# NEPHELINE SYENITE MAGMA DIFFERENTIATION WITH CONTINENTAL CRUSTAL ASSIMILATION FOR THE CABO FRIO ISLAND INTRUSIVE COMPLEX, STATE OF RIO DE JANEIRO, BRAZIL

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> Introduction Regional geology Lithologic and petrographic characteristics Chemical analyses Major elements Minor elements Crystallisation fractionation Radiometric dating Discussion Conclusion

**ABSTRACT** - This article presents chemical composition and magma differentiation process of the alkaline rocks of the Cabo Frio Island and the adjacent areas, State of Rio de Janeiro, Brazil, with special attention to continental crust assimilation. The intrusive body is made up mainly of nepheline syenite, alkaline syenite, and trachyte. The country orthogneiss is intruded also by subvolcanic vent breccia, as well as by lamprophyre, trachyte, and phonolite dykes. The alkaline syenite is distributed at the contact zone in which abundant digested host rock xenoliths are present. Most of the nepheline syenite and phonolite samples are highly silica undersaturated with moderate proportion of  $(Na+K)/Al_{mol}$  and  $K_2O/(Na_2O+K_2O)_{wt\%}$ , being classified to be potassic nepheline syenite. The  ${}^{40}Ar$ - ${}^{39}Ar$  age for the nepheline syenite is 54.83±0.35 Ma. The variation diagrams indicate fractionation crystallisation of titanite, ilmenite, apatite, and clinopyroxene during the magma cooling of the intrusive body. The nepheline syenite and phonolite are originated from highly differentiated magmas whose compositions are close to the terminal point of the silica undersaturated field. Continental crust assimilation is remarkable. Some alkaline syenite and trachyte samples are constituted by about 50% of the wall rock materials. The continental crust assimilation took place at the last phase of fractionation crystallisation of the nepheline syenite magma. This composition is thermodynamically instable and it could be originated from super-reheating or rapid fluid content elevation caused by new magma injection into the magma chamber.

Keywords: Nepheline syenite; Alkaline syenite; Fractionation crystallization; Crustal assimilation; Ar-Ar age; Cabo Frio Island.

**RESUMO** - *Motoki, A., Araújo, A.L., Sichel, S.E., Vargas, T., Aires, J.R., Iwanuch, W., Mello, S.L.M., Motoki, K.F., Jourdan, F., Motoki, K.F., Silva, S. Diferenciação do magma de nefelina sienito com assimilação da crosta para o corpo intrusivo da Ilha de Cabo Frio, RJ. Este artigo apresenta a composição química e evolução magmática das rochas alcalinas da Ilha de Cabo Frio, RJ, e das áreas adjacentes, com atenção especial para a assimilação da crosta continental. O corpo intrusivo principal é composto de nefelina sienito, álcali sienito e traquito. O ortognaisse encaixante é intrudido também por brecha de conduto subvulcânico e diques de lamprófiro, traquito e fonolito. O álcali sienito é distribuído na zona de contato em que ocorrem muitos xenólitos digeridos da rocha encaixante. A maioria das amostras de nefelina sienito e fonolito é altamente subsaturada em sílica com moderada proporção molecular de (Na+K)/Al e de K<sub>2</sub>O/(Na<sub>2</sub>O+K<sub>2</sub>O) em peso, sendo classificadas como nefelina sienito potássico. A idade <sup>40</sup>Ar-<sup>39</sup>Ar para o nefelina sienito é 54.83±0.35 Ma. Os diagramas de variação indicam a cristalização fracionada de titanita, ilmenita, apatita e clinopiroxênio durante o resfriamento magmático no corpo intrusivo. O nefelina sienito e traquito foram originados do magma de grau avançado em diferenciação cuja composição é próxima ao ponto terminal do campo subsaturado em sílica. A assimilação da crosta continental é relevante e algumas amostras de álcali sienito e traquito são constituídas por cerca de 50% de materiais provenientes da rocha encaixante. A assimilação crustal ocorreu na fase final da cristalização fracionada do magma de nefelina sienito. Esta composição é termodinamicamente instável e poderia ser originada de super-reaquecimento do magma ou elevação rápida do teor de fluídos que foi causado por injeção de novo pulso de magma à câmara magmática.* 

Palavras chave: Nefelina sienito; Álcali sienito; Cristalização fracionada; Assimilação crustal; Idade Ar-Ar; Ilha de Cabo Frio.

## **INTRODUCTION**

In the State of Rio de Janeiro, northeastern part of the State of São Paulo, and southern portion of the State of Minas Gerais, Brazil, there is a WNW-ESE ward alignment of felsic alkaline rocks, called Poços de Caldas-Cabo Frio alkaline rock alignment (Figure 1; Sadowski & Dias Neto, 1981; Almeida, 1986; Thomáz Filho & Rodrigues, 1999; Riccomini et al., 2004). The intrusive complex of Cabo Frio Island, the main target of this paper, is situated at the eastern end of the magmatic alignment (Motoki & Sichel, 2008).



**FIGURE 1.** Felsic alkaline intrusive bodies of the State of Rio de Janeiro, Brazil, after Motoki et al. (2010). The Canaã body is made up exceptionally of Cambrian nepheline syenite gneiss.

The alignment is made up of a dozen of alkaline intrusive bodies of the Cretaceous to Early Cenozoic (Sonoki & Garda, 1988; Motoki et al., 2007a), such as: Itatiaia (Brotzu et al., 1997), Morro Redondo (Brotzu et al., 1989), Tinguá, Mendanha (Motoki et al., 2007a), Itaúna (Motoki et al., 2008a), Tanguá, Soarinho, Rio Bonito (Valença, 1980; Motoki et al., 2010), Morro dos Gatos (Motoki et al., 2012a), Morro de São João (Brotzu et al., 2007; Mota et al., 2009), and Cabo Frio Island (Sichel et al., 2008). Only the Canaã body is composed of nepheline syenite gneiss of the Cambrian. The alkaline rocks are constituted mainly by nepheline syenite with eventual presence of alkaline syenite, trachyte, phonolite, and ventfilling welded tuff breccia (Motoki et al., 2007b; 2008b).

The alkaline rock bodies form morphologic elevations with relative height of 300 to 900 m, called alkaline massifs, because of the strong erosive resistance (Motoki et al., 2008c; Aires et al., 2012). Some of them form non-metallic ore deposits for special quality construction material (Petrakis et al., 2010). Such rocks are of scarce world occurrence and their magma evolution is relatively little studied. The present-day exposures correspond to the subvolcanic structures of 3 to 4 km of the depth of the eruption or intrusion time (Motoki & Sichel, 2006; Motoki et al., 2007c).

These alkaline rocks show peculiar manner of fractionation crystallisation. In common case, the contents of Na<sub>2</sub>O and K<sub>2</sub>O increase together according to the magma differentiation. The increase of K<sub>2</sub>O is remarkable. However, in case of the nepheline syenite magmas, the Na content increases and the K content decreases. In addition, a strong effect of continental crust assimilation is generally observed. The co-existence of silica over-saturated and under-saturated rocks, crossing over the thermal divide, cannot be explained by fractionation crystallisation, being an important research theme of alkaline rock igneous petrology. It is notable that the relation between the fractionation crystallisation and continental wall rock assimilation is very

specific in each alkaline intrusive body of the State of Rio de Janeiro. For example, the magmas of the Tanguá and Morro de São João bodies are less fractionated and that of the Soarinho body is under strong continental assimilation.

The authors have performed fieldworks, petrographic observations, and chemical analyses of the alkaline rocks of the Cabo Frio Island. The comparative geochemical studies of the alkaline rocks of the State of Rio de Janeiro are important from the viewpoint of the relation between fractionation crystallisation and crustal assimilation. This article presents chemical analyses of the alkaline rocks of the Cabo Frio Island and other intrusive bodies and shows laser-spot <sup>40</sup>Ar-<sup>39</sup>Ar dating. Based on the new results and the previous data (e.g. Motoki et al., 2010), the authors discuss geochemical evolution process for the nepheline syenite magmas with special attention of assimilation of the continental crust country rocks.

## **REGIONAL GEOLOGY**

The metamorphic basement of this area is constituted mainly by the orthogneiss of the Região dos Lagos Unit of the Cabo Frio Terrane. The metamorphic age is about 530 Ma and the original intrusive age is about 2000 Ma (Schmitt et al., 2008, Motoki, unpublished U-Pb data). The orthogneiss is cut by tectonic breccia of the late stage of Pan-African continental collision event (Motoki et al., 2011; 2012b). They are cut by early Cretaceous tholeiitic mafic dykes that correspond to a part of feeder dykes of continental flood basalt of the Paraná Province (e.g. Piccirillo & Melfi, 1988; Peate et al., 1992; Turner et al., 1994; Stewart et al., 1996). The basement and the dykes are intruded by the nepheline syenite and alkaline syenite plutons. The syenitic intrusions are cut by phonolite, trachyte, and lamprophyre dykes, and subvolcanic breccia.

The intrusive complex of the Cabo Frio Island is present at the coordinates of 23°S, 42°'W, about 126 km to the east of the Rio de Janeiro city, southeastern Brazil. The body has NE-SW elongation, with extension of 3.7 km and width of 2.0 km (Figure 2).



**FIGURE 2**. Geologic map of the alkaline intrusive body of the Cabo Frio Island and surrounded area, modified from Motoki et al. (2009).

The main intrusive body occupies most of the area of the Cabo Frio Island. The southwestern, southern, and eastern corners of the island are underlain by the country rocks, which are composed mainly of basement orthogneiss and partially of Early Cretaceous tholeiite dykes, Early Cenozoic lamprophyre dykes, and vent-filling welded subvolcanic tuff breccia. Because of the advance of field studies, the distribution area of the nepheline syenite main body is smaller than the previous works (e.g. Lima, 1976). In the continental side of the Pontal da Atalaia peninsula, no extension of the main nepheline syenite body is observed (Motoki et al., 2008d). At this peninsula, there is a dyke of about 10 m in width made up of holo-leucocratic nepheline syenite.

The field observations have recognised the following rock bodies: 1) Metamorphic basement; 2) Early Cretaceous tholeiite dykes; 3) Early Cenozoic lamprophyre dykes; 4) Subvolcanic breccia; 5) Nepheline syenite main intrusive body and auto-metamorphic trachyte dykes and sills; 6) Phonolite dykes (Photo 1). The intrusions of auto-metamorphic dykes and sills are considered to be simultaneous with the main nepheline syenite body. Different from the other alkaline complexes, the subvolcanic breccia of the Cabo Frio Island and lamprophyre dyke are older than the main intrusive body of nepheline syenite (Figure 3).



**PHOTO 1.** Field view of the main rock types of the Cabo Frio Island: A) Nepheline syenite; B) Lamprophyre dyke and auto-metamorphic trachyte sill intruding into the orthogneiss of the metamorphic basement; C) Subvolcanic vent-filling tuff breccia; D) Mafic xenolith. Gn orthogneiss of the metamorphic basement; Tr - auto-metamorphic trachyte sill; Lp - lamprophyre dyke; Px - mafic xenolith; Sn - nepheline syenite.

#### A. Cabo Frio Island

#### B. Mendanha Intrusive Complex





The lamprophyre dykes are found in the metamorphic basement either at the Cabo Frio Island or the Pontal da Atalaia Peninsula. They are 50 cm to 1 m wide and cut by trachyte dykes and sills (Photo 1B). In the main intrusive body, these dykes are not observed and only phonolite dykes are present. The vent-filling subvolcanic breccia is exposed at south-western end of the Cabo Frio Island intruding into the metamorphic basement. The subvolcanic breccia includes no clasts of nepheline syenite and alkaline syenite ant it is not cut by the

lamprophyre dykes. The trachyte dykes and sills are frequent in the metamorphic basement close to the contact zone. They are considered to be the extension of the main intrusive body (Motoki et al., 2008b) and are strongly affected by deuteric alteration. The phonolite dykes are fresh and cut all of the above-mentioned bodies, representing the youngest magmatic activity. They have radial layout from the main nepheline syenite pluton. At the north-eastern end of the Praia do Farol Beach, mafic alkaline rock xenoliths are observed (Photo 1D).

## LITHOLOGIC AND PETROGRAPHIC CHARACTERISTICS

The Cabo Frio Island alkaline intrusive body is composed predominantly of grossgrained nepheline syenite of light grey macroscopic colour (Photo 1A). This rock is made up of alkaline feldspar, nepheline, clinopyroxene, amphibole, and biotite, with accessory minerals of magnetite, titanite, and apatite, however zircon is scarce. The clinopyroxene is light green in parallel nicol, indicating aegirine-augite composition, and frequently surrounded by amphibole, suggesting the reaction between the clinopyroxene and hydrated magma. This texture is commonly observed in the alkaline syenite and nepheline

syenite of other intrusive complexes (e.g. Motoki, 1986; Motoki et al., 2010).

Alkaline syenite is similar to the nepheline syenite but without modal nepheline. This rock is light grey in macroscopic colour and difficult to be distinguished from the nepheline syenite by naked eye observations. Its distribution is limited only along the contact zone. The rock is composed of alkaline feldspar, clinopyroxene and amphibole, with magnetite and apatite as accessory minerals. The abundance of host rock xenoliths is remarkable and they show notable plastic deformation by the host magma heat (Photo 2).



**PHOTO 2**. Plastically deformed and digested host gneiss xenoliths in the alkaline syenite at the south-western contact zone of the Cabo Frio Island intrusive complex. The contrast is increased and the brightness is decreased.

