Geochim. Brasil., **8**(1): 21-39, 1994

THE GEOCHEMISTRY OF ALKALINE VOLCANIC-SUBVOLCANIC ROCKS FROM THE BRAZILIAN FERNANDO DE NORONHA ARCHIPELAGO, SOUTHERN ATLANTIC OCEAN

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Recebido em: 06/93. Aprovado para publicação em: 02/94

ABSTRACT

The Fernando de Noronha Archipelago consists of two volcanic formations; the Remédios Formation (12 to 8 Ma old), constituted by a basal pyroclastic unit and an intrusive Subvolcanic Central Complex, capped by the post-erosional Quixaba Formation (3 to 1.8 Ma old), with flows and a few smaller intrusions.

Most intrusive Remédios rocks belong to two petrographic series: a *ne*-normative to *qz*-normative, mildly potassic, alkali basalt-trachyandesite-trachyte series, and a sodic undersaturated basanite and tephrite-tephritic phonolite-phonolitic tephrite-phonolite association. Possible parental magmas have the compositions of alkali basalt (Nb:Zr = ± 1:6) and basanite-tephrite (Nb:Zr = ± 1:3) or limburgite (Nb:Zr = ± 1:4). Chemical data of amphibole-rich tephrites (with matrix amphibole) suggest "contamination" of dry tephritic material with a volatile-rich "lamprophyric" liquid. Two kinds of lamprophyres occur in the Remédios Formation: the P_2O_5-rich tephritic or melanocratic lamprophyres and the more evolved P_2O_5-poorer typical lamprophyres.

Extensive Quixaba flows of ankaratrites (type A) show restricted chemical composition (SiO_2 = 37-38%; MgO = 9-12%). Type B ankaratrites are more varied (SiO_2 = 39-45%). Ba/Nb versus La/Nb plots indicate that both types are derived from different parental magmas and mantle sources. A basanite pipe intruding ankaratrites and the basanite rocks that compose the islets of the São José, Cuscus and de Fora represent the final stages of the Quixaba volcanism.

RESUMO

O Arquipélago de Fernando de Noronha apresenta duas formações vulcânicas, a Formação Remédios (12 a 8 Ma), composta por uma unidade basal de rochas piroclásticas e um Complexo Subvulcânico Central, capeada pela Formação pós-erosional Quixaba (3 a 1,8 Ma), contendo derrames e algumas pequenas intrusões.

As rochas intrusivas da Formação Remédios pertencem a duas séries petrográficas: a série álcali basaltos-traquiandesitos-traquitos, moderadamente potássica, com nefelina ou quartzo na norma, e a série sódica, subsaturada, de basanitos e tefritos-tefritos fonolíticos - fonolitos tefríticos - fonolitos. Possíveis magmas progenitores apresentam composições de álcali basalto (Nb:Zr ± 1:6) e basanito-tefrito (Nb:Zr ± 1:3) ou limburgito (Nb:Zr ± 1:4). Os dados químicos de tefritos ricos em anfibólio (com anfibólio na matriz) sugerem "contaminação" de material tefrítico anidro com líquido "lamprofírico" rico em voláteis. Dois tipos de lamprófiros ocorrem na Formação Remédios: os tefríticos ou melanocráticos, ricos em P_2O_5 e os lamprófiros típicos, mais evoluídos e mais pobres em P_2O_5.

Os extensos derrames de ankaratrito da Formação Quixaba (tipo A) possuem composição química restrita (SiO_2 = 37-39%; MgO = 9-12%). Os do tipo B são mais variados (SiO_2 = 39-45%). As relações Ba/Nb e La/Nb indicam que esses tipos provêm de magmas progenitores e fontes mantélicas diferentes. O "pipe" de basanito, que corta ankaratritos, e os derrames de basanitos, que compõem as ilhotas São José, Cuscus e de Fora, representam os estádios finais do vulcanismo.

INTRODUCTION

The Brazilian Fernando de Noronha Archipelago, located 345 km off the Brazilian coast at latitude 3°51'S and longitude 32°25'W, consists of a main island and several islets, with a total area of about 18.4 km² (Fig. 1).

The Archipelago was mapped by Almeida (1955), who defined two main volcanic units, the older Remédios (12.3 to 8 Ma; Cordani, 1970) and the younger Quixaba (3.3 to 1.8 Ma; Cordani, 1970) formations, separated by an erosional hiatus (Almeida, 1955; cf. also a summary of Almeida's work, with comments, by Mitchell-Thomé, 1970). Similar features were found in other oceanic islands, which present a more or less exposed "Central Igneous Complex" and a younger volcanic cover (e.g. Cabo Verde Islands, Furnes & Stillman, 1987), corresponding, in Fer-

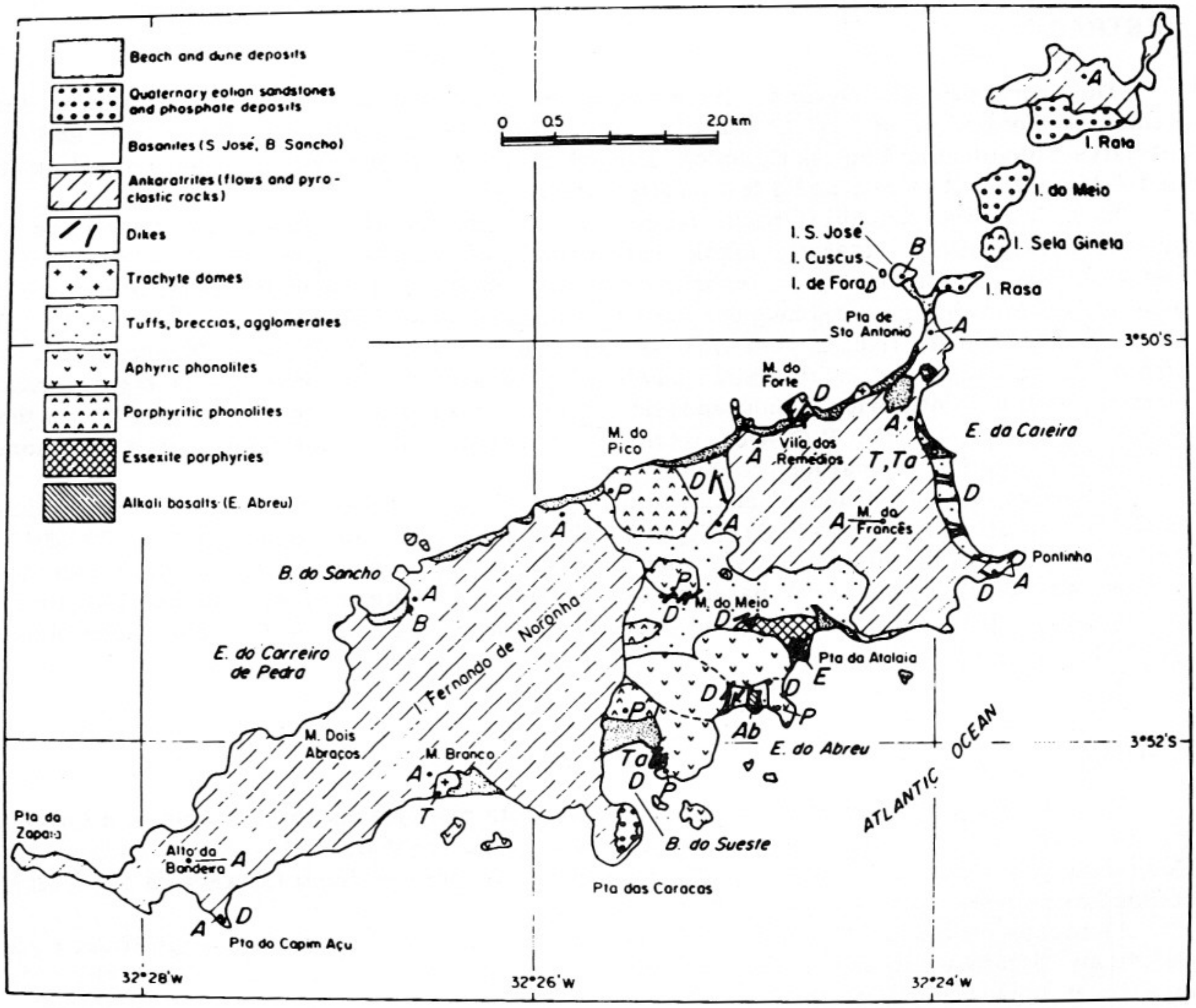

Figure 1 – Geological map of the Fernando de Noronha Archipelago (simplified after Almeida, 1955), showing the location of samples with chemical analysis (Tables 2 and 3). Only some of the numerous dike locations present in the B. do Sueste, E. do Abreu, Pta. da Atalaia and in the northern part of the E. das Caieiras are shown. Abreviations. B: Baía and E. Enseada (Bay). I. Ilha (Island), M: Morro (Mount), Pta. Ponta (Point).

nando de Noronha, approximately to the two mentioned formations.

The large variability in terms of petrography and possible genetic relationships of the highly alkaline undersaturated rocks of Fernando de Noronha was clearly shown since the early studies of Almeida (1955).

In the Remédios Formation, at least two petrographically distinct series are recognized (Ulbrich, 1993), one made up by the sodic undersaturated basanite-tephrite-phonolite series and the other composed by a K-enriched alkali basalt-trachyandesite-trachyte association. The Quixaba volcanism, on the other hand, is predominantly of a nephelinitic (ankaratritic) nature. Series such as the ones mentioned here are frequently observed in oceanic islands (cf. for instance, Wilson, 1989).

Gerlach et al. (1987) separate the Fernando de Noronha rocks in two *isotopic groups*, one corresponding to the alkali basalt-trachyte series and the other including all the sodic alkaline rocks of the Remédios and Quixaba Formations. The alkali basalt-trachyte group, with restricted isotopic ranges, presents more radiogenic Sr-isotopic ($^{87}Sr/^{86}Sr$ = 0.70457-0.70485) composition and less radiogenic Nd-isotopic ($^{143}Nd/^{144}Nd$ = 0.51271-0.51285) and Pb-isotopic ($^{206}Pb/^{204}Pb$ = 19.132-19.282) compositions than the second group. The isotopic data of the second group show no particular trend (Gerlach et al., 1987).

Recent geological observations, as well as a general petrographic account, are given in Ulbrich (1993). A brief summary follows, using mainly the nomenclature proposed by the IUGS Subcommission on the Systematics of Igneous Rocks (e.g. Le Maitre, 1989), and also preserving some of the varietal names frequently found in the literature on oceanic islands.

The Remédios Formation is constituted by a basal group of pyroclastic rocks (lapilli tuffs, breccias and agglomerates) invaded by dikes of phonolitic tephrites (to tephritic phonolites) and a sheet-like intrusion of coarse-grained equivalents (essexite porphyry), by several domes and some dikes of either porphyritic or aphyric phonolites and by dikes and plugs of alkali basalts, trachybasalts, trachyandesites and trachytes. Also present are a large variety of ultrabasic to basic alkaline dike rocks: limburgites, with clinopyroxene, magnetite and olivine set in a glassy groundmass; tephrites and basanites grading into amphibole-rich tephrites due to increasing amounts of amphibole in the matrix; tephritic or melanocratic lamprophyres with amphibole phenocrysts and an almost amphibole-free matrix, and typical lamprophyres, with a panidiomorphic texture, abundant amphibole (both as phenocryst and matrix mineral) and a more felsic groundmass than that shown by the melanocratic lamprophyres (cf. Table 1 and Fig. 1).

The Quixaba Formation shows mainly type A and B ankaratrites (melanocratic olivine nephelinites with some biotite flakes), the first ones presenting more olivine phenocrysts and lesser amounts of clinopyroxene than the B type. Type A ankaratrites are intruded by ankaratrite and nephelinite dikes and also by a basanite pipe (the Baía do Sancho occurrence; Ulbrich & Ruberti, 1992).

Dikes and flows of ultrabasic rocks, with little or no stratigraphic control, were attributed to the Quixaba volcanism on petrographic grounds (Ulbrich, 1993). They include several ankaratrite dikes that only cut rocks of the Remédios Formation ("tannbuschites" of Almeida, 1955; cf. Table 1), and the basanite flows that compose the islets of São José, Cuscus and de Fora.

The present paper reports major and trace element analysis of Fernando de Noronha rocks. The purpose of this work is to discuss the possible genetic relationships among rocks of the Remédios Formation, on the one hand, and of the Quixaba Formation, on the other, and to compare the chemical features of the Remédios and Quixaba magmatic cycles, with a characterization of the possible parental magmas.

METHODOLOGY

Samples and analytical methods

Eighty-five samples covering the main petrographic types, described in Ulbrich (1993), were selected for chemical analysis.

In order to obtain a representative collection of data, the selection included 26 samples of ankaratrites and 13 samples of phonolites from all the locations shown in Figure 1. In addition, most of the ultrabasic-basic dikes intruding the Remédios Formation were also analyzed; sample locations are listed in Table 1.

Although only fresh rocks were selected for analysis, most of them show some alteration or secondary minerals. Olivine is a fresh mineral in the ankaratritic and limburgitic dikes, but is altered in all the amphibole-rich tephritic rocks. In some ankaratritic flows and, particularly, in the basanites of the Baía do Sancho, olivine is substituted by serpentine and/or goethite. Small amounts of zeolites are conspicuously present in the ultrabasic-basic dikes; in some, analcime is an important constituent. Another common feature of the dikes and to a lesser extent of most ankaratrites is the presence of irregularly-shaped amygdules or globular structures filled with zeolites acompanied by carbonates and sometimes also with subordinate chlorite.

To minimize the content of alteration patches or secondary materials, crushed cm-sized chips of the rocks were handpicked under a binocular microscope. The chips were then further crushed in an agate mill to less than 100 mesh.

The rock powders were prepared at the Institute of Geosciences, University of São Paulo. Major and trace element analyses were carried out using Philips PW 1400 XRF spectrometers in two different

Table 1 – Location of sampled ultrabasic-basic dikes of the Remédios (R) and Quixaba (Q) Formations.

Location	Dike rock type	Wall rock
Coastal areas		
Enseada da Caieira	Ankaratrites, (Q) limburgites, (R) tephrites, basanites, (R) tephritic lamprophyres, (R) typical lamprophyres (R)	Pyroclastic rocks
Pontinha	Nephelinite (Q)	Ankaratrite flow
Enseada do Abreu	Ankaratrites, (Q) tephrites, basanites, (R) tephritic lamprophyres (R)	Pyroclastic rocks, phonolite dome
Ponta do Atalaia	Tephrites, (R) tephritic lamprophyres (R), typical lamprophyres (R)	Essexite porphyry sill, pyroclastic rocks
Baía do Sueste	Limburgites (R)	Phonolite dome
Morro do Forte	Tephritic lamprophyres (R) typical lamprophyres (R)	Phonolite dome
Vila dos Remédios	Ankaratrite (Q)	Ankaratrite flow
Ponta do Capim Açú	Ankaratrite (Q)	Ankaratrite flow
Interior of the main island		
Morro do Meio	Tephrites, (R) typical lamprophyres (R)	Phonolite dome, pyroclastic rocks
Essexite porphyry sill	Tephrites (R), tephritic lamprophyres (R)	Essexite porphyry sill, pyroclastic rocks
Close to the Morro do Pico	Typical lamprophyres (R), olivine nephelinite (Q)	Pyroclastic rocks

laboratories.

The ultrabasic-basic dikes of the Remédios Formation (39 samples), including the ankaratritic dikes, were analyzed on glass fusion beads for major elements and on powder briquettes for trace elements at the "Istitut für Geowissenschaften", in Mainz, Germany (for methodology, see Verma et al., 1992). Fe^{2+} was determined by titration with potassium dichromate at the Chemistry Laboratory of the Institute of Geosciences, São Paulo, Brazil. The remaining rocks of the Remédios Formation and those of the Quixaba Formation, totalling 50 samples, were analyzed by one of us (E. Ruberti) in the University of Cagliari, Italy, at the "Istituto de Giacimenti Minerari"; major and trace element analyses were performed on powder briquettes and Fe^{2+} was determined by titration with potassium permanganate (methodology in Franzini et al., 1972).

