contain higher Al^{IV} and Ti concentrations, approaching the eastonite-siderophylite series (Fig. 6). In general, Si and Al^{IV} cationic proportions are insufficient to fill the tetrahedral site, with the position being completed by Fe^{3+}or Ti^{4+}, as it has been noted in several alkaline occurrences from Southeastern Brazil (see, for instance, Morbidelli *et al.* 1995).

Quartz

This mineral is present in variable amounts as individual crystals or as interstitial aggregates. SiO_2-oversaturated syenitic rocks have amphibole as the main mafic mineral and quartz in association with alkali feldspar, forming a typical granophyric texture.

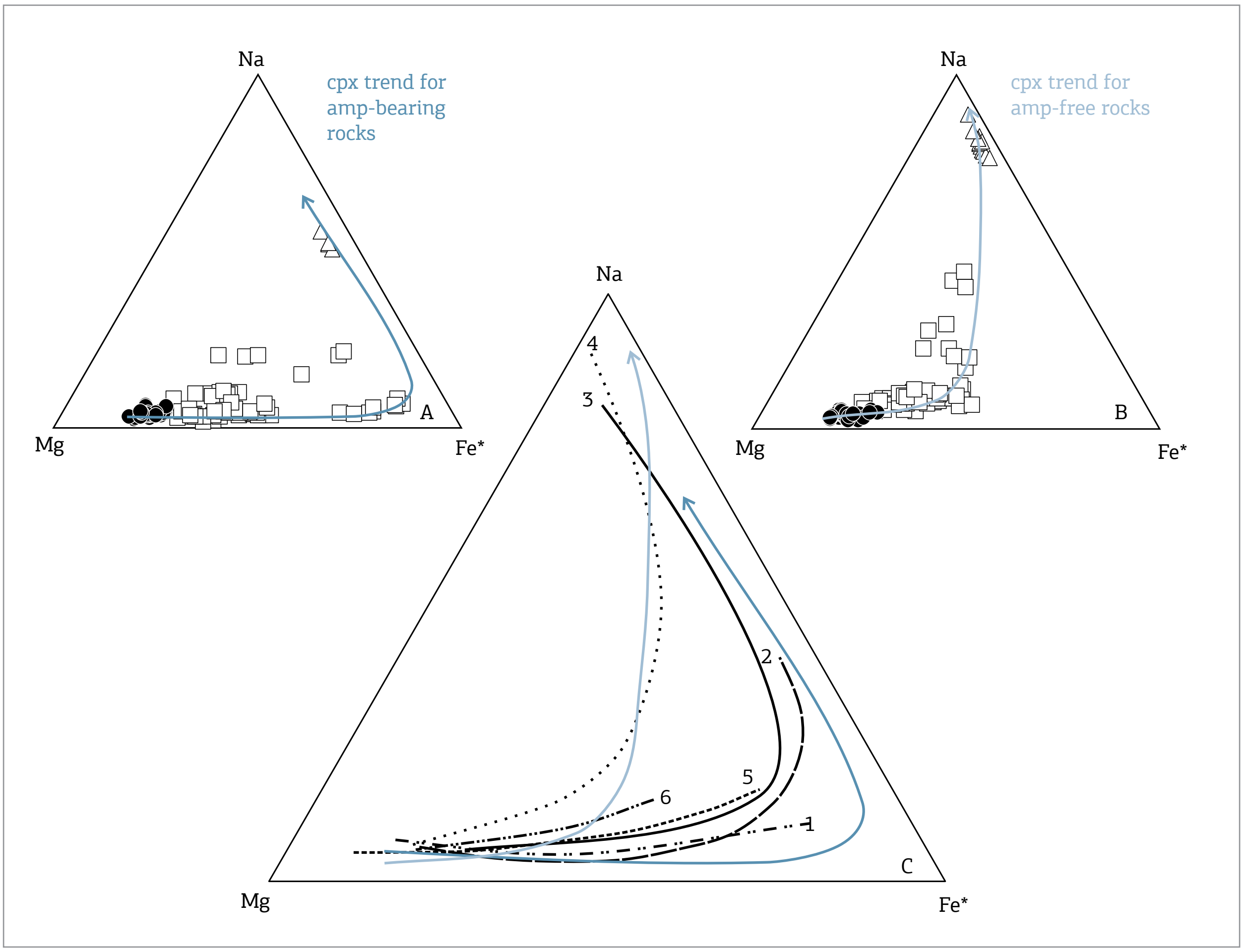

Figure 5. (A) Cristallization trend of Búzios clinopyroxenes for amphibole-free lithotypes. (B) Cristallization trend of Búzios clinopyroxenes for amphibole-bearing lithotypes. *Symbols:* (A) open square, syenite; (B) open circle, trachyte; open triangle, nepheline (sodalite) microsyenite and phonolite; (C) full circle, mafic-ultramafic rocks. (C) Comparison of the different Búzios clinopyroxene trends with the main evolutionary trends for clinopyroxenes of alkaline complexes from southeastern Brazil. Fe* = (Fe^{2+}+Mn+Fe^{3+}-Na). References: 1. São Sebastião Island (Bellieni *et al.* 1990); 2. Vitória Island (Motoki 1986); 3. Monte de Trigo Island (Enrich 2005); 4. Passa Quatro (Brotzu *et al.* 1992) and Itatiaia (Brotzu *et al.* 1997); 5. Morro Redondo (Brotzu *et al.* 1989); 6. Morro de São João (Brotzu *et al.* 2007). Dark blue line, clinopyroxene trend for Búzios amphibole-bearing rocks; light blue line: clinopyroxene trend for Búzios amphibole-free rocks.

Feldspathoids

This mineral group contains nepheline as the most abundant constituent, but sodalite and analcite are also recognized. The latter phase is present in the groundmass or as *ocelli* in lamprophyric rocks, with the mineral occurring in close contact with glass and secondary minerals (carbonates and zeolites). Cancrinite is the main alteration product of nepheline and occupies the boundaries of its crystals or occurs concentrated along its fractures. Alves (1997) reported nepheline crystals with minor quartz (Q_{6-7}) and main nepheline (Ne_{73-74}) endmembers, indicating equilibrium temperature higher than 775ºC for the mineral (Hamilton 1961).

Olivines

Olivines are scarce and almost restricted to the lamprophyric rocks, forming megacrystals or aggregates in association with clinopyroxene, plagioclase, phlogopite, and opaques. The few data available in Alves (1997) point to a composition in the crysolite field (Forsterite: 76-84 mol%) and CaO content lower than 0.38 wt%.