## CHEMICAL ANALYSES

In total, 20 samples of felsic alkaline rocks and 6 samples of mafic to intermediate composition form the Cabo Frio Island, Itatiaia, and Morro de São João intrusive complexes and adjacent areas have been analysed. In addition, 4 nepheline syenite samples of the Itatiaia complex, 2 nepheline syenite samples of the Morro de São João complex, and 1 pyroxenite of the same intrusive complex have been analysed for the purpose of comparison. The chemical analyses have been performed at the geochemical laboratory of the Geosol<sup>TM</sup> S.A., Belo Horizonte, State of Minas Gerais, Brazil, using X-ray fluorescence (XRF) for major and trace elements. The XRF apparatus for geochemical laboratories, such as Rigaku ZSX-

101E and Rigaku ZSX Primus II, have relative analytical error ranging from 0.5% (K<sub>2</sub>O) to 5% (SiO<sub>2</sub>) for major elements. The relative errors for the trace elements are about 5% and the detection limit is 0.5 to several ppms. (e.g. Mochizuki, 1997; Rigaku, 2012).

For the CIPW Norm calculation, the  $Fe^{3+}/Fe_{total}$  molecular ratio is estimated based on the atomic absorption analyses for the samples of Vitória Island body (Motoki, 1986) and Poços de Caldas intrusive complex (Ulbrich, 1984). The felsic alkaline rocks of the Cabo Frio Island have (Na+K)/Al molecular ratio around 1.0, and the  $Fe^{3+}/Fe_{total}$  is estimated to be 0.35, according to the method of Motoki et al. (2010).

#### **MAJOR ELEMENTS**

The Table 1 presents chemical composition of the major and minor elements for the alkaline rocks of the intrusive complexes of the Cabo Frio Island, and the Table 2, Itatiaia Morro de São João. The magma and differentiation index (D.I.) refers to the sum of all CIPW Norm felsic minerals (Thornton & Tuttle, 1960). The Silica Saturation Index (SSI) is calculated according to the definition of Motoki et al. (2010) by the following form:

$$\begin{split} SSI = & 1000 (SiO_2/60.0835 - \\ Al_2O_3/101.9601 - \\ & 5(Na_2O/61.9785 + K_2O/94.1956) - CaO/56.077 - \\ & MgO/40.304 - MnO/70.937 - \\ & FeO/71.844 + 2Fe_2O_3/159.687). \end{split}$$

The analysed rocks are classified into two distinct groups, felsic alkaline rocks and mafic to intermediate ones. The felsic rocks, nepheline syenite, alkaline syenite, phonolite, and trachyte, have distinctly low TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>\* (total Fe recalculated as Fe<sub>2</sub>O<sub>3</sub>), MgO, and CaO, and high SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and K<sub>2</sub>O than the mafic ones, as lamprophyre, amphibolite, and pyroxenite. For example, the average MgO contents of the felsic alkaline rocks of the Cabo Frio Island, Itatiaia, and Morro de São João are, respectively, 0.45, 0.33, and 0.59 wt%, and that of the mafic rocks of the Cabo Frio Island and Morro de São João bodies are, respectively, 3.14 and 2.70 wt% (Figure 4). The diagram of  $SiO_2$  vs. CaO (Figure 4C) shows two different trends for the felsic alkaline rocks, high-SiO<sub>2</sub> trend and low-SiO<sub>2</sub> one, but their details are unknown. In general, these diagrams show geochemical tendency of

mafic mineral fractionation crystallisation, but not so clearly.

<b>TABLE 1</b> . Main and trace elements for the felsic alkaline rocks of the Cabo Frio Island and the
adjacent areas, Itatiaia, and Morro de São João intrusive complex rock bodies, State of Rio de
Janeiro, Brazil. Obs.: n.a not analysed; n.d below the analytical detection limit.

	Nepheline syenite									
	CBF-	CBF-	CBF-	CBF-	CBF-	CBF-	CBF-	CBF-	CBF-	CBF-
Wt%	15	15B	30A	33	34P	34A	41	13	18	19
SiO <sub>2</sub>	54.70	53.30	55.00	58.10	55.70	56.00	55.10	58.30	60.40	61.20
TiO <sub>2</sub>	0.38	0.49	0.38	0.36	0.32	0.43	0.45	1.20	0.75	0.71
$Al_2O_3$	21.10	22.20	20.90	21.40	21.90	20.00	20.90	18.10	19.60	18.20
$Fe_2O_3^*$	2.41	2.60	3.18	3.11	2.55	2.96	2.75	5.30	2.60	3.70
MnO	0.19	0.13	0.20	0.24	0.17	0.19	0.17	0.17	0.18	0.14
MgO	0.17	0.35	0.23	0.23	0.19	0.26	0.26	1.40	0.70	0.60
CaO	1.40	1.80	1.20	1.10	0.71	1.40	1.40	3.00	2.00	1.80
Na <sub>2</sub> O	9.70	9.90	10.20	6.50	8.40	8.90	9.10	5.80	6.40	6.20
$K_2O$	6.90	7.00	6.60	6.80	6.90	6.80	7.20	4.90	5.80	6.30
$P_2O_5$	0.06	0.09	0.06	0.05	0.05	0.05	0.06	0.35	0.17	0.15
Total	97.01	97.86	97.95	97.89	96.89	96.99	97.39	98.52	98.60	99.00
ppm										
Cr	21	17	9	36	7	7	6	4	10	5
Ni	4	3	3	4	3	3	3	4	3	3
V	20	26	24	23	24	18	26	24	15	12
Rb	196	157	261	233	226	282	191	73	124	106
Sr	86	128	242	210	339	111	264	1339	607	428
Ba	68	49	218	130	258	46	221	4926	2025	1834
Zr	484	258	1154	1484	908	1047	479	234	474	376
Y	53	19	28	32	31	21	22	33	31	25
Nb	202	154	349	453	335	245	303	65	145	103
Th	93	17	57	81	57	69	36	6	17	13
U	4	4	13	16	11	14	9	n.d.	3	3
Cu	5	5	6	7	4	5	6	8	5	5
Pb	19	15	32	59	24	39	15	8	16	13
Zn	65	41	123	168	97	125	73	85	69	71
Sn	2	2	2	3	2	1	1	1	2	3
S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Mg#	0.12	0.21	0.13	0.13	0.13	0.15	0.16	0.34	0.35	0.24
D.I.	85.75	85.76	84.94	92.97	92.05	84.99	85.93	85.77	92.42	89.90
K/Na	1 1 1	1 07	1 1 1	0.94	0.07	1 10	1.00	0.82	0.86	0.04
Κ	1.11	1.07	1.14	0.04	0.97	1.10	1.09	0.02	0.00	0.94
NK/A	1.11	1.07	1.14	0.84	0.97	1.10	1.09	0.82	0.86	0.94
SSI	-486	-552	-506	-170	-362	-389	-448	-41	-72	-56

NK/A: (Na+K)/Al mol.

K/NaK: K<sub>2</sub>O/(Na<sub>2</sub>O+K<sub>2</sub>O)

$$\label{eq:SSI} \begin{split} SSI = & 1000 (SiO_2/60.0835 - Al_2O_3/101.9601 - 5 (Na_2O/61.9785 + K_2O/94.1956) - CaO/56.077 - MgO/40.304 - MnO/70.937 - FeO/71.844 + 2Fe_2O_3/159.687). \end{split}$$

	Alkaline syenite			Phonolite						
xx/±0/	CBF-	CBF-	CBF-	CBF-	CBF-	CBF-	CBF-	CBF-	CBF-	CBF-
W1%	13	18	19	29A	21	27	30	31	32A	17
SiO <sub>2</sub>	58.30	60.40	61.20	55.10	54.08	56.10	55.40	55.20	54.70	54.83
TiO <sub>2</sub>	1.20	0.75	0.71	0.32	0.46	0.32	0.38	0.47	0.27	0.35
$Al_2O_3$	18.10	19.60	18.20	20.70	21.47	21.00	20.90	21.10	20.70	21.47
$\text{Fe}_2\text{O}_3^*$	5.30	2.60	3.70	2.86	2.92	2.91	3.02	2.85	2.56	1.92
MnO	0.17	0.18	0.14	0.24	0.17	0.25	0.19	0.16	0.16	0.26
MgO	1.40	0.70	0.60	0.15	0.47	0.18	0.25	0.21	0.12	0.34
CaO	3.00	2.00	1.80	1.00	1.40	0.95	1.20	1.30	1.00	1.01
Na <sub>2</sub> O	5.80	6.40	6.20	9.80	8.19	10.10	9.70	9.10	9.90	9.58
K <sub>2</sub> O	4.90	5.80	6.30	6.40	6.68	6.70	6.80	7.00	6.30	6.62
$P_2O_5$	0.35	0.17	0.15	0.05	0.07	0.05	0.05	0.05	0.05	0.00
Total	98.52	98.60	99.00	96.62	95.91	98.56	97.89	97.44	95.76	96.38
ppm										
Cr	4	10	5	7	7	9	12	7	6	15
Ni	4	3	3	3	3	4	3	3	6	15
V	24	15	12	21	22	27	22	20	23	105
Rb	73	124	106	265	257	247	250	245	213	176
Sr	1339	607	428	42	43	258	231	46	213.8	503
Ba	4926	2025	1834	68	47	241	172	64	106	393
Zr	234	474	376	1046	1044	629	928	1051	591	632
Y	33	31	25	29	29	30	23	30	19	26
Nb	65	145	103	368	422	223	303	375	249	265
Th	6	17	13	63	63	36	60	63	32	34
U	n.d.	3	3	n.d.	12	7	10	12	7	6
Cu	8	5	5	5	3	6	7	4	4	21
Pb	8	16	13	34	34	25	34	33	21	18
Zn	85	69	71	141	138	87	114	138	19	100
Sn	1	2	3	3	3	3	2	3	2	3
S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Mg#	0.34	0.35	0.24	0.09	0.24	0.11	0.14	0.13	0.08	0.26
D.I.	85.77	92.42	89.90	86.89	85.86	87.56	77.94	78.40	77.74	70.08
K/Na K	0.46	0.48	0.50	0.40	0.45	0.40	0.41	0.43	0.39	0.41
NK/A	0.82	0.86	0.94	1.11	0.96	1.14	1.12	1.07	1.12	1.07
SSI	-41	-72	-56	-480	-469	-459	-165	-372	-61	-164

**TABLE 1.** Continues.

 $\label{eq:NK/A: (Na+K)/Al mol. K/NaK: K_2O/(Na_2O+K_2O) \\ SSI=1000(SiO_2/60.0835-Al_2O_3/101.9601-5(Na_2O/61.9785+K_2O/94.1956)-CaO/56.077-MgO/40.304-MnO/70.937-FeO/71.844+2Fe_2O_3/159.687).$ 

	Trac	hyte	Lamprophyre						
wt%	CBF-29	CBF-22	CBF-25	CBF-06	CBF-35	CBF-36	CBF-16		
SiO <sub>2</sub>	56.80	60.10	46.20	51.21	54.40	48.50	44.00		
$TiO_2$	1.30	0.75	3.10	1.09	1.70	1.90	2.50		
$Al_2O_3$	18.40	16.70	22.00	19.91	17.00	17.50	15.20		
$Fe_2O_3^*$	5.60	4.73	5.40	5.53	7.47	9.70	10.90		
MnO	0.15	0.15	0.19	0.20	0.18	0.22	0.20		
MgO	1.50	0.99	4.20	2.05	2.50	3.20	4.80		
CaO	3.70	2.30	8.00	4.04	4.60	6.80	8.30		
Na <sub>2</sub> O	5.60	5.70	4.00	7.10	5.20	4.10	4.10		
$K_2O$	4.60	5.30	2.90	5.90	4.00	4.40	3.50		
$P_2O_5$	0.41	0.21	1.40	0.30	0.80	0.93	1.70		
Total	98.06	96.93	97.39	97.33	97.85	97.25	95.20		
Ppm									
Cr	7	33	9	12	7	6	15		
Ni	2	14	4	3	3	6	15		
V	18	65	27	22	20	23	105		
Rb	244	109	247	250	245	213	176		
Sr	31	386	258	231	46	213.8	503		
Ba	33	858	241	172	64	106	393		
Zr	1121	399	629	928	1051	591	632		
Y	30	30	30	23	30	19	26		
Nb	378	97	223	303	375	249	265		
Th	63	14	36	60	63	32	34		
U	13	4	7	10	12	7	6		
Cu	4	12	6	7	4	4	21		
Pb	32	11	25	34	33	21	18		
Zn	136	66	87	114	138	19	100		
Sn	2	2	3	2	3	2	3		
<u> </u>	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.		
	0.25	0.00	0.61	0.40	0.40	0.40	0.47		
Mg#	0.35	0.29	0.61	0.42	0.40	0.40	0.47		
D.I.	86.89	85.86	87.56	77.94	78.40	77.74	70.08		
K/Na K	0.40	0.41	0.41	0.42	0.45	0.43	0.52		
NK/A	0.77	0.91	0.44	0.91	0.76	0.66	0.69		
SSI	-480	-469	-459	-165	-372	-61	-164		

**TABLE 1.** Continues.

NK/A: (Na+K)/Al mol.

