CLINOPYROXENES FROM ALKALINE ROCKS OF JAPAN

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ABSTRACT

Twenty clinopyroxenes from ultramafic and mafic inclusions in the basaltic and the alkali basalt-trachyte volcanic rocks, which belong to the alkaline rocks from Japan, have been separated and analyzed chemically. All of them are Ca-rich clinopyroxenes. Two crystallization trends, the diopside-ferropigeonite series and the diopside-hedenbergite series, are recognized from these Japanese clinopyroxenes.

From the studies of clinopyroxenes from the alkaline rocks of Japan, Morotu (Yagi, 1953), and Pantelleria (Carmichael, 1962), the following three crystallization trends of clinopyroxenes can be traced: 1) diopside-ferropigeonite, 2) diopside-hedenbergite, and 3) diopside-aegirine. The fields of Ca-rich and Na-rich clinopyroxenes are separated by a wide region of immiscibility. The first two series of clinopyroxenes coexist with olivines from the early to later stages, but not generally with amphiboles. In contrast, the third series of clinopyroxenes coexists with calciferous amphiboles (hornblende, kaersutite and hastingsite) and alkali amphiboles (arfvedsonite and riebeckite) in the middle and later stages. These trends are controlled by temperatures and oxygen partial pressures in the alkali basalt magma. Trends 1 and 2 correspond to higher temperatures and lower oxygen partial pressures; trend 3 corresponds to lower temperatures and higher oxygen partial pressures.

INTRODUCTION

The clinopyroxenes of igneous rocks are of great petrogenetic significance, but although the clinopyroxenes from the tholeiite magmas have been studied by many investigators, the study of clinopyroxenes from the alkali basalt magma has been neglected. A systematic study of the crystallization trends of the clinopyroxenes from the alkali basalt magma and their mutual relationships to other mafic silicates was first made by Yagi (1953) in his investigation of rocks from the Morotu area of Sakhalin. The clinopyroxenes of Garbh, Eilean, England and Black Jack, Australia were later studied by Murray (1953) and Wilkinson (1956).

The present investigation deals with the clinopyroxenes from the alkali basalt-trachyte series of Japan. The principal purpose is to establish crystallization trends and mutual relationships of the clinopyroxenes during the middle and late stages of fractionation of alkali basalt magmas.

OUTLINE OF PETROGRAPHIC FEATURES

Most Cenozoic volcanic rocks of Japan belong to the tholeiitic, high alumina-basalt, or calc-alkalic rock series, but alkaline rocks occur in a

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small province along the coast of the Sea of Japan. The type localities are the Oki and Iki Islands, northwestern Japan. The former consists mainly of alkali rhyolites, comendites and trachytes, whereas the latter consists mainly of alkali basalts and mugearites. The petrology of these islands has been described in detail by Tomita (1935) and Aoki (1959), respectively. The clinopyroxenes described here were collected mainly from Iki Island and adjacent areas.

Alkali basalts and mugearites are widely distributed on Iki Island and adjacent areas, where they are associated with small amounts of trachyte and alkali rhyolite. The alkalic rocks of these areas are divided into the following two types; alkali basalt-mugearite-trachyte association (kaersutite-free group) and trachybasalt-trachyandesite-trachyte-alkali rhyolite association (kaersutite-bearing group). The former, which is produced by crystallization-differentiation of an alkali-olivine basalt magma, is the more common type. The rocks are similar to those of Hawaii but are slightly lower in soda and higher in potash. The kaersutite-bearing group is believed to have been formed by contamination of an alkali olivine basalt magma by granitic rocks during the middle stages of fractionation.

The essential mineral constituents of the entire range of rocks in the alkali basalt-trachyte association are plagioclase, anorthoclase, olivine, and clinopyroxene. Small amounts of cristobalite may occur in some trachytes. The rocks grade into each other and differ principally in the relative proportions and chemical composition of the primary minerals. Although subcalcic augite or pigeonite has not yet been reported in alkaline rocks, subcalcic ferroaugite (zoned from ferroaugite to ferropigeonite) is found in the groundmass of trachytes from Kakarashima Island.

The mineral assemblage of the trachybasalt-alkalic rhyolite association is more complex and is characterized by kaersutite. The phenocryst minerals of the trachybasalt and trachyandesite are olivine, clinopyroxene, kaersutite, plagioclase and iron ore; the groundmass consists essentially of plagioclase, anorthoclase, clinopyroxene and olivine. In trachytes and alkalic rhyolites, phenocryst minerals are anorthoclase, plagioclase, kaersutite, clinopyroxene and titanian biotite; the groundmass consists essentially of anorthoclase, kaersutite and silica minerals. The silicic rocks contain no olivine, but in some there may be an orthopyroxene. The trachybasalt-alkali rhyolite series is slightly higher in potash but otherwise does not differ markedly in chemical composition from the alkali basalt-trachyte series. The mineralogic and chemical features of the kaersutites have been described in detail by Aoki (1963b).

Basic rocks in this district locally contain peridotite, pyroxenite and gabbro inclusions, up to 10 cm in size.

Mineral Separation

Twenty-one clinopyroxenes and three amphiboles have been chemically analyzed. The pyroxenes and amphiboles were crushed to -150 to 300 mesh for subsequent mineral separation. The analyzed samples were separated in a Frantz isodynamic separator and with methylene iodide and Clerici's heavy liquids. Purity of the analyzed clinopyroxenes from ultramafic and mafic inclusions and amphiboles is estimated to be more than 99.5 per cent, but phenocryst clinopyroxenes contain slightly higher impurity amounts.

The purification of fine-grained groundmass clinopyroxenes was especially difficult since it was found almost impossible to eliminate small amounts of interstitial anorthoclase. According to Hess (1949) a satisfactory analysis can be recognized by the fact that the number of cations for every 6 oxygen atoms in the Z and WXY groups is 2.00 ± 0.02. The author has therefore used only those analyses of clinopyroxenes that satisfy this criterion and do not contain more than 0.3 per cent K_2O.

Chemical analyses of twenty-seven clinopyroxenes from ultramafic and mafic inclusions in the basaltic rocks and the volcanic rocks which belong to the alkaline rocks from Japan are given in Table 1 and their atomic ratios in Table 2. Twenty of the analyses are new.

Crystallization of the Clinopyroxenes

Previous concepts of the crystallization trends of clinopyroxenes from an alkalic magma have been based on the substitutions of Mg-Fe^{2+} in early and middle stages and of Ca·Mg-Na·Fe^{3+} or Ca·Fe^{2+}-Na·Fe^{3+} in later stages. Progressive substitution is thought to lead to aegirine-augite (Yagi, 1953; Yoder and Tilley, 1962). In the trends of crystallization of Japanese clinopyroxenes, however, two series of diopside-hedenbergite and diopside-ferropigeonite display the substitutions of Mg-Fe^{2+} and Ca-Fe^{2+} respectively. The diopside-ferropigeonite series is rare (Figs. 1 and 2). The composition of groundmass clinopyroxenes at the earliest stage of crystallization of alkali basalt magmas is about $Ca_{45}Mg_{40}Fe_{15}$ (Table 1, no. 17). The composition of the phenocrysts first crystallized from the magma is $Ca_{45}Mg_{46}Fe_9$ to $Ca_{45}Mg_{43}Fe_{12}$. Its Fe^{+2} is slightly higher than the chromian diopside from olivine nodules (Table 1, no. 1) and approaches that of augite from peridotite, pyroