PYROXENES FROM THE ALKALINE ROCKS OF ITAPIRAPUÃ, SÃO PAULO, BRAZIL

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ABSTRACT

The results of chemical analyses including determination of trace elements and some optical data are given for 10 pyroxenes from plutonic alkaline rocks of Itapirapuã, São Paulo, Brazil. They are members of the diopside-hedenbergite-acmite series. The general fractionation trend, as suggested by Ca:Mg:Fe and Na+K:Mg:Fe diagrams and textural evidence, is soda augite→aegirine-augite→aegirine. Chemical formulae seem to indicate that, within the series, the aegirine-rich members are relatively high in Si and correspondingly lower in tetrahedrally coordinated Al ions. Regular variations have also been demonstrated for some trace elements: Nb, Zr and Sr.

INTRODUCTION

In the alkaline Cretaceous nepheline syenite complex of Itapirapuã, São Paulo, Brazil, the most widespread ferromagnesian silicates are sodic pyroxenes. Most of the pyroxenes described in this paper were extracted from nepheline syenites (with felsic index ranging from 47.4 to 91.7); one additional sample (1a) was obtained from a biotite melteigite (a nonfeldspathic, basic alkaline rock), and another (22a) from cancrinite mariupolite (cancrinite-albite syenite). Pyroxene crystals are commonly optically zoned, pale in the cores, dark green on the rims; but, as far as possible, samples for analyses were selected from unzoned or weakly zoned material. Samples 1a and 2a represent mean compositions (phenocrysts plus groundmass crystals) of pyroxene in porphyritic rocks with phenocrysts up to 2 mm long.

The nomenclature adopted here for the sodic pyroxenes is that proposed by Tröger (1956). According to this author, the aegirine-augite field ranges from 25 to 75 percent of the $NaFe^{3+}Si_2O_6$ component.

METHODS OF STUDY

Most samples were crushed to 170–270 mesh; specimens 13a and 16a to 270–325 mesh. Separation of the pyroxene was carried out with a Frantz isodynamic separator and Clerici solution. The purity of the samples was estimated as 99 percent, the main impurity being melanite. The refractive index was determined in white light by oil immersion and the optic angle measured directly with a Leitz universal stage. The figures represent an average of about 8 measurements, and the estimated error is not much better than ±.003 and ±3° respectively for the values quoted.

Chemical analyses for major elements were carried out by conventional methods while spectrographic determinations for 14 trace elements have been done using the technique given in Herz and Dutra (1960).

CHEMICAL COMPOSITION AND OPTICS

Results of chemical analyses are listed in Table 1, in order of increasing aegirine content. Table 2 gives the structural formulae, based on 6 oxygen atoms (cf. Burnham *et al.*, 1967) as well as the atomic ratios Ca:Mg:Fe and Na+K:Mg:Fe. The Na+K:Mg:Fe values were computed by a modification of Carmichael's (1962) method, which was suggested by Aoki (1964). According to the latter, in the calculation of the atomic ratio, Na should be combined with equal amount of Fe^{3+} to form the $NaFe^{3+}Si_2O_6$ component. The excess Na over Fe^{3+}, which forms

TABLE 1. CHEMICAL ANALYSES OF ITAPIRAPUĀ PYROXENES

Weight %		Soda augite	Aegirine-augite									Aegirine
		1a	2a	6a	7a	14a	12a	16a	17a	13a		22a
SiO_2		48.15	49.19	50.01	48.81	49.24	49.72	50.68	50.82	50.48		51.35
TiO_2		1.35	1.01	0.55	0.70	0.60	0.45	0.99	0.60	0.60		1.10
Al_2O_3		4.07	3.02	1.97	2.16	2.00	2.19	3.18	2.32	2.88		2.15
Fe_2O_3		5.66	10.01	12.34	13.03	16.92	17.72	18.43	20.32	23.72		28.66
FeO		5.40	7.45	7.37	6.81	9.92	8.02	6.32	4.86	3.62		2.24
MnO		0.24	0.41	0.64	0.62	0.71	0.50	1.06	0.97	0.76		tr
MgO		11.61	6.62	5.72	5.00	1.95	2.50	2.37	2.32	1.52		0.10
CaO		20.02	19.40	16.01	18.27	11.93	11.05	9.32	8.26	5.70		1.25
Na_2O		2.30	3.40	5.20	4.72	6.72	7.42	7.52	8.37	10.81		12.66
K_2O		0.34	0.24	0.20	0.52	0.24	0.24	0.54	0.48	0.21		0.15
H_2O^+		0.59	0.10	0.18	0.21	0.23	0.31	0.14	0.14	0.16		0.12
H_2O^-		0.08	0.07	0.05	0.19	0.17	0.01	—	0.19	0.18		0.17
Total		99.81	100.92	100.72	101.04	100.63	99.04	100.55	99.65	100.64		99.95

S^a	ppm											
3	Ga	16	17	14	13	46	20	30	30	22		38
1	Cr	96	20	nd	16	nd	nd	nd	nd	nd		2
3	V	230	360	260	200	400	280	400	340	154		44
10	Nb	30	70	16	50	40	16	108	116	166		114
1	Ni	62	8.8	6	14	12	8	14	10	8		4
1	Co	32	22	30	10	30	22	18	16	18		8
0.3	Cu	8	6	22	18	28	22	26	24	95		32
1	Sc	26	18	nd	8	nd	nd	nd	nd	nd		nd
10	Zr	760	1260	1120	720	2400	1240	1920	2400	2600		2400
10	Y	30	94	38	38	66	20	22	36	36		nd
30	La	nd	nd	nd	nd	100	nd	nd	ns	196		nd
10	Sr	960	1160	920	800	600	800	500	280	420		230
5	Pb	nd	16	32	30	40	20	76	40	30		nd
5	Ba	96	112	90	160	40	52	52	69	46		120

[a] Limit of sensitivity.

Analysts: Major elements—Silvia Lourdes Moro; Trace elements—Cláudio Vieira Dutra.

TABLE 2. FORMULAE OF THE ANALYZED PYROXENES (ON
THE BASIS OF SIX OXYGEN ATOMS)

		1a	2a	6a	7a	14a	12a	16a	17a	13a	22a
	Si	1.830	1.865	1.932	1.889	1.930	1.939	1.943	1.996	1.938	1.975
T	Al	0.170	0.134	0.068	0.098	0.070	0.061	0.057	0.004	0.062	0.025
	Ti	—	0.001	—	0.013	—	—	—	—	—	—
	Al	0.013	—	0.021	—	0.021	0.039	0.085	0.900	0.067	0.072
	Ti	0.039	0.028	0.016	0.008	0.016	0.014	0.027	0.016	0.018	0.032
M1	Fe^{3+}	0.162	0.284	0.354	0.378	0.496	0.517	0.529	0.590	0.684	0.826
	Fe^{2+}	0.171	0.234	0.234	0.220	0.324	0.260	0.202	0.155	0.115	0.072
	Mn	0.007	0.017	0.021	0.021	0.023	0.016	0.034	0.032	0.025	—
	Mg	0.662	0.375	0.329	0.290	0.115	0.145	0.136	0.135	0.087	0.006
	Ca	0.814	0.787	0.657	0.756	0.501	0.461	0.382	9.341	0.235	0.022
M2	Na	0.169	0.250	0.386	0.353	0.510	0.559	0.559	0.627	0.804	0.941
	K	0.016	0.011	0.009	0.025	0.012	0.012	0.025	0.023	0.009	0.007
T		2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
M1		1.05	0.94	0.97	0.92	0.99	0.99	1.01	1.03	1.00	1.01
M2		1.00	1.05	1.05	1.13	1.02	1.03	0.97	0.99	1.05	0.97
% Al in T		8.5	6.7	3.4	4.9	3.5	3.0	2.8	0.2	3.1	1.2
% Ti in T		—	—	—	0.6	—	—	—	—	—	—
		Atomic %									
Ca		44.9	46.4	41.2	45.4	34.3	32.9	29.7	27.2	20.5	5.3
Mg		36.4	22.1	20.6	17.4	7.9	10.4	10.6	10.8	7.6	0.6
Fe^a		18.7	31.5	38.2	37.2	57.8	56.7	59.7	62.0	71.9	94.1
Na+K		16.2	28.8	27.7	41.6	51.7	55.1	58.7	64.6	75.0	91.4
Mg		66.0	41.4	35.1	31.9	12.0	15.5	15.0	14.8	9.6	0.7
Fe^b		17.8	29.8	27.2	26.5	36.3	29.4	26.3	20.6	15.4	7.9
% of Aeg. comp.		16	26	35	38	50	52	53	59	68	83

$Fe^a = Fe^{2+} + Fe^{3+} + Mn$

$Fe^b = Fe^{2+} + Mn + [Fe^{3+} - (Na+K)]$

with Al the $NaAlSi_2O_6$ component, must be excluded. The Fe includes
Fe^{2+}, Mn and Fe^{3+}, if any, remaining after the proper amount was added
to Na for the $NaFe^{3+}Si_2O_6$ component. Optical data are set out in Table 3.