Fe-Ti oxide minerals

These minerals are represented by magnetite that is highly variable in TiO_2 (syenitic rocks, 0.40–7.78 wt%; mafic-ultramafic dikes, 17.05–24.25 wt%) and found as isolated grains or coexisting with ilmenite lamellae (TiO_2 in syenitic rocks, 44.05–52.23 wt%; mafic dikes, 47.37–50.13 wt%) (Alves 1997). Magnetite is widespread in Búzios lithotypes, whereas ilmenite occurs more frequently in syenitic rocks. Temperature calculations by the author using Buddington and Lindsley's (1964) geothermometry suggested values between 580 and 680ºC and –log fO_2 ~18–21 for the syenites; for the mafic dikes, the results are between 870 and 960ºC and –log fO_2 ~11–13.

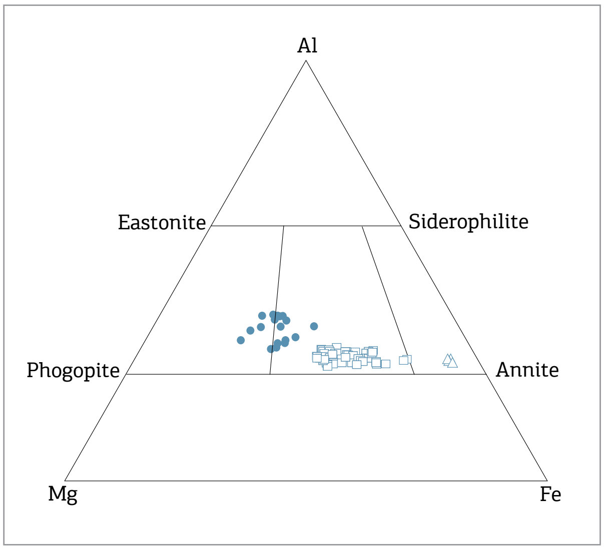

Figure 6. Chemical analyses of Búzios micas in the Al-Mg-Fe diagram (after Alves 1997). *Symbols:* (A) open square, syenite; (B) open circle, trachyte; open triangle, nepheline (sodalite) microsyenite and phonolite; (C) full circle, mafic-ultramafic rocks.

Accessory minerals

The main accessory minerals are titanite, apatite, zircon, allanite and fluorite. Additionaly, an assemblage of mostly silicate minerals bearing Zr, Ti, Nb, and Rare Earth Elements (REE) is identified in association with nepheline (sodalite) microsyenite and phonolite dikes of agpaitic affinity as indicated in Table 1. The whole set of minerals includes låvenite, mosandrite, rosenbuschite and wöhlerite, which are Na-, Ca- and F-rich sorosilicates with variable amounts of Zr, Nb, Ti and REE (e.g., Merlino & Perchiazzi 1988; Christiansen *et al.* 2003; Bellezza *et al.* 2009); eudialyte, a Zr-, Fe-, Mn-, Ca-, Na- and Cl-rich cyclosilicate (e.g., Johnsen *et al.* 2003; Schilling *et al.* 2011); and astrophyllite, a Ti-, Fe-, Mn- and K-rich heterophyllosilicate (e.g., Piilonen *et al.* 2003). Other rare accessory to post-magmatic minerals of the felsic dikes are britholite-(Ce), aenigmatite, pyrochlore, fergusonite-(Y), synchysite-(Ce) and bastnäsite-(Ce). Several of them are also typical of similar rocks from the nearby alkaline massif of Monte de Trigo Island (Enrich 2005; Enrich *et al.*, 2016).

GEOCHEMISTRY

The chemical analyses of the Búzios rocks are taken after Alves (1997) (for the data source, access the site: http://www.teses.usp.br/teses/disponiveis/44/44135/tde-18092015-174733/pt-br.php) and plotted in the Total-alkali–silica (TAS) classification diagram (cf. Le Maitre 1989; Fig. 7). Two rock assemblages are easily distinguished, with the first group composed of lithologies more enriched in SiO_2 (syenites and felsic dikes) and the second one consisting of less enriched types (mafic-ultramafic dikes), including basic to ultrabasic rocks. The first set can also be divided into syenites to nepheline (sodalite) syenites (trachytes to phonolites) and alkaline granites (rhyolites), the latter lithotypes showing chemical similarities with the basement charnockites. A potassic affinity is indicated for mostly rocks in Middlemost's (1975) K_2O *vs.* Na_2O diagram (Fig. 8), with the exceptions corresponding to several more sodic samples of both felsic and mafic-ultramafic dikes. A bimodal pattern also characterizes the alkalis distribution for syenitic and mafic-ultramafic rocks, with the latter lithologies generally less enriched in K_2O and Na_2O in relation to the syenites.

Based on values for the agpaitic index (A.I.=Na_2O+K_2O/Al_2O_3, molar ratio), most of the Búzios lithologies are classified as belonging to the miaskitic series. However, some nepheline syenites and especially peralkaline phonolites exhibit typical agpaitic features (cf. Sörensen 1960), as suggested by chemical evidences (A.I.>1.0) and the presence of exotic mineral phases bearing large-ion lithophile element (LILE), high field strength elements (HFSE) and REE (Enrich *et al.* 2007a,b).

Variation diagrams (Figs. 9 to 10) for major and trace elements against Mg# [$MgO_{mol.}/(MgO_{mol.}+FeO_{Tmol.})*100$] show again the bimodal distribution of the elements and the existence of well-defined negative correlations for SiO_2, Na_2O, Rb, Nb, Zr, La, Ce, and Nd, and positive ones for TiO_2, FeO_T, MgO, CaO, P_2O_5, Cr, Ni, Ba, and Sr.

The distribution of incompatible elements normalized to the primitive mantle (cf. McDonough and Sun 1995) for the Búzios rocks is displayed in Figure 11. Positive anomalies are indicated for Nb, La-Ce, Nd, and Zr, and pronounced negative spikes occur for Ba, Sr, and Ti. The positive anomaly for Ba and the negative one for Zr also characterize the mafic dikes, and the felsic dikes both undersaturated and supersaturated in silica show approximately the same behavior. On the whole, these patterns are very similar to those described in other alkaline rocks from Southeastern Brazil,

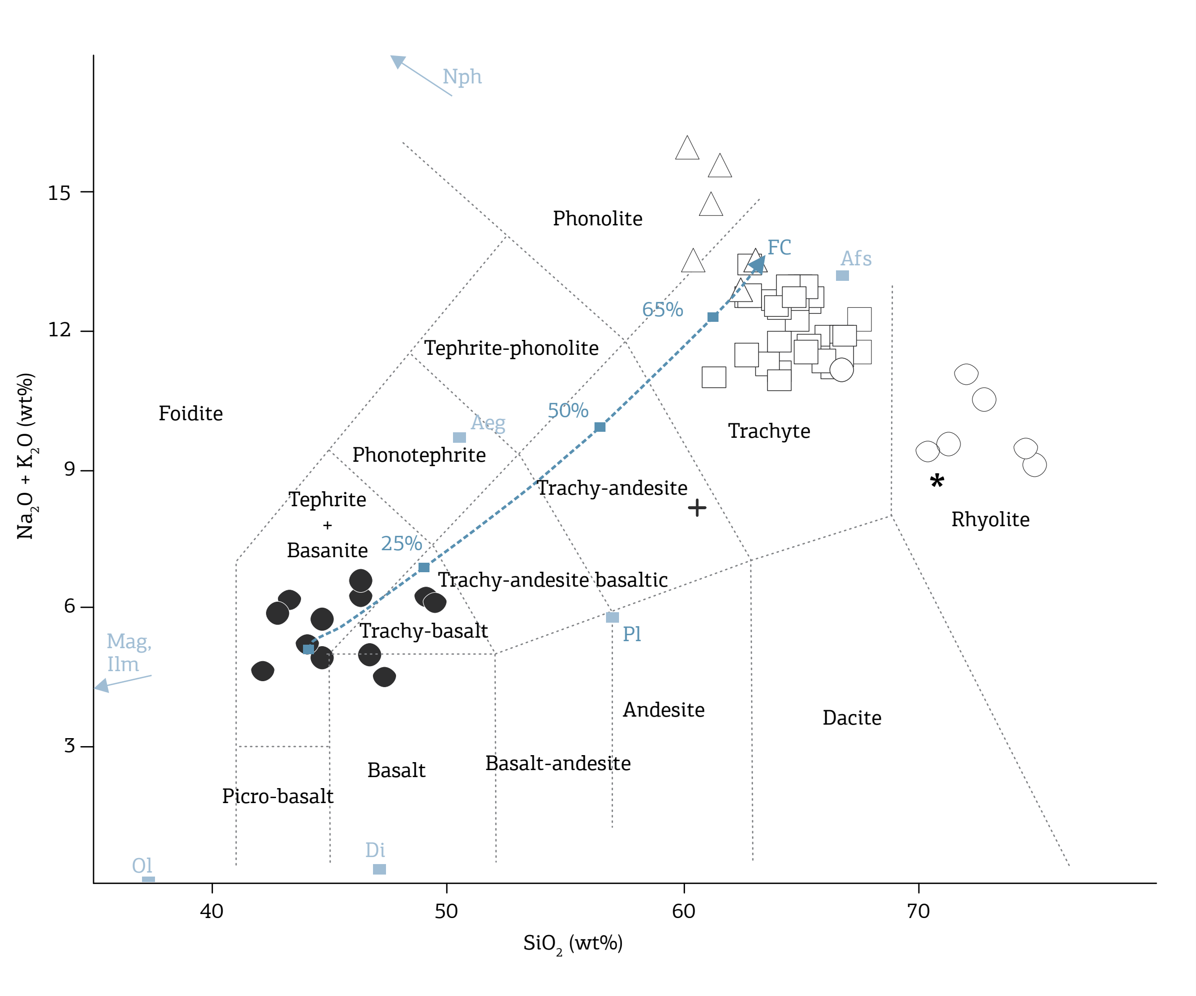

Figure 7. TAS (Na_2O+K_2O vs. SiO_2, in wt%) diagram (cf. Le Maitre 1989) for the Búzios rocks (after Alves 1997). Symbols: open square, syenite; open circle, trachyte and rhyolite dikes; open triangle, nepheline (sodalite) microsyenite and phonolite dikes; full circle, mafic-ultramafic dikes; cross, mangerite host rock; asterisk, average composition of charnockitic rocks from the Ubatuba area (cf. Neumann 1993). Dark blue dashed line: models of fractional crystallization performed using the MELTS algorithm for initial liquid compositions calculated based on the basanite 326a compositions. The numerals on these lines refer to the percentage of fractionation of solid phases of the system. The conditions inferred for those models are $T_{initial}$ ~1200°C, P=1 kbar, fO_2= QFM. The data were recalculated on an anhydrous basis in all diagrams. Mineral poles based on average compositions from Alves (1997).

particularly the major syenitic occurrences from the Serra do Mar Province (Enrich *et al.* 2005).

PETROLOGY

The plutonic and hypabyssal syenitic rocks from Búzios are highly evolved as judged by their Mg# (<0.38) and very low Cr and Ni contents (<11 and <21 ppm, respectively). Even the mafic-ultramafic dikes are evolved rocks (Mg#<0.65, Ni<235 ppm).

The bimodal alkaline magmatism found in the Buzios Island massif, with syenitic and felsic fine-grained rocks prevailing over mafic-ultramafic lithologies, is probably linked to fractional crystallization processes from parental basic alkaline magmas. Fractional crystallization from a parental magma of basanitic composition has been proposed as the main evolution process for Early (Juquiá, Beccaluva *et al.* 1992; Ponte Nova, Azzone *et al.* 2016) and Late (Lages, Traversa *et al.* 1996; Monte de Trigo Island, Enrich 2005; Morro Redondo, Brotzu *et al.* 1989; Passa Quatro, Brotzu *et al.* 1992; Piratini, Barbieri *et al.* 1987; São Sebastião Island, Bellieni *et al.* 1990) alkaline occurrences from Southern Brazil.

The MELTS thermodynamic models of fractional crystallization (Ghiorso & Sack 1995; Asimow & Ghiorso 1998) were applied to evaluate the possible relationships of basanite dikes and the syenitic rocks from the Búzios

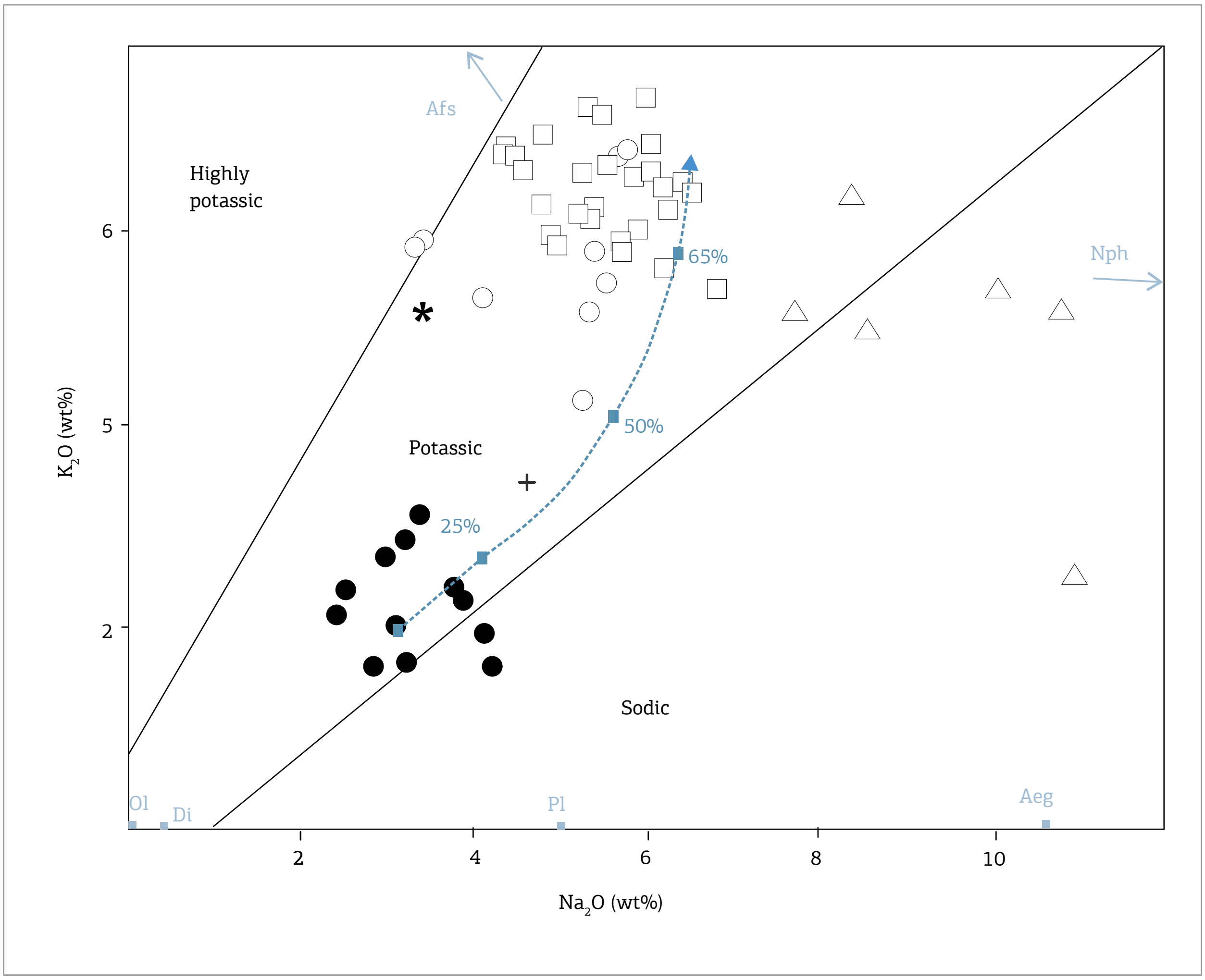

Figure 8. Búzios rocks in the K_2O *vs.* Na_2O Middlemost's (1975) diagram (after Alves 1997). Symbols: open square, syenite; open circle, trachyte and rhyolite dikes; open triangle, nepheline (sodalite) microsyenite and phonolite dikes; full circle, mafic-ultramafic dikes; cross, mangerite host rock; asterisk, average composition of charnockitic rocks from the Ubatuba area (cf. Neumann 1993). Dark blue dashed line: models of fractional crystallization performed using the MELTS algorithm for initial liquid compositions calculated based on the basanite 326a compositions. The numerals on these lines refer to the percentage of fractionation of solid phases of the system. Mineral poles based on average compositions from Alves (1997).

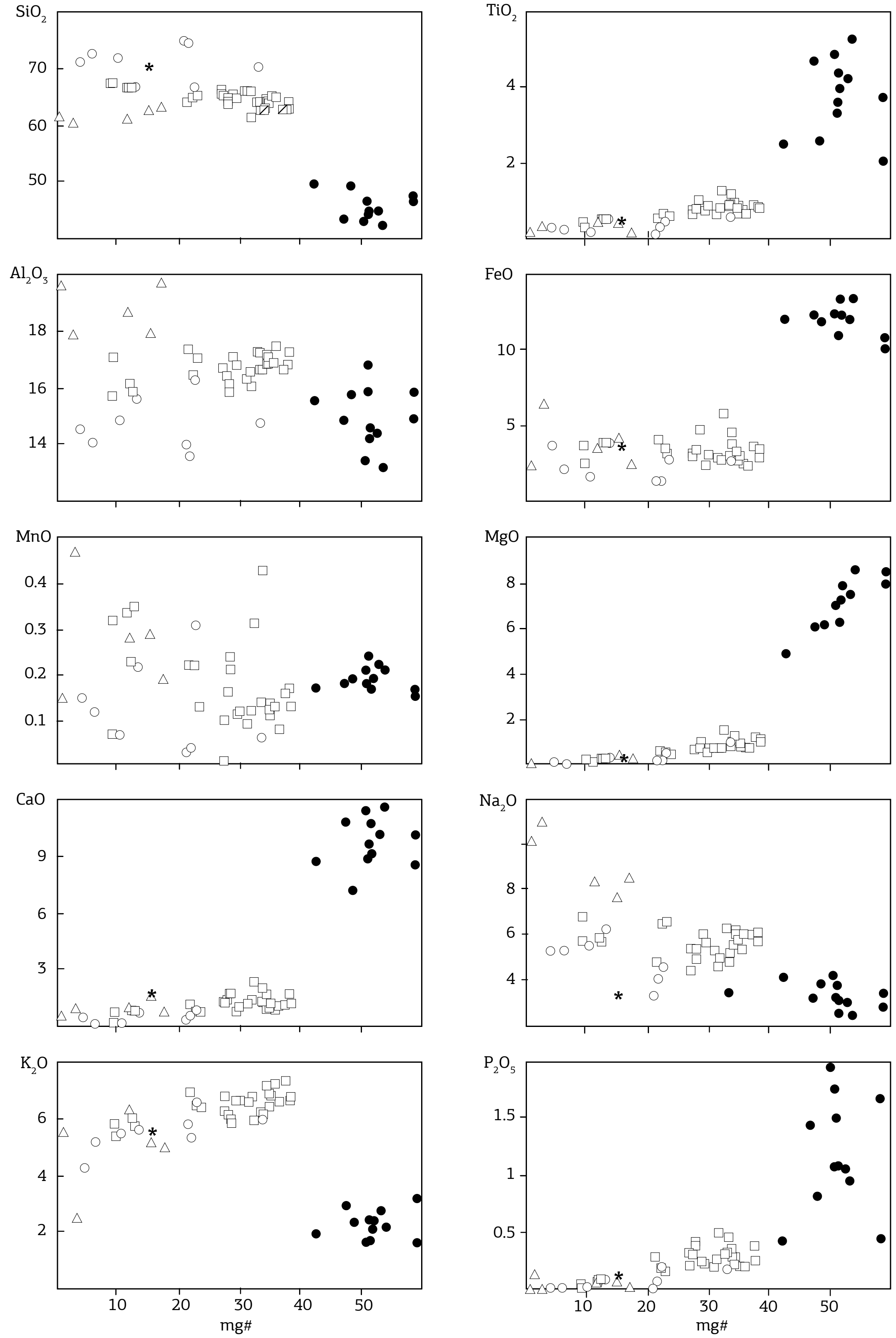

Figure 9. Variation diagrams of major elements against Mg# for the Búzios rocks (after Alves 1997). Symbols: open square, syenite; open circle, trachyte and rhyolite dikes; open triangle, nepheline (sodalite) microsyenite and phonolite dikes; full circle, mafic-ultramafic dikes; cross, mangerite host rock; asterisk, average composition of charnockitic rocks from the Ubatuba area (cf. Neumann 1993).

