Some Geochemical Features of the Alkaline Rocks of Itapirapuã, São Paulo, Brazil *

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(With 11 text-figures)

INTRODUCTION

The area in Brazil commonly known as Ribeira Valley, occupying the southern and northeastern parts of the States of São Paulo and Paraná respectively (Fig. 1), includes several centers of alkaline intrusions, the most outstanding being Tunas and Itapirapuã. The

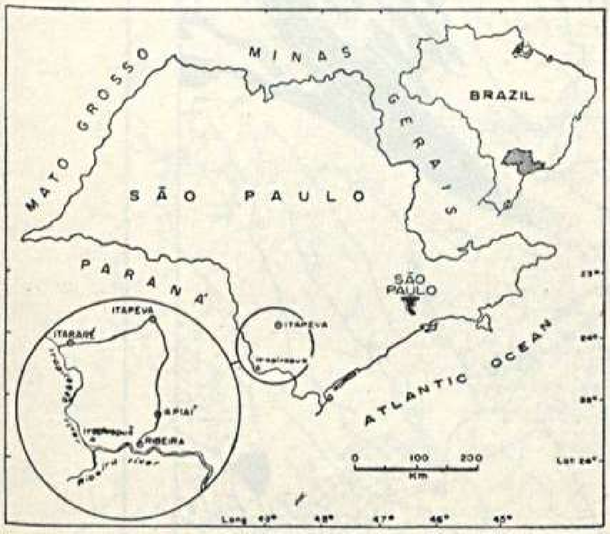

Fig. 1 – Index map showing the investigated area.

alkaline bodies, as seen in Figure 2, are intruded into metasedimentary rocks belonging to the Precambrian Açungui Group or into granitic rocks (Três Córregos-Itapirapuã batholith). Except for the above occurrences, where plutonic varieties showing medium to coarse grain size are the most frequent petrographic type, the alkaline rocks are fine-grained, chiefly phonolites and tinguaites.

This article deals with the geochemical features of the Itapirapuã rocks, especially those having a bearing on their origin. A general account of the district is given by GOMES (in press).

The Itapirapuã massif is irregular in shape, and covers an area of about 2.5 square miles (Fig. 3). It is entirely surrounded by granitic rocks ranging in composition from adamellite to granodiorite. The contact relations between the alkaline rocks and the granitic types are badly defined as a consequence of the deep weathering and dense vegetation in the area; however, some mineralogical and chemical changes (discussed later) were recognized in the granitic rocks cropping out near the contact zone.

Nepheline syenites, occasionally bearing titaniferous garnet (melanite), are the dominant petrographic variety while more basic rocks, represented principally by biotite melteigite (a non-feldspathic alkaline rock) and melanite malignite (a syenite carrying large amounts of ferromagnesian minerals), are less abundant. Small tinguaite dykes, several decimeters wide, cut the plutonic syenites as well as the granitic country-rock. Two magmatic breccia zones mainly associated with melanite-nepheline syenites, and extending over an area of a few square meters, crop out at the southern portion of

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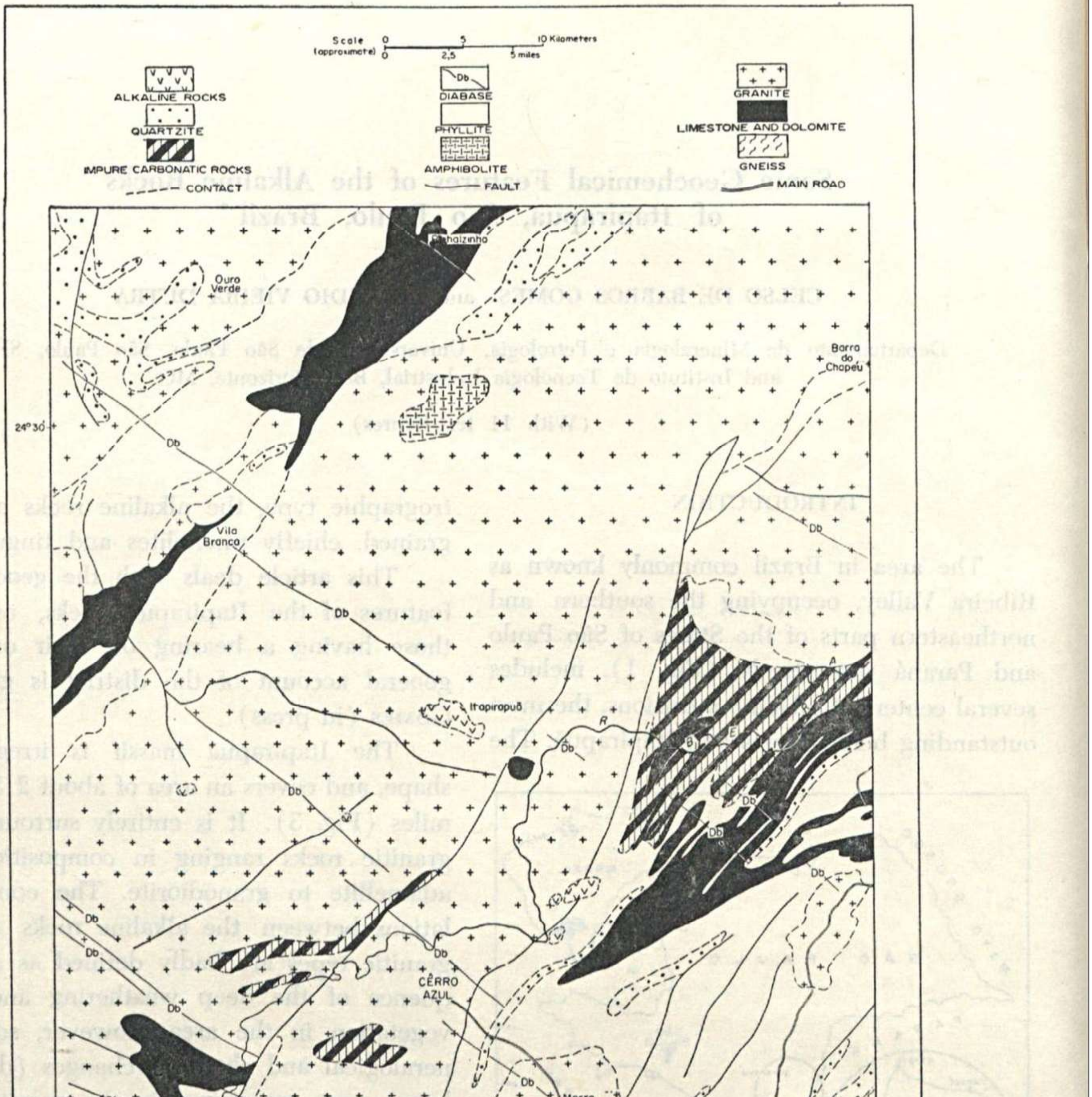

Fig. 2 — Geologic map of the Ribeira Area (Compiled from BITTENCOURT ET AL., in preparation).

the complex in addition to a funnel-shaped ore body composed of idiomorphic granular magnetite. Carbonatites occur as small irregular veins, clearly intersecting medium-grained nepheline syenite in the central part of the body. Apparently they cover a very restricted area, and usually show syenitic fragments, better seen in semi-weathered material, in the interior of the veins. The carbonatites exhibit a very simple composition, with calcite (the only carbonate phase identified) and orthoclase as chief constituents, and with apatite, magnetite, and pyrrhotite as accessories. Some very unusual rocks, characterized by abundance in alkali feldspar, albite, and calcic minerals (melanite and wollastonite), and described as pulaskite, cancrinite mariupolite, and wollastonite-melanite-nepheline syenite respectively, are also found within the alkaline intrusion.