Ca:Mg:Fe plots of the Itapirapuã pyroxenes fall close to curve 1 in
Fig. 1. This agrees well with Tyler and King's (1967) fractionation
curve (2) for Uganda alkaline rocks which is assumed to have a similar
genetic significance. Shown for comparison as curve 3 is the pyroxene

TABLE 3. OPTICAL PROPERTIES OF THE ANALYZED PYROXENES

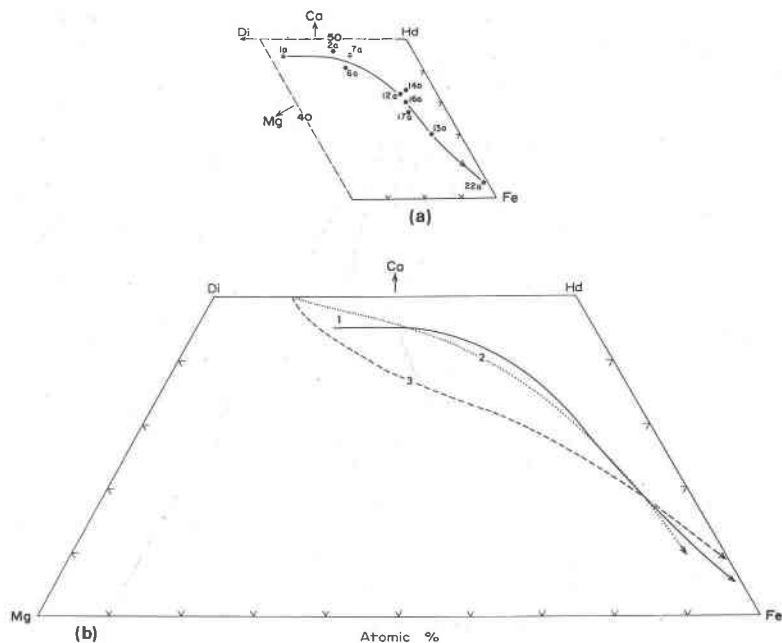		1a	2a	6a	7a	14a	12a	16a	17a	13a	22a
β	1.713	1.722	1.736	1.736	1.757	1.762	1.764	1.765	1.782	1.797
2V	55(+)	80(+)	90°	90°	82(−)	82(−)	81(−)	72(−)	70(−)	64(−)

FIG. 1. Crystallization trends of clinopyroxenes on the Ca:Mg:Fe diagram. (a) Plot of the pyroxenes of the Itapirapuã district with numbers as listed on tables. (b) Fractionation trends for pyroxenes from magmatic provinces as follows: 1) Itapirapuã; 2) Uganda (Tyler and King, 1967); 3) Morotu (Yagi, 1953).