Chemical data used in this work

The chemical data were screened for the effects of alteration products and for anomalous enrichment or depletion in major and trace elements.

Post-magmatic and/or hydrothermal alteration seems to be able to leach selectively some of the more "mobile" elements, such as the alkalies, Ca and Rb, among others. On the other hand, they may selectively incorporate other elements (e.g. Cl, F). Ba enrichment, possibly by secondary processes, was found by Chaffey et al. (1989) in the Santa Helena alkaline rocks.

Anomalous amounts of some of these trace elements (Sr or Rb and mainly Ba) were determined in some Fernando de Noronha dike and ankaratrite samples, and cannot be correlated with the mineralogy of the rocks (e.g., contents of feldspars).

In other cases, a rather wide scatter of elements may point out discrepancies due to unidentified analytical errors or to the effect of secondary processes. Samples departing from the general trend in diagrams depicting an evolutionary petrogenetic sequence must also be considered with caution (cf. discussion in Chen & Frey, 1985; Chaffey et al., 1989; Weaver, 1990).

Very high LOI values determined at 1000°C are registered in many dike samples, particularly lamprophyres and other rocks with abundant amphibole and/or sodalite group minerals or analcime. Independent determinations of H_2O^+, SO_3 and CO_2 justify in many cases these high LOI values, but the figures obtained for some samples remain suspect and may be related to an incomplete removal of vug fillings during separation procedures; in some cases LOI may include other elements (alkali loss?; I. McReath, personal communication).

As a result of the screening process, the chemical data of nine samples were discarded. Representative analyses of rocks of the Remédios and Quixaba Formations are presented in Tables 2 and 3.

MAJOR AND TRACE ELEMENTS GEOCHEMISTRY

The chemical data were recalculated on a volatile-free basis, with total FeO adjusted to $Fe_2O_3/FeO = 0.3$. The compositions of the dikes and small intrusions of the Remédios Formation are plotted in Harker variation diagrams in Figure 2 and those belonging to the flows and dikes of the Quixaba Formation are shown in Figure 3, including the São José and Baía do Sancho basanites. For comparison purposes, the Remédios limburgite dikes and the ultrabasic ankaratrite dikes (attributed to the Quixaba volcanism) are represented in both figures.

In the following discussion, the Fernando de Noronha subvolcanic-volcanic rocks are grouped according to their chemical and petrographical features, in order to establish possible differentiation series (cf. also Ulbrich, 1993).

Tephrites-basanites, amphibole-rich tephrites and lamprophyres

Tephrites, basanites and amphibole-rich tephrites are mainly characterized by a continuous increase in amphibole in the matrix, either as isolated prisms or concentrated in vug-like areas (Ulbrich, 1993). The chemical trend in major elements (Fig. 2) correlates with petrographic variations such as decrease in olivine content from basanites to tephrites, relative proportions of mafic to felsic minerals and also changes in the composition of the feldspar (calcic plagioclase or anorthoclase).

The increase in some incompatible trace elements appears to be directly related to the increase in amphibole in the samples. Figure 4 shows that the amphibole-free (or amphibole-poor) tephrites and basanites (see Table 2) also present rather constrained Nb:Zr values (ratio about 1:3, cf. data surrounded by a circle in Fig. 4), while the data of dike rocks richer in matrix amphibole depart from that ratio giving values closer to 1:4.

The chemical trend shown in Figure 4 by the amphibole-free basanites and tephrite to the amphibole-rich tephrites displays a continuous variation and suggests, as well as the petrographic features described in Ulbrich (1993), a complex sequence reminiscent of mixing of tephritic material with a (lamprophyric?) liquid rich in incompatible elements and volatiles, rather than differentiation controlled by crystal fractionation.

The tephritic or melanocratic lamprophyres present amphibole in the

Table 2 – Representative analysis of rocks from the Remédios Formation.

	Alkali basalt	Essexites		Phonolites		Trachyandesite	Trachytes		Limburgite	Basanite
Body	d	sill		domes		plug	plugs		d	d
Sample No.	WFN3	FN10	FN11	FN127	FN65	FN42	FN28a	FN61	WFN2	WFN21
SiO_2 (%)	41.92	49.88	51.93	55.85	56.08	59.90	60.68	61.34	42.70	39.59
TiO_2	3.95	1.64	1.32	0.51	0.17	0.40	0.39	0.41	3.52	3.31
Al_2O_3	10.38	17.33	18.97	21.28	20.68	19.80	19.47	20.00	11.66	11.70
Fe_2O_3	14.36	2.16	2.12	1.65	2.05	2.21	1.31	1.75	12.81	11.80
FeO		4.09	2.99	1.16	0.16	0.50	0.75	0.60		
MnO	0.16	0.15	0.15	0.13	0.24	0.12	0.13	0.14	0.17	0.19
MgO	9.41	5.06	3.20	0.80	0.73	1.44	0.32	0.68	9.93	9.32
CaO	12.75	5.72	4.77	2.12	0.61	1.82	1.88	1.71	10.73	14.00
Na_2O	1.96	5.72	6.20	8.35	9.84	4.78	6.80	5.56	3.15	2.61
K_2O	1.41	3.31	4.48	5.87	4.43	4.99	5.90	5.25	2.24	0.54
P_2O_5	0.33	0.42	0.35	0.10	0.02	0.06	0.05	0.05	0.87	0.72
LOI	3.23	3.64	2.99	1.68	4.12	3.85	1.96	2.20	1.88	5.90
Total	99.86	99.12	99.47	99.50	99.13	99.87	99.64	99.69	99.66	99.68
Fe_2O_3*	5.44								4.60	5.51
FeO*	8.12								6.82	5.38
SO_3	0.05								0.01	0.09
CO_2	0.78								0.15	0.58
Cr (ppm)	451	110	62	n.d.	n.d.	n.d.	n.d.	n.d.	293	258
Ni	161	83	55	8	n.d.	3	n.d.	1	213	451
Co	60								52	63
V	430	122	100	47	9	31	36	34	298	306
Cu	68								62	49
Pb	n.d.	13	10	15	35	10	8	15	6	6
Zn	112	99	100	101	225	119	87	123	141	119
Rb	32	80	121	199	346	174	210	190	72	14
Ba	232	650	665	417	19	950	1065	1135	544	584
Sr	601	1031	1168	736	180	699	725	1030	1086	745
Nb	38	96	110	111	187	108	99	116	85	92
Zr	229	469	571	737	1687	824	885	905	378	291
Y	26	21	19	18	32	23	14	24	38	28
Th	5								10	10
U	n.d.								3	3
La		109	123	93	174	138	105	139		
Ce		139	147	100	156	153	116	164		
mg#	56.3	59.9	53.8	35.0	39.4	50.9	22.8	35.9	61.3	56.6
Nb/Zr	0.17	0.21	0.19	0.15	0.11	0.13	0.11	0.13	0.22	0.32
La/Nb		1.13	1.11	0.84	0.93	1.28	1.06	1.20		
Ba/Nb	6.11	6.75	6.03	3.77	0.10	8.82	10.79	9.77	6.40	6.35
Ba/La		5.98	5.42	4.48	0.11	6.88	10.14	8.14		

(Continued Table 2)