K/NaK:  $K_2O/(Na_2O+K_2O)$ 

$$\label{eq:SSI} \begin{split} SSI = & 1000 (SiO_2/60.0835 - Al_2O_3/101.9601 - 5 (Na_2O/61.9785 + K_2O/94.1956) - CaO/56.077 - MgO/40.304 - MnO/70.937 - FeO/71.844 + 2Fe_2O_3/159.687). \end{split}$$

	Mo	orro de São J	oão	Itatiaia				
	Nepheline syenite		Pyroxenite	Nepheline syen		ite	Phonolite	
wt%	MSJ-01	MSJ-04	MSJ-03	ITT-01	ITT-03	ITT-04	ITT-05	
SiO <sub>2</sub>	51.98	54.90	45.90	51.98	54.90	45.90	51.98	
TiO <sub>2</sub>	0.92	0.55	3.26	0.92	0.55	3.26	0.92	
$Al_2O_3$	21.80	21.65	17.71	21.80	21.65	17.71	21.80	
$\text{Fe}_2\text{O}_3^*$	2.84	1.70	8.98	2.84	1.70	8.98	2.84	
MnO	0.18	0.21	0.18	0.10	0.15	0.21	0.10	
MgO	0.32	0.43	0.43	0.85	0.32	2.70	0.85	
CaO	1.57	1.56	1.57	2.98	1.80	8.37	2.98	
Na <sub>2</sub> O	8.58	6.45	6.40	3.04	8.20	5.06	3.04	
K <sub>2</sub> O	7.39	9.34	9.42	11.81	7.60	5.91	11.81	
$P_2O_5$	0.06	0.08	0.10	0.13	0.12	0.74	0.13	
Total	97.97	97.52	97.34	96.45	96.99	98.84	96.45	
ppm								
Cr	517	180	144	193	244	255	237	
Ni	4272	661	2162	275	266	1119	25	
V	3187	291	1262	94	70	254	43	
Rb	81	631	438	953	692	778	2170	
Sr	14	16	47	29	45	31	53	
Ba	63	131	175	223	268	175	375	
Zr	6	15	11	29	22	20	48	
Y	1	4	3	6	4	3	12	
Nb	14	5	20	4	4	5	2	
Th	4	14	7	18	16	15	31	
U	44	88	114	98	110	87	258	
Cu	3	2	3	3	4	2	4	
Pb	157	1436	2947	899	610	216	115	
Zn	517	180	144	193	244	255	237	
Sn	4272	661	2162	275	266	1119	25	
S	3187	291	1262	94	70	254	43	
М #	0.27	0.07	0.27	0.01	0.05	0.00	0.11	
Mg#	0.37	0.27	0.37	0.21	0.25	0.26	0.11	
D.I. V/Ne	88.88	89.36	64.06	90.28	89.92	89.98	87.13	
K/INA V	0.00	0.40	054	0.46	0.50	0.60	0.25	
	0.80	0.48	0.54	0.40	0.39	0.00	0.35	
INK/A	0.82	1.00	0.83	0.99	0.97	0.97	1.10	
221	-301	-408	-361	-439	-359	-364	-491	

**TABLE 2.** Main and trace elements for the felsic alkaline rocks of the Itatiaia and the Morro de<br/>São João intrusive complex rock bodies, State of Rio de Janeiro, Brazil.

NK/A: (Na+K)/Al mol. K/NaK: K2O/(Na2O+K2O)

$$\begin{split} SSI = 1000 (SiO_2/60.0835 - Al_2O_3/101.9601 - 5 (Na_2O/61.9785 + K_2O/94.1956) - CaO/56.077 - MgO/40.304 - MnO/70.937 - FeO/71.844 + 2Fe_2O_3/159.687). \end{split}$$



FIGURE 4. Variation diagrams that suggest fractionation crystallisation of clinopyroxene and/or amphibole for the alkaline rocks of the intrusive rock bodies of Cabo Frio Island, Itatiaia, and Morro de São João: A) CaO vs. MgO; B) Fe<sub>2</sub>O<sub>3</sub>\* vs. MgO; C) CaO vs. SiO<sub>2</sub>; D) D.I. vs. Mg#. The D.I. is the sum of all of the CIPW norm felsic minerals and the Mg# corresponds to molecular proportion of Mg/(Fe+Mg).

The Figure 5 presents the classification diagram of Na<sub>2</sub>O+K<sub>2</sub>O vs. SiO<sub>2</sub> of Le Bas et al. (1986). The average  $SiO_2$  of the felsic rocks of the Cabo Frio Island body is 56.3 wt%. Although they are highly felsic with average differentiation index (D.I., Thornton & Tuttle, 1960, the sum of all of the CIPW Norm felsic minerals) of 87.56 wt%, the silica contents are equivalent to andesite. Most of the samples are projected on the phonolite and trachyte fields, and these rocks are classified to be nepheline svenite, phonolite, alkaline syenite. and trachyte. The Na<sub>2</sub>O and K<sub>2</sub>O contents are high, with respective average values of 8.26 and 6.40 wt%. Many samples have Na<sub>2</sub>O+K<sub>2</sub>O higher than 12 wt%. Norm nepheline is high in average 20.13 wt%, being more undersaturated than those of the felsic alkaline rocks of the Tanguá and Rio Bonito intrusive complexes. The nepheline syenite samples CBF-15, CBF-15A, CBF-30, and phonolite ones CBF-30, 31, have high Norm nepheline, respectively of 29.72, 36.43, 29.33, 28.34, and 38.70 wt%. The rocks from the lamprophyre dykes are present on the tephriphonolite, phonotephrite, tephrite, and trachy andesite fields. The sample CBF-16 has the lowest SiO<sub>2</sub> content of 44.00%.



**FIGURE 5.** Geochemical classification diagram of Na<sub>2</sub>O+K<sub>2</sub>O vs. SiO<sub>2</sub> (Le Bas et al., 986) for the alkaline rocks of the intrusive complexes of Cabo Frio Island, Itatiaia, and Morro de São João. The previous data are after Motoki et al. (2010) and Valença (1980).

The Na<sub>2</sub>O vs. K<sub>2</sub>O diagram shows that the most of the felsic rocks of the Cabo Frio Island body fall on the potassic series field, with the average K<sub>2</sub>O/(Na<sub>2</sub>O+K<sub>2</sub>O)<sub>wt%</sub> ratio of 0.44 (Figure 6). They are more sodic than the felsic rocks of the Tanguá and Rio Bonito bodies and still more sodic than the Itaúna body. Most of them are classified to be potassic nepheline syenite or phonolite. On the other hand, the sample MSJ-01 of the Morro de São João has pseudo leucite crystals and very high  $K_2O/(Na_2O+K_2O)_{wt\%}$  ratio, being classified to be an ultrapotassic rock.



**FIGURE 6.** The Na<sub>2</sub>O vs. K<sub>2</sub>O diagram plot (Middlemost, 1975) for the alkaline rocks of the intrusive complexes of the Cabo Frio Island, Itatiaia, and Morro de São João. The previous data are after Motoki et al. (2010) and Valença (1980).

The  $Al_2O_3$  content is high, in average 20.35, 21.66, and 21.73 wt% for the felsic rocks

of the Cabo Frio Island, Itatiaia, and Morro de São João. The mafic rocks have relatively low Al<sub>2</sub>O<sub>3</sub>, in average 18.32 wt%. On the alkalialumina diagram, a half of the samples are classified to be peralkaline and the other to be subalkaline-subaluminous (Figure 7). In comparison with the felsic rocks of the Tanguá, Rio Bonito, and Itaúna complex, those of the Cabo Frio Island are more peralkaline and many samples have Norm acmite. The mafic to intermediate rocks are highly subalkaline and subaluminous. The alkaline syenite and trachyte also show similar tendency, but not so remarkably.



**FIGURE 7**. Alkali-alumina saturation on the Al/(Na+K+1/2Ca)<sub>mol</sub>. vs. Al/(Na+K)<sub>mol</sub>. diagram of Shand (1943) for the alkaline rocks of the Cabo Frio Island, Itatiaia, and Morro de São João intrusive complexes. The previous data are after Motoki et al. (2010) and Valença (1980).

## MINOR ELEMENTS

The Ba contents of the nepheline syenite and alkaline syenite is in average 619 ppm. It is lower than the nepheline syenite and alkaline syenite bodies of the other regions, such as the Vitória Island (Motoki, 1986), but higher than Tanguá and Rio Bonito bodies. The alkaline syenite without nepheline and some samples of trachytic and phonolitic dykes have high Ba content, more than 2000 ppm. The felsic nonalkaline rocks generally have low Sr and Ba, and the Sr shows positive correlation to Ba (Figure 8A). This tendency is observed in the felsic alkaline rocks of the Tanguá and Rio Bonito bodies. However, it is not expressive in the alkaline mafic rocks of this area (Figure 8B).



**FIGURE 8.** Ba-Sr relation for the alkaline rocks of the Cabo Frio Island, Itatiaia, and Morro de São João intrusive complexes, State of Rio de Janeiro, Brazil: A) Samples with relatively low Sr and Ba; B) All analysed rocks.

# FRACTIONATION CRYSTALLISATION

The chemical analyses point out that the felsic rocks and mafic to intermediate ones of this alkaline rock province form two distinct magma differentiation trends without direct linkage.

On the Na<sub>2</sub>O+ $K_2O$  vs. SiO<sub>2</sub> diagram, the felsic rocks exhibit a negative correlation trend and the mafic to intermediate rocks show a widely dispersed positive one (Figure 5). The positive trend is commonly observed in basalt andesite and can be and attributed to fractionation of mafic minerals, although a considerable scattering is observed. The negative trend of the felsic rocks is not due to fractional crystallization but is a characteristic of the nepheline syenite magmas of the State of Rio de Janeiro (Motoki et al., 2010).

On the other hand, the Na<sub>2</sub>O vs. K<sub>2</sub>O diagram, the felsic rocks form a negative correlation trend and alkaline syenite, trachyte, and mafic to intermediate rocks constitute a positive one (Figure 6). The negative trend is considered to be of fractionation of leucite and potash feldspar. This phenomenon is characteristic in the fractionation crystallisation of highly differentiated nepheline syenite magma (Motoki et al., 2010). On the other

hand, the sample of the Morro de São João body, which contains pseudo leucite, is of little fractionated nepheline svenite magma. This diagram is able to reveal the felsic mineral fractionation of the nepheline syenite magma but unable to distinguish the crustal assimilation of the felsic magmas and mafic fractionation mineral of the mafic to intermediate magmas.

The alkali-alumina saturation diagram demonstrates a positive correlation for the felsic rocks (Figure 6). They are highly differentiated nepheline syenite and phonolite with very low MgO, CaO, and Fe<sub>2</sub>O<sub>3</sub>\* and low  $K_2O/(Na_2O+K_2O)_{wt\%}$  ratio (Figure 9). That is, at the last stage of highly differentiated nepheline syenite magma, the magma tends to become more peralkaline, that is, of higher molecular (Na+K)/Almol. ratio. This tendency was pointed out in the nepheline syenite of the Poços de Caldas intrusive complex (Ulbrich, 1984). In fact, the rocks of the Cabo Frio Island are the most differentiated felsic alkaline rocks among those of the State of Rio de Janeiro. On the other hand, the nepheline syenite of the Morro de São João and the Tanguá complex are the least differentiated.



FIGURE 9. The relation between alkali-alumina saturation and fractionation crystallisation for the alkaline rocks of the Cabo Frio Island, Itatiaia, and Morro de São João intrusive bodies: A) (Na+K)/Al<sub>mol.</sub> vs. MgO<sub>wt%</sub>; B) (Na+K)/Al<sub>mol.</sub> vs. K<sub>2</sub>O/(Na<sub>2</sub>O+K<sub>2</sub>O)<sub>wt%</sub>.

The CaO content shows strong positive correlation with MgO and Fe<sub>2</sub>O<sub>3</sub>\* (total Fe recalculated as  $Fe_2O_3$ ), with the R<sup>2</sup> respectively of 0.9292 and 0.8067 (Figure 4A, B), and a moderately negative correlation to SiO<sub>2</sub>, with the  $R^2$  of 0.6110 (Figure 4C). These tendencies are common either for the felsic or for the mafic to intermediate alkaline rocks, suggesting the fractionation of Ca-rich mafic minerals, such as clinopyroxene and amphibole. The modest correlation between negative the D.I. (Differentiation, Thornton & Tuttle, 1960) supports the above-mentioned idea. (Figure 4D).

The CaO demonstrates remarkable positive correlation to  $TiO_2$  and relevant correlation to  $P_2O_5$ , with the  $R^2$  respectively 0.9598 and 0.8686 (Figure 10A, B). These correlations suggest respectively crystallisation of titanite and apatite. The correlation between  $Fe_2O_3$  and  $TiO_2$  is high, with the  $R^2$  of 0.7102, indicating fractionation of ilmenite (Figure 10C). The high correlation indexes indicate that the crystallisation of these minerals occurred either in the felsic or the mafic to intermediate rocks. They are found in the separated mineral grain fractions and the thin sections under microscope observations.

There is certain positive correlation between Na<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub>, with the  $R^2$  of 0.3179 (Figure 10D), pointing out nepheline and/or sodic alkaline feldspar fractionation, with the exception of the samples of Itatiaia and Morro de São João. The positive correlation between  $K_2O$  and  $Al_2O_3$  is also modestly high, with the  $\mathbf{R}^2$ of 0.3682 (Figure 10E), indicating fractionation of leucite and/or potassic alkaline feldspar. The correlation between CaO and  $Al_2O_3$ , with the R<sup>2</sup> of 0.3652 (Figure 10F), can suggest plagioclase fractionation. However, this observation can be explained also by combined fractionation of alkaline feldspar and clinopyroxene or amphibole. In fact, the rocks contain alkaline feldspar, clinopyroxene, and amphibole but no plagioclase. Plagioclase is found only in the mafic to intermediate rocks.