Modal analyses indicate that feldspathoids, including altered nepheline, and feldspars constitute the principal salic minerals while sodic pyroxenes belonging to the aegirine-aegirine-augite series and melanite make up the most important ferromagnesians. Occasionally biotite, wollastonite, and pectolite are also present.

Geochronological work, carried out by Gomes and Cordani (1965) using the K/Ar method, gave an age of 104 m.y. (Upper Cretaceous) for the Itapirapuã rocks. Within the age range for the Brazilian alkaline occurrences, this massif occupies a unique position, intermediate to the two modes – 122-133 m.y., Early Cretaceous, and 51-82 m.y., Late Cretaceous to Early Tertiary – as established by Amaral et al (1967).

Fig. 3 – Geologic map and sample location of Itapirapuã district.

METHODS OF STUDY

Chemical analyses for the major elements were carried out by GLÓRIA BERENICE BRAZÃO DA SILVA, SÍLVIA LOURDES MORO and BENEDITO FERREIRA ALVES using conventional methods. The trace elements were determined by CLÁUDIO V. DUTRA utilizing the technique described in HERZ AND DUTRA (1960).

Molecular norms were computed in conformity with the CIPW method, forming calcite instead of cancrinite for all the rocks containing CO_2. The chemical analyses have been recalculated on a water-free basis for cation proportions, and all the data are expressed in parts per million.

GEOCHEMISTRY

Chemical analyses of the Itapirapuã rocks are arranged in order of increasing felsic index, $F = \frac{(Na + K) \times 100}{Na + Ca + K}$ (cf. SIMPSON, 1954), in TABLE I. Spectrographic data for 17 trace elements, atomic ratios relating major and minor elements, agpaitic indices as well as the specific gravity for the analyzed specimens are also listed. Chemical analyses (in weight per cent of oxides) and molecular norms are set down in TABLE II. The location of the samples within the alkaline body is shown in Figure 3. The chemical and modal compositions of the cancrinite mariupolite, pulaskite, and wollastonite-melanite-nepheline syenite are given in TABLE III. An average composition for the principal rock types of the district is illustrated in TABLE IV.

Agpaitic indices, as given by the $\frac{Na_2O + K_2O}{Al_2O_3}$ ratio, have values ranging from 0.58 to 0.89, and, together with mineralogical features, such as the abundance of calcic minerals, they constitute strong evidence, according to GERASIMOVSKII (1956) and SÖRENSEN (1960), for the miaskitic character of Itapirapuã rocks.

DISTRIBUTION OF THE ELEMENTS

Plots of major and trace elements as well as selected ratios among them are shown graphically on Figures 4 through 9; the felsic index is used as the abscissa. In a triangular variation diagram Fe:Alk:Mg (Fig. 10) the rocks show a regular trend toward the Alk corner, with the later rocks situated near to the Fe-Alk join.

Silicon and Oxygen: Both elements increase smoothly throughout series (Fig. 4) with the ratio of Si to O ranging from 1:2, at mafic end, to 1:1.8, at felsic end.

Aluminum and Gallium: The Al curve behaves like those given for Si and O (Fig. 4). Ga increases slightly toward the felsic end while the Ga/Al ratio, ranging from 0.11 to 0.40, and averaging 0.25, remains almost constant (Fig. 7). Gallium accumulation in the course of magmatic fractionation is a very common feature of many rock series (GOLDSCHMIDT AND PETERS, 1931; SHAW, 1957; BORISENOK, 1959; SIEDNER, 1965).

Magnesium, Nickel, Iron, Cobalt, Chromium, Vanadium, Titanium and Scandium: Except for V, whose concentration increases in the early middle stages, all these elements decrease progressively throughout series (Fig. 5). Sc/Mg, Co/Mg, and Ni/Mg, despite the fact that the last ratio seems to go up at he mafic end, remain practically horizontal and turn up abruptly at the felsic end (Fig. 8). Fe/Mg (Fig. 9), V/Mg and Cr/Mg increase steadily throughout series and, except for the Cr/Mg ratio, behave similarly to the other curves at the felsic end (Fig. 8). Co/Fe and Cr/Fe diminish gradually toward the felsic rocks while the V/Fe ratio increases during the initial and intermediate stages (Fig. 9).

Calcium and Strontium: The Ca curve decreases linearly throughout series whereas Sr shows some scatter at the felsic end (Fig. 6). The Sr/Ca + K ratio (Fig. 7) appears to be constant despite the large dispersion in late

TABLE I

Chemical Analyses (All Data are given in parts per million)