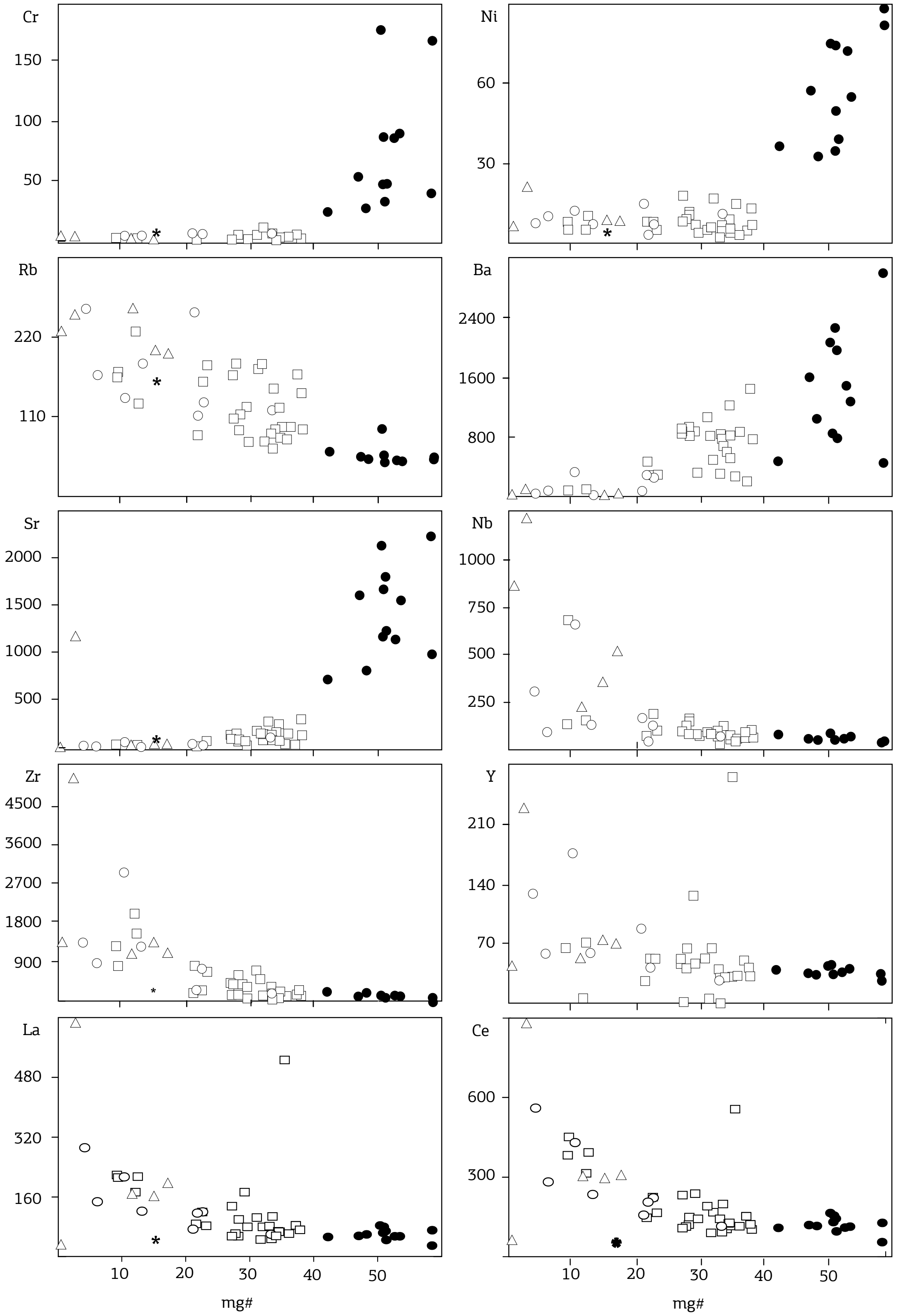

Figure 10. Variation diagrams of trace elements against Mg# for the Búzios rocks (after Alves 1997). Symbols: open square, syenite; open circle, trachyte and rhyolite dikes; open triangle, nepheline (sodalite) microsyenite and phonolite dikes; full circle, mafic-ultramafic dikes; cross, mangerite host rock; asterisk, average composition of charnockitic rocks from the Ubatuba area (cf. Neumann 1993).

Island massif (Table 2). These models also indicate the evolutionary trends of the assumed basanite parental melt and the crystallization sequences. The initial composition selected for the models corresponds to that of dike 326a, which is thought to represent a primitive non-cumulus liquid in the intrusion. Although other dikes show a more primitive composition, they are considered to represent a melt bearing an important volume of megacrysts, which could be assigned as antecrysts (Menezes *et al.* 2015); hence, they are not a good indication of the parental magma composition. The initial T (~1200–1150ºC) of the assumed parental magma was estimated based on the pyroxene saturation thermometer (Putirka 2008). A low-pressure condition (P=1 kbar) was also indicated for most Búzios rocks, as suggested by the Al^{VI} contents (usually <0.1 a.f.u.) and the calculated cell volumes (VCell>440 Å^3, following Nimis, 1995) of the clinopyroxenes. The fO_2 buffer fixed for these models was the QFM, compatible with petrographic observations and similar to the one adopted by Trumbull *et al.* (2003) and Menezes *et al.* (2015). Low levels of H_2O (1.0 wt%) and CO_2 (0.2 wt%) were assumed based on petrographic evidences.