**FIGURE 10.** Variation diagrams with high correlation index for the alkaline rocks of the Cabo Frio Island, Itatiaia, and Morro de São João alkaline intrusive complexes: A) TiO<sub>2</sub> v.s. CaO; B) P<sub>2</sub>O<sub>5</sub> vs. CaO; C) TiO<sub>2</sub> vs. Fe<sub>2</sub>O<sub>3</sub>\*; D) Na<sub>2</sub>O vs. Al<sub>2</sub>O<sub>3</sub>; E) K<sub>2</sub>O vs. Al <sub>2</sub>O<sub>3</sub>; F) CaO vs. Al<sub>2</sub>O<sub>3</sub>.

The Figure 11 shows the relation of the above-mentioned two fractionation crystallisation trends. The mafic mineral fractionation forms a gentle negative correlation trend on the field with MgO>1.0 wt%. The mafic to intermediate rocks of the Cabo Frio

Island are scattered along the gentle negative correlation line. This trend is common in the igneous rocks in general, in addition to these mafic to intermediate alkaline rocks. The most mafic sample is CBF-16, with MgO=4.8 and  $K_2O/(Na_2O+K_2O)_{wt\%}=0.46$ .



**FIGURE 11.** Fractionation crystallisation diagram based on the indicator K<sub>2</sub>O/(Na<sub>2</sub>+K<sub>2</sub>O)<sub>wt%</sub> for felsic minerals, such as leucite and potash feldspar, and MgO for mafic minerals for the alkaline rocks of the Cabo Frio Island and other alkaline intrusive complexes of the State of Rio de Janeiro. The previous data are from Motoki et al. (2010a) and Valença (1980).

On the other hand, the felsic mineral fractionation forms the steep positive correlation trend on the field with MgO<1.0. The felsic rocks of the Cabo Frio Island and Itatiaia fall on the well-differentiated felsic rock field with low  $K_2O/(Na_2O+K_2O)_{wt\%}$ . Those of the Morro de São João, Tanguá, Rio Bonito, Soarinho, and Itaúna are situated on the less-differentiated felsic rock field with high  $K_2O/(Na_2O+K_2O)_{wt\%}$ . This trend is observed

specifically in the felsic alkaline rocks, and not common in non-alkaline rocks.

In this diagram, the fractionation trend for the felsic alkaline rocks and that for the mafic to intermediate alkaline rocks are not continuous, suggesting that the nepheline syenite magma is not directly delivered from the fractionation crystallization of the mafic alkaline magma. The origin of the less differentiated felsic magma is still unknown.

## **RADIOMETRIC DATING**

The authors have performed a laser-spot step-heating <sup>40</sup>Ar-<sup>39</sup>Ar dating for biotite of the Cabo Frio Island nepheline syenite. The dating has been accomplished at John de Laeter Centre, Department of Applied Geology, Curtin University, Perth, Australia. The samples selected for the dating are highly undersaturated rock in order to avoid the influence of the wall rock. The laser spot step-heating  $^{40}$ Ar- $^{39}$ Ar dating for the biotite crystal of the Cabo Frio Island shows a coherent plateau of 54.83±0.35 Ma with the MSWD of 0.49 (Figure 12).



**FIGURE 12**. <sup>40</sup>Ar-<sup>39</sup>Ar step-heating diagram for the biotite crystal of nepheline syenite of the Cabo Frio Island nepheline syenite.

The <sup>40</sup>Ar-<sup>39</sup>Ar age affirms the generally tendency that the ages become younger from the west to the east along the Pocos de Caldas-Cabo Frio alignment, which was pointed out by the data base of Sonoki & Garda (1988). This observation was attributed to supposed hot-spot chain from Poços de Caldas to Trindade Island (Herz, 1977; Thompson et al., 1998; Thomáz Filho & Rodrigues, 1999). However, the Vitória-Trindade Chain is of E-W trend and the South America plate movement relative to hotspots, so-called absolute motion, is of NW-SE (O'Connor direction & Roex, 1992; Steinberger, 2000).

Although the Poços de Caldas-Cabo Frio alkaline magmatic alignment and the Vitória-Trindade Chain are parallel, between them there is 380 km of offset. The western half span of this Vitória-Trindade Chain strikes N77°W. In its western extension, there is the São Mateus Vocanic Province, State of Espírito Santo, of the Late Cretaceous to Early Cenozoic, which is composed of sub-aquatic rhyolitic pyroclastic flows (Motoki et al., 2007d; Novais et al., 2008). The felsic magma could be originated from the continental crust melting caused by the mafic alkaline magmatism (Motoki et al., 2012c).

Moreover, the Poços de Caldas-Cabo Frio are constituted by felsic alkaline rocks, such as nepheline syenite and phonolite, but the Vitória-Trindade chain are made up of mafic alkaline ones, such as alkaline picrite, basanite, nephelinite, and ankaramite (Marques et al., 1999; Siebel et al., 2000; Foddor & Hanan, 2000; Skolotnev et al., 2010).

Above-mentioned observations indicate that the Poços de Caldas-Cabo Frio magmatic alignment does not continue to the Vitória-Trindade Chain and they are not a single volcanic chain of hot-spot track. This problem remains still unsolved.

#### DISCUSSION

Motoki et al. (2010) proposed the geochemical evolution in three stages for highly differentiated nepheline syenite magma based on the chemical analyses of the intrusive complexes of Tanguá, Rio Bonito, Soarinho, and Itaúna, State of Rio de Janeiro, Brazil: 1) Leucite fractionation; 2) Potash feldspar fractionation; 3) Continental crust assimilation. The Figure 13 visualises the above-mentioned processes on the terminal residual diagram of Hamilton & Mackenzie (1960).



FIGURE 13. Geochemical evolution of highly differentiated nepheline syenite magma for the felsic rocks of the Cabo Frio Island and other alkaline intrusive complexes of the State of Rio de Janeiro: A) Projection on the SiO<sub>2</sub>-NeAlSi<sub>3</sub>O<sub>8</sub>-KfAlSi<sub>3</sub>O<sub>8</sub> diagram (Schairer & Bowen, 1935; Hamilton & Mackenzie, 1960); B) Magma evolution trends. The previous data are from Motoki et al. (2010) and Valença (1980).

This figure indicates that the relatively less differentiated felsic alkaline magma is potassium-rich and has Norm leucite. Such magma can crystallise leucite and the residual liquid evolutes to the direction of the cotectic curve, decreasing  $K_2O/(Na_2O+K_2O)_{wt\%}$  ratio. The rocks in this stage, called Stage 1, are few and are found at several localities of the Morro de São João and Tanguá intrusive complexes.