	Tephrites			Amphibole-rich tephrites		Tephritic lamprophyres		Typical lamprophyres	
Body	d	d	d	d	d	d	d	d	d
Sample No.	WFN14	WFN19	WFN36	WFN26	WFN59	WFN30	WFN57	WFN17	WFN52
SiO_2 (%)	41.30	42.48	43.84	41.21	43.60	40.47	42.91	45.50	46.32
TiO_2	2.69	2.98	3.07	3.23	2.69	3.40	3.86	2.29	2.08
Al_2O_3	13.50	13.56	14.38	12.48	14.80	15.34	14.24	18.60	17.59
Fe_2O_3	10.60	10.57	11.08	12.04	9.88	11.30	12.67	7.15	7.67
FeO									
MnO	0.17	0.15	0.16	0.19	0.18	0.21	0.20	0.15	0.19
MgO	7.55	6.63	7.30	9.63	5.88	5.35	6.32	3.78	2.99
CaO	11.50	10.53	9.72	11.73	9.75	11.10	10.94	5.75	7.81
Na_2O	4.33	3.34	4.05	3.15	4.53	4.04	3.64	2.55	3.74
K_2O	2.21	2.25	2.03	1.97	2.84	2.74	1.40	4.59	4.09
P_2O_5	0.59	0.67	0.71	0.70	0.79	0.98	1.08	0.68	0.58
LOI	4.90	6.40	3.60	3.08	4.48	4.23	2.37	8.20	6.76
Total	99.34	99.56	99.94	99.41	99.42	99.16	99.63	99.24	99.82
Fe_2O_3*	4.16	4.34	1.90	5.30	3.58	3.97	3.81	3.06	2.30
FeO*	5.74	5.50	8.26	6.10	5.62	4.42	5.60	3.59	4.83
SO_3	0.1	0.07	n.d.	0.13	0.14	0.12	0.02	0.14	0.02
CO_2	0.74	0.68	0.17	0.21	0.15	0.36	0.7	0.04	0.32
Cr (ppm)	319	204	131	393	232	129	55	n.d.	21
Ni	208	127	107	191	125	75	59	13	20
Co	43	40	37	44	32	24	36	17	16
V	227	250	248	290	236	186	307	163	153
Cu	44	62	72	61	46	37	47	25	25
Pb	5	6	5	4	10	9	6	14	14
Zn	112	113	112	124	130	124	145	114	n.d.
Rb	64	74	45	47	108	59	11	147	127
Ba	779	718	738	772	933	1048	674	1240	1094
Sr	1079	980	1105	1383	1552	1830	1499	1463	1895
Nb	98	96	101	100	129	154	116	177	163
Zr	325	315	318	362	456	487	414	514	573
Y	29	32	31	34	38	35	46	38	38
Th	9	10	11	11	16	17	10	27	26
U	3	3	2	4	4	5	2	8	7
La									
Ce									
mg#	56.6	55.7	56.6	61.2	54.2	55.8	55.5	55.5	43.6
Nb/Zr	0.30	0.30	0.32	0.28	0.28	0.32	0.28	0.34	0.28
La/Nb									
Ba/Nb	7.95	7.48	7.31	7.72	7.23	6.81	5.81	7.01	6.71
Ba/La									

FN samples analyzed in Cagliari; WFN samples analyzed in Mainz; Fe_2O_3* and FeO* determined in São Paulo; d: dike; mg# = 100 Mg/(Mg + Fe); n.d.: not detected

Table 3 – Representative analyses of rocks from the Quixaba Formation.

		Ankaratrite			Flows		Nephelynite	Ni- and Cr-rich ankaratrites		Basanites	
Body	A	A	A	B	B	B	d	d	d	I.S. José pipe	B. do Sancho flow
Sample No.	FN41	FN67	FN110	FN29	FN83	FN115	FN80	WFN27	WFN45	FN15	FN79
SiO_2 (%)	37.13	37.07	38.32	39.21	44.20	40.27	39.43	39.58	40.78	44.82	44.90
TiO_2	3.64	3.66	3.50	3.91	2.92	3.11	3.32	2.90	2.85	2.73	2.65
Al_2O_3	11.57	11.93	12.00	11.95	12.94	12.83	17.23	10.21	9.50	12.93	13.61
Fe_2O_3	5.21	2.91	5.05	4.72	4.84	7.53	4.61	12.84	11.80	8.80	3.17
FeO	7.33	9.29	6.72	8.09	6.73	4.39	5.07			2.84	8.23
MnO	0.21	0.20	0.19	0.20	0.17	0.18	0.17	0.19	0.17	0.18	0.17
MgO	11.89	11.52	12.74	11.33	9.40	10.13	5.36	13.55	13.67	8.46	9.45
CaO	14.13	13.45	13.15	12.04	10.59	12.10	10.84	12.49	12.85	10.67	10.83
Na_2O	2.50	4.12	4.19	3.78	4.85	4.78	4.02	2.85	2.61	3.58	3.63
K_2O	1.35	1.02	1.95	1.08	1.43	0.81	1.65	0.85	0.64	0.91	1.08
P_2O_5	1.40	1.51	1.10	1.23	0.64	0.94	1.76	0.70	0.75	0.89	0.66
LOI	2.79	2.50	0.83	2.37	0.81	2.00	5.98	3.40	3.80	3.18	1.26
Total	99.15	99.18	99.74	99.91	99.52	99.07	99.44	99.56	99.42	99.99	99.64
Fe_2O_3*								4.11	2.45		
FeO*								7.60	8.33		
Cr (ppm)	319	304	352	491	292	253	n.d.	512	686	319	318
Ni	159	158	166	225	165	212	8	359	451	281	247
Co								62	65		
V	305	300	313	320	261	302	228	278	291	223	216
Cu								70	67		
Pb	5	8	n.d.	13	10	n.d.	5	n.d.	5	n.d.	6
Zn	114	119	97	109	116	96	100	116	116	108	108
Rb	69	42	44	15	27	5	41	31	18	16	25
Ba	911	973	818	669	736	754	1612	517	490	618	478
Sr	1208	1200	974	925	812	817	1480	779	993	1109	833
Nb	129	121	109	90	66	86	179	73	80	68	69
Zr	384	373	316	350	240	269	398	220	265	315	244
Y	28	29	23	26	21	21	31	26	28	21	22
Th								7	8		
U								2	3		
La	89	86	76	51	92	66	132			54	46
Ce	167	159	121	114	121	100	191			107	104
mg#	63.8	63.3	60.0	62.1	60.2	61.8	50.9	68.1	69.8	58.4	60.3
Nb/Zr	0.34	0.32	0.34	0.26	0.28	0.32	0.45	0.33	0.30	0.22	0.28
La/Nb	0.69	0.72	0.70	0.57	1.39	0.77	0.74			0.79	0.66
Ba/Nb	7.06	8.08	7.50	7.47	11.11	8.74	9.01	7.08	6.13	9.07	6.95
Ba/La	10.19	11.29	10.76	13.07	7.99	11.38	12.22			11.52	10.50

A: type A ankaratrite; B: type B ankaratrite; d: dike; n.d.: not detected. Other details in Table 2.