The early-crystallized minerals in the applied MELTS models are olivine, spinel and clinopyroxene, whereas apatite and plagioclase represent other fractionated phases. The trend of the modelled liquid indicates a progressive decrease in the amounts of MgO, TiO_2 and CaO and, subordinately, an increase in concentrations of SiO_2, Al_2O_3 and alkalis (K_2O and Na_2O; Figs. 7 and 8). To reach a syenite composition starting from the basanite would require the fractionation of ~7 wt% olivine, ~24 wt% clinopyroxene, ~22 wt% plagioclase, ~13 wt% spinel, and ~3 wt% apatite (~65% fractionation of solid phases; Table 2). Although outcrops of gabbroic cumulates that could corroborate the fractionation models are lacking in Búzios, it should be noted that these types of rocks crop out on the neighboring islands of Monte de Trigo (Enrich *et al.* 2005, 2009) and São Sebastião (Bellieni *et al.* 1990) and are also very common in several other alkaline districts from Southeastern Brazil, such as Jacupiranga, Juquiá and Pariquera-Açu (Morbidelli *et al.* 2000; Gomes *et al.* 2011) and Ponte Nova (Azzone *et al.* 2013, 2016).

It is also important to note the clear compositional gap shown in the variation diagrams of the Búzios rocks, especially for major elements (Fig. 9), pointing to the absence of compositions between 50 and 60 wt% SiO_2 (an interval referred in the literature as the "Daly gap", cf. Chayes, 1977). This gap can be interpreted as a consequence of the viscosity increase during the magmatic evolution that would prevent the migration of magma

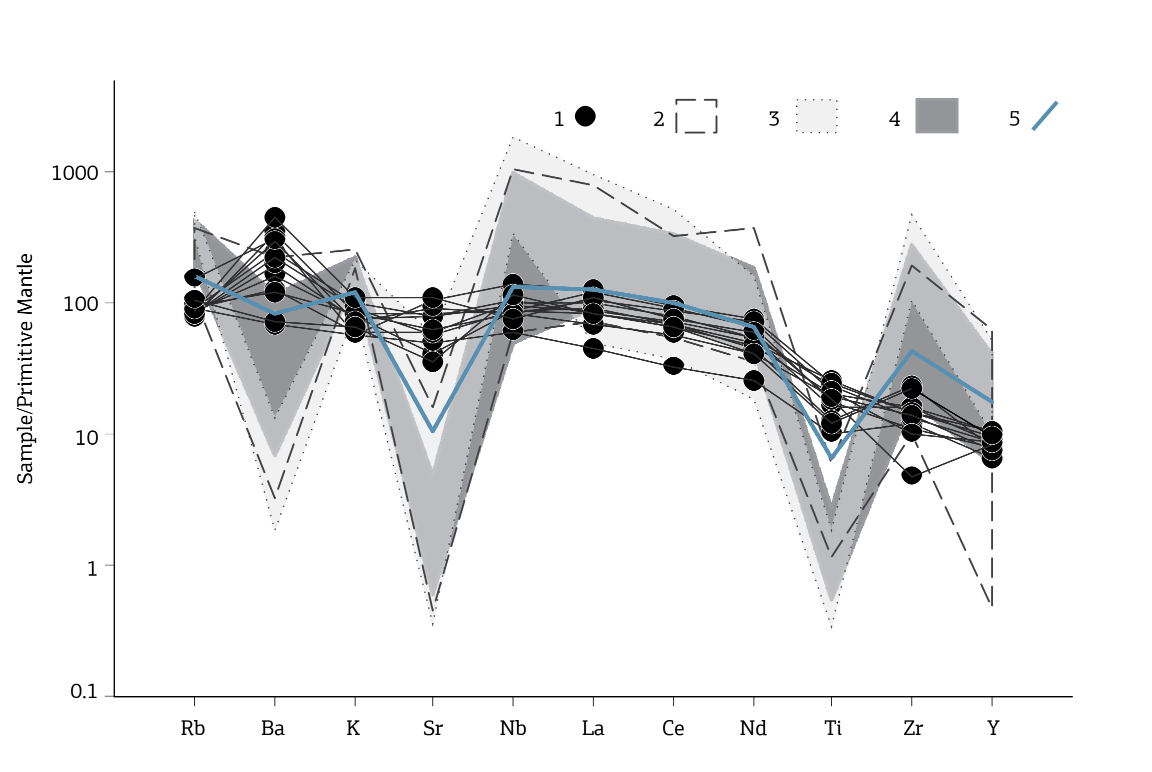

Figure 11. Primitive mantle-normalized trace elements patterns (cf. McDonough & Sun 1995) for the Búzios rocks (after Alves 1997). Legends: 1. Mafic-ultramafic dikes; 2. syenites; 3. phonolites; 4. rhyolites; 5. mangerite host rock.

with intermediate compositions to low crustal levels (e.g., Thompson *et al.* 2001). Alternatively, it could be the result of two distinct parental magmas, a mafic and a felsic one (e.g., Legendre *et al.* 2005). This latter hypothesis usually leads to the mixture of mafic and felsic melts. However, there is no description of field, petrographic or chemical evidences of magma mixing in the area (Alves 1997; Alves & Gomes 2001).

In the petrogeny residual system (Fig. 12, after Hamilton & Mackenzie 1965), the Búzios felsic rocks are compatible with major fractionation of alkali feldspar and plot differently with respect to the low-pressure Ab-Or thermal barrier. A trend towards the phonolitic minimum characterizes the SiO_2-undersaturated association (felsic dikes of nepheline/sodalite-bearing rocks), whereas a trend towards the rhyolitic minimum is associated with the SiO_2-oversaturated rocks (felsic dikes of rhyolites). According to Alves (1997), the first trend seems to be related to the normal evolution of the syenitic magma. Mineral vectors on the Na_2O *vs.* K_2O diagram (Fig. 8) also indicate the alkali feldspar fractionation from a syenitic magma towards a phonolite liquid and suggest that some syenites are alkali feldspar cumulates. The second trend

Table 2. Summary of thermodynamic fractional crystallization models developed using the MELTS algorithm (Ghiorso and Sack, 1995) from a basanitic liquid compositionally similar to sample 326a. The starting composition is found under isobaric conditions (1 kbar) and with fO_2 conditions equal to the QFM buffer. Abbreviations: Ap, apatite; Cpx, clinopyroxene; Ol, olivine; Pl, plagioclase; Spl, spinel group.