S		Biotite melteigite	Melanite malignite	Melanite-nepheline syenites (3–9)							Nepheline Syenites (10–17)								Tinguaites	
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
	Si^{4+}	194.10^3	203.10^3	212.10^3	226.10^3	218.10^3	211.10^3	219.10^3	229.10^3	232.10^3	236.10^3	237.10^3	229.10^3	251.10^3	254.10^3	252.10^3	252.10^3	247.10^3	248.10^3	248.10^3
	Al^{3+}	87.10^3	94.10^3	89.10^3	95.10^3	102.10^3	97.10^3	93.10^3	104.10^3	108.10^3	113.10^3	116.10^3	123.10^3	105.10^3	123.10^3	112.10^3	116.10^3	129.10^3	115.10^3	121.10^3
	Ti^{4+}	17.10^3	13.10^3	8.10^3	6.10^3	6.10^3	9.10^3	6.10^3	6.10^3	6.10^3	3.10^3	3.10^3	2.10^3	3.10^3	1.10^3	1.10^3	4.10^3	2.10^3	3.10^3	2.10^3
	Fe^{3+}	36.10^3	47.10^3	55.10^3	53.10^3	29.10^3	52.10^3	57.10^3	30.10^3	41.10^3	44.10^3	24.10^3	11.10^3	36.10^3	19.10^3	31.10^3	29.10^3	19.10^3	9.10^3	24.10^3
	Mg^{2+}	23.10^3	19.10^3	10.10^3	1.10^3	11.10^3	10.10^3	9.10^3	8.10^3	5.10^3	—	3.10^3	3.10^3	4.10^3	1.10^3	—	1.10^3	1.10^3	1.10^3	1.10^3
	Fe^{2+}	36.10^3	15.10^3	15.10^3	5.10^3	14.10^3	13.10^3	14.10^3	13.10^3	3.10^3	6.10^3	6.10^3	8.10^3	6.10^3	10.10^3	3.10^3	10.10^3	4.10^3	17.10^3	7.10^3
	Na^{+}	54.10^3	52.10^3	51.10^3	47.10^3	68.10^3	66.10^3	57.10^3	55.10^3	49.10^3	65.10^3	70.10^3	86.10^3	67.10^3	58.10^3	46.10^3	62.10^3	70.10^3	77.10^3	73.10^3
	Ca^{2+}	98.10^3	89.10^3	83.10^3	68.10^3	67.10^3	63.10^3	52.10^3	48.10^3	44.10^3	29.10^3	28.10^3	26.10^3	18.10^3	16.10^3	18.10^3	14.10^3	12.10^3	12.10^3	9.10^3
	K^{+}	19.10^3	29.10^3	37.10^3	57.10^3	40.10^3	35.10^3	52.10^3	63.10^3	66.10^3	57.10^3	61.10^3	59.10^3	54.10^3	50.10^3	81.10^3	61.10^3	62.10^3	57.10^3	48.10^3
3	Be^{2+}	nd	11	10	11	7.2	9.3	5.8	6.5	8	3.6	4	3.6	11	3.4	5	6.5	8.5	9.4	11
3	Ga^{3+}	18	22	22	27	21	11	37	30	34	36	31	28	27	28	24	24	27	37	36
1	Cr^{3+}	96	5	15	10	12	6	13	9	7.4	2,8	1.3	9	3.4	2.8	1.4	nd	1.4	1.3	1.3
3	V^{3+}	168	230	270	400	180	172	156	200	200	164	76	70	80	70	108	84	88	44	54
1	Mo^{4+}	11	nd	17	12	12	12	6	6.8	7.8	7	5	6	5	6	7	4.3	4.3	15	8
10	Nb^{5+}	170	200	104	180	133	630	155	225	190	155	62	25	180	31	50	175	190	150	180
3	Sn^{4+}	19	25	19	24	9.5	7.8	28	14	14	16	4.6	4	24	4	4	6.3	9.5	4.7	6.3
1	Ni^{2+}	60	11	11	18	8	8	8.6	3	3.1	6.5	2.7	2.4	5.2	2.7	2.8	3.1	3.1	3.2	4.7
1	Co^{2+}	13	13	7.8	3	7.4	6.3	6	5.2	4.7	5	3.3	3.3	4	1.6	1.5	2.7	2.8	3.3	2.3
0.3	Cu^{2+}	150	160	60	48	140	150	150	80	80	140	140	20	80	100	44	32	140	110	80
1	Sc^{3+}	26	8.6	and	nd	nd	5.2	nd	4	3.2	4	3.2	nd	6.6	2	3.2	nd	3.2	2.6	nd
10	Zr^{4+}	340	500	740	830	370	345	280	370	410	500	250	150	870	240	200	350	450	440	630
10	Y^{3+}	62	115	124	280	54	90	48	49	58	43	13	35	63	5.5	14	24	36	20	35
30	La^{3+}	420	420	220	nd	180	220	160	136	68	252	88	nd	460	68	68	nd	106	170	154
10	Sr^{2+}	920	700	760	570	840	740	640	590	490	820	780	1000	620	740	570	560	570	370	540
5	Pb^{2+}	38	38	19	17	43	110	36	34	51	142	19	19	43	13	51	17	34	83	83
5	Ba^{2+}	380	2000	1200	3200	2800	5400	3000	4800	3200	3600	3200	3000	1080	320	3200	1200	1540	100	200
	Ga × 1000/Al	0.21	0.23	0.25	0.28	0.21	0.11	0.40	0.29	0.31	0.32	0.27	0.23	0.26	0.22	0.21	0.21	0.21	0.32	0.30
	Cr × 1000/Mg	4.1	0.26	1.4	7.1	1.1	0.59	1.4	1.1	1.5	—	0.45	3.5	0.85	2.1	—	—	2.3	1.9	1.2
	V × 1000/Mg	7.2	12.1	25.9	285.7	16.7	17.2	17.3	25.0	40.0	—	26.2	26.9	20.0	53.8	—	140	146.6	62.9	49.1
	Ni × 1000/Mg	2.6	0.58	1.1	12.8	0.74	0.80	0.95	0.37	0.62	—	0.93	0.92	1.3	2.1	—	5.2	5.2	4.6	4.3
	Co × 1000/Mg	0.56	0.68	0.75	2.1	0.68	0.63	0.66	0.65	0.94	—	1.1	1.3	1.0	1.2	—	4.5	4.7	4.7	2.1
	Sc × 1000/Mg	1.1	0.44	—	—	—	0.51	—	0.51	0.59	—	1.1	—	1.7	1.5	—	—	5.3	3.7	—
	Fe/Mg	3.1	3.3	6.8	41.0	4.0	6.5	7.9	5.4	8.8	—	10.6	7.4	10.5	22.4	—	65.0	38.3	37.9	27.7
	Cr × 1000/Fe	1.3	0.08	0.21	0.17	0.27	0.09	0.18	0.21	0.17	0.06	0.04	0.47	0.08	0.09	0.04	—	0.06	0.05	0.04
	V × 1000/Fe	2.3	3.7	3.8	7.0	4.1	2.6	2.2	4.6	4.5	3.3	2.5	3.6	1.9	2.4	3.2	2.1	3.8	1.7	1.8
	Co × 1000/Fe	0.18	0.21	0.11	0.05	0.17	0.09	0.08	0.12	0.11	0.10	0.10	1.7	0.09	0.05	0.04	0.07	0.12	0.12	0.07
	Sc × 1000/Fe	0.36	0.14	—	—	—	0.08	—	0.09	0.07	0.08	0.10	—	0.21	0.07	0.94	—	0.14	0.10	—
	Y × 1000/Ca	0.63	1.3	1.5	4.1	0.80	1.4	0.92	1.0	1.3	1.5	0.46	1.3	3.5	0.34	0.61	1.7	3.0	1.6	3.9
	Sr × 100/Ca	0.94	0.79	0.91	0.84	1.2	1.2	1.2	1.2	1.1	2.8	2.8	3.8	3.4	4.6	3.2	4.0	4.7	3.1	6.0
	Sr × 100/Ca+K	0.78	0.48	0.63	0.45	0.78	0.75	0.61	0.53	0.44	0.95	0.89	1.2	0.77	1.1	0.57	0.74	1.2	0.53	0.94
	Ba × 100/K	2.0	3.5	3.2	5.6	7.0	12.0	5.8	7.6	4.8	6.3	5.3	5.0	1.7	0.64	3.9	2.0	2.5	0.17	0.41
	$Fe^{2+} + Fe^{3+}$	42.8	38.4	41.7	35.2	26.9	36.9	37.1	25.4	26.8	28.9	18.6	11.5	25.4	21.0	21.1	23.8	14.6	16.4	20.0
	Alk	43.3	49.6	52.2	63.9	66.4	57.4	58.1	70,0	69.9	71.1	79.6	87.0	72.3	78.0	78.9	75.8	85.0	83.2	79.3
	Mg	13.9	12.0	6.1	0.9	6.7	5.7	4.8	4.6	3.3	—	1.8	1.5	2.3	1.0	—	0.4	0.4	0.4	0.7
	Na+K/Al (1)	0.58	0.59	0.67	0.74	0.72	0.72	0.80	0.77	0.71	0.73	0.77	0.81	0.79	0.57	0.75	0.72	0.70	0.80	0.68
	Specific gravity	2.91	2.91	2.83	2.76	2.71	2.80	2.78	2.78	2.77	2.69	2.65	2.59	2.73	2.63	2.65	2.69	2.70	2.55	2.58
	(Na+K) × 100/ Na+K+Ca	42.6	47.4	51.5	60.6	61.5	61.6	67.7	71.3	72.5	80.9	82.4	84.7	87.1	87.2	87.4	89.9	91.7	91.8	93.1

