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Geochemical behaviour of trace elements during fractional crystallization and crustal assimilation of the felsic alkaline magmas of the state of Rio de Janeiro, Brazil

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ABSTRACT

This paper presents geochemical behaviour of trace elements of the felsic alkaline rocks of the state of Rio de Janeiro, Brazil, with special attention of fractional crystallization and continental crust assimilation. Fractionation of leucite and K-feldspar increases Rb/K and decreases K2O/(K2O+Na2O). Primitive nepheline syenite magmas have low Zr/TiO2, Sr, and Ba. On the Nb/Y vs. Zr/TiO2 diagram, these rocks are projected on the field of alkaline basalt, basanite, and nephelinite, instead of phonolite. Well-fractionated peralkaline nepheline syenite has high Zr/TiO2 but there are no zircon. The diagrams of silica saturation index (SSI) distinguish the trends originated form fractional crystallization and crustal assimilation. In the field of SSI<-200, Zr/TiO2 and Ba/Sr have negative correlations to SSI in consequence of fractional crystallization. In the field of SSI>-200, they show positive correlations due to continental crust assimilation. Total REEs (Rare Earth Elements) is nearly 10 times that of granitic rocks, but LaN/SmN and LaN/YbN are similar. REE trend is linear and Eu anomaly is irrelevant. The pegmatitic liquid generated by country rock partial melting is SiO2-oversaturated and peraluminous with high Ba, Sr, Ba/Sr, Zr/TiO2, and SSI, with high content of fluids. This model justifies the peraluminous and SiO2-oversaturated composition of the rocks with relevant effects of continental crust assimilation.

Key words: nepheline syenite, alkaline syenite, trace elements, rare earth elements, fractional crystallization, continental crust assimilation.

INTRODUCTION

Geochemical behaviour of trace elements are sometimes different from major elements. Absolute and relative abundance of determined trace elements, such as Zr, Y, Nb, Ga, and Sc, are stable during alteration processes of metamorphism, hydrothermalism and weathering. The behaviour of immobile elements are sometimes related to those of major elements. For example, Zr/Ti is related to SiO_2 and Nb/Y is related to alkaline elements (e.g. Floyd and Winchester 1975, Winchester and Floyd 1977). The content can be used as a proxy for K_2O and Co content for SiO_2 (Hastie et al. 2007).

Immobile elements, especially high field strength elements (HFSE, e.g. Zr, Nb, Hf, Ta, and Ti), are convenient for classification of altered rocks

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(e.g. Gast 1968, Pearce and Cann 1973, Pearce and Parkinson 1993). There are some classification diagrams based on these elements (e.g. Winchester and Floyd 1977, Floyd and Winchester 1978). Original rock composition can be estimated even from strongly altered volcanic rock samples and ash-fall deposits (e.g. Caddah et al. 1994, Alves 2005, Kitsopoulos 2010). On the other hand, large ion lithophile elements (LILE, e.g. K, Rb, Sr, and Ba) and the light rare earth elements, especially Ba, are mobile and easily transferred by fluids. In addition, certain elements, such as REEs, show geochemical behaviour different from major elements, providing unique information on magma generation and evolution.

Geochemistry of immobile elements is also useful to estimate tectonic settings of basaltic and granitic rocks (e.g. Hanson 1978, Pearce et al. 1984, Pearce 1996). However, detailed behaviour of trace elements in alkaline rocks are unknown (e.g. Wolff 1984, Bryan 2006). Specifically, geochemical studies on felsic alkaline rocks, such as nepheline syenite, alkaline syenite, phonolite, and trachyte are few.

Recent geochemical researches for the Cretaceous to Early Cenozoic felsic alkaline rocks of the state of Rio de Janeiro, Brazil, have accumulated a significant amount of major and trace element data, which are enough for the genetic discussions (e.g. Motoki et al. 2010, Sichel et al. 2012). This paper presents the behaviour of trace and rare earth elements of these alkaline rocks with additional analytical data. Based on them, the authors discuss fractional crystallization and continental crust assimilation of the nepheline syenite magmas.

SERRA DO MAR ALKALINE MAGMATIC PROVINCE

Felsic alkaline rocks, such as nepheline syenite, alkaline syenite, phonolite, and trachyte, are rare in field occurrences. In the coastal region of the state of Rio de Janeiro and São Paulo, southeastern Brazil, there are about 20 occurrences of alkaline intrusive bodies, called Serra do Mar alkaline rock province (Ulbrich and Gomes 1981). These bodies intrude into Pan-African metamorphic basement of granitic orthogneiss and pelitic paragneiss (Heilbron et al. 2000, Valladares et al. 2008), post-tectonic granite (Valeriano et al. 2011), silicified tectonic breccia (Motoki et al. 2011), and Early Cretaceous mafic dykes (Guedes et al. 2005, Motoki et al. 2009).

The Serra do Mar alkaline rock province is constituted by two magmatic alignments (Fig. 1a): A) Poços de Caldas-Cabo Frio and B) Monte de Trigo-Vitória Island. In spite of the weathering vulnerability of the constituent minerals, they have strong erosive resistance originated from mechanical strength and weathering passivity (Petrakis et al. 2010). Therefore, the intrusive bodies form massifs of 300 m to 1500 m of relative height, called alkaline massifs (Aires et al. 2012).

Poços de Caldas-Cabo Frio alignment is about 490 km long and has WNW-ESE trend (Fig. 1a, alignment A). Intrusive bodies are composed mainly of nepheline syenite and trachyte, with local occurrences of alkaline syenite on the first and lamprophyre dykes on the second. (e.g. Ulbrich 1984, Brotzu et al. 1997, 2007, Motoki et al. 2007a). They expose bottom level of flattened funnel-shaped plutons (Motoki and Sichel 2006, 2008). The fission track datings for apatite indicate that the present exposures correspond to the subvolcanic intrusive bodies of about 3 km of depth from the surface of the intrusive time. The felsic alkaline bodies of the state of Rio de Janeiro belong on Poços de Caldas-Cabo Frio alignment (Fig. 1b).

The Monte de Trigo-Vitória Island alignment is about 60 km long and of WNW-ESE trend (Fig. 1a, alignment B). Different from the Poços de Caldas-Cabo Frio alignment, the intrusions are constituted mainly by alkaline syenite with eventual presence of modal quartz (Alves and Gomes 2001).

Some of the intrusive complexes of Poços de Caldas-Cabo Frio alignment are associated with

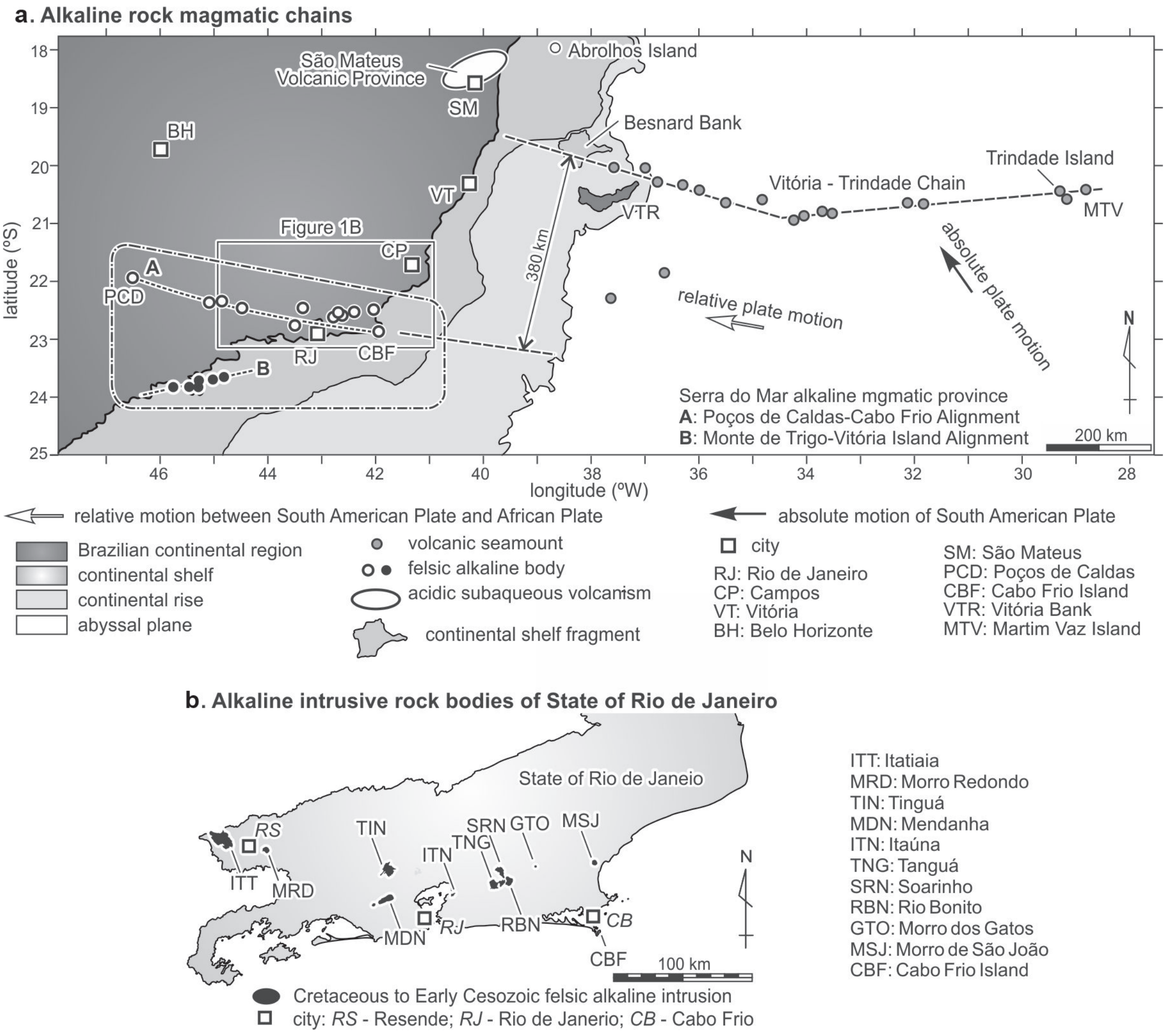


Figure 1 - Locality map for the Cretaceous to Early Cenozoic felsic alkaline intrusive bodies of the state of Rio de Janeiro, modified from Sichel et al. (2012): **a**) Alkaline magmatic alignments of Serra do Mar province and Vitória-Trindade Chain; **b**) Felsic alkaline intrusive bodies of the state of Rio de Janeiro. The subaqueous pyroclastic flows of the São Mateus Volcanic Province follow that specified by Novais et al. (2007).

strongly welded and secondary-flowed vent-filling subvolcanic tuff breccia at Poços de Caldas (Ulbrich 1984, Loureiro and Santos 1988), Itatiaia (Brotzu et al. 1997), Mendanha (Motoki et al. 2007b), Itaúna (Motoki et al. 2008), Morro dos Gatos (Motoki et al. 2012, Geraldes et al. 2013), and Cabo Frio Island (Sichel et al. 2008) complexes.

BEHAVIOUR OF THE MAJOR ELEMENTS

The geochemical data for the present paper are originated from Valença (1980), Motoki et al. (2010, 2013) and Sichel et al. (2012). Additional trace element data of Tanguá intrusive complex are presented (Table I). The samples were analysed by atomic absorption (Valença 1980), X-ray fluorescence, ICP-AES (Motoki et al. 2010, Sichel et al. 2012) for major and trace elements, and ICP-MS (Motoki et al. 2010, Sichel et al. 2012; present data) for trace and rare earth elements.

The geochemical behaviour of major elements of these alkaline rocks are widely different from non-alkaline rocks, such as granite and granodiorite.

TABLE I
New analyses of trace (A) and rare earth elements (B) for nepheline syenite of Tanguá intrusive complex, state of Rio de Janeiro, Brazil. The major elements of the same samples were presented by Sichel et al. (2012).

TABLE IA
Trace elements for nepheline syenite of Tanguá complex.

(ppm)	Tg-2	TNG32	TNG36A	TNG37	TNG38	TNG39A	TNG39B	Tg-1	TNG41	TNG42	TNG43	TNG44	TNG45	TNG46	TNG47
Ag	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
As	5	0	0	0	0	0	0	0	0	0	11	0	0	0	0
B	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Be	2	1	0	1	1	0	2	1	2	1	2	0	1	1	1
Bi	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ca	0.79	0.74	0.77	0.7	0.82	0.85	0.96	0.8	1.02	1.14	0.93	0.88	0.87	0.73	0.88
Cd	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Co	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fe	2.35	2.37	2.3	2.58	2.47	2.18	2.42	1.91	2.67	2.59	2.47	2.22	2.11	1.82	2.09
K	0.51	0.56	0.54	0.95	0.51	0.6	0.53	0.81	0.76	0.72	0.52	0.42	0.58	0.56	0.52
Li	3	4	2	10	2	2	4	3	3	3	5	2	3	3	4
Mg	0.19	0.1	0.1	0.26	0.11	0.19	0.14	0.16	0.15	0.17	0.12	0.23	0.13	0.09	0.13
Mn	0.1	0.09	0.07	0.1	0.05	0.06	0.06	0.06	0.07	0.07	0.13	0.06	0.06	0.05	0.06
Mo	10	7	13	10	3	9	4	12	6	5	1	9	4	4	7
Na	1.04	1.31	1.44	1.49	1.89	1.29	2.27	1.08	2.2	2.22	1.03	0.72	2.44	2.73	2.58
P	0.05	0.04	0.07	0.06	0.11	0.06	0.1	0.03	0.09	0.1	0.02	0.08	0.07	0.06	0.06
Sb	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sc	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Se	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ti	0.25	0.2	0.24	0.31	0.19	0.28	0.22	0.21	0.29	0.29	0.19	0.3	0.21	0.19	0.23
Tl	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
W	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Zr	104	107	106	116	92	98	146	115	213	169	112	105	122	115	210
Cs	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cl	0	0	339	196	1036	204	725	288	686	809	301	0	0	415	1455
Hf	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ta	69	0	26	16	15	29	18	0	13	0	13	19	16	10	0
Ga	19	22	15	22	65	19	23	59	22	15	12	8	14	14	23

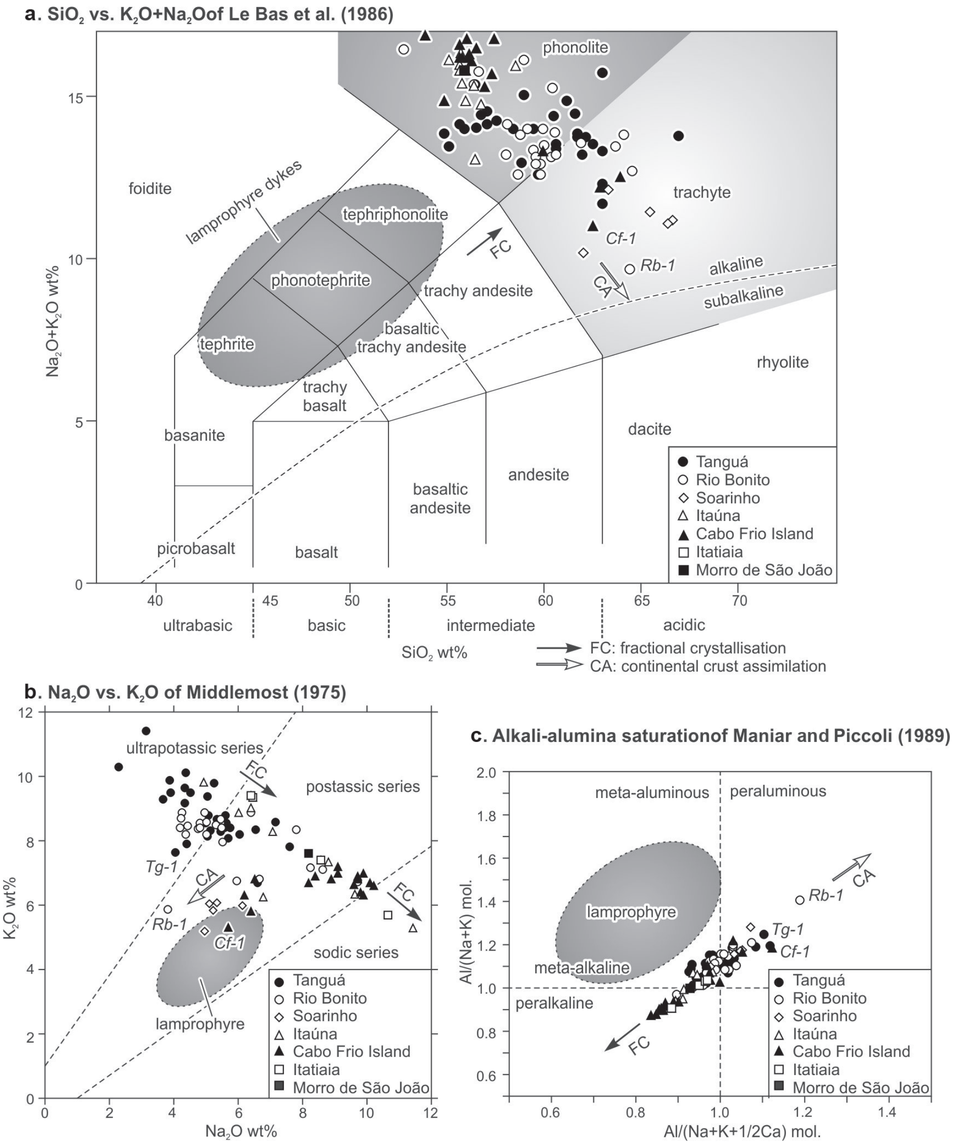
Table IB
Rare earth elements for nepheline syenite of Tanguá complex. The total REEs is in ppm.

	Nepheline syenite of Tanguá														
(ppm)	Tg-2	TNG32	TNG36 A	TNG37	TNG38	TNG39A	TNG39B	Tg-1	TNG41	TNG42	TNG43	TNG44	TNG45	TNG46	TNG47
La	256.1	154.3	181.4	164.3	158.7	175.2	199.5								
Ce	589.4	291.1	362.1	346.3	300.3	352.8	362.7	112.7	192.8	194.6	350.2	207.7	165.6	153.5	155.9
Pr	84.77	35.18	46.74	50.29	36.73	43.44	41.87	197.8	348.9	357.3	354	440.9	279.2	266.3	270.2
Nd	308.5	122.2	161.4	194.9	125.6	146.1	134.8	23.87	40.95	42.05	64.17	58.08	30.98	29.76	30.78
Sm	49.1	16.7	23.8	32.8	18.4	21.1	19.7	74.8	136	143.4	194.3	192.8	101.3	93.5	94.1
Eu	8.3	4.9	8.28	8.69	6.08	6.5	6.71	10.8	19	20.5	23.1	27.9	13.7	12.9	14.3
Gd	35.43	12.25	17.58	23.72	13.89	15.62	15.2	3.2	6.58	6.77	6.14	7.79	5.17	4.73	5.19
Tb	4.87	1.62	2.65	3.24	1.84	2.26	1.89	7.55	14.7	15.54	18.8	20.71	10.31	9.91	10.72
Dy	26.79	9.91	14	16.76	10.39	12.61	11.35	0.97	1.93	1.96	2.67	2.96	1.34	1.12	1.51
Ho	3.24	1.25	1.84	2	1.32	1.77	1.58	6.21	11.19	11.83	16.51	16.22	8.29	7.94	8.58
Er	8.07	3.65	5	5.02	3.63	4.73	4.47	0.71	1.55	1.5	2.01	2.02	1.11	1.15	1.17
Tm	0.81	0.5	0.6	0.66	0.37	0.66	0.48	2.25	4.33	4.53	7.15	6.17	3.35	3.42	3.23
Yb	5.3	2.8	3.8	3.3	3.1	3.6	3.7	0.24	0.45	0.57	0.91	0.71	0.46	0.53	0.35
Lu	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1.8	3.5	3.4	5.4	4.3	3	2.8	2.8
T. REEs	1381	656	829	852	680	786	804	443	782	804	1046	989	624	588	599
La_N/Sm_N	3.26	5.77	4.76	3.13	5.39	5.19	6.32	6.52	6.34	5.93	9.47	4.65	7.55	7.43	6.81
La_N/Yb_N	32.83	37.44	32.43	33.82	34.78	33.06	36.63	42.53	37.42	38.88	44.06	32.81	37.50	37.24	37.82
Gd_N/Yb_N	5.41	3.54	3.74	5.82	3.63	3.51	3.32	3.39	3.40	3.70	2.82	3.90	2.78	2.86	3.10
Eu/Eu*	0.49	0.85	1.01	0.77	0.95	0.89	0.98	0.86	0.99	0.95	0.76	0.81	1.09	1.05	1.05
(Sm/ Sm*)*	1.18	0.70	0.80	1.24	0.73	0.74	0.63	0.65	0.64	0.69	0.45	0.82	0.53	0.54	0.59

N.A.: Not analyzed.

The SiO_2 content ranges from 52.43 to 63.57 wt%, covering almost the entire zone of the intermediate rocks. Such a variation is attributed generally to different grades of mafic mineral fractionation. If so, these rocks should form a positive correlation trend in SiO_2 vs. Na_2O+K_2O diagram. However, in fact, they form a negative trend (Fig. 2a) and the fractional crystallization is not a main factor of the geochemical variation. The sample Cf-1 of Cabo Frio Island complex, Rb-1 of Rio Bonito complex, and the rocks of Soarinho complex have characteristically low Na_2O+K_2O relative to SiO_2. These rocks have Norm quartz, being similar to granitic rocks. The Cf-1 was collected from border of the intrusive bodies and the Rb-1 was extracted from a pyroclastic dyke.

The felsic alkaline rocks have high K_2O relative to Na_2O. Most of the samples of Tanguá and Rio


a. SiO_2 vs. $K_2O+Na_2O$of Le Bas et al. (1986)

b. Na_2O vs. K_2O of Middlemost (1975)

c. Alkali-alumina saturationof Maniar and Piccoli (1989)

Figure 2 - Geochemical classification diagrams for felsic alkaline rocks of the state of Rio de Janeiro: **a**) Na_2O+K_2O vs. SiO_2 (wt%) diagram of Le Bas et al. (1986); **b**) Na_2O vs. K_2O wt% of Middlemost (1975); **c**) Alkali-alumina saturation diagram of Maniar and Piccoli (1989). The data are originated from Valença (1980), Motoki et al. (2010, 2013), and Sichel et al. (2012).

Bonito complexes are ultrapotassic and those of Cabo Frio Island complex are potassic (Fig. 2b). The samples from the central part of the intrusive bodies, especially those of Cabo Frio Island, are peralkaline nepheline syenite (Fig. 2c). In contrast, the samples of Soarinho, Rb-1 of Rio Bonito, Tg-1 of Tanguá, and Cf-1 of Cabo Frio Island have remarkably low alkalis and high alumina. The Tg-1 is an alkaline syenite collected from the contact zone of Tanguá intrusive body.

The geochemical data range from strongly SiO_2-undersaturated alkaline composition to oversaturated non-alkaline composition, forming a continuous trend. Such a distribution, crossing over the thermal divide, is unable to be explained by fractional crystallization. Motoki et al. (2010, 2013) and Sichel et al. (2012) pointed out the effects of assimilation of continental crust country rocks. The relation between fractional crystallization and crustal assimilation for these alkaline rocks is expressed by the residual diagram of Norm quartz, nepheline, and kaliophilite (Fig. 3).

The relatively primitive nepheline syenite magma has high $K_2O/(Na_2O+K_2O)$ wt%, low (Na+K)/Al mol. and crystallizes leucite. This mineral is observed now as pseudoleucite in Itatiaia, Tanguá, and Morro de São João bodies. According to the fractionation of leucite, the residual liquid changes from potassic to sodic, and the magma composition approaches the cotectic curve, called Stage 1. On the cotectic curve, the residual liquid continues to become more sodic due to K-rich alkaline feldspar fractionation, called Stage 2. The residual magma becomes more SiO_2-undersaturated, more peralkaline, and more sodic than potassic. It can arrive at the area close to the terminal point (Fig. 3, *Ns*). At any phase of Stage 2, crustal assimilation events can take place, transforming the magma composition from SiO_2-undersaturated to oversaturated and form peralkaline to peraluminous, called Stage 3. The samples Rb-1, Cf-1, and those of Soarinho complex, have high grade crustal assimilation, with a ratio of about 50 wt%.

Continental crust granite and orthogneiss are SiO_2-oversaturated and meta-aluminous, and pelitic paragneiss is SiO_2-oversaturated and peraluminous. These country rocks have geochemical characteristics opposite to nepheline syenite in alkali-silica and alkali-alumina relations. The geochemical distribution trend of these rocks crosses over the quartz-nepheline and the aegirine-

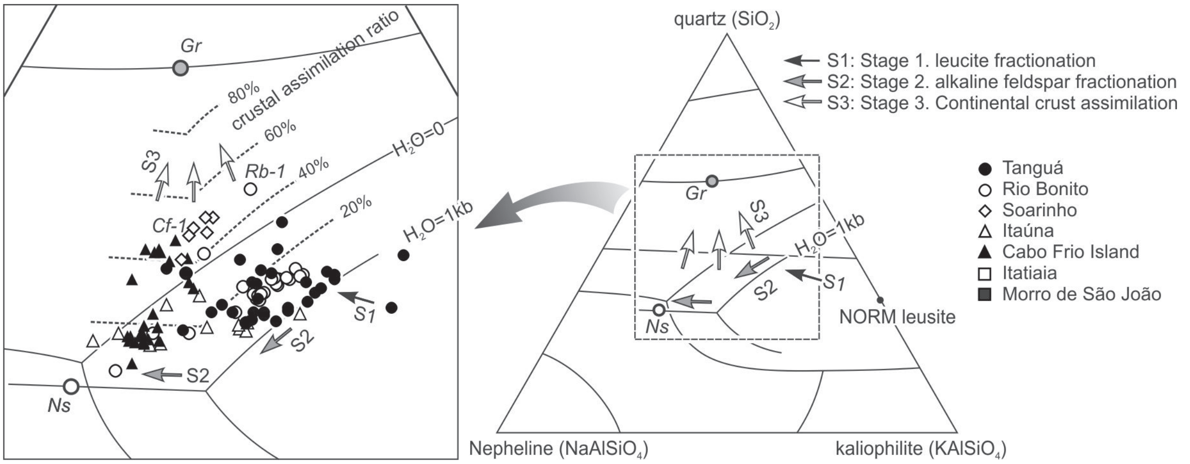


Figure 3 - Projection of the alkaline rocks of state of Rio de Janeiro on the residual diagram of Norm quartz, nepheline, and kaliophilite (Hamilton and MacKenzie 1960) and geochemical evolution of the nepheline syenite magma, modified from Sichel et al. (2012).

muscovite thermodynamic incompatibilities (Fig. 4). The silica saturation index (SSI) on this figure expresses the degree of its quantitative grade of felsic alkaline rocks (Motoki et al. 2010). The rocks with SSI<0 are SiO_2-undersaturated with Norm nepheline, and those with (Na+K)/Al mol. >1.0 are peralkaline with Norm acmite. On the other hand, the felsic rocks with SSI>0 are SiO_2-oversaturated with Norm quartz, and those with (Na+K)/Al mol. <1.0 are meta-aluminous or peraluminous with eventual occurrence of Norm corundum. The samples Tg-1, Cf-1, Cf-2, and those of Soarinho complex have SSI>0 and (Na+K)/Al mol. <1.0, and are projected on the domain and area of non-alkaline rocks. They are under strong effects of crustal assimilation and occur generally along the border zone of the intrusive complexes. The subvolcanic pyroclastic rocks, such as Rb-1, a strongly SiO_2-oversaturated and peraluminous composition.

The degree of the fractionation of leucite and K-rich alkaline feldspar in Stage 1 and Stage 2 is represented by $K_2O/(K_2O+Na_2O)$ wt% ratio, and that of mafic minerals, by Mg#, Mg/(Mg+Fe) mol. There is weak positive correlation between $K_2O/(K_2O+Na_2O)$ and Mg#. This observation suggests that both of the fractionation processes occurred in the nepheline syenite magma but not so concurrently. The fractionation of mafic minerals took place at an early stage and those of alkaline feldspar at a later stage. The peralkalinicity represented by (Na+K)/Al mol. has a good correlation to $K_2O/(K_2O+Na_2O)$. By means of the potassium alkaline feldspar fractionation during Stage 2, the residual magma became more sodic, more SiO_2-undersaturated, and more peralkaline.

The grade of crustal assimilation during Stage 3 is expressed by the SSI. Owing to this process, the magma becomes less SiO_2-undersaturated and less peralkaline. In extreme cases, the magma develops into SiO_2-oversaturated and peraluminous.

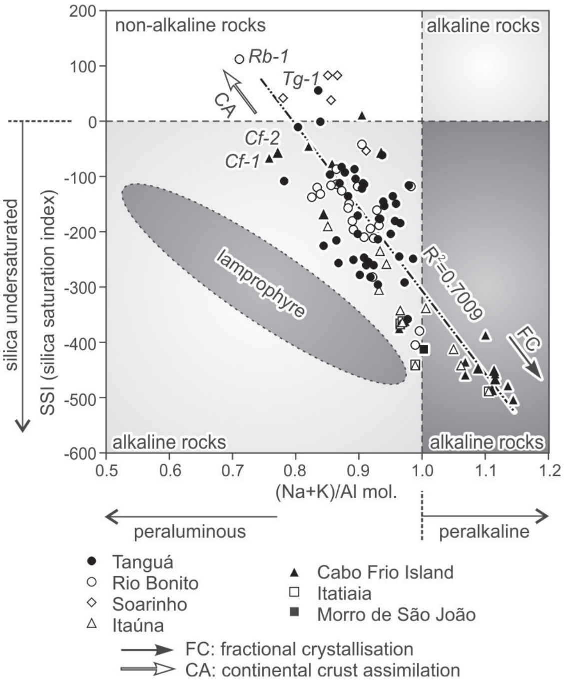


Figure 4 - SSI (silica saturation index; Motoki et al. 2010) vs. (Na+K)/Al mol. diagram for the felsic alkaline rocks of the state of Rio de Janeiro, modified from Sichel et al. (2012). $SSI=1000(SiO_2/60,0835-Al_2O_3/101,9601-5(Na_2O/61,9785+K_2O/94,1956)-CaO/56,077-MgO/40,304-MnO/70,937-FeO/71,844+2Fe_2O_3/159,687)$ wt%.

The continuous geochemical distribution crossing over the thermodynamic incompatibilities cannot be originated from fractional crystallization. However, it can be formed by the magma super-reheating (Motoki et al. 2010, 2013, Sichel et al. 2012). The SiO_2-undersaturated hot magma can melt the wall rock generating SiO_2-oversaturated magma. When the magma temperature is superior to the liquidus, these magmas can mix, forming thermodynamically unstable alkaline syenite. The resorption shape of clinopyroxene in the nepheline syenite and alkaline syenite, supports this model. The volatile materials extracted from the country rocks by the nepheline syenite magma heat, decrease the liquidus temperature, which makes the magma mixture of incompatible composition easier. The reaction rim of amphibole around clinopyroxene in the syenitic rocks corroborates this idea.

HIGH-FIELD STRENGTH ELEMENTS

High field strength elements (HFSE) are present generally in accessory minerals of high density, high crystallization temperature, and high resistance to alteration, such as zircon, titanite, apatite, and monazite. The concentrations and relative abundances of HSFE are stable during weathering, hydrothermalism and metamorphism, so they are called immobile elements. The HFSEs are useful for geochemical classification and geotectonic discrimination even for altered samples of igneous rocks.

The HSFE-based classifications for the felsic alkaline rocks have a relevant relation to those based on major elements. The nepheline syenite, alkaline syenite, phonolite, and trachyte of the intrusive complexes of Cabo Frio Island, Itaúna, Itatiaia, and Morro de São João are projected on the field of phonolite and trachyte (Fig. 5a, b). However, the rocks of Tanguá and Rio Bonito complexes have unexpectedly low Zr and are projected on the field of trachy-andesite, andesite, basalt, alkaline basalt, and basanite (Fig. 5a, b, d). The felsic alkaline rocks with high-grade continental crust assimilation tend to be plotted on the areas close to the domains of non-alkaline rocks, as rhyolite and dacite. The HFSE behaviour can express fractional crystallization of the felsic alkaline magmas, but it is difficult to show the continental crust assimilation.

Figure 6a presents tectonic setting discrimination diagrams based on trace elements. Most of the studied rocks are projected on the within-plate

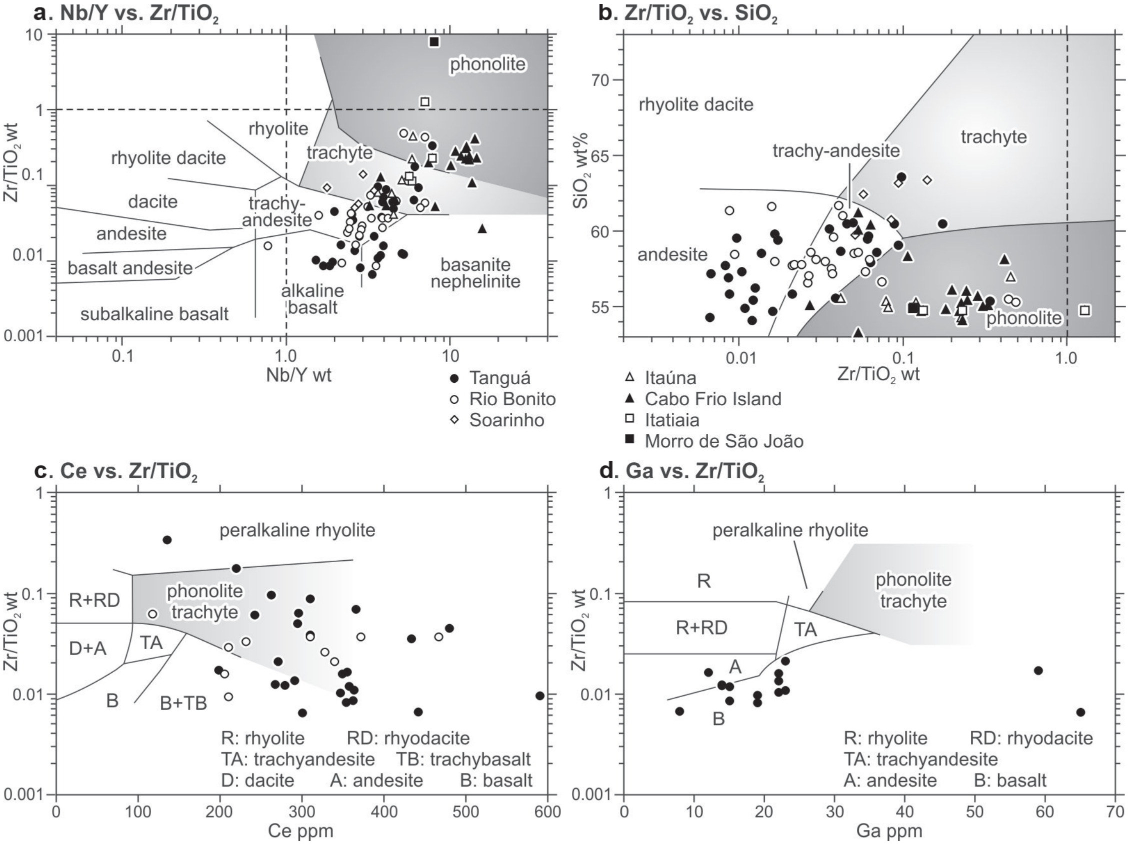


Figure 5 - Classification of the felsic alkaline rocks of the state of Rio de Janeiro based on immobile elements (Winchester and Floyd 1977): **a**) Nb/Y vs. Zr/TiO$_2$; **b**) Zr/TiO$_2$ vs. SiO$_2$; **c**) Ce vs. Zr/TiO$_2$; **d**) Ga vs. Zr/TiO$_2$. The geochemical data follow that of Valença (1980), Motoki et al. (2010, 2013), and Sichel et al. (2012).

magmatism area. The samples of Cabo Frio Island and Itatiaia intrusive complexes have high Nb and Rb and those of Rio Bonito and Tanguá have lower Nb. The samples of Tanguá are less fractionated, with high $K_2O/(K_2O+Na_2O)$, and have notably low Rb. The samples Rb-1 and Tg-1 are plotted on the fields of non-alkaline rocks of volcanic arc and syn-collision granite, because of a great influence of continental crust assimilation.

The R_1 vs. R_2 diagram (Batchelor and Bowden 1985) shows that most of the data are projected in the area of intraplate alkaline rocks (Fig. 6b). The low R_1 values are due to the high alkalis relative to silica. Some of the samples with strong influence of continental crust assimilation, such as Rb-1, Tg-1, and those of Soarinho complex, are projected in the domain of late tectonic granite.

LARGE ION LITHOPHILE ELEMENTS

The large ion lithophile elements (LILE) are present generally in major silicate minerals, such as feldspars and micas. These elements are highly mobile during weathering and hydrothermal alteration, and are convenient for the studies of partial melting, fractional crystallization, metassomatic alteration, and fluid component behaviour.

Some of the LILEs provide important information about the magmatic evolution process. For example, Rb/K ratio indicates the grade of magma fractionation (e.g. Abbott 1966, Shaw 1968) and Rb/Ba and Rb/Sr are plagioclase fractionation indicators. Figure 7 shows variation diagrams for Rb/K mol., Rb/Ba mol., and Zr/TiO_2. The former two ratios are based on LILE and the

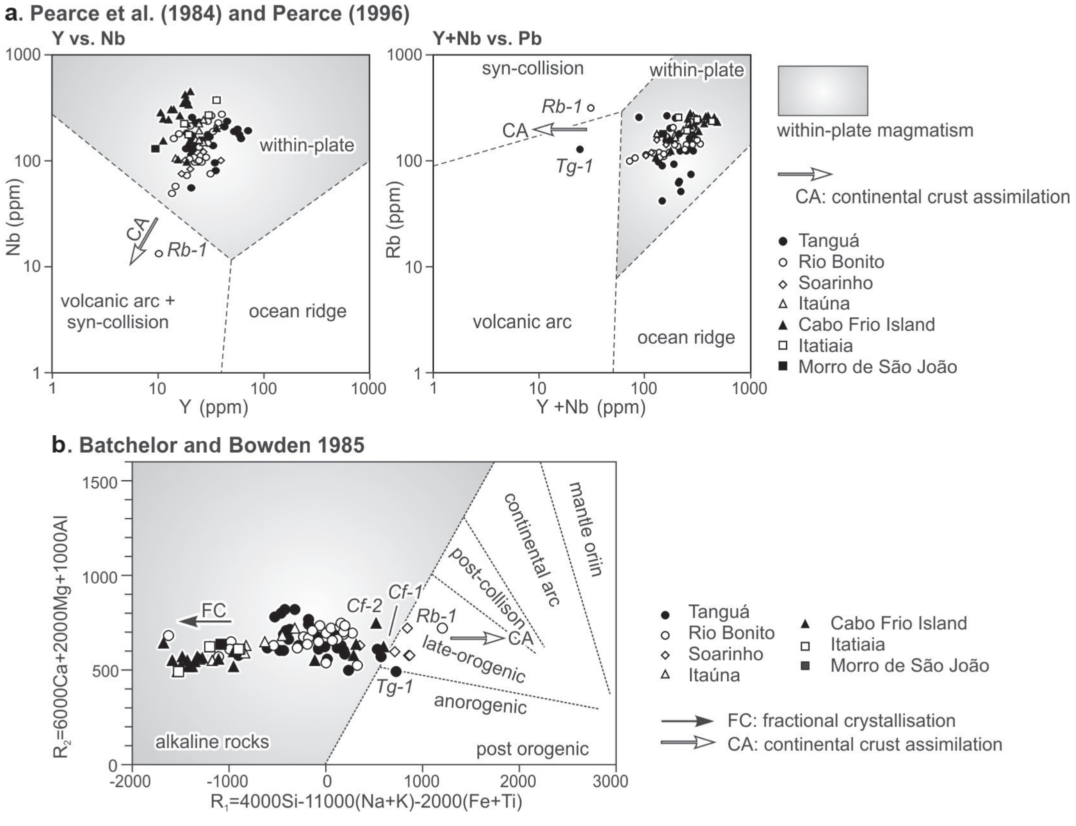


Figure 6 - Tectonic environment discrimination diagrams for the felsic alkaline rocks of the state of Rio de Janeiro after: **a**) Pearce et al. (1984), Pearce (1996); **b**) Batchelor and Bowden (1985).

latter, on HFSE. The abscissa $K_2O/(K_2O+Na_2O)$ wt% represents degree of fractional crystallization of leucite and K-rich alkaline feldspar during Stage 1 and Stage 2 (Fig. 3).

The Rb/K ratios for the felsic alkaline rocks have a good negative correlation to $K_2O/(K_2O+Na_2O)$, with $R^2=0.461$ (Fig. 7a), which is of the opposite sense to non-alkaline granitic rocks. The samples of Cabo Frio complex have high Rb/K and those of Tanguá and Rio Bonito have low Rb/K. The HFSE-based parameter Zr/TiO_2 also shows a similar characteristic, with $R^2=0.562$ (Fig. 7c). The concentration of Sr and Ba, especially Ba, are widely variable, and Rb/Sr and Rb/Ba show no clear correlation to $K_2O/(K_2O+Na_2O)$ (Fig. 7b). These observations suggest that the fractionation of leucite and K-rich alkaline feldspar is a relevant and the plagioclase fractionation is not very expressive. Petrographic observations indicate that plagioclase is quite rare in these rocks (Sichel et al. 2012).

On the other hand, some LILE contents provide information of the crustal assimilation process. The Sr and Ba contents tend to increase according to the SSI. That could explain by, increase of continental crust assimilation. Their upper limits elevate linearly by SSI (Fig. 8a, b, dashed line). However, the concentrations of these elements are distributed randomly in the area beneath the upper limit,

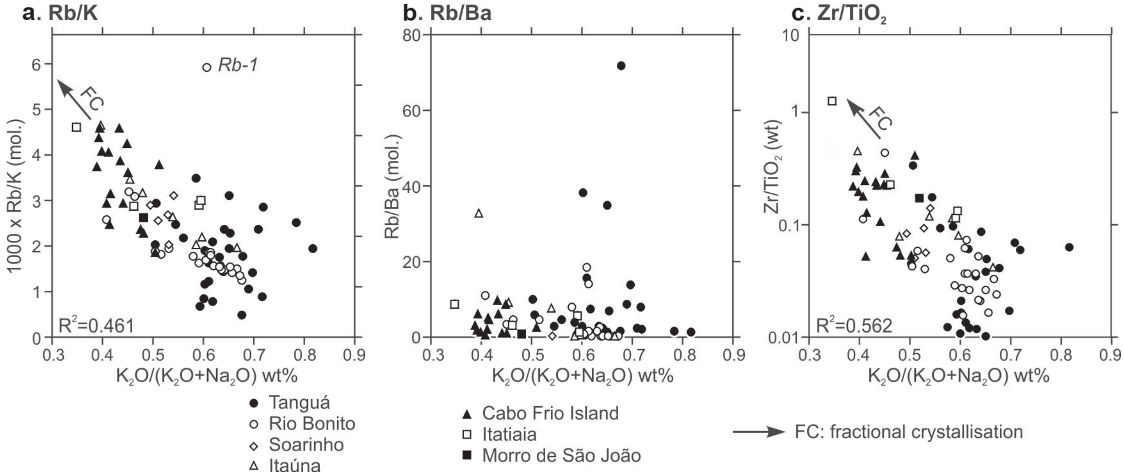


Figure 7 - Variation diagrams based on trace elements for the felsic alkaline rocks of the state of Rio de Janeiro: **a**) Rb/K mol.; **b**) Rb/Ba mol.; **c**) Zr/TiO_2 wt. The abscissa $K_2O/(K_2O+Na_2O)$ wt% represents fractionation crystallization grade of felsic minerals.

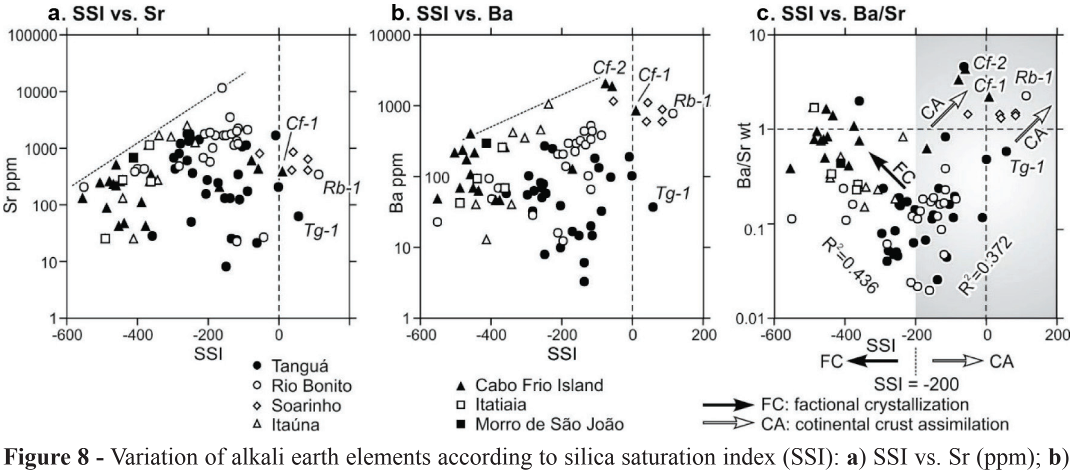


Figure 8 - Variation of alkali earth elements according to silica saturation index (SSI): **a**) SSI vs. Sr (ppm); **b**) SSI vs. Ba (ppm); **c**) SSI vs. Ba/Sr (ppm ratio).

probably due to high mobility and heterogeneous distribution of these elements in these alkaline rocks.

The Ba/Sr diagram distinguishes the trends of fractionation crystallization and continental crust assimilation. In the area of SSI<-200, this ratio increases according to the reduction of SSI due to fractional crystallization, with $R^2=0.372$ (Fig. 8c, FC). On the other hand, in the area of SSI>-200, Ba/Sr increases according to elevation of SSI because of continental crust assimilation (Fig. 8c, CA), with $R^2=0.436$. The critical point is SSI=-200. The samples Rb-1, Rg-1, Cf-1, Cf-2, and the rocks of Soarinho complex have high Ba, high Ba/Sr, and high SSI because of relevant influence of fluids and continental crust assimilation.

The diagrams of HFSE vs. LILE for basaltic and granitic rocks can discriminate magma source and tectonic condition (e.g. Floyd and Winchester 1975, Whale et al. 1987, Förster et al. 1997). Figure 9 shows the diagrams of Nb and Rb. The studied felsic alkaline rocks are projected in the area between volcanic arcs (Fig. 9a, VA) and within plate magmatisms (WP). Most of them are distributed along the WP line. Exceptionally, the sample Rb-1 is plotted on the VA line, which corresponds to granite of subduction zones and continental collision zones. This was probably due to strong effects of continental crust assimilation. The Nb/Y vs. Rb/K diagram confirms these observations (Fig. 9b).

RARE EARTH ELEMENTS

Rare earth element analyses are available for the selected samples of Tanguá and Rio Bonito complex (Fig. 10a, b). The total REEs is high, in average 669 ppm, which is about 10 times higher than that of granitic rocks. The average La_N/Sm_N and La_N/Yb_N (CI chondrite normalized values) are, respectively, 6.26 and 47.6, being similar to granitic rocks. Most of the samples have linear REE variation from La to Yb (Fig. 10c).

The samples Tg-6 and Rb-2 have lower total REEs, with respective concentrations of 241 and 247 ppm. The former has lower La, Ce, and Pr than the other samples, with lower La_N/Sm_N of 2.61, and lower heavy REEs especially from Dy to Yd, with higher Gd_N/Yb_N of 10.31, showing a convex-upward REE pattern. In contrast, the latter have low Nd to Dy, with higher La_N/Sm_N of 18.18 and lower Gd_N/Yb_N of 1.64, demonstrating a concave REE pattern. These samples have no remarkable geochemical features in major elements.

The difference of the two samples is well expressed on the Gd_N/Yb_N vs. La_N/Sm_N diagram (Fig. 10d). The projected data of the analyzed rocks form a well-defined linear trend with $R^2=0.644$ in direction perpendicular to the line of $La_N/Sm_N = Gd_N/Yb_N$ (dashed line on the figure). This observation indicates that the general enrichment of LREEs is almost the same for all of the samples but the REE pattern ranges widely from concave to convex.

Figure 11a proposes a new parameter which represents the convexity of the REE pattern: $(Sm/Sm^*)^*=10^{(\log(SmN)-(\log(LaN)\ x\ 8/13\ +\ \log(YbN)\ x\ 5/13))}$. The parameter $Sm/Sm^*=Sm_N/(La_N\ x\ 8/13 + Yb_N\ x\ 5/13)$, defined by similar way of Eu/Eu*, but it is of normal scale and does not represent the convexity on the log-scale REE diagram. The samples with (Sm/Sm*)*>1 have convex-upward REE pattern, and those with (Sm/Sm*)*<1, concave pattern. The samples Tg-2, Tg-3, Tg-4, and Tg-6 show convex REE pattern with respective (Sm/Sm*)* of 1.18, 1.38, 1.52, and 1.92 (Fig. 10c, 11b). The Rb-2 has notably concave pattern, (Sm/Sm*)*=0.23 with a remarkably low total REEs of 247 ppm.

Concave REE pattern is generally attributed to garnet fractionation (e.g. Kay and Gast 1973, Hawkesworth et al. 1979, Terakado 1980). They are generally mafic and ultramafic rocks and show heavy REE depletion represented by Er. However, the Rb-2 has no notable heavy REE depletion. The concave pattern is represented by low Sm, Eu, and Gd.

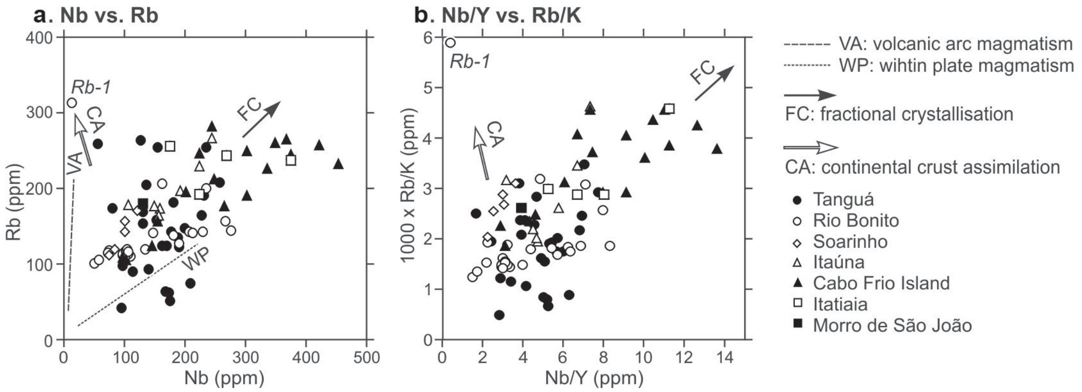


Figure 9 - Diagrams of LILE vs. HFSE: **a**) Nb vs. Rb (ppm); **b**) Nb/Y vs. Rb/K (ppm).

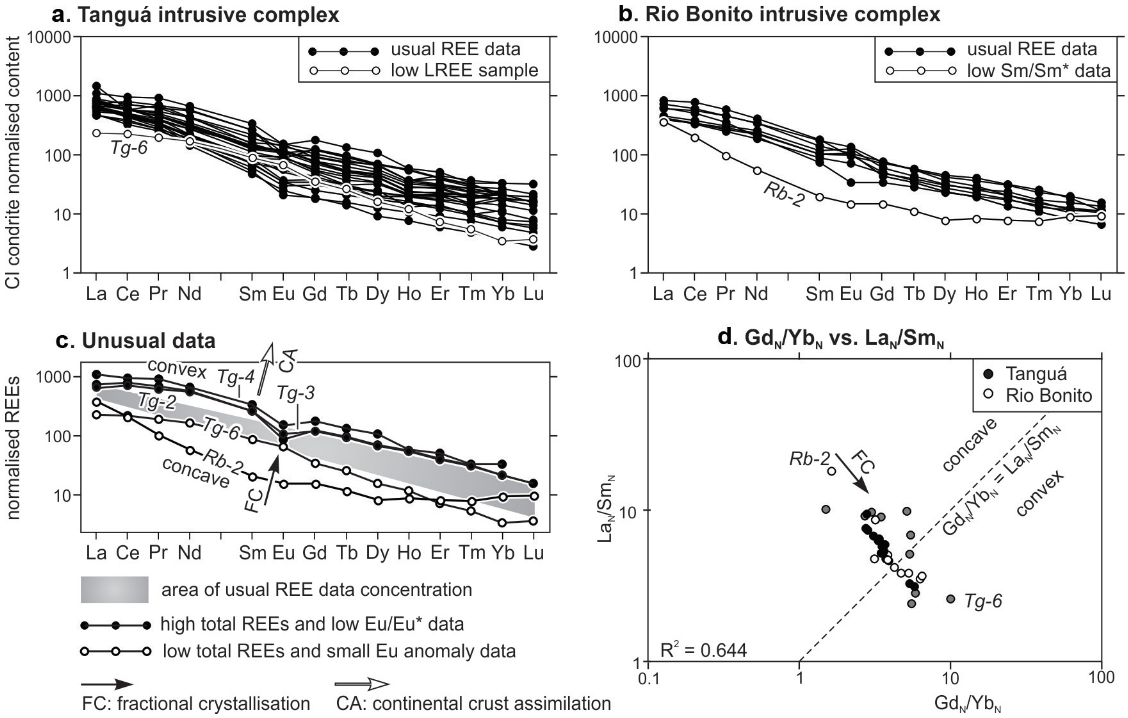


Figure 10 - Normalized rare earth elements for the felsic alkaline rocks of state of Rio de Janeiro: **a**) Tanguá intrusive complex; **b**) Rio Bonito intrusive complex; **c**) Unusual REE patterns; **d**) Gd_N/Yb_N vs. La_N/Sm_N diagram. The CI chondrite data are from McDonough and Sun (1995).

The Eu anomalies of these samples are generally small, with average Eu/Eu* of 0.95, and therefore, plagioclase fractionation is irrelevant. The diagram of total REEs vs. Eu/Eu* shows that the Eu anomaly has linear upper limit of negative gradient (Fig. 11c). The samples Tg-2, Tg-3, and Tg-4 of Tanguá complex have high total REEs, respectively 1381, 1018, and 934 ppm, and significant negative Eu anomaly, respectively Eu/Eu*=0.58, 0.45, and 0.56.

Total REE values increase either by fractional crystallization or by continental crust assimilation. The total REEs and (Sm/Sm*)* have no clear relation either to the magma fractionation indexes, such as La_N/Sm_N, La_N/Yb_N, Rb/K, Mg#, and $K_2O/(K_2O+Na_2O)$, or to the continental crust assimilation indexes, as SSI.

The samples of Tanguá complex present negative correlation on the diagram of SSI vs. Eu/Eu* with $R^2=0.431$ (Fig. 11d), indicating that

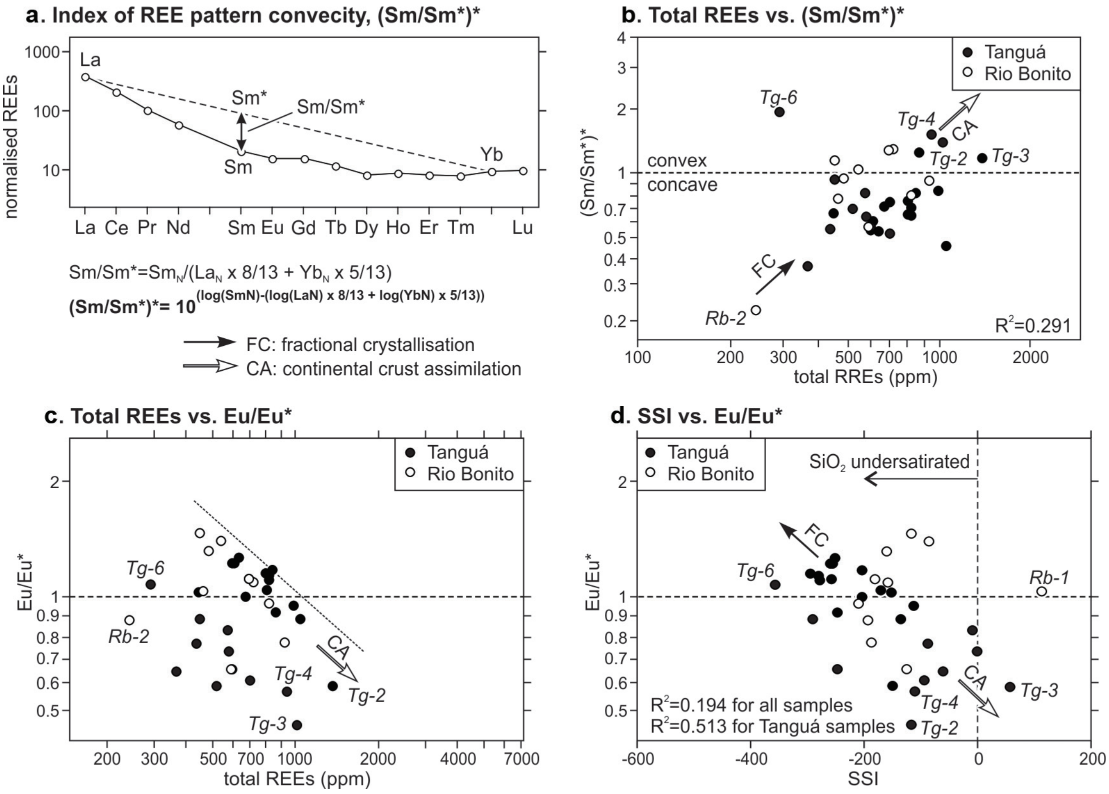


Figure 11 - (Sm/Sm*)* and Eu/Eu* for the samples of Tanguá and Rio Bonito alkaline complex, state of Rio de Janeiro: **a**) Definition of (Sm/Sm*)* which represents convexity of REE pattern; **b**) Total REEs vs. (Sm/Sm*)*; **c**) Total REEs vs. Eu/Eu*; **d**) SSI vs. Eu/Eu*.

the rocks with relevant crustal assimilation tend to show slight effect of plagioclase fractionation, being similar to granitic rocks.

The sample Rb-2 has characteristically low total REEs and concave pattern. The SSI of this sample is -195, $K_2O/(K_2O+Na_2O)$, wt% is 0.61, and the differentiation index is 84.26. These values suggest that this rock is originated from primitive nepheline syenite magma. In general, according to fractional crystallization total REEs increases, La_N/Sm_N decreases, (Sm/Sm*)* increases, and the REE pattern becomes from concave to linear. In spite of the geochemical indications of less fractionated nepheline syenite magma, the sample Rb-2 is extracted from a syenitic aplite vein. Similar phenomena are found in recent geochemical data of other syenitic aplite veins. This apparently controversial fact, is still in discussion.

In contrast, the sample, Tg-3 has high total REEs, convex pattern, and negative Eu anomaly. This sample has positive SSI of 56 and SiO_2-oversaturated with strong effects of continental crust assimilation. According to the assimilation, total REEs and (Sm/Sm*)* increases, Eu/Eu* decreases, and REE pattern becomes from linear to convex.

MULTI-ELEMENTS SPIDER DIAGRAMS

The felsic alkaline rocks of state of Rio de Janeiro are under complex effects of fractional crystallization and continental crust assimilation. The multi-elements spider diagrams (Fig. 12) show peculiar patterns. General concentrations of these incompatible elements are high, being more than 10 to 100 times of average oceanic island basalt. The normalized Sr, Ba, and P are 10 to 100 times lower

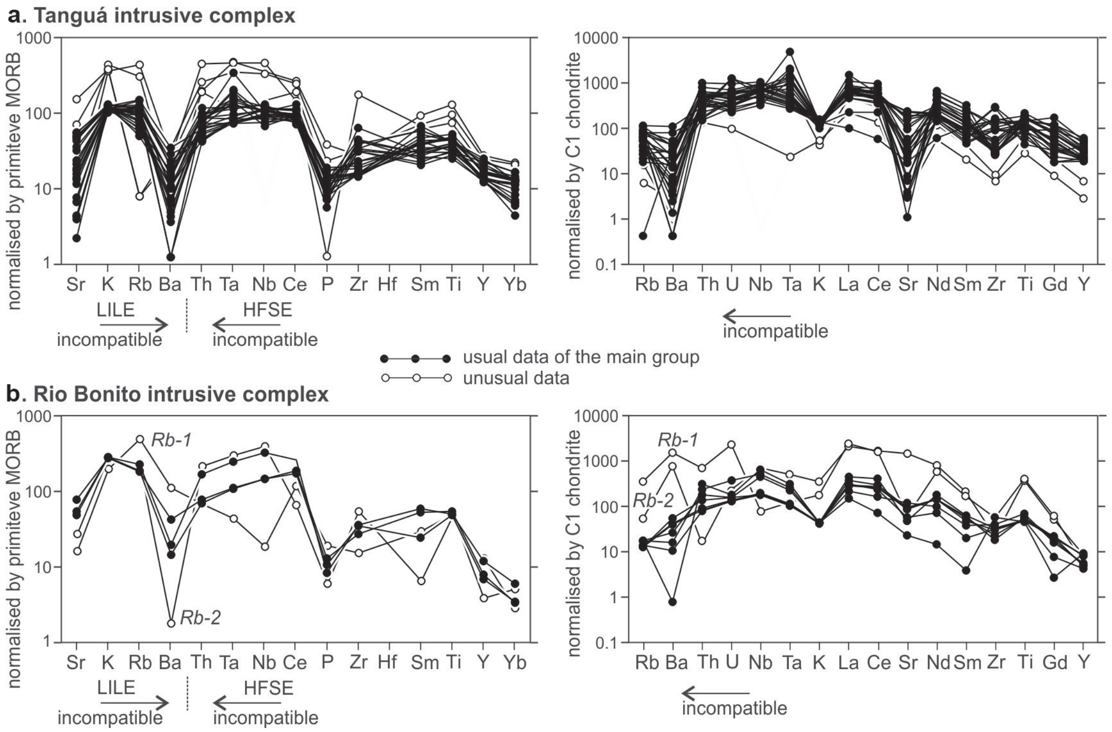


Figure 12 - Multi-elements spider diagrams for the samples of Tanguá and Rio Bonito intrusive complexes, state of Rio de Janeiro.

than the adjacent elements. The content variations of these three elements are very wide. The Ba variation could be due to highly heterogeneous fluid activity in the intrusive bodies, which is indicated by petrographic observations (Motoki et al. 2010).

Some samples show different trace element concentration patterns from the main group. The samples Rb-1 is characterized by very high incompatible elements and high Ba, showing strong influence of fluids. On the other hand, the Rb-2 is marked by low Ba. The major element behaviour indicate that the former sample is under strong effect of continental crust assimilation and the latter, originated from less fractionated nepheline syenite magma.

LOW ZR/TIO$_2$ OF THE PRIMITIVE NEPHELINE SYENITE

Nepheline syenite samples of Tanguá and Rio Bonito intrusive complexes have unexpectedly low Zr/TiO$_2$ ratio. Different from the other alkaline complexes, such as Cabo Frio Island, These rocks are projected on the areas of trachy-andesite, alkaline basalt, basanite, and nephelinite, and not of phonolite (Fig. 5a, b). There are two possible geneses for the low Zr/TiO$_2$: 1) The nepheline syenite magmas of this region have originally low Zr; 2) Zircon fractionation in the magma chamber decreased Zr content.

Figure 13 shows Zr/TiO$_2$ variation diagrams with abscissas of K$_2$O/(K$_2$O+Na$_2$O), (K+Na)/Al, and SSI. They represent, respectively, grade of fractional crystallization, peralkalinicity, and continental crust assimilation.

According to the fractionation of leucite during Stage 1 and that of K-rich alkaline feldspar during Stage 2, the Zr content and Zr/TiO$_2$ ratio increase (Fig. 13a). The Zr/TiO$_2$ increases also according to elevation of peralkalinicity (Fig. 13b). Although the peralkaline syenite has higher Zr content than

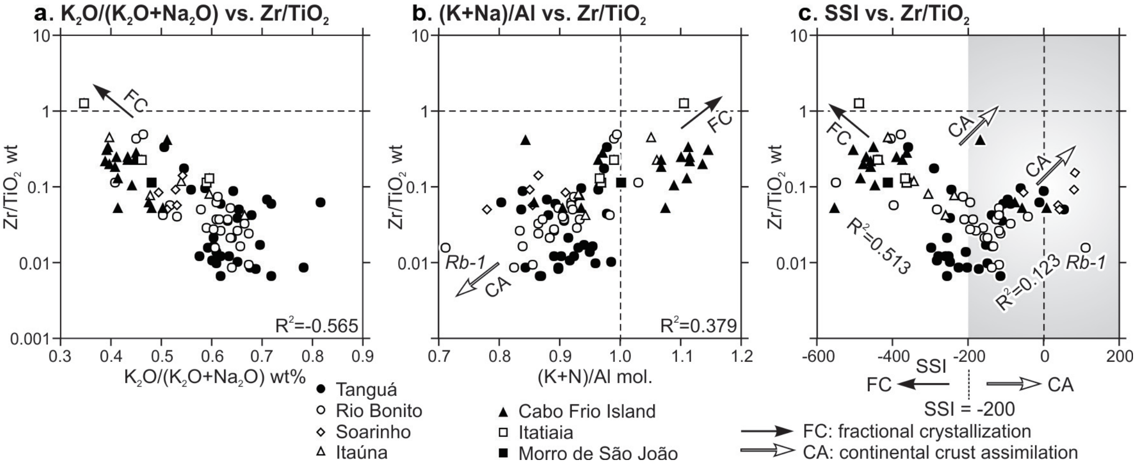


Figure 13 - Zr/TiO_2 wt ratio variation according to: **a**) $K_2O/(K_2O+Na_2O)$ wt%; **b**) (K+Na)/Al mol.; **c**) silica saturation index (SSI).

the meta-alkaline rocks, they contain scarce or no zircon crystals. This phenomenon is commonly observed in the other felsic alkaline complexes (Belousova et al. 2001). Only some alkaline syenite and quartz syenite samples have very small amounts of zircon, and the Zr of nepheline syenite should be present in mafic minerals.

The diagram of SSI vs. Zr/TiO_2 distinguished the trends of fractional crystallization and continental crust assimilation. The fractional crystallization (FC) from a negative correlation trend with $R^2=0.513$ in the domain of SSI<-200, and the continental crust assimilation from a positive correlation trend with $R^2=0.123$ in the domain of SSI>-200. The behaviour of Zr/TiO_2 on this diagram are similar to those of Ba/Sr (Fig. 13c), but the trend is clearer. In both cases, the critical SSI value is -200 (Fig. 8c, 13c).

PARTIAL MELTING OF THE COUNTRY ROCK

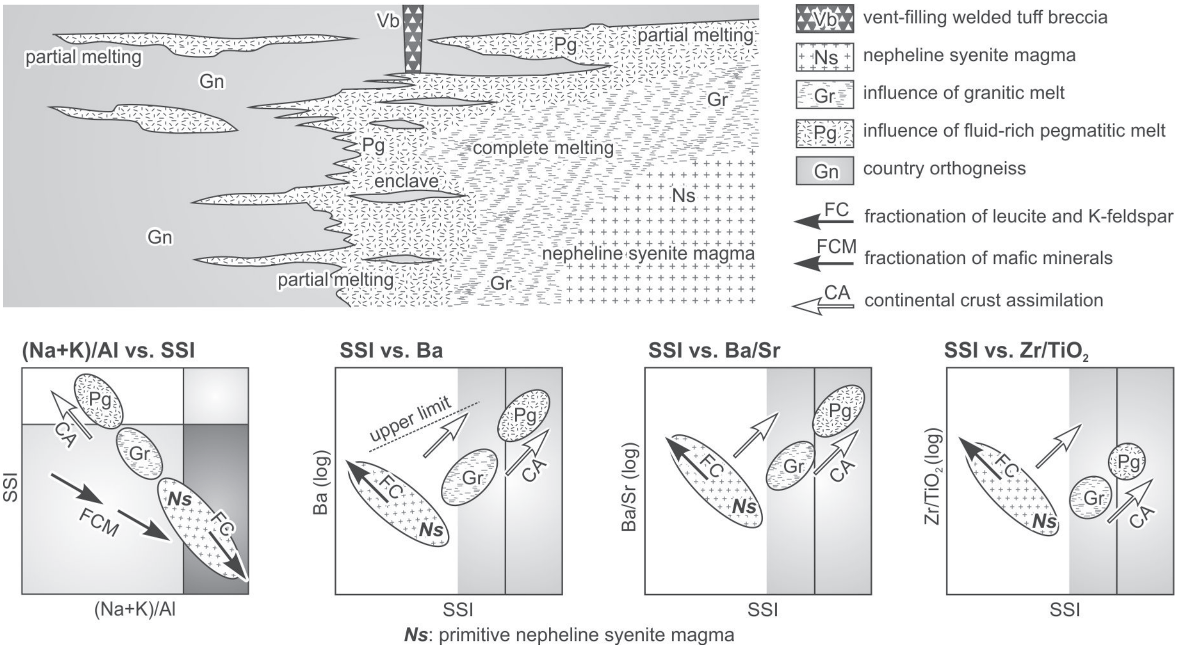
Motoki et al. (2010, 2013), and Sichel et al. (2012) proposed that the geochemical variation trend of these felsic alkaline rocks, which crosses over the two thermodynamic incompatibilities, is originated from magma super-reheating, country rock melting, and the consequent continental crust assimilation. These papers assumed complete melting of the country rock. This idea can explain the continuous variation from SiO_2-undersaturated to oversaturated composition. It can also justify the variation from peralkaline to peraluminous composition in the case of the samples of Tanguá, Rio Bonito, and Soarinho complex, whose country rock is paragneiss with abundant modal muscovite and garnet.

However, Itatiaia, Itaúna, and Cabo Frio Island complexes are intrusive into orthogneissic basement of granitic composition, which is not peraluminous but meta-aluminous. Therefore, some peraluminous alkaline syenite, such as Cf-1 and Cf-2 (Fig. 8), cannot be justified by the above-mentioned idea. The SSI vs. (Na+K)/Al diagram indicates that all of the studied rocks, all of the felsic alkaline rocks, from a continuous trend from peralkaline to peraluminous fields regardless of the country rock type, whether it is peraluminous pelitic paragneiss or meta-peraluminous orthogneiss. The authors propose the model of country rock partial melting for the solution.

Along the contact plane, complete melting of country rock can occur because of strong thermal effects of the super-reheated magma. However, at the location of the country rock little distant from the contact between the orthogneiss and the alkaline synite, the thermal effects of the magma are less expressive and the country rock melting could be partial. Even the country rock is meta-peraluminous orthogneiss, the melt generated by partial fusion with strong fluid influence could generate pegmatite. This liquid is peraluminous and SiO_2-oversaturated with high concentration of incompatible elements, especially fluid-mobile ones. Therefore, the felsic alkaline magma with continental crust assimilation have high Ba, Ba/Sr, Zr/TiO_2, SSI, and low (Na+K)/Al mol. In the case of complete melting of country rock, such geochemical features should not appear. This model justifies the major elements and the trace element ones of the Figure 8 and Figure 13c. The very wide variation of Ba and Sr (Fig. 8a, b) can be attributed to different degrees of host rock partial melting. The Figure 14 schematically illustrates the proposed model.

The subvolcanic pyroclastic rock Rb-1 of Rio Bonito complex shows strong characteristics of continental crust assimilation and have Norm quartz (8.28 wt%) and corundum (1.48 wt%). The high Ba (769.9 ppm) and Ba/Sr (2.26) suggest remarkable influence of fluid. The explosive eruption that formed vent-filling welded tuff breccia and welded pyroclastic dykes (Motoki et al. 2007a, b) could be originated from the fluid-rich pegmatitic liquid, generated by the low-degree partial melting of country gneiss. Similar phenomena are observed in recent geochemical data of vent-filling welded pyroclastic rocks of the other felsic alkaline intrusive bodies.

A rock with strong effects of continental crust assimilation do not always have all of the above-mentioned geochemical characteristics, as high SSI, low (Na+K)/Al, high Sr and Ba, high total REEs, convex REE patterns, and low Eu/Eu*. There are samples with all of these features, such as Rb-1, do exist also samples with show only few of them. This observation cannot be justified simply by different degrees of continental assimilation. The variety of country rock types and of partial melting degree should be complexly related to the



Ns: primitive nepheline syenite magma

Figure 14 - Schematic illustration for the contact zone of the nepheline syenite intrusive bodies and its geochemical interpretations on the diagrams of (Na+K) vs. SSI, SSI vs. Ba, SSI vs. Ba/Sr, and SSI vs. Zr/TiO_2, which are related, respectively, to Fig. 4, 8b, 8c, and 13c.

chemical composition of the felsic alkaline rocks with continental assimilation effects.

CONCLUSIONS

The behaviour of trace elements of the Cretaceous to Early Cenozoic felsic alkaline rocks of the state of Rio de Janeiro, Brazil, show the following features:

1. The Rb/K and Zr/TiO_2 ratios increase according to the reduction of $K_2O/(K_2O+Na_2O)$. Adversely the cases of non-alkaline granitic magmas, the $K_2O/(K_2O+Na_2O)$ of the nepheline syenite magma decrease by fractional crystallization of felsic minerals.
2. The nepheline syenitic rocks of Tanguá and Rio Bonito complex are less fractionated. On the diagram of Nb/Y vs. Zr/TiO_2, these rocks are projected on the areas of trachy-andesite, alkaline basalt, basanite, and nephelinite, because of the low Zr contents.
3. The SSI vs. Zr/TiO_2 diagram shows distinct trends of fractional crystallization and continental crust assimilation. In the field of SSI<-200, negative correlation trend is observed because of fractional crystallization. In the domain of SSI>-200, positive trend is found due to continental crustal assimilation. This diagram distinguishes the two trends with critical SSI value of -200.
4. The Sr and Ba contents have very wide variation and have no relation to fractional crystallization indexes. The SSI vs. Ba/Sr diagram distinguishes the trends of crustal assimilation and fractional crystallization in the similar way of SSI vs. Zr/TiO_2 diagram.
5. Total REEs are generally high, about 10 times that of granitic rocks. The La_N and Yb_N are similar to those of granitic rocks. The REE pattern is linear with small Eu anomaly because of irrelevant plagioclase fractionation. The less fractionated nepheline syenite, has low total REEs and concave REE pattern. According to the magma fractionation, total REEs and (Sm/Sm*)* increase. The samples with strong continental assimilation have high total REEs, concave REE pattern, and slight negative Eu anomaly.
6. The SiO_2-oversaturated magma generated by the country rock melting is peraluminous with high Ba, Ba/Sr, Zr/TiO_2, and total REEs. The low-degree partial melting of country rock can generate fluid-rich peraluminous pegmatitic melt, even from the orthogneiss country rocks of meta-aluminous composition. The hyper-liquidus temperature of the magma enables the mixture between the magmas of thermodynamically incompatible compositions.

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RESUMO

Este trabalho apresenta os comportamentos geoquímicos de elementos traços das rochas alcalinas félsicas do Estado do Rio de Janeiro, Brasil, com atenção especial da cristalização fracionada e assimilação da crosta continental. O fracionamento de leucita e de feldspato alcalino potássico aumenta Rb/K e reduz K2O/(K2O+Na2O). Os magmas primitivos de nefelina sienito têm baixa Zr/TiO2, Sr e Ba. No diagrama de Nb/Y v.s. Zr/TiO2, essas rochas são projetadas nos campos de álcali basalto, basanito e nefelinito, ao invés do campo de fonolito. O nefelina sienito peralcalino, que é bem fracionado, possui alta Zr/TiO2 porém não há zircão. Os diagramas do índice de saturação de sílica (ISS) distinguem as sequências originadas da cristalização fracionada e da assimilação crustal. No campo de ISS<-200, Zr/TiO2 e Ba/Sr apresentam seqüências de correlação negativa ao SSI por consequência da cristalização fracionada. No campo de ISS>-200, essas mostram correlações positivas devido à assimilação da crosta continental. O teor total de ETR's (Elementos Terras Raras) é cerca de 10 vezes de rochas graníticas, porém LaN/SmN e LaN/YbN são similares. A seqüência de elementos terras raras é linear e a anomalia de Eu é irrelevante. O líquido pegmatítico gerado pela fusão parcial da rocha encaixante é supersaturado em SiO2 e peraluminoso com altos Ba, Sr, Ba/Sr, Zr/TiO2 e SSI com alto teor de fluídos. Este modelo justifica a composição peraluminosa e supersaturada em SiO2 das rochas com relevante efeito da assimilação da crosta continental.

Palavras-chave: nefelina sienito, álcali sienito, elementos traços, elementos terras raras, cristalização fracionada, assimilação da crosta continental.

REFERENCES

ABBOTT MJ. 1966. K and Rb in a continental alkaline igneous rock suite. Geochim Cosmochim Ac 31: 1035-1041.

AIRES JR, MOTOKI A, MOTOKI KF, MOTOKI DF AND RODRIGUES JG. 2012. Geomorphological analyses of the Teresópolis Plateau and Serra do Mar Cliff, State of Rio de Janeiro, Brazil with the help of summit level technique and ASTER GDEM, and its relation to the Cenozoic tectonism. Anuário do IGEO - UFRJ 35(2): 105-123.

ALVES DB. 2005. Sedimentação vulcanoclástica do Cretáceo superior da Bacia de Campos, sudeste do Brasil. Anais do III Simpósio de Vulcanismo e Ambientes Associados. Cabo Frio, Brazil, CD, 5 p.

ALVES FR AND GOMES CB. 2001. Ilha dos Búzios, Litoral Norte do Estado de São Paulo: Aspectos Geológicos e Petrográficos. Revista do IGEO - USP, Série Científica, São Paulo, Brasil 1: 101-114.

BATCHELOR RA AND BOWDEN P. 1985. Petrogenetic interpretation of granitic rocks series using multícationic parameters. Chem Geol 48: 43-55.

BELOUSOVA EA, GRIFFIN WL, O'REILLY SY AND FISHER NI. 2001. Igneous zircon: trace element composition as an indicator of source rock type. Contrib Mineral Petrol 143: 602-622.

BROTZU P, GOMES CB, MELLUSO L, MORBIDELLI L, MORRA V AND RUBERTI E. 1997. Petrogenesis of coexisting SiO_2-undersaturated to SiO_2-oversaturated felsic igneous rocks: the alkaline complex of Itatiaia, southern eastern Brazil. Lithos 40: 133-156.

BROTZU P, MELLUSO L, BENNIO L, GOMES CB, LUSTRINO M, MORBIDELLI L, MORRA V, RUBERTI E, TASSINARI C AND D'ANTONIO M. 2007. Petrogenesis of the Early Cenozoic potassic alkaline complex of Morro de São João, southeastern Brazil. J S Am Earth Sci 24: 93-115.

BRYAN SE. 2006. Petrology and Geochemistry of the Quaternary Caldera-forming, Phonolitic Granadilla Eruption, Tenerife (Canary Islands). J Petrol 47(8): 1557-1589.

CADDAH LFG, ALVES DB, HANASHIRO M AND MIZUSAKI AMP. 1994. Caracterização e origem do Marco "3-Dedos" (Santoniano) da Bacia de Campos. Bol Geoc Petr 8(2): 315-334.

FLOYD PA AND WINCHESTER JA. 1975. Magma type and tectonic setting discrimination using immobile elements. Earth Planet Sc Lett 27: 211-218.

FLOYD PA AND WINCHESTER JA. 1978. Identification and discrimination of altered and metamorphosed volcanic rocks using immobile elements. Chem Geol 21(1-3): 291-306.

FÖRSTER HJ, TISCHENDORF G AND TRUMBULL RB. 1997. An evaluation of the Rb vs. (Y + Nb) discrimination diagram to infer tectonic setting of silicic igneous rocks. Lithos 40(2-4): 261-293.

GAST PW. 1968. Trace element fractionation and the origin of tholeiitic and alkaline magma types. Geochim Cosmochim Ac 32(10): 1057-1086.

GERALDES MC, MOTOKI A, VARGAS T, IWANUCH W, BALMANT A AND MOTOKI KF. 2013. Geology, petrography, and emplacement mode of the Morro dos Gatos alkaline intrusive rock body, State of Rio de Janeiro, Brazil. Geociências, Rio Claro, 32-34 p.

GUEDES E, HELIBRON M, VASCONCELOS PM, VALERIANO CM, ALMEIDA JCH, TEIXEIRA W AND THOMÁZ FILHO A. 2005. K-Ar and $^{40}Ar/^{39}Ar$ ages of dykes emplaced in the onshore basement of the Santos Basin, Resende area, SE. Brazil: implications for the south Atlantic opening and Tertiary reactivation. J S Am Earth Sci 18: 371-182.

HAMILTON DL AND MACKENZIE WS. 1960. Nepheline solid solution in the system $NaAlSiO_4$-$KAlSiO_4$-SiO. J Petrol 1: 56-72.

HANSON G. 1978. The application of trace elements to the petrogenesis of igneous rocks of granitic composition. Earth Planet Sc Lett 38(1): 26-43.

HASTIE AR, KERR AC, PEARCE JA AND MITCHELL SF. 2007. Classification of altered volcanic island arc rocks using immobile trace elements: Development of the Th-Co discrimination diagram. J Petrol 48(12): 2341-2357.

HAWKESWORTH CJ, O'NIONS RK AND ARCUTLUS RJ. 1979. Nd and Sr isotope geochemistry of island arc volcanics, Grenada, Lesser Antilles. Earth Planet Sc Lett 45: 237-248.

HEILBRON M, MOHRIAK W, VALERIANO CM, MILANI E, ALMEIDA JCA AND TUPINAMBÁ M. 2000. From collision to extension: the roots of the southeastern continental margin of Brazil. In: Mohriak WU and Talwani M (Eds), Geophysical Monograph. Am Geophy Un 115: 1-32.

KAY RW AND GAST PW. 1973. The rare earth content and origin of alkali-rich basalt. Geol J 81: 653-682.

KITSOPOULOS K. 2010. Immobile trace elements discrimination diagrams with zeolitized volcaniclastics from the Evros - Thrace - Rhodope volcanic terrain. Bulletin of the Geological Society of Greece, Proceedings of the 12th International Congress, CD, 10 p.

LE BAS MJ, LE MAITRE RW, STRECKEISEN A AND ZANETTIN B. 1986. A Chemical Classification of Volcanic. Rocks based on the Total-Alkali-Silica Diagram. J Petrol 27: 745-750.

LOUREIRO FEL AND SANTOS RC. 1988. The intra-intrusive uranium deposits of Poços de Caldas, Brazil. Ore Geol Rev 3: 227-240.

MANIAR PD AND PICCOLI PM. 1989. Tectonic discrimination of granitoids. Geol Soc Am Bull 101: 635-64.

MCDONOUGH WF AND SUN S. 1995. The composition of the Earth. Chem Geol 120: 223-253.

MIDDLEMOST EAK. 1975. The basalt clan. Earth-Sci Rev 11: 337-364.

MOTOKI A, ARAÚJO AL, SICHEL SE, MOTOKI KF AND SILVA S. 2013. Nepheline syenite magma differentiation process by continental crustal assimilation for the Cabo Frio Island intrusive complex, State of Rio de Janeiro, Brazil. Geociências 32(2): 195-218.

MOTOKI A, GERALDES MC, IWANUCH W, VARGAS T, MOTOKI KF, BALMANT A AND RAMOS MN. 2012. Pyroclastic dyke and welded crystal tuff of the Morro dos Gatos alkaline intrusive complex, State of Rio de Janeiro, Brazil. REM: Rev Esc Minas 65(1): 35-45.

MOTOKI A AND SICHEL SE. 2006. Avaliação de aspectos texturais e estruturais de corpos vulcânicos e subvulcânicos e sua relação com o ambiente de cristalização, com base em exemplos do Brasil, Argentina e Chile. REM: Rev Esc Minas 59(1): 13-23.

MOTOKI A AND SICHEL SE. 2008. Hydraulic fracturing as possible mechanism of dyke-sill transition and horizontal discordant intrusion: an example of Arraial do Cabo area, State of Rio de Janeiro, Brazil. Geofís Int 47(1): 3-25.

MOTOKI A, SICHEL SE AND PETRAKIS GH. 2009. Genesis of the tabular xenoliths along contact plane of the mafic dykes of Cabo Frio area, state of Rio de Janeiro, Brazil: Thermal delamination or hydraulic shear fracturing? Geociências 28(1): 15-26.

MOTOKI A, SICHEL SE, SOARES RS, NEVES JLP AND AIRES JR. 2008. Geological, lithological, and petrographical characteristics of the Itaúna Alkaline Intrusive Complex, São Gonçalo, State of Rio de Janeiro, Brazil, with special attention of its emplace mode. Geociências 27(1): 33-44.

MOTOKI A, SICHEL SE, VARGAS T, AIRES JR, IWANUCH W, MELLO SLM, MOTOKI KF, SILVA S, BALMANT A AND GONÇALVES J. 2010. Geochemical evolution of the felsic alkaline rocks of Tanguá, Rio Bonito, and Itaúna intrusive bodies, State of Rio de Janeiro, Brazil. Geociências 29(3): 291-310.

MOTOKI A, SOARES R, LOBATO M, SICHEL SE AND AIRES JR. 2007b. Weathering fabrics in felsic alkaline rocks of Nova Iguaçu, State of Rio de Janeiro, Brazil. REM: Rev Esc Minas 60(3): 451-458.

MOTOKI A, SOARES R, NETTO AM, SICHEL SE, AIRES JR AND LOBATO M. 2007a. Genetic reconsideration of the Nova Iguaçu Volcano model, State of Rio de Janeiro, Brazil: eruptive origin or subvolcanic intrusion? REM: Rev Esc Minas 60(4): 583-592.

MOTOKI A, VARGAS T, IWANUCH W, SICHEL SE, BALMANT A AND AIRES JR. 2011. Tectonic breccia of the Cabo Frio area, State of Rio de Janeiro, Brazil, intruded by Early Cretaceous mafic dyke: Evidence of the Pan-African brittle tectonism? REM: Rev Esc Minas 64(1): 25-36.

NOVAIS LCC, ZELENKA T, SZATMARI P, MOTOKI A, AIRES JR AND TAGLIARI CV. 2007. Ocorrência de rochas vulcânicas ignimbríticas na porção norte da Bacia do Espírito Santo: evolução do modelo tectono-sedimentar. Bol Geoc Petr 16(1): 139-156.

PEARCE JA. 1996. Sources and settings of granitic rocks. Episodes 19(4): 120-125.

PEARCE JA AND CANN JR. 1973. Tectonic setting of basic volcanic rocks determined using trace element analyses. Earth Planet Sc Lett 19(2): 290-300.

PEARCE JA, HARRIS NBW AND TINDLE AG. 1984. Trace element discrimination diagrams for the tectonic interpretation of granitic rocks. J Petrol 25: 956-983.

PEARCE JA AND PARKINSON IJ. 1993. Trace element models for mantle melting: application to volcanic arc petrogenesis. Geol Soc London Spec Publ 76: 373-403.

PETRAKIS GH, MOTOKI A, SICHEL SE, ZUCCO LL, AIRES JR AND MELLO SLM. 2010. Ore geology of special quality gravel and artificial sand: examples of alkaline syenite of Nova Iguaçu, State of Rio de Janeiro, and rhyolite of Nova Prata, State of Rio Grande do Sul, Brazil. Geociências 29(1): 21-32.

SHAW DM. 1968. A review of K-Rb fractionation trends by covariance analysis. Geochim Cosmochim Ac 32(6): 573-601.

SICHEL SE, MOTOKI A, IWANUCH W, VARGAS T, AIRES JR, MELO DP, MOTOKI KF, BALMANT A AND RODRIGUES JG. 2012. Fractionation crystallization and continental crust assimilation by the felsic alkaline rock magmas of the State of Rio de Janeiro, Brazil. Anuário do IGEO – UFRJ 35(2): 84-104.

SICHEL SE, MOTOKI A, SAVI DC AND SOARES RS. 2008. Subvolcanic vent-filling welded tuff breccia of the Cabo Frio Island, State of Rio de Janeiro, Brazil. REM: Rev Esc Minas 61(4): 423-432.

TERAKADO Y. 1980. Fine structure of rare earth elements patterns of Tahitian rocks. Geochem J 14: 155-166.

ULBRICH HHGJ. 1984. A petrografia, a estrutura e quimismo de nefelina sienitos do Maciço Alcalino de Poços de Caldas, MG-SP. Livre Docência thesis, Instituto de Geociências da Universidade de São Paulo, Brazil.

ULBRICH HHGJ AND GOMES CB. 1981. Alkaline rocks from continental Brazil. Earth-Sci Rev 17(1-2): 135-154.

VALENÇA JG. 1980. Geology, petrography and petrogenesis of some alkaline igneous complexes of Rio de Janeiro State, Brazil. Thesis, Doctor in Geosciences. West Ontario University, London, Ontario, Canada, 247 p.

VALERIANO CM, TUPINAMBÁ M, SIMONETTI A, HEILBRON M, ALMEIDA JCH AND EIRADO LG. 2011. U-Pb LA-MC-ICPMS geochronology of Cambro-Ordovician post-collisional granites of the Ribeira belt, southeast Brazil: Terminal Brasiliano magmatism in central Gondwana supercontinent. J S Am Earth Sci 32: 416-428.

VALLADARES CS, MACHADO N, HEILBRON M, DUARTE BP AND GAUTHIER G. 2008. Sedimentary provenance in the central Ribeira belt based on laser-ablation. Gondwana Res 13: 516-526.

WHALE JB, CURRIE KL AND CHAPPELL W. 1987. A-type granites: geochemical characteristics, discrimination and petrogenesis. Contrib Mineral Petrol 95: 407-419.

WINCHESTER JA AND FLOYD PA. 1977. Geochemical discrimination of different magma series and their differentiation products using immobile elements. Chem Geol 20: 325-343.

WOLFF JA. 1984. Variation in Nb/Ta during differentiation of phonolitic magma, Tenerife, Canary Island. Geochim Cosmochim Ac 48(6): 1345-1348.