When the magma comes up to the the leucite crystallisation cotectic curve. finishes. The magma evolution occurs along the cotectic curve from potassic to sodic composition, crystallising potash feldspar. The residual liquid decreases K<sub>2</sub>O/(Na<sub>2</sub>O+K<sub>2</sub>O)<sub>wt%</sub> becomes undersaturated. and more The  $K_2O/(Na_2O+K_2O)_{wt\%}$  of the crystallised potash feldspar is of about 0.75 and according to the magma evolution it decreases up to 0.7. The rocks in this stage, called Stage 2, are commonly found in the felsic alkaline complexes of this region. If the crustal assimilation does not take place, the magma composition evolves to the terminal point of the

lowest temperature, which is represented by the Ns point with  $K_2O/(Na_2O+K_2O)_{wt\%}$  of about 0.3.

During the Stage 2, if the magma temperature suddenly rises up, partial melting of the wall rock can take place along the contact zone. The generated magma is felsic and oversaturated in silica, represented by the Gr point composition. The mixture of this magma of granitic composition pulls the composition of the nepheline syenite magma from silica-undersaturated to oversaturated field, crossing over the thermal divide. It is considered that the alkaline syenite and alkaline syenite with quartz are formed by means of this process.

The assimilation of continental crust is relevant, supported by the deformed host rock xenoliths which are found along the contact zone (Photo 2). In the case of alkaline syenite CFB-13, CBF-19, CBF-19, and trachyte CBF-22, CBF-29, the assimilation rate is close to 50 wt%. This ratio is superior to that of the Tanguá, Rio Bonito, Itaúna, Morro de São João, and Itatiaia bodies, and comparable to that of the Soarinho body.

In the case of Cabo Frio Island intrusive body, the  $K_2O/(Na_2O+K_2O)_{wt\%}$  ratio of the felsic rocks is enough low. The leucite fractionation, which characterise the Stage 1, is not observed. Some samples are projected close to the *Ns* terminal point. The felsic alkaline rocks of the Cabo Frio Island are highly differentiated, showing a strong contrast with the Tanguá and Morro de São João bodies, which contain pseudo leucite.

The crustal assimilation crossing over the thermal divide cannot take place during normal magma cooling and fractionation crystallisation. For generation of such magma, nepheline syenite magma must cross over two thermodynamic incompatibility zones (Figure 14): 1) Alkali-silica saturation thermal divide between quartz and nepheline; 2) Alkalinealumina saturation barrier between aegirine and muscovite. In order to cross over the thermodynamic barriers. the magma temperature must be higher than the minimum, which requires magma super-reheating or melting temperature decrease (Motoki, 1986; Motoki et al., 2010; Sichel et al., 2012). They can occur by new injection of high-temperature and/or volatile-rich magma into the unconsolidated nepheline syenite magma chamber. This event, called Stage 3, can take place in any phase of the Stage 2.



**FIGURE 14**. The diagram of Silica Saturation Index (SSI) vs. (Na+K)/Al (mol) for the alkaline rocks of the Cabo Frio Island and other alkaline intrusive complexes of the State of Rio de Janeiro. The SSI (silica saturation index) was defined by Motoki et al. (2010) and the calculation form is shown on the Table 1 and 2. The previous data are from Motoki et al. (2010) and Valença (1980).

Brotzu et al. (1997) proposed that hightemperature and less differentiated nepheline syenite magma with normative leucite could melt the continental crust wall rocks, generating co-existing silica-undersaturated and silicaoversaturated rocks in the Itatiaia intrusive body. According to this model, the assimilated rock, such as alkaline syenite and quartz syenite, should have high  $K_2O/(Na_2O+K_2O)_{wt\%}$ ratio. However, the rocks of the Cabo Frio Island are of low  $K_2O/(Na_2O+K_2O)_{wt\%}$  and this idea is difficult to apply.

In the case of the Tanguá, Rio Bonito, Soarinho, and Itaúna bodies, the intrusive body was formed by successive multiple magma injection, causing multiple magma superreheating events. In the case of Cabo Frio Island, the magma super-reheating occurred only once at the last phase of the Stage 2. The Poços de Caldas felsic alkaline intrusive complex rock body, State of Minas Gerais and São Paulo, has no silica oversaturated rocks (Ulbrich, 1984), suggesting that the magma super-reheating did not occur.

The intrusive complex of the Cabo Frio Island contains xenoliths-like mafic rocks in nepheline syenite (Photo 1D). The Morro de São João body also has xenolith-like pyroxenite of similar field occurrence mode. These mafic rocks could be originated from the hightemperature magma injected into the nepheline syenite magma chamber before its cooling and consolidation. Because of the temperature difference, the pyroxenite magma was frozen, rapidly consolidated, and auto-brecciated, forming the angular xenolith-like shape. These gross-grained alkaline mafic rocks are partially assimilated by the nepheline syenite magma, transforming into deformed enclaves which are made of pyroxenite, amphibolite. up lamprophyre, and monzonite, locally called melano-svenite (Araujo, 1995).

The geochemical data of the alkaline rocks of the Cabo Frio Island, Itatiaia, and Morro de São João intrusive bodies lead to the following conclusions:

1. The intrusive complex of the Cabo Frio Island is constituted mainly by nepheline syenite and partially by alkaline syenite at the contact zone with country orthogneiss, with the presence of dykes and sills of phonolite and trachyte. The distribution of the main intrusive body is limited within the island with no continuity to the Pontal da Atalaia Peninsula. In the island, the host orthogneiss is exposed at the western. southern. south-eastern. eastern, and north-eastern parts.

2. More than a half of the analysed rocks are silica undersaturated with moderate  $(Na+K)/Al_{mol}$ and  $K_2O/(Na_2O+K_2O)_{wt\%}$ ratios. They are classified to be potassic nepheline syenite. These rocks are peralkaline. These observations indicate that they are highly advanced in fractionation crystallisation. On the other hand, the nepheline syenite magma was superheated by the mafic to ultramafic magma, and melted the country orthogneiss. If the superheated magma temperature was enough high and superior to the thermal divide, the silica-undersaturated nepheline syenite magma could mix chemically with the silica oversaturated magma originated from the country rock partial melting, generating the alkaline syenite magma. The minimum temperature elevation for the total assimilation of the country rock is only 50°C.

# CONCLUSION

According to the magma fractionation, the residual magma tends to become more peralkaline elevating (Na+K)/Al mol. ratio.

3. The variation diagrams for the main elements strongly indicate the in-situ crystallisation of titanite, ilmenite, apatite, and clinopyroxene or amphibole during the magma cooling at the magma chamber which corresponds to the pluton.

4. The laser spot step-heating <sup>40</sup>Ar-<sup>39</sup>Ar age for biotite crystal is 54.83±0.35 Ma.

assimilation effect 5. The of continental crust country rock is relevant and some of the samples are composed of about 50% of assimilated materials. These rocks, alkaline syenite and trachyte, are thermodynamically unstable, and could be formed by a new injection of hightemperature or fluid-rich magma. Different from the cases of Tanguá and Rio Bonito bodies, the continental crust assimilation event for the Cabo Frio Island took place at the last phase of fractionation crystallisation process.

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