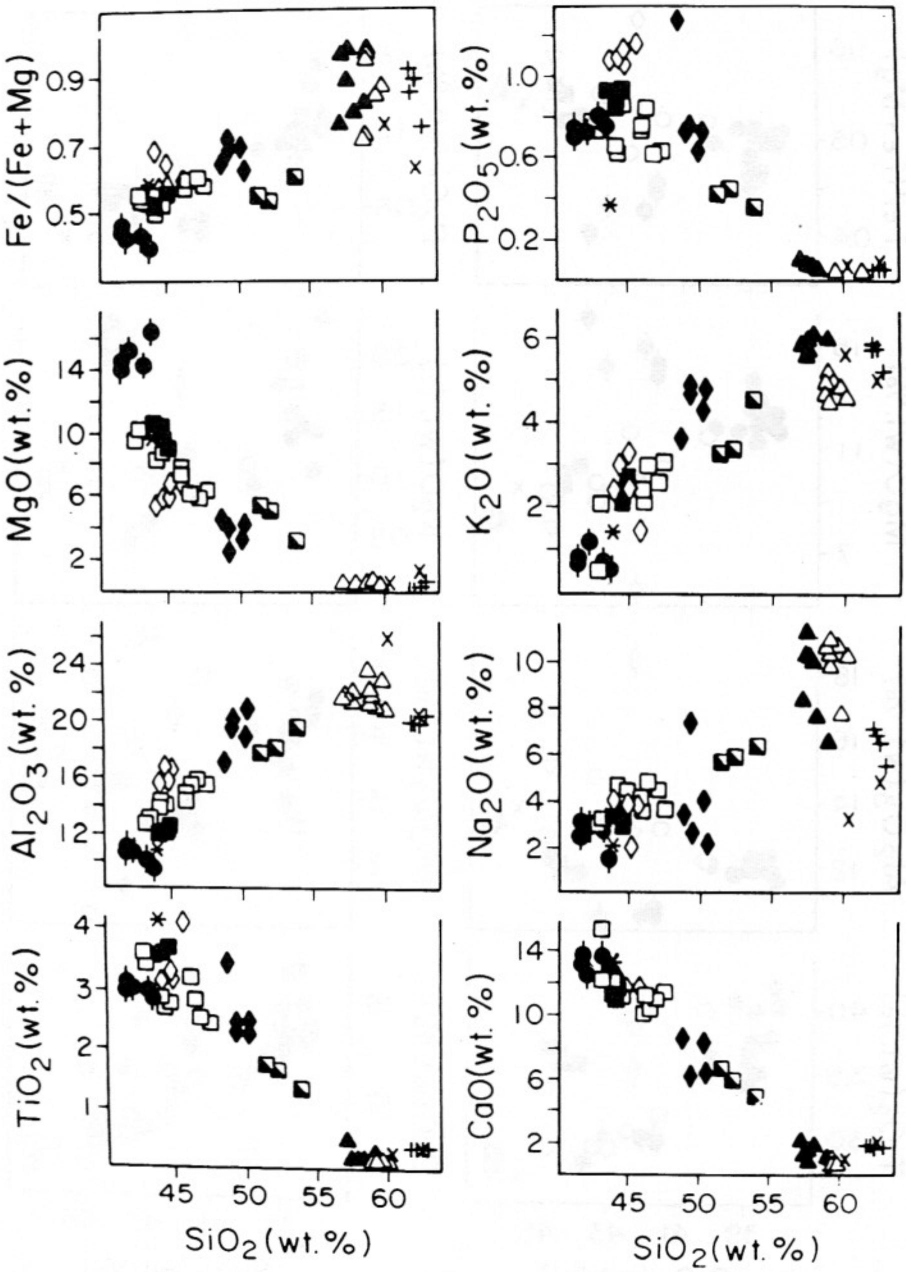

Figure 2 – Whole-rock major element variation for domes, plugs and dikes of the Remédios Formation; also plotted are the ankaratrite dikes (as Ni- and Cr-rich ankaratrites) whose stratigraphic position is discussed in the text. Crossed filled circles: Ni- and Cr-rich ankaratrites; filled squares: limburgites; open squares: basanites, tephrites and amphibole-rich tephrites; open diamonds: melanocratic or tephritic lamprophyres; filled diamonds: typical lamprophyres; asterisk: alkali basalt; half-filled squares: essexite porphyries; filled triangles: porphyritic phonolites; open triangles: aphyric phonolites; x: trachyandesites; crosses: trachytes.

phenocryst assemblage, as idiomorphic crystals or resorbed grains, and a matrix of tephritic composition practically without amphibole; they carry also sodalite and apatite (Ulbrich, 1993). This group of rocks has also a different major element composition, with somewhat lower MgO and higher Al_2O_3 and P_2O_5 than tephritic rocks with equivalent SiO_2 content (Fig. 2). Although the Nb:Zr ratio of some tephritic lamprophyres overlaps that of the amphibole-rich tephrites, the samples

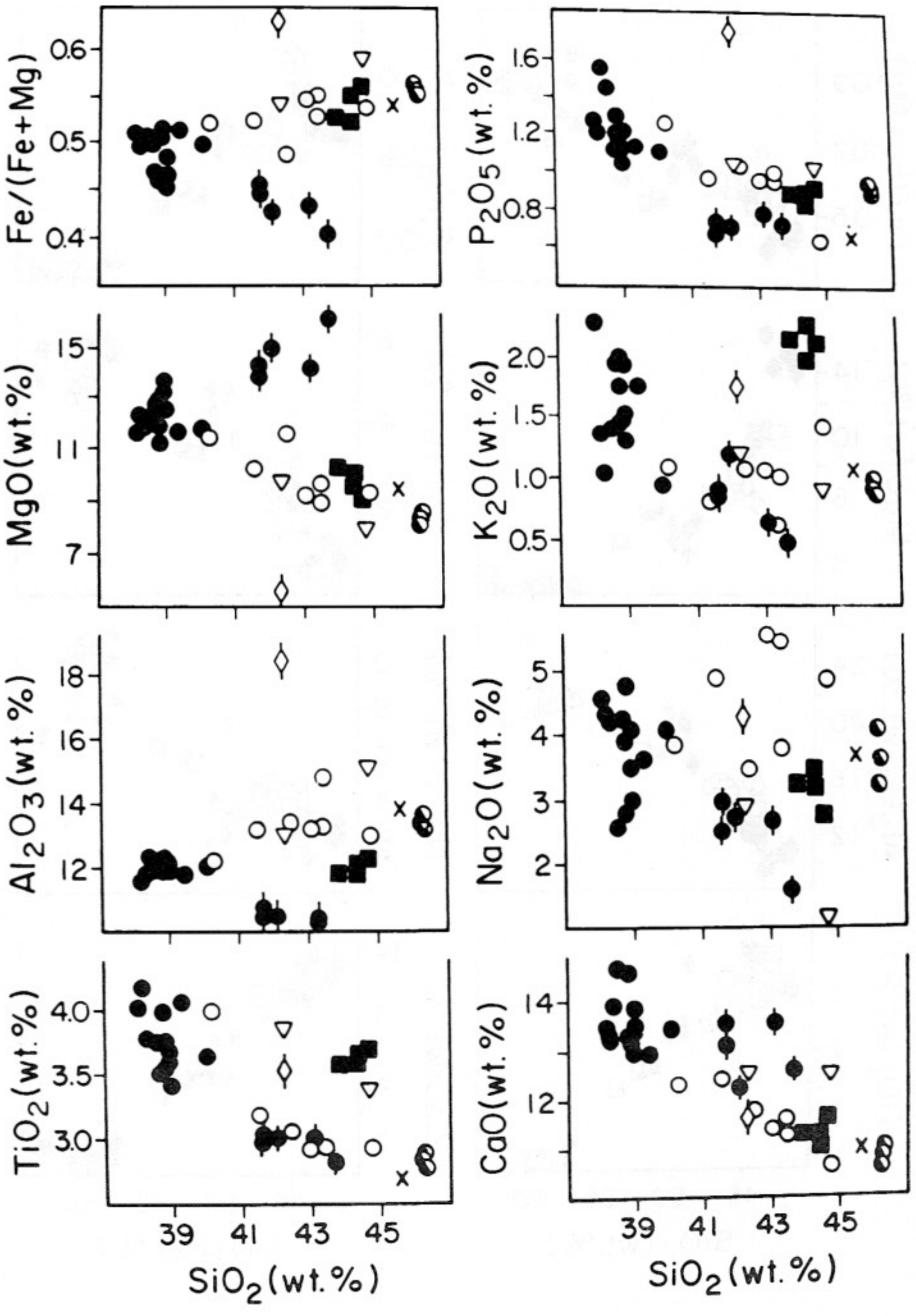

Figure 3 – Whole-rock major element variation for the rocks of the Quixaba Formation: ankaratrites and São José basanitic flows, ankaratritic and nephelinitic dikes and Baía do Sancho basanitic pipe. Also included are data of the limburgites of the Remédios Formation and of the Ni- and Cr-rich ankaratrites (see text). Filled circles: type-A ankaratrites; open circles: type-B ankaratrites; open inverted triangles: ankaratrite dikes; open diamond with bars: nephelinite dike; crossed filled circles: Ni- and Cr-rich ankaratrite dikes; filled squares: limburgite dikes; x: São José basanite; half-filled circles: Baía do Sancho basanites.

richer in trace elements have a Nb:Zr ratio close to 1:3 (Fig. 4).