(S) sensivity limit; (nd) not detected; (—) not found; (1) Agpaitic index.

TABLE II

Chemical Analyses of Rocks and Molecular Norms

weight per cent	Biotite melteigite	Melanite malignite	Melanite-nepheline syenites (3–9)							Nepheline syenites (10–17)								Tinguaites	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
SiO_2	40.9	43.4	44.4	47.5	45.7	44.2	46.3	48.1	49.0	49.8	50.1	48.0	53.6	53.9	53.6	52.8	53.0	53.0	52.5
TiO_2	2.75	2.15	1.28	1.00	1.07	1.50	1.00	1.00	0.93	0.55	0.44	0.37	0.50	0.12	0.24	0.60	0.35	0.58	0.35
Al_2O_3	16.1	17.70	16.5	17.5	18.8	18.0	17.3	19.2	20.2	21.0	21.6	22.7	19.7	24.0	21.1	21.4	24.3	21.6	22.5
Fe_2O_3	5.06	6.70	7.68	7.37	4.08	7.34	7.98	4.23	5.80	6.22	3.45	1.55	5.19	2.67	4.35	4.02	2.69	1.35	3.33
FeO	4.55	1.99	1.95	0.60	1.81	1.60	1.75	1.61	0.40	0.71	0.79	1.03	0.80	1.30	0.44	1.24	0.51	2.16	0.87
MnO	0.23	0.27	0.29	0.21	0.24	0.28	0.22	0.13	0.14	0.21	—	0.07	0.20	—	0.10	0.19	0.18	—	—
MgO	3.82	3.24	1.69	0.24	1.76	1.65	1.50	1.28	0.89	—	0.47	0.42	0.63	0.21	—	0.10	0.10	0.12	0.18
CaO	13.5	12.40	11.40	9.31	9.22	8.64	7.20	6.55	6.05	4.00	3.87	3.59	2.51	2.20	2.55	1.90	1.69	1.69	1.24
Na_2O	7.13	6.96	6.72	6.20	8.96	8.76	7.54	7.32	6.50	8.63	9.37	11.30	9.05	7.80	6.21	8.18	9.50	10.40	9.67
K_2O	2.26	3.47	4.40	6.76	4.68	4.13	6.25	7.45	7.91	6.81	7.23	7.00	6.46	5.97	9.68	7.16	7.44	6.88	5.75
H_2O+	0.95	1.00	2.24	1.63	1.70	0.45	0.37	1.00	0.60	2.04	0.32	2.54	0.55	0.56	0.71	0.24	0.32	0.84	0.32
H_2O-	0.11	0.41	0.92	0.33	0.41	0.03	0.09	0.01	0.10	0.30	0.12	0.26	0.03	0.18	0.10	0.05	0.05	0.29	0.11
P_2O_5	1.61	0.93	0.96	0.07	0.67	0.61	0.67	0.35	0.35	0.08	0.19	0.14	0.17	0.21	0.43	0.12	0.05	0.29	0.32
CO_2	0.47	0.27	0.39	1.08	0.90	0.90	0.98	0.75	0.30	0.11	1.12	1.16	0.69	0.56	0.50	0.06	0.33	1.43	1.90
S	—	0.15	—	—	—	0.33	0.03	0.06	0.10	0.13	•	0.43	0.11	•	0.03	0.02	0.02	•	•
Total	99.4	101.04	100.82	99.80	100.00	98.42	99.18	99.05	99.27	100.59	99.07	100.56	100.19	99.68	100.04	98.08	100.53	100.60	99.04
Or	12.51	13.62	26.13	40.03	21.13	24.46	27.80	29.47	42.26	40.03	38.09	25.58	38.36	35.56	57.27	42.81	43.92	40.59	33.92
Ab	—	—	2.62	2.10	—	1.31	—	—	—	5.24	—	—	12.84	27.25	6.03	15.20	9.43	14.15	32.49
An	5.28	6.67	1.95	—	—	—	—	—	2.50	—	—	—	—	7.23	1.11	0.28	1.67	—	—
Lc	0.65	5.45	—	—	5.23	—	6.98	11.34	3.49	—	3.71	12.21	—	—	—	—	—	—	—
Ne	32.66	31.81	29.25	26.69	38.06	36.78	29.54	30.96	29.82	35.22	38.34	42.32	28.26	21.02	25.14	29.25	38.34	31.81	19.03
Nc	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.85	2.86
C	—	—	—	—	—	—	—	—	—	—	—	—	—	1.94	—	—	—	—	3.16
Ac	—	—	—	—	5.08	4.16	8.32	4.16	—	2.31	7.39	4.16	10.16	—	—	—	—	3.70	—
Ns	—	—	—	0.70	—	—	—	—	—	—	—	2.93	—	—	—	—	—	1.59	—
Di Wo	11.02	9.40	4.87	0.60	5.10	4.76	4.29	3.71	2.55	—	1.39	1.97	1.86	—	—	0.23	0.23	—	—
Di En	9.50	8.10	4.20	—	4.40	4.10	3.70	3.20	2.20	—	1.20	1.00	1.60	—	—	0.20	0.20	—	—
Di Fs	—	—	—	—	—	—	—	—	—	—	—	0.92	—	—	—	—	—	—	—
Ol Fo	—	—	—	—	—	—	—	—	—	—	—	—	—	0.35	—	—	—	0.21	0.40
Ol Fa	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2.25	—
Wo	9.63	10.67	14.50	15.43	9.86	9.40	6.26	7.19	6.67	8.00	3.71	2.32	1.51	—	2.44	3.60	1.67	—	—
Cs	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Mt	7.42	0.34	3.25	—	3.25	0.46	3.25	2.55	—	0.93	1.16	—	1.60	3.71	0.93	2.78	1.16	—	1.86
Hm	—	6.48	5.44	7.36	0.16	5.60	2.88	0.96	5.76	4.80	0.16	—	0.48	0.16	3.68	2.08	1.92	—	2.08
Il	5.17	4.10	2.43	1.67	2.13	2.89	1.98	1.82	0.84	1.06	0.91	0.76	0.91	0.30	0.46	1.22	0.61	1.06	0.61
Pf	—	—	—	0.27	—	—	—	—	0.88	—	—	—	—	—	—	—	—	—	—
Ap	3.70	2.02	2.35	—	1.68	1.34	1.68	0.67	0.67	—	—	—	—	—	1.01	—	—	0.67	0.67
Pr	—	0.30	—	—	—	0.60	—	0.12	0.18	0.24	—	0.36	0.12	—	—	—	—	—	—
Cc	1.10	0.60	0.90	2.50	2.00	2.00	2.30	1.70	0.70	0.20	2.50	2.70	1.60	1.30	1.10	—	0.70	2.40	1.60
H_2O	1.06	1.41	3.16	1.96	2.11	0.48	0.46	1.02	0.70	2.34	0.44	2.80	0.58	0.74	0.81	0.29	0.37	1.13	0.43
Total	99.70	100.97	101.05	99.31	100.19	98.34	99.46	98.87	99.22	100.37	98.56	100.03	99.88	99.56	99.98	97.94	100.22	100.41	99.11