Steps	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
T (°C)	**1176**	**1156**	**1136**	**1116**	**1096**	**1076**	**1056**	**1036**	**1016**	**996**	**976**	**956**	**936**	**916**	**896**
***Fractionated solids* (f%)**	**0.0**	**1.5**	**3.2**	**7.5**	**24.1**	**34.1**	**41.7**	**48.6**	**53.7**	**57.7**	**61.0**	**63.8**	**66.3**	**68.4**	**70.4**
MELT compositions															
SiO_2	43.52	43.59	43.73	44.98	47.91	50.60	52.63	54.39	55.82	56.99	57.98	58.81	59.49	60.04	60.48
TiO_2	4.31	4.37	4.41	3.95	2.75	2.04	1.64	1.40	1.22	1.08	0.96	0.86	0.78	0.72	0.66
Al_2O_3	14.08	14.29	14.53	14.93	16.27	17.57	18.04	17.91	17.68	17.38	17.03	16.67	16.31	15.95	15.59
Fe_2O_3	2.21	2.23	2.24	2.10	1.74	1.45	1.24	1.07	0.93	0.81	0.71	0.63	0.55	0.47	0.41
FeO	10.18	10.08	9.90	8.77	6.93	5.69	4.73	3.92	3.27	2.74	2.31	1.94	1.62	1.35	1.12
MnO	0.17	0.17	0.16	0.17	0.20	0.23	0.26	0.28	0.31	0.32	0.34	0.35	0.37	0.38	0.39
MgO	7.17	6.65	6.09	5.45	4.15	3.23	2.61	2.14	1.80	1.52	1.30	1.12	0.97	0.84	0.74
CaO	10.54	10.69	10.87	11.21	9.88	8.21	7.02	6.11	5.38	4.78	4.28	3.86	3.50	3.21	2.96
Na_2O	3.08	3.13	3.18	3.33	4.01	4.59	5.03	5.39	5.68	5.89	6.05	6.17	6.25	6.30	6.31
K_2O	2.06	2.09	2.12	2.22	2.70	3.11	3.51	3.96	4.37	4.76	5.14	5.50	5.86	6.21	6.55
P_2O_5	1.49	1.51	1.54	1.61	1.88	1.53	1.32	1.19	1.10	1.03	0.99	0.96	0.94	0.95	0.96
H_2O	0.99	1.00	1.02	1.07	1.30	1.47	1.64	1.84	2.04	2.23	2.41	2.59	2.78	2.96	3.16
CO_2	0.20	0.20	0.20	0.21	0.26	0.30	0.34	0.38	0.43	0.47	0.51	0.55	0.58	0.62	0.67
Total	100.00	100.00	99.99	100.00	99.98	100.02	100.01	99.98	100.03	100.00	100.01	100.01	100.00	100.00	100.00
% of solid phases (in equilibrium with each step)															
Cpx				0.66	12.39	6.86	3.1	1.13	0.6	0.32	0.17	0.11	0.08	0.06	0.05
Ol		1.46	1.52	1.23	0.09	0.06	0.31	0.54	0.4	0.33	0.29	0.23	0.18	0.14	0.11
Spl			0.16	2.45	4.06	2.07	1.39	1.05	0.71	0.5	0.35	0.27	0.21	0.16	0.13
Pl							2.3	3.81	3.18	2.74	2.41	2.14	1.93	1.77	1.94
Ap					0.14	1	0.57	0.38	0.25	0.17	0.13	0.1	0.07	0.05	0.04
% of accumulated fractionated phases from previous steps															
Cpx					0.65	13.04	19.89	22.98	24.11	24.71	25.03	25.19	25.3	25.38	25.43
Ol			1.46	2.98	4.21	4.29	4.36	4.67	5.2	5.6	5.93	6.22	6.45	6.63	6.77
Spl				0.16	2.61	6.66	8.73	10.11	11.16	11.87	12.36	12.7	12.97	13.17	13.33
Pl								2.29	6.1	9.29	12.03	14.43	16.57	18.5	20.26
Ap						0.14	1.13	1.69	2.07	2.31	2.48	2.61	2.7	2.76	2.81

could be the result of moderate water pressures adequate to promote the oversaturation of the magma in lower temperature zones (e.g., at the margins of the intrusion), leading to the destabilization of the clinopyroxene and formation of amphibole and/or biotite, with SiO_2 in excess. Studying the Itatiaia massif, which also contains SiO_2-undersaturated and SiO_2-oversaturated rocks, Brotzu *et al.* (1997) suggested that a fractionation process dominated by silica-poor and alkali-rich amphibole is a possible way to straddle the Ab-Or join in the Qz-Ne-Ks diagram. The authors postulated that variations in mineral composition, mainly of amphibole, of the least differentiated syenites excluded the possibility of a direct link between the two suites, and proposed for such lithologies a genesis from distinct mafic parental magmas showing different degrees of SiO_2 saturation. This conclusion could also be applied to the Búzios rocks.

The bridging of the thermal barrier may also be explained by AFC processes (DePaolo 1981). In some alkaline intrusions from Southeastern Brazil, such as Itatiaia (Brotzu *et al.* 1997) and Cananeia (Spinelli & Gomes 2009), silica-oversaturated syenitic rocks occurring as small dikes appear to have been influenced by crustal contamination or AFC processes, as mainly indicated by the high $^{87}Sr/^{86}Sr$ initial ratios (>0.705, cf. Ruberti *et al.* 2005). Unfortunately, no isotopic data are available for the Búzios rhyolitic rocks. Crustal assimilation processes are believed to play an important role in the genesis of other alkaline intrusions of Southern Brazil, as suggested by Motoki (1986) and Motoki *et al.* (2015) for the neighboring Vitória Island and the Cabo Frio massif, as well as by Azzone *et al.* (2016) for the mafic-ultramafic complex of Ponte Nova.

The last alkaline magmatic activity in Búzios is represented by the numerous dikes that vary compositionally from lamprophyres to SiO_2-undersaturated (phonolites) to SiO_2-oversaturated (rhyolites) rocks. Such dikes could either