The petrographically distinct group of typical alkaline lamprophyres is more evolved than all the tephritic dike rocks (SiO_2 ± 50%; Fig. 2), showing low values of MgO, CaO and Na_2O (except for one sample rich in Na_2O) and low Ni and Cr contents, coupled with higher Al_2O_3 and K_2O (Fig. 2). These rocks have moderate

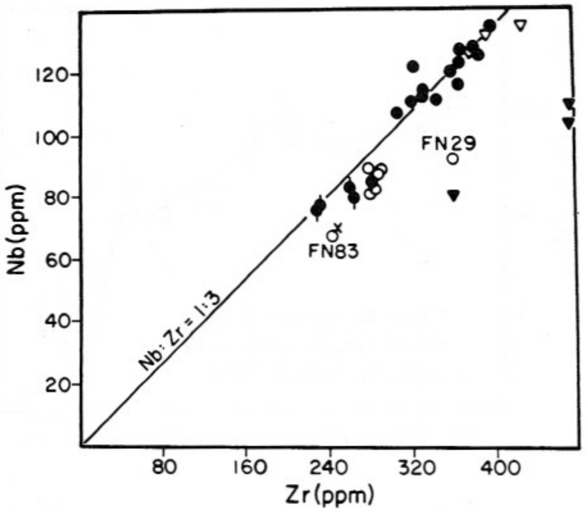

Figure 4 – Variation in Zr vs. Nb in ultrabasic-basic dikes of the Remédios Formation; also plotted are the Ni- and Cr-rich ankaratrites and the alkali basalt data. Symbols as in Figure 2. Circled area shows data of amphibole-free basanites and tephrites.

to low P_2O_5 and high trace element contents with a variable Nb:Zr ratio (Fig. 4).

The presented chemical and petrographic data (cf. also Ulbrich, 1993) point to several possible genetic relationships:

1. Fractionation of olivine ± clinopyroxene ± calcic plagioclase plus "contamination" on tephritic material with a lamprophyric liquid may account for the chemical variations observed in the basanite, tephrite and amphibole-rich tephrite dikes.

2. The melanocratic or tephritic lamprophyres form a distinct group of P_2O_5-rich rocks. Apatite, although sometimes observed as microphenocrysts, is a late groundmass phase in these dikes and should not be an important fractionating phase. The typical alkaline lamprophyres, on the other hand, are rather poor in P_2O_5, which may represent a characteristic chemical feature of these rocks, not generated by previous crystal fractionation of apatite in P_2O_5-richer tephritic parents. This suggests that at least two independent lamprophyric liquids may have existed derived from one or more basanitic-tephritic parents.

There are also other complicating factors that have to be considered when attempting a more detailed analysis of the chemical data: a) the tephritic dikes are highly porphyritic rocks of slightly different compositions, with subordinate glass in the groundmass (which contains either plagioclase or anorthoclase or shows analcime, probably substituting for feldspathoid) and may, in part, be the result of crystal concentration processes (hence not representing true magma compositions); b) the lamprophyric dikes, on the other hand, commonly carry low-pressure cumulate enclaves (biotite and/or amphibole-bearing rocks) some of which may have been overlooked during sample preparation, introducing a bias in the chemical analysis; c) in general, the dikes are compositionally somewhat zoned, so that the analyses of some samples may not represent the true composition of the dikes.

Limburgites

These dike rocks have major element chemistry similar to the more mafic tephrites and basanites, being only slightly poorer in Al_2O_3 and richer in P_2O_5 (Fig. 2), but have different contents of some trace elements (Table 2), with a Nb/Zr ratio of over 1:4 (Fig. 4). These rocks certainly belong to the Remédios Formation, since they show on the whole the same alkaline enrichment as the Remédios undersaturated basanitic-tephritic rocks (cf. Na_2O and K_2O contents in Fig. 2). They cannot be correlated chemically with the Quixaba dike rocks (compare especially the K_2O content of the limburgites with those of other Quixaba samples in Fig. 3). A "limburgite" collected in the vicinity of the Morro do Atalaia was dated as a younger rock (2.62 ± 0.33 Ma; Cordani, 1970), but may actually represent a misnamed "tannbuschite" dike, here classified as Ni- and Cr-rich ankaratrite dikes and attributed to the Quixaba volcanism in our work (cf. Ulbrich, 1993 and discussion on ankaratrites, below).

Essexite porphyries and phonolites

Essexite porphyries and phonolites represent the crystallization of alkali-rich melts with $Na_2O > K_2O$. The tephritic-basanitic or the limburgitic dikes may represent parental magmas; of the two possibilities, a limburgitic magma with the same Nb:Zr ratio of the essexites (Table 2) is the most possible candidate.

Fractionation of the limburgite phenocryst assemblage (olivine + clinopyroxene + titanomagnetite) plus apatite should account for the major and trace element content of the essexites. Apatite occurs as well-formed needles in the groundmass of the limburgites, but it is possible that unsampled dikes in the region present intermediate compositions between limburgites and essexites, with apatite as a liquidus phase. The removal of this early apatite may account for the lower amounts of phosphorous shown by the essexites.

The continuous fractionation of the mentioned liquidus assemblage, together with some plagioclase, can produce the compositions shown by the porphyritic phonolites from essexitic parental material (Fig. 2). The aphyric phonolites are more evolved and represent a final differentiation stage in this series.

The MORB-normalized diagram of minor and trace elements of the essexitic and phonolitic rocks (Fig. 5) shows that there is a continuous depletion of Sr and Ti due to plagioclase, clinopyroxene and titanomagnetite fractionation.

The decrease in Ba content from essexites to porphyritic phonolites could be attributed to biotite removal or to initial alkali feldspar fractionation. Biotites occur in the groundmass of essexites, and alkali feldspar crystallizes after plagioclase in some coarser tephritic phonolites (cf. Ulbrich, 1993).

The porphyritic phonolites are poorer in SiO_2, La, Ce, Zr, Rb, Y, Zn and Pb, and richer in CaO, P_2O_5, TiO_2, Ba, Sr and K_2O than the aphyric phonolites (Table 2; Fig. 5). The alkalies, particularly Na_2O, show some scatter in Figure 2, that could indicate leaching due to alteration. It is remarkable that only some aphyric phonolites are truly peralkaline rocks ($Na_2O + K_2O/Al_2O_3 > 1$), although all of them present the same mineralogy. Identical observations were made by Marsh in Namibia (Marsh, 1987).

There is a small decrease in La and Ce from essexites to porphyritic phonolites, which may be due to removal of light REE-enriched phases (apatite and maybe also titanite). The passage of the porphyritic to the aphyric phonolites also involves fractionation of titanite, which is relatively abundant in the porphyritic phonolites and rare in the aphyric rocks.

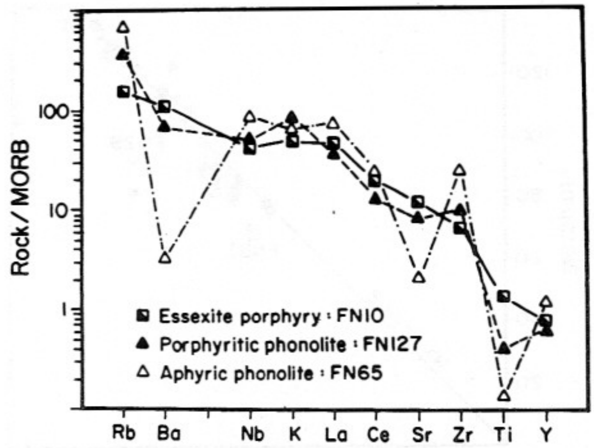

Figure 5 – MORB-normalized distribution patterns of Rb, Ba, Nb, K., La, Ce, Sr, Zr, Ti, and Y for Fernando de Noronha essexite and phonolites. N-type MORB composition is from Sun & McDonough (1989).

The aphyric phonolites, however, are slightly enriched in La and Ce, suggesting that, in these highly evolved compositions, the light REE (and maybe also Zr and Nb) concentrate in other minerals. Petrographic observations showed the presence of an unidentified accessory mineral belonging to the rare-metal silicate group in some aphyric phonolites (Ulbrich, 1993).

Another interesting feature of the aphyric phonolites is that they have lower K contents than the less differentiated porphyritic rocks. This feature appears to be quite common during the evolution of phonolites and, as Marsh (1987) pointed out, may indicate that the alkali feldspar phenocrysts are richer in K than the original magma (the "orthoclase effect" of Bailey & Schairer, 1964). Consequently, the amount of K in the magma decreases with fractionation of alkali feldspars. On the other hand, the Rb content increases from the porphyritic to the aphyric phonolites, suggesting that the K-feldspar/magma Rb distribution coefficient must be less than 1; this observation is supported by the work of Wörner et al. (1983), who found that the values of $K^{Rb}_{feldspar}$ vary from 0.55 to 1.25 in phonolites from the Laacher See volcano.

Alkali basalts, trachyandesites and trachytes

The olivine-rich alkali basalt (sample WFN3, Table 2, Fig. 2) has low SiO_2 and high MgO contents, similar to those of the tephrites; on the other hand, it is richer in TiO_2 and poorer in P_2O_5, Al_2O_3 and alkalies, having about 7% normative nepheline. Compared to the other ultrabasic rocks of the Archipelago it has low trace element contents (except Ni, Cr and V) with a Nb:Zr ratio of about 1:6 (Table 2, Fig. 4). Primitive mantle-normalized trace element distributions (Fig. 6) show a close relationship with the average OIB composition (Sun & McDonough, 1989).

The evolution of alkali basalts to rocks with increasing, but moderate, alkali content is common in continental and oceanic environments producing derivative rocks with either *ne* or *qz* in the norm (cf. Wilson, 1989).

This rock series is represented in Fernando de Noronha by rare alkali basalt-trachybasalts and abundant trachyandesite-trachytes with more than 60% SiO_2 and low MgO and CaO (Fig. 2), characterizing a bimodal distribution.

The data in Figure 2 for the more evolved rocks of this series show some scatter in Fe/Fe + Mg and also in Na_2O. The variability of Na_2O is probably the result of leaching.

All rocks of this series present small amounts of modal feldspathoid, a member of the sodalite family, partly resorbed in some rocks, or rounded and zeolitized in others. The analyzed trachyandesite sample is *qz* normative (*qz* = 7%), while the trachytes vary from *qz* normative (4% *qz*) to *ne* normative (3-7% *ne*). Weaver (1990) also found *qz* normative trachytes in Fernando de Noronha. The available data are insufficient to clear up this point, but the presence of modal feldspathoids indicates that both trachytes and trachyandesites are slightly undersaturated rocks.

Figure 7 compares trace element data of an alkali basalt, a trachyandesite and a trachyte. The depletion of Ti in the evolved rocks may result from continuous fractionation of clinopyroxene and Ti-Fe oxides, while other elements (K, Sr, Ba, Nb, La, Ce, Zr) are enriched in the trachyandesite and trachytes (see Table 2) in accordance with usual differentiation trends. The depletion of La and Ce from trachyandesite to trachyte is probably due to titanite crystallization.

Ankaratrite flows and basanite, ankaratrite and nephelinite dikes

The composition of the two different ankaratritic types that form the flows of the Quixaba Formation are presented in Figure 3. Type-A ankaratrites present olivine phenocrysts and clinopyroxene only in the matrix. Type B ankaratrites are lighter coloured, with phenocrysts of olivine and clinopyroxene and also higher amounts of total clinopyroxene. The flows that cover

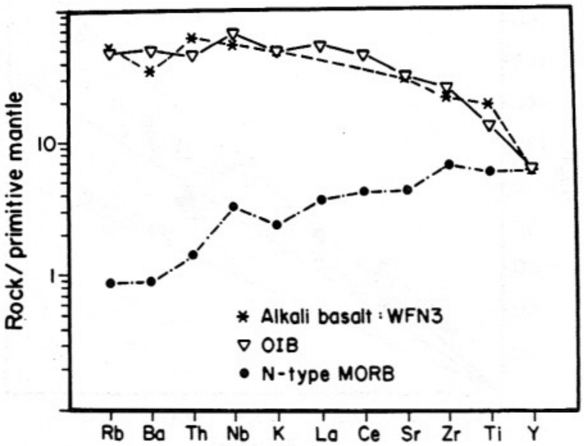

Figure 6 – Comparison of the primitive mantle normalized distribution pattern of Rb, Ba, Th, Nb, K, Sr, Zr, Ti and Y for the alkali basalt of Fernando de Noronha, the average oceanic island basalt (OIB) and N-type MORB. Normalization values and data of OIB and N-type MORB are from Sun & McDonough (1989).

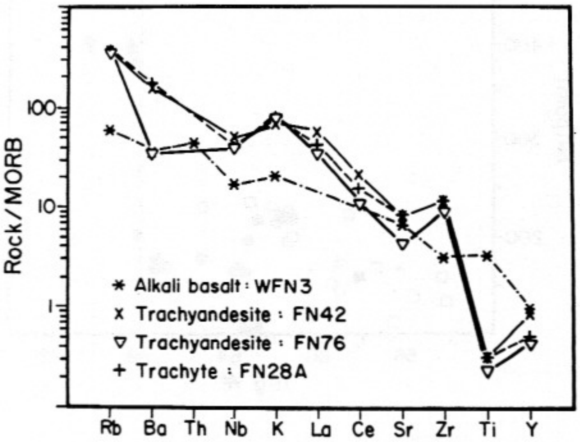

Figure 7 – MORB-normalized distribution patterns of some trace elements for alkali basalt, trachyandesites and trachyte. N-type MORB normalization values are from Sun & McDonough (1989).

the eastern and western parts of the main island are composed of type A ankaratrites. Type B rocks were sampled only in the western part of the main island, restricted to the upper flows of the Alto da Bandeira and Capim Açú areas (Fig. 1).

As seen in Figure 3, the widely distributed type A ankaratrites present very restricted SiO_2 and MgO contents; variations in the amounts of some elements (K_2O, TiO_2, P_2O_5) are the result of observed differences in biotite, apatite and perovskite content of rocks recovered from different localities and also from different flows.

In general, type A ankaratrites are richer in Mg, TiO_2, P_2O_5, CaO and K_2O, and poorer in SiO_2 and Al_2O_3 than the other type. Type B ankaratrites, although of restricted occurrence, show a larger variation in silica content, and the whole set of data establishes a differentiation trend from rocks with more MgO, TiO_2, P_2O_5 and CaO to rocks poorer in those elements. The alkalies are somewhat scattered, but there is a clear increase in Na_2O in these rocks.

The major element chemical compositions of the basanites of São José and Baía do Sancho are very similar; these rocks are clearly more evolved than the ankaratrites.

Several ankaratrite dikes and the nephelinite dike of Pontinha were also plotted in Figure 3. The nephelinite, devoid of olivine and richer in nepheline and apatite, shows consequently low MgO and high Fe/(Fe + Mg), P_2O_5, Al_2O_3 and alkalies. The ankaratrites that intrude the pyroclastic rocks of the Remédios Formation (also plotted in Fig. 2) are here classified as the "Ni - and Cr-rich ankaratrites" (cf. Table 3) and represent the tannbuschites of Almeida (1955). These ankaratrites show the highest mg# values (68-72) and Ni (± 400 to 550) and Cr (± 500 to 720) contents of all the ultrabasic rocks of the Archipelago (Figs. 3, 8). These compositions do not represent those of primary magmas and are probably the results of phenocryst accumulation processes (Hart & Davies, 1978).