TABLE III

Chemical and Modal Composition of Pulaskite (1), Cancrinite mariupolite (2) and Wollastonite-melanite-nepheline syenite (3)

Weight per cent	1	2	3		1	2	3
SiO_2	56.2	55.4	41.3	alkali feldspar	83.3	—	9.7
TiO_2	0.52	0.35	1.85	albite (An_3)	—	53.0	—
Al_2O_3	16.3	20.0	15.2	nepheline	4.3	tr	54.2
Fe_2O_3	4.89	6.08	7.53	cancrinite	0.3	33.7	—
FeO	1.72	0.40	1.43	pyroxene	3.1	12.3	8.2
MnO	0.15	0.17	0.24	melanite	3.7	0.5	13.8
MgO	0.89	0.10	2.32	sphene	0.5	tr	—
CaO	3.03	1.52	17.2	magnetite	2.5	—	tr
Na_2O	2.96	10.3	7.14	apatite	—	—	1.4
K_2O	11.6	2.72	4.18	wollastonite	—	—	8.4
H_2O+	1.23	1.50	0.32	calcite	1.1	0.3	1.6
H_2O-	0.25	0.14	0.12	biotite	0.4	—	tr
P_2O_5	0.10	0.24	1.19	fluorite	tr	tr	—
CO_2	0.72	1.06	0.29	chlorite	tr	—	—
S	—	0.11	0.11	mineral A*	—	0.2	—
				aggregate	0.6	tr	2.7
Total	100.56	100.09	100.34	* not identified			
ppm							
Be	7.2	10	7.2				
Ga	37	45	25				
Cr	nd	1.4	5				
V	140	18	220				
Mo	5	4.3	7				
Nb	560	154	100				
Sn	nd	6.3	nd				
Ni	4.7	1.5	10				
Co	nd	1.5	7.5				
Cu	34	68	110				
Sc	5	nd	6.8				
Zr	400	590	340				
Y	230	13	124				
La	nd	170	170				
Sr	480	680	560				
Pb	nd	41	nd				
Ba	3500	3600	320				

differentiates while the Sr/Ca curve increases smoothly and, finally, more rapidly at the felsic end.

Yttrium: After reaching a maximum concentration in the intermediate rocks, Y diminishes progressively toward the felsic rocks. Except for the increase at the felsic end, the Y/Ca curve shows no variation throughout series (Fig. 7).

Sodium: Na increases progressively with a slight spread at the felsic end (Fig. 6).

Potassium and Barium: K increases smoothly throughout series, and Ba, after passing through a maximum at the end of the intermediate stage, decreases rapidly to the felsic rocks (Fig. 6). The Ba/K curve (Fig. 9) behaves similarly to Ba.

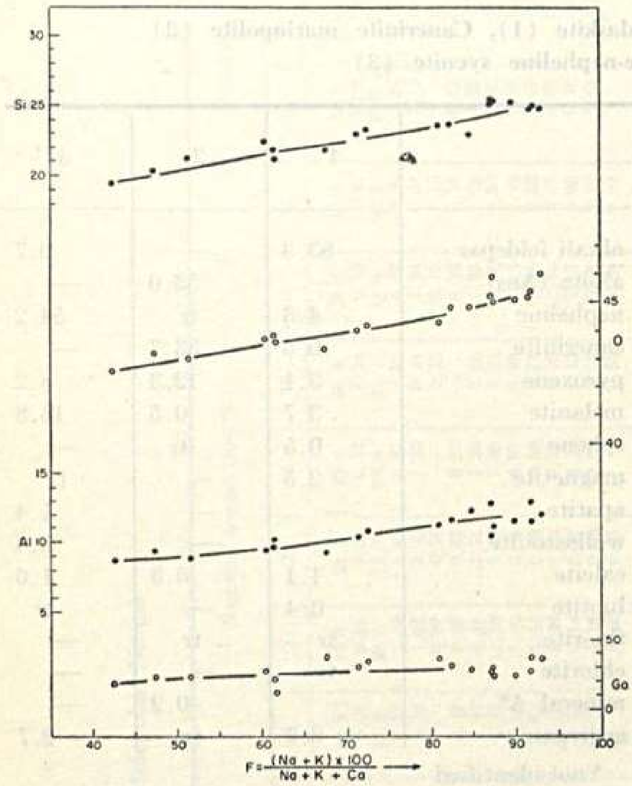

Fig. 4 – Variation diagram of Si, O, Al and Ga in Itapirapuã. Major elements in weight per cent and trace elements in parts per million.