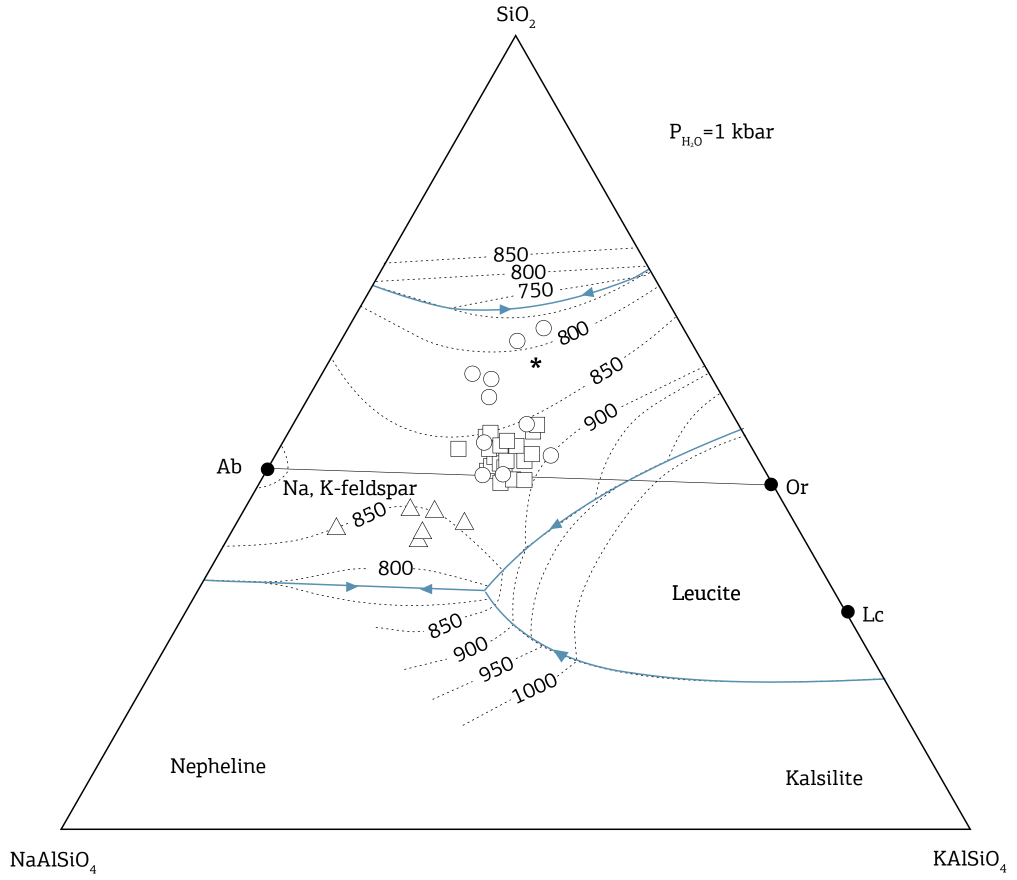

Figure 12. The Búzios rocks plotted in the normative Qz-Ne-Ks residual system at P_{H20}=1 kbar (after Hamilton and MacKenzie 1965). Isotherms and cotectic lines after Hall (1987). Symbols: open square, syenite; open circle, trachyte and rhyolite dikes; open triangle, nepheline (sodalite) microsyenite and phonolite dikes; asterisk, average composition of charnockitic rocks from the Ubatuba area (cf. Neumann 1993).

be part of a single magmatic sequence formed by fractional crystallization or represent different pulses of undersaturated alkaline magmas.

FINAL REMARKS

Geological evidence indicates that Precambrian formations of the Ribeira Belt were probably intruded by different pulses of alkaline magma on Búzios Island. The emplacement of these magmas, and also of other alkaline rocks on the neighboring islands, is clearly controlled by regional tectonics, as already suggested by Almeida (1983) and Riccomini *et al.* (2005).

Similar to other alkaline centers from Southeastern Brazil (Morbidelli *et al.*, 1995), which show the presence of volcanic structures and lithotypes (e.g., Itatiaia, Piratini, Poços de Caldas, Tunas) or of cumulate rocks occupying shallow stratigraphic positions (e.g., Jacupiranga), the syenitic magmatic activity in Búzios was developed under low-pressure conditions.

The Búzios alkaline rocks can be placed into two main assemblages. The first and most abundant group includes plutonic felsic types, mostly alkali feldspar syenites and minor amounts of quartz-alkali feldspar syenites. Also belonging to this association are dikes, widely variable in composition, with microsyenites and trachytes as the main petrographic types. The second assemblage consists of mafic to ultramafic rocks that occur as small lamprophyric dikes (alkali basalts, basanites, tephrites, and trachybasalts). In contrast to Monte de Trigo and São Sebastião Islands, and like Vitória Island, Búzios does not have outcrops of plutonic alkaline basic rocks.

Mineralogically, the Búzios lithologies have alkali feldspar (mesoperthite), clinopyroxenes (diopsidic to aegirinic in composition), amphiboles (Mg-hornblende evolving towards more calcic-sodic types), micas (Mg-biotites to Fe-biotites), opaques (magnetite and ilmenite), and quartz as principal phases, with feldspathoids (nepheline and subordinate sodalite) occasionally present in fine-grained syenites, and plagioclase in more basic rocks. In the lamprophyric varieties, the amphibole is kaersutite, olivine occurs, and the biotite is Ti-rich. In addition to ore phases, the accessory mineralogy of the syenitic rocks includes apatite, titanite, zircon, fluorite, and rare Ti-Zr-REE silicate phases, while zeolites and carbonates are the more common alteration products. Also notable is the presence of globules and *ocelli* of variable mineralogical composition (analcite, glass and/or carbonates) in the lamprophyric rocks.

Excluding the lamprophyric rocks, textural evidence indicates that, after the formation of opaques, clinopyroxenes are the first mafic minerals to be crystallized in the magma. They occur as isolated crystals or are clearly surrounded by amphibole/biotite grains in the more advanced stages of magmatic crystallization. Alkali feldspar appears to have been formed simultaneously with both mafic minerals.

Zoning is particularly common in the clinopyroxenes, with the central areas of the crystals exhibiting lighter greenish colours. Changes in color reflect the variations in the chemical composition as follows: the increase in Fe and Na contents and the concomitant decrease in Mg from the cores to the rims of the crystals.

The chemical analyses of the Búzios rocks show a compositional gap in SiO_2 content (between 50 and 60 wt%), which corresponds to the interval between syenites and mafic-ultramafic dikes. This bimodal distribution is also suggested for other major elements, particularly FeO, MgO, CaO, and K_2O. Overall, the rocks are typically potassic, although some dikes can be chemically classified as sodic, peralkaline and agpaitic in composition.

The fractional crystallization of gabbroic cumulates from a basanite melt is considered to be responsible for the formation of the syenite magma of the island. MELTS models indicate the fractionation of ~7 wt% olivine, ~24 wt% clinopyroxene, ~22 wt% plagioclase, ~13 wt% spinel, and ~3 wt% apatite (~65% fractionation of solid phases) to reach the syenite compositions.

Similar to other Brazilian alkaline districts (e.g., Itatiaia), Búzios has SiO_2-undersaturated and SiO_2-oversaturated rocks represented by felsic dikes of phonolitic and rhyolitic composition, respectively. In the normative Qz-Ne-Ks petrogeny residual diagram, these compositions exhibit distinct behavior, trending towards the eutectic phonolitic minimum and the rhyolitic minimum, respectively. The first trend is possibly associated with the normal evolution of the syenitic magma, with extensive fractionation of alkali feldspar. On the other hand, the trend towards the granitic eutectic may be due to alkali feldspar fractionation or to fractionation of amphibole, or it may be the result of AFC processes, a hypothesis that cannot be discarded because the almost total absence of isotopic data for the Búzios rocks.

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