The variations in Zr and Nb of the type A and B ankaratritic lavas and of the São José basanite flows are shown in Figure 9, together with data of the Ni- and Cr-rich ankaratrites, as well as Weaver's (1990) "nephelinites" (equivalent to our type A ankaratrites) and "basanites" (our type B ankaratrites; see discussion of nomenclature in Ulbrich, 1993). The figure shows that type A rocks (including the "nephelinites" of Weaver) are richer in Nb than type B ankaratrites. The data of type

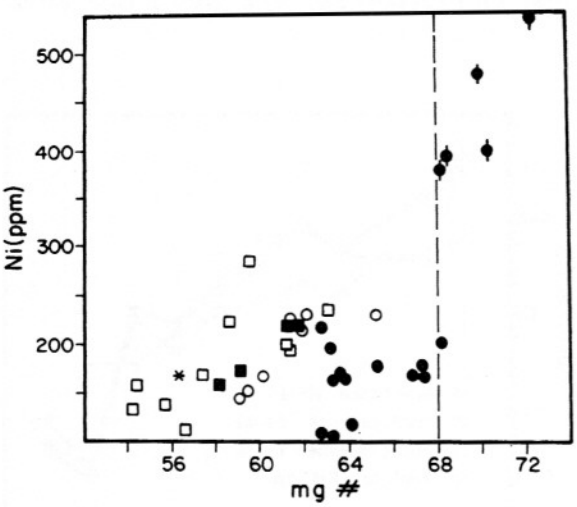

Figure 8 – Ni vs. mg# values for ultrabasic-basic dikes, including alkali basalt of the Remédios Formation, ankaratrite lavas (types A and B) and Ni- and Cr-rich ankaratrites of the Quixaba Formation. Symbols as in Figures 2 and 3.

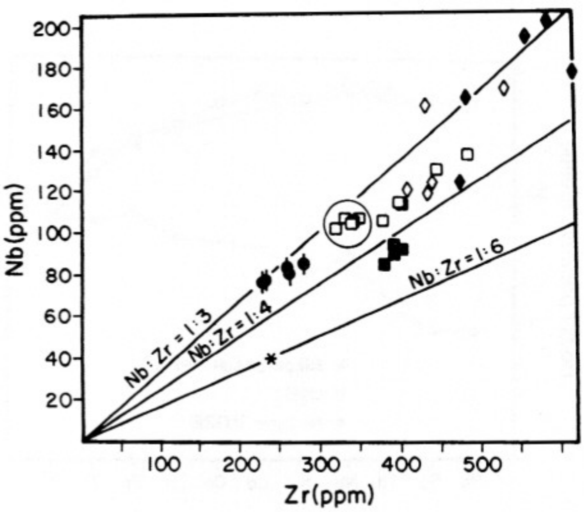

Figure 9 – Variation in Zr vs. Nb abundances in rocks of the Quixaba Formation. Symbols as in Figure 3. Also included are data of "nephelinite" (open inverted triangle) and "basanite" (filled inverted triangle) of Weaver (1990). For details, see text.

B rocks and the "basanites" of Weaver (1990) are more scattered.

The relationship of La and Ba with respect to Nb for the ankaratritic and basanitic lavas appear in Figure 10, showing that type A ankaratrites and São José basanites occupy a restricted area, while type B ankaratrites data are variable and extend to very high values of Ba/Nb and La/Nb. The large differences in these ratios between type A (and basanites) and type B rocks indicate that they derive from different primary magmas originated from varied mantle sources (Sun & McDonough, 1989, and bibliography therein; Weaver, 1990). The high La/Nb values of the type B ankaratrites could register either the presence of a residual titanate mineral in the mantle source or the "contamination" of the primary liquids with subducted sediments (Weaver et al., 1986; Sun & McDonough, 1989). Available data are insufficient to discuss the problem further.

SUMMARY AND CONCLUSIONS

1. The rocks making up the Remédios Formation crystallized from parental magmas that are different from those that constitute the post-erosional Quixaba Formation, as shown by petrographic and chemical characteristics.

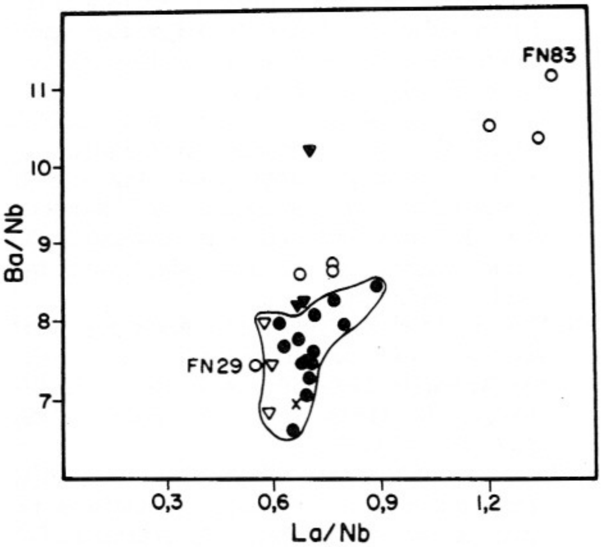

Figure 10 – Plot of Ba/Nb and La/Nb for type-A and B ankaratrites (filled and open circles, respectively), compared with data given by Weaver (1990, open and filled inverted triangles, respectively Weaver's "nephelinites" and "basanites"); x: São José basanite flow.

2. At least two different chemical series are found within the Remédios Formation, as also pinpointed by petrography. One consists of the Na-enriched and undersaturated tephrite (basanite)-tephritic phonolite-phonolite trend (and coarse-grained equivalents such as the essexite porphyry), while the other presents alkali basalts-trachyandesites-trachytes, resulting in a mildly potassic, slightly undersaturated (to slightly oversaturared?) series.

3. Parental magmas of the two series may be limburgitic or basanitic-tephritic and alkali basalt magmas, the first ones enriched in incompatible elements in comparison to the second one. Petrographic and field data (cf. Ulbrich, 1993) indicate that many intermediate magma chambers existed in the complex volcanic structure that gave rise to the Archipelago, thus suggesting that not only one, but several chemically similar parental magmas may have existed for each of the proposed rock series. Thus, the limburgites, although similar to the tephrites, show differences in both the Nb/Zr ratio and the general content of trace elements (Table 2; Figs. 2, 3, 4).

4. Limburgites are positioned chemically within the trend of the sodic Remédios series, to which they probably belong. The essexite porphyries are also related to the limburgites (and tephrites), on the one hand, and to the more evolved phonolites, on the other. The porphyritic and aphyric phonolites crystallized from common magmas; the differences in chemistry among the two can be explained by feldspar, pyroxene and titanite fractionation (Table 2; Figs. 2,5).

5. Chemical variations between basanites, tephrites and amphibole-rich tephrites (with amphibole in the matrix) are probably due to crystal fractionation plus "contamination" of tephritic material with a lamprophyric liquid rich in incompatible elements and volatiles. The melanocratic or tephritic lamprophyres (with phenocrystic amphibole) are P_2O_5-rich; no clear correlation exists between these rocks and the more evolved typical lamprophyres, suggesting that at least two independent lamprophyric liquids may have existed, derived from one or several tephritic-basanitic parents.

6. The Quixaba volcanism, mainly

generated type-A ankaratrites, which are different from the more localized type-B ankaratrites, as shown by element ratios (Fig. 10); these two types probably represent two chemically distinct parental magmas, generated from different mantle sources. The Ni- and Cr-rich ankaratrite dikes, here attributed to the Quixaba event, are the result of olivine and clinopyroxene accumulation processes. On the other hand, the nephelinite dike (showing no modal olivine) was derived from the ankaratrite magma by removal of olivine.

7. The São José basanite flow, carrying abundant mantle xenoliths (cf. also Ulbrich, 1993), possibly represents a primary magma, akin in chemical features to the Bafa do Sancho basanite pipe. These rocks were derived from very similar mantle sources as the A-type ankaratrites (Fig. 10).

ACKNOWLEDGMENTS

V. Marfngolo gratefully acknowledges the advice and financial support of Dr. G. Brey for the analytical work and for his stay at the Max-Planck Institute für Chemie in Mainz, Germany. E. Ruberti thanks Dr. C. Garbarino for help during sample preparation and analytical work at the Istituto di Giacimenti Minerari, Università di Caligari, Italy. Thanks are also due to unknown referees for their critical comments on the manuscript. The field trip to Fernando de Noronha and E. Ruberti's stay in Italy were supported by the São Paulo Financial Agency - FAPESP.

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