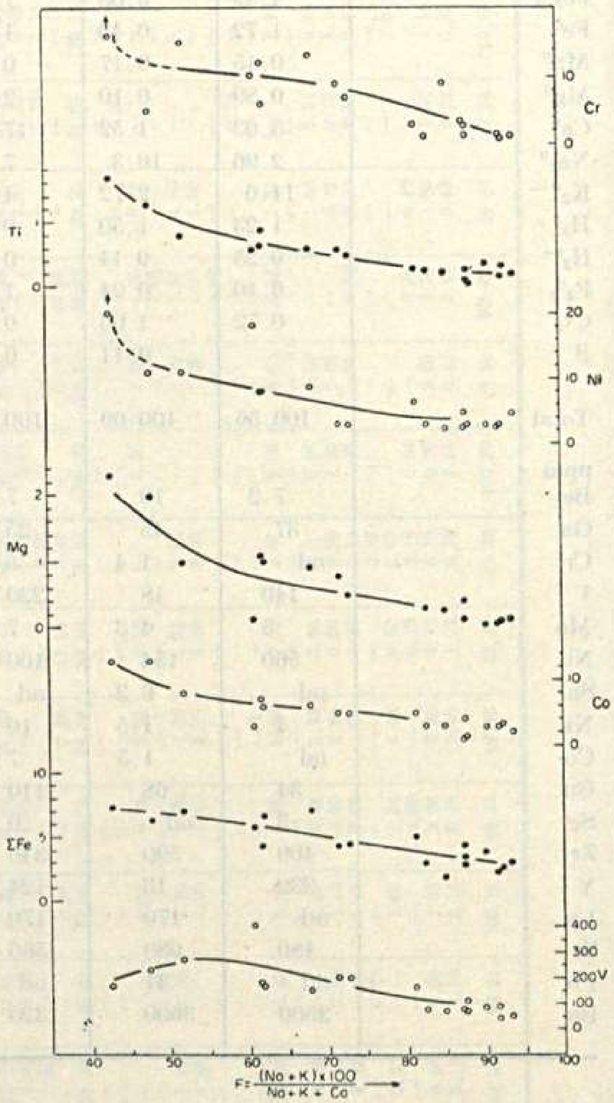

Fig. 5 – Variation diagram of Cr, Ti, Ni, Mg, Co, Fe and V in Itapirapuã rocks.

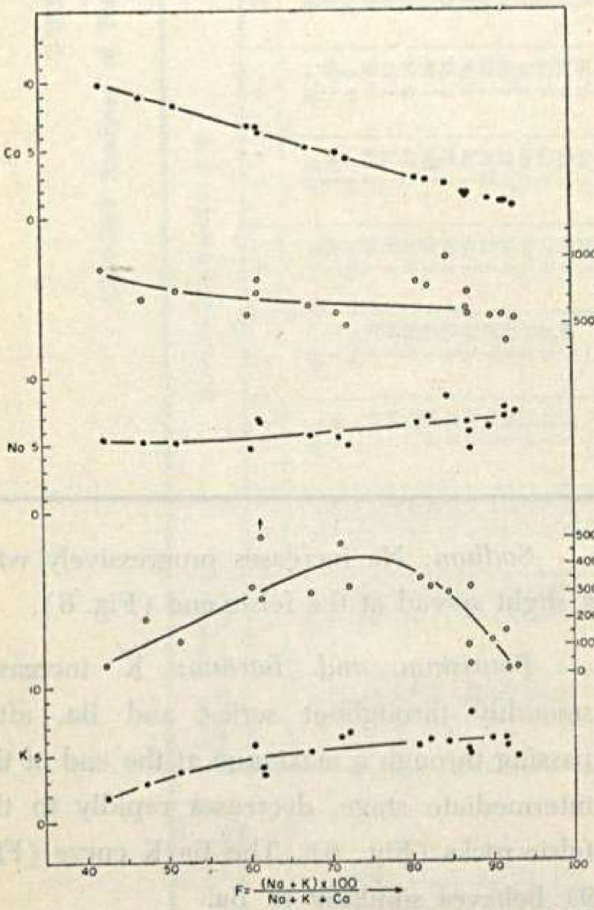

Fig. 6 – Variation diagram of Ca, Sr, Na, Ba and K in Itapirapuã rocks.

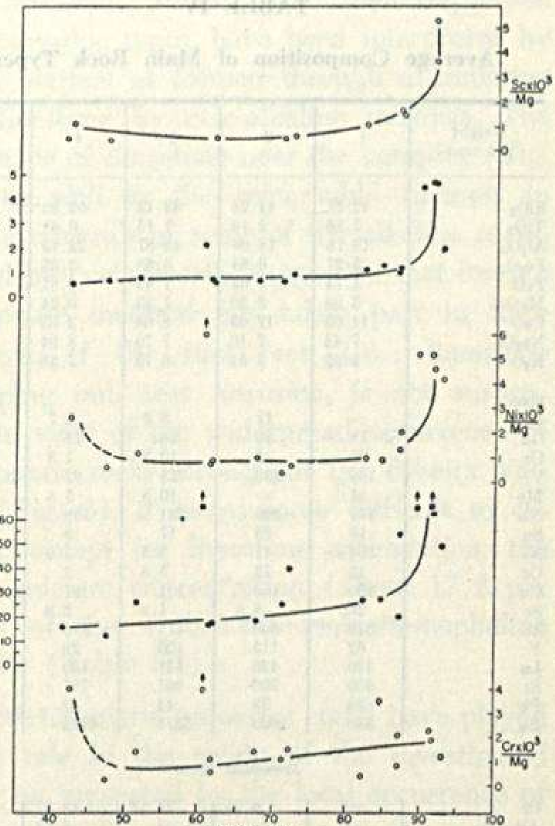

Fig. 8 — Variation diagram of Sc/Mg, Co/Mg, Ni/Mg and Cr/Mg in Itapirapuã rocks.

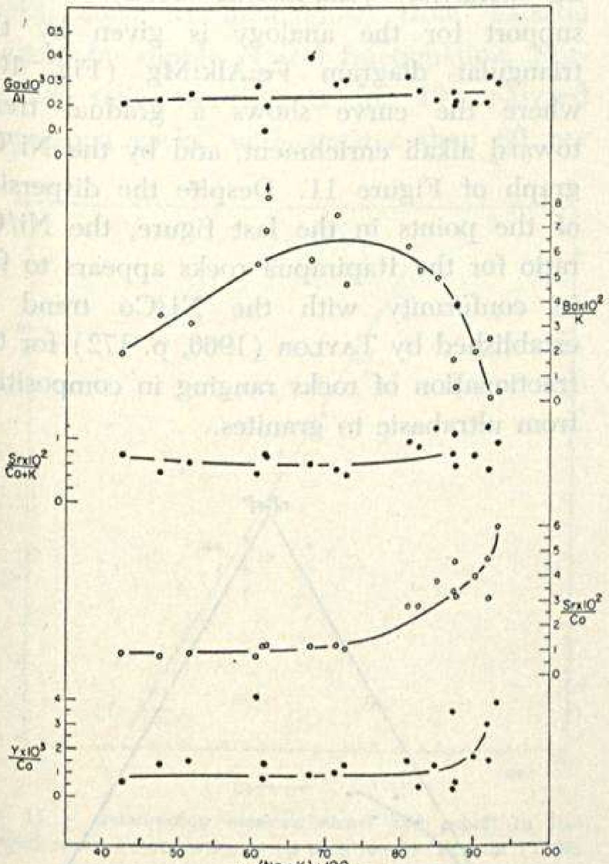

Fig. 7 — Variation diagram of Ga/Al, Ba/K, Sr/Ca + K, Sr/Ca and Y/Ca in Itapirapuã rocks.

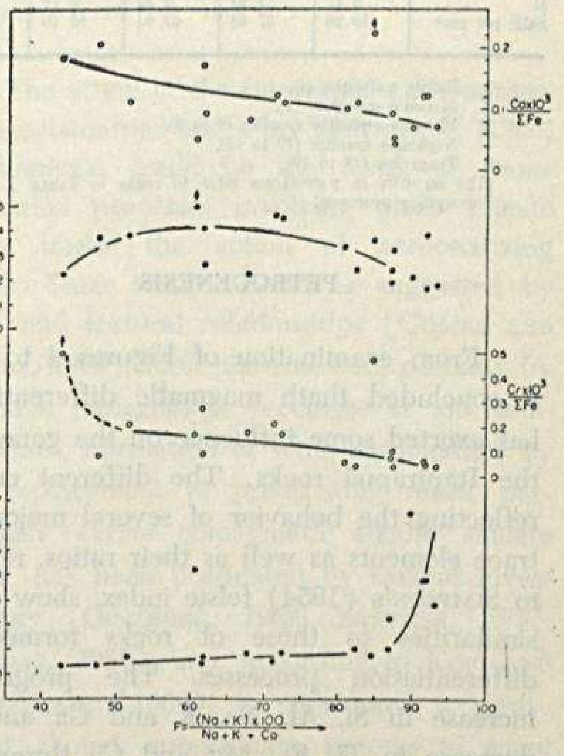

Fig. 9 — Variation diagram of Co/Fe, V/Fe, Cr/Fe and Fe/Mg in Itapirapuã rocks.

TABLE IV

Average Composition of Main Rock Types

Weight per cent	1	2	3	4	5
SiO_2	42.57	44.28	48.13	52.99	54.35
TiO_2	2.86	2.19	1.15	0.41	0.47
Al_2O_3	16.76	18.06	18.87	22.45	22.72
Fe_2O_3	5.27	6.84	6.58	3.85	2.41
FeO	4.74	2.03	1.44	0.87	1.55
MgO	3.98	3.30	1.33	0.24	0.15
CaO	14.05	12.65	8.64	2.85	1.50
Na_2O	7.42	7.10	7.70	8.94	10.33
K_2O	2.35	3.54	6.15	7.38	6.50
ppm					
Be	—	11	8.3	5.7	10.2
Ga	18	22	26	28	36
Cr	96	5	10.3	2.8	1.3
V	168	230	225	92	49
Mo	11	—	10.5	5.6	11.5
Nb	170	200	231	108	165
Sn	19	25	17	9	5.5
Ni	60	11	8.5	3.6	3.9
Co	13	13	5.8	3	2.8
Cu	150	160	101	87	95
Sc	26	8.6	1.8	2.8	1.3
Zr	340	500	478	376	535
Y	62	115	100	29	27
La	420	420	141	130	162
Sr	920	700	661	707	455
Pb	38	38	44	42	83
Ba	380	2000	3371	2142	150
Molecular norm					
Or	—	6.95	24.18	43.37	38.36
Ab	—	—	—	8.64	11.53
An	5.28	6.95	—	—	—
Lc	10.90	11.12	10.25	—	—
Ne	34.08	32.38	33.51	35.69	37.49
Ac	—	—	2.77	0.92	0.91
Di Wo	11.48	9.51	4.29	0.70	1.97
Di En	9.90	8.20	3.70	0.60	0.40
Di Fs	—	—	—	—	1.72
Wo	15.43	13.80	14.04	5.22	1.16
Mt	6.96	0.23	1.39	1.62	0.46
Hm	0.48	6.72	4.64	2.40	—
Il	5.47	4.10	2.13	0.76	0.91
Salic per cent	50.26	57.40	67.94	87.70	87.38

1. Biotite melteigite (1).
2. Melanite malignite (2).
3. Melanite-nepheline syenites (2 to 9).
4. Nepheline syenites (10 to 17).
5. Tinguaites (18 to 19).

(The numbers in parentheses refer to rocks in TABLE I used in compiling averages).

PETROGENESIS

From examination of Figures 4 to 9, it is concluded thath magmatic differentiation has exerted some influence on the genesis of the Itapirapuã rocks. The different curves, reflecting the behavior of several major and trace elements as well as their ratios, relative to SIMPSON's (1954) felsic index, show many similarities to those of rocks formed by differentiation processes. The progressive increase in Si, Al, Na, K and Ga and the decrease in Ti, Fe, Mg and Ca throughout series, as well as the tendency of some trace elements, viz., Cr, Ni, Co and V, to be enriched in more basic rocks, are in agreement with the chemical variations that usually take place during crystal fractionation of a basaltic magma (NOCKOLDS AND ALLEN, 1954; TURNER AND VERHOOGEN, 1960). Also analogous to magmatic differentiation are the positive correlations between Fe/Mg, Y/Ca and Sr/Ca and the felsic index, and negative ones between Cr/Fe and Co/Fe and the same index (TAYLOR, 1966), as well as the Ba behavior (LEMAITRE, 1962). Further support for the analogy is given by the triangular diagram Fe:Alk:Mg (Fig. 10), where the curve shows a gradual trend toward alkali enrichment, and by the Ni/Co graph of Figure 11. Despite the dispersion of the points in the last figure, the Ni/Co ratio for the Itapirapuã rocks appears to fall in conformity with the Ni/Co trend as established by TAYLOR (1966, p. 172) for the fractionation of rocks ranging in composition from ultrabasic to granites.

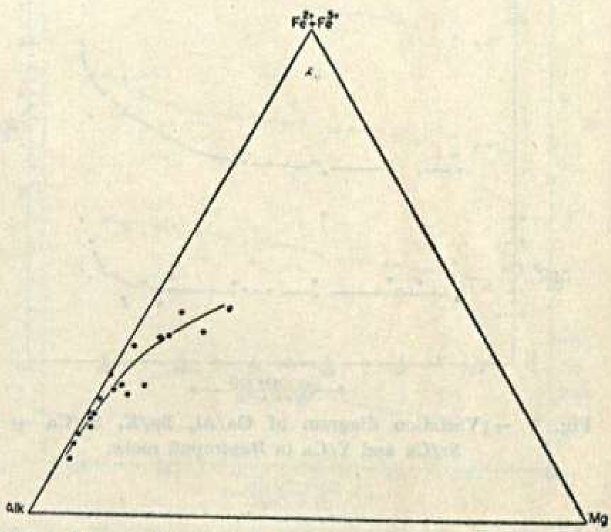

Fig. 10 – Triangular variation diagram Fe:Mg:Alk in Itapirapuã rocks.

Despite the fact that the stratigraphic position of many analyzed samples, especially the most basic rocks, still remains unknown, it is important to note that the fine-grained varieties, the most acid petrographic types throughout series (specimens 16 and 17 as well as the tinguaites 18 and 19), occur as small dykes cutting coarse-grained nepheline syenites.

The belief that alkaline rocks are derived from an alkali olivine basalt parent magma is advocated by such recent studies as WILLIAMS (1959), ERICSON AND BLADE (1963) and VERWOERD (1966). On the other hand, some authors (KING AND SUTHERLAND, 1960; KING, 1965; BAILEY AND SCHAIRER, 1966) have emphasized the apparent impracticability of deriving strongly undersaturated alkaline rocks, such as melteigites, from balsatic magma by simple crystal fractionation. Normative salic constituents for 10 analyzed Itapirapuã rocks, with greater than 80 per

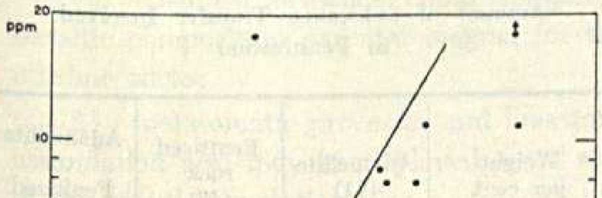

Fig. 11 – Relationship between nickel and cobalt in Itapirapuã rocks. Fractionation trend as given by TAYLOR (1966, p. 172).

cent salic constituents, have been recalculated in terms of $NaAlSiO_4$, $KAlSiO_4$, and SiO_2, and the data plotted graphically on the nepheline-kaliophilite-silica diagram. Nepheline syenites representing the last stages of fractional crystallization of natural systems undersatured in silica are expected to lie in the low-melting region of the diagram (TURNER AND VERHOOGEN, 1960, p. 396); however, excluding the tinguaite 19, all the plotted rocks fall outside the low-temperature trough.

Miaskitic rocks, like the Itapirapuã petrographic types, have been interpreted by some writers as formed through assimilation of limestone by calc-alkaline magmas. The presence of limestone near the complex (Fig. 3), as well as the remarkable richness in calcic minerals of some of the alkaline rocks, could be preliminarily suggestive that foreign carbonate material has taken part in their genesis. If the first fact, i.e., limestone cropping out near intrusion, is not surprising in view of the widespread occurrence of carbonatic rocks throughout the Ribeira Valley (Fig. 2), it seems more difficult to explain, except for limestone assimilation, the high calcium concentration (about 17.2 per cent) of the wollastonite-melanite-nepheline syenite (Table III).

Metasomatic processes could have played some role in the origin of the investigated rocks as suggested by the local occurrence of sodium and potassium enriched varieties (cancrinite mariupolite and pulaskite respectively) and the country-rock fenitization (see below).

CARBONATITES

The origin of the Itapirapuã carbonatites, metacarbonatites adopting VERWOERD's (1966) terminology, could be the result of transformation processes involving older silicate rocks under the action of carbonatizing fluids. Their emplacement, as suggested by field and textural relationships (GOMES AND DUTRA, 1969), took place at least partially by selective replacement processes at low temperature. Formation of some carbonatites by the replacement of pre-existing rocks, particularly earlier comagmatic alkalic silicate types, has been postulated by several investigators (GINZBURG, 1962; SAETHER, 1957; McCALL, 1959), and, according to KING AND SUTHERLAND (1960), is considered a significant, though subordinate, process in many of the African complexes.

Fenitization

Mineralogical and chemical evidence indicates that the enclosing granitic rocks, especially near the north and south borders of the alkaline intrusion, were subjected to fenitization processes. In these rocks, the decrease in quartz content is accompanied by the simultaneous formation of asbestiform riebeckite, and occasionally of aegirine-augite, with a composition ranging from 30 to 40 per cent of the aegirine molecule. Within the feldspar group, the plagioclase content increases while microcline decreases through the process. Modal data for two rocks are listed in Table V. In addition to mineralogy,

TABLE V

Modal Analyses

	Adamellite (41)	Fenitized rock (42)
Quartz	26.8	12.0
Microcline	31.8	17.7
Oligoclase	31.4	52.7
Biotite	6.4	8.9
Riebeckite	0.2	3.6
Hornblende	0.1	1.9
Sphene	0.6	0.8
Ore minerals	0.7	0.9
Epidote	0.6	0.4
Allanite	0.1	tr
Apatite	0.3	0.2
Zircon	tr	tr
Calcite	tr	0.9
Chlorite	—	tr
Sericite	0.3	tr

textural changes, such as undulatory quartz, turbid feldspar, and development of small irregular fissures, were also noted. Riebeckite has been found concentrated along these veinlets as well as forming narrow rims around hornblende and biotite crystals. This last fact besides its formation along cleavage fractures clearly indicates that riebeckite is replacing both minerals. Due to the scarcity of fresh outcrops, it was impracticable to delineate the width of the fenitization zone, but it is believed that it reaches at least one hundred meters. The presence of quartz in the metasomatic rocks makes evident the low grade of the fenitization process in Itapirapuã. The metasomatic transfers, as established only from two analyses (samples 41 and 42, Fig. 3), show that Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O and P_2O_5 have been added whereas SiO_2, TiO_2 and K_2O have been removed through the process. Except for Cu, which remained constant, the concentrations of all analyzed trace elements were increased during fenitization. Chemical data are given in Table VI.

TABLE VI

Amount of Substance Transfer Involved in Fenitization

Weight per cent	Adamellite (41)	Fenitized rock (42)	Adamellite to Fenitized rock
SiO_2	70.4	60.0	− 10.4
TiO_2	0.53	0.16	− 0.37
Al_2O_3	14.1	17.0	+ 2.9
Fe_2O_3	0.92	2.60	+ 1.68
FeO	1.80	3.38	+ 1.58
MnO	tr	tr	—
MgO	0.89	2.11	+ 1.22
CaO	3.22	4.90	+ 1.68
Na_2O	3.33	4.66	+ 1.33
K_2O	4.16	3.48	− 0.68
H_2O^+	0.22	0.25	—
H_2O^-	0.20	0.25	—
P_2O_5	0.52	0.78	+ 0.26
CO_2	tr	0.15	—
S	tr	tr	—
Total	100.29	99.72	
ppm			
Be	3.6	5.4	
Ga	14	22	
Cr	18	36	
V	30	74	
Mo	nd	5	
Nb	8	25	
Sn	4	9.5	
Ni	3.6	13	
Co	5	10	
Cu	140	140	
Sc	4	14	
Zr	230	340	
Y	9.5	40	
La	88	180	
Sr	390	490	
Pb	19	34	
Ba	1720	2860	

GENERAL CONSIDERATIONS

The origin of the Itapirapuã rocks, like many alkaline provinces around the world, remains still a subject of some speculation. There is no sufficient justification for attempting to decide in favor of one or another hypothesis for the genesis of alkaline rocks on the basis of the data accumulated through this study; however, it must be emphasized that the different variation diagrams are clearly indicative that magmatic differentiation was a very active rock-forming process at Itapirapuã. The following points would also be particularly relevant in any genetic considerations:

1) chemical evidence could suggest a basaltic composition parental magma for the alkaline rocks;

2) metasomatic processes and limestone assimilation also may have played some role in the complex evolution.

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SUMMARY

Twenty-two chemical analyses, including determination of 17 trace elements, are given for representative plutonic rocks of the alkaline district of Itapirapuã, São Paulo, Brazil. Variation diagrams relating major and minor elements to Simpson's (1954) felsic index are presented and discussed. Some information is given on the petrology of the alkaline rocks and carbonatites, as well as the fenitized country-rocks.

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