trend from the Morotu district (Yagi, 1953). The fractionation trend for the Itapirapuã minerals is based on the supposition that the selected rocks represent differentiated material arranged in order of increasing felsic index. Early fractionation in the Itapirapuã series, if the above assumption is correct, involves substitution of $NaFe^{3+}Si_2O_6$ and some $CaFe^{2+}Si_2O_6$ for $CaMgSi_2O_6$ until the composition reaches $Ca_{45}Mg_{18}Fe_{37}$. Thereafter, $NaFe^{3+}Si_2O_6$ steadily substitutes mainly for $CaMgSi_2O_6$ and and partially for $CaFe^{2+}SiO_6$. The late progressive increase in aegirine content is brought out in a Na+K:Mg:Fe plot (Fig. 2). Besides the curves for Morotu and Uganda, this diagram also shows the fields of Na- and Ca-rich pyroxenes according to Aoki (1964). Four analyzed minerals from Itapirapuã are situated inside Aoki's immiscibility area, a wide region separating the two fields, and the remainder occupy the field of Na-rich pyroxenes. The fractionation trends for pyroxenes derived from alkaline provinces have some features in common, being characterized initially by a progressive enrichment of Na-Fe, and later by a vertical increase in Na towards the aegirine corner.
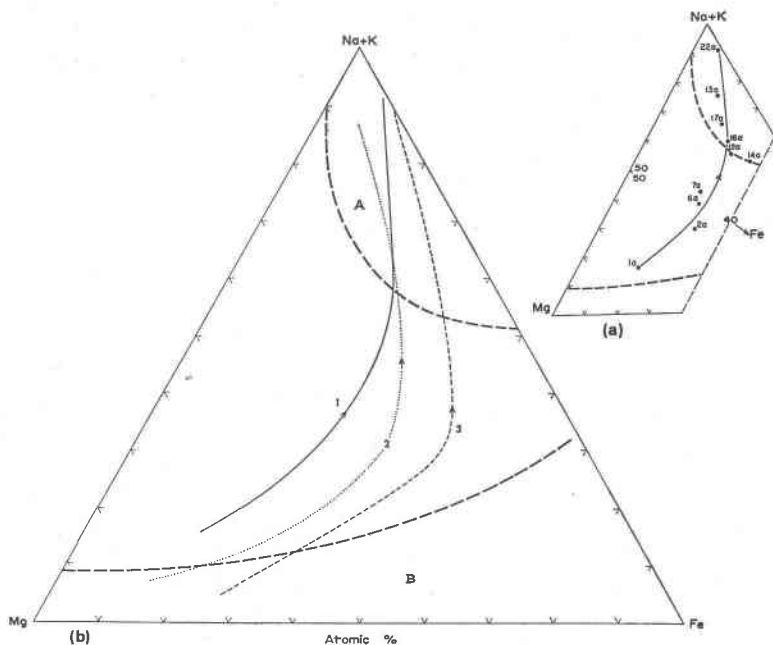
Fɪɢ. 2. Crystallization trends of clinopyroxenes on the Na+K:Mg:Fe diagram. (a) Plot of the pyroxenes of the Itapirapuã district with numbers as listed on tables. (b) Fractionation trends for pyroxenes from magmatic provinces as follows: 1) Itapirapuã; 2) Uganda (Tyler and King, 1967); 3) Morotu (Yagi, 1953). Fields of Na-rich (A) and Ca-rich (B) pyroxenes according to Aoki (1964).

The T group in the investigated samples is occupied principally by Si and Al, and Ti has been assumed tetrahedrally coordinated only in two specimens, *viz.* pyroxenes 2a and 7a (Table 2). Si and Al occur in variable proportions within the T group, with Al reaching its highest percentage, about 8.5, in sample 1a. The role of Al and Ti in the tetra-hedral sites has been discussed by Kushiro (1960) as a result of a sta-tistical study of the chemical composition of clinopyroxenes from igneous rocks. One of Kushiro's chief conclusions was that during magmatic crystallization the proportion of Si increases and that of Al in the tetra-hedral position decreases. Unfortunately, aegirine-augites were not in-cluded in Kushiro's study, but the behavior of Si and Al in the Brazilian minerals, with the former element tending to rise and Al^{IV} diminishing through the course of fractionation (Table 2), seems to indicate that the above relationship could also be valid for sodic pyroxenes.

Except for Zr, Nb and Sr, no regular changes in trace element composition were registered for the analyzed pyroxenes. By examining the tables, it is possible to see that Nb and Zr increase and Sr decreases

proportionally to the aegirine content. The tendency of the former elements to be enriched in NaFe-rich pyroxenes is in agreement with their geochemical behavior, which predicts an increase in their concentration in residual solutions.

When plotted against the number of Fe^{3+} ions per formula unit ($NaFe^{3+}$ Si_2O_6 component), the optical data given in Table 3 show a very regular trend, especially for the refractive index β, with the figures increasing progressively toward the aegirine end (cf. Gomes, in press, Fig. 9). These relationships are in agreement with graphs relating chemical composition and optical properties given in the standard references for pyroxenes of the aegirine-augite-aegirine series. The most frequent pattern of zoning shows a darker green color on the rims of the crystals than in the central parts, besides a more aegirine-rich composition of the borders as suggested by optical data.

GENERAL CONSIDERATIONS

As seen in the figures, the course of crystallization for the itapirapuá pyroxenes is, in many respects, comparable to that shown by those from Morotu. These latter pyroxenes were described and analyzed by Yagi (1953) from a genetic series of dolerites, monzonites, and syenites, and their fractionation trend is considered by many workers as illustrating a more extreme type of alkali enrichment. In this paper, Yagi concluded that diopside, hedenbergite, and acmite may form complete solid solutions with some complications caused by the incongruent melting of acmite. Subsequently, the same author (Yagi, 1958, 1962) carried out some experimental work in the binary system acmite-diopside, and more recently (Yagi, 1966), as a result of phase-equilibrium studies in this system, has emphasized the fact that in the temperature ranges studied during the experiments, no immiscibility region, as postulated by Aoki (1964, p. 1214), was found separating the Na-rich and the Ca-rich pyroxenes. More recently Nolan (1969) found experimental evidence showing the presence of a complete solid solution series in the subsolidus region of the system acmite-hedenbergite-diopside, thereby invalidating the immiscibility gap between Na- and Ca-rich pyroxenes proposed by Aoki (1964).

According to Yagi (1966, p. 993), most of the sodic pyroxenes from plutonic alkali rocks are usually aegirine-augites and rarely aegirines and soda augites. So far, soda augite and aegirine have been found only in two rocks within the Itapirapuá district, whereas aegirine-augite, showing a wide range in composition, is by far the commonest pyroxene in the complex.

It is therefore suggested that the pyroxenes from the Itapirapuá alka-

line rocks form a continuous series within the diopside-hedenbergite-acmite system, ranging in composition from soda augite to aegirine-augite and finally aegirine. Except for the absence of diopsidic augite, the course of crystallization seems to conform to the third fractionation trend of clinopyroxenes from alkaline rocks as established by Aoki (1964, p. 1213), *i.e.*, diopsidic augite→soda auite→aegirine-augite→aegirine. According to Aoki (1964) as well as Yagi (1966), crystallization in the mentioned trend takes place under low temperature and high oxygen partial pressure conditions, with the former decreasing gradually and the latter increasing toward the aegirine-rich members.

REFERENCES

AOKI, K. (1964) Clinopyroxenes from alkaline rocks of Japan. *Amer. Mineral.* **49,** 1199–1223.

BURNHAM, C. W., J. R. CLARK, J. J. PAPIKE AND C. T. PREWITT (1967) A proposed crystallographic nomenclature for clinopyroxene structures. *Z. Cristallogr.* **125,** 109–119.

CARMICHAEL, I. S. E. (1962) Pantelleritic liquids and their phenocrysts. *Mineral. Mag.* **33,** 86–113.

GOMES, C. B. (in press) Petrologia do macico alcalino de Itapirapuã, São Paulo, Brasil *Fac. Fil. Cienc. Lett. Mineral. Petrol.* **20,**

HERZ, N. AND C. V. DUTRA (1960) Minor element abundance in a part of the Brazilian shield. *Geochim. Cosmochim. Acta* **21,** 81–98.

KUSHIRO, I. (1960) Si-Al relations in clinopyroxenes from igneous rocks. *Amer. J. Sci.* **258,** 548–554.

NOLAN, J. (1969) Physical properties of synthetic and natural pyroxenes in the system diopside-hedenbergite-acmite. *Mineral. Mag.* **37,** 216–229.

TRÖGER, W. E. (1956) *Optische Bestimmung der Gesteinsbildenden Minerale, Teil I.* E. Schweizerbart'sche Verlagsbuchhandlung. Stuttgart.

TYLER, R. C. AND B. C. KING (1967) The pyroxenes of the alkaline igneous complexes of eastern Uganda. *Mineral. Mag.* **36,** 5–21.

YAGI, K. (1953) Petrochemical studies on the alkalic rocks of the Morotu district, Sakhalin. *Geol. Soc. Amer. Bull.* **64,** 769–810.

—— (1958) Synthetic pyroxenes of the acmite-diopside system. *J. Mineral. Soc. Japan* **3,** 763–769.

—— (1962) A reconnaissance of the systems acmite-diopside and acmite-nepheline. *Carnegie Inst. Wash. Year Book* **61,** 98–99.

—— (1966) The system acmite-diopside and its bearing on the stability relations of natural pyroxenes of the acmite-diopside series. *Amer. Mineral.* **51,** 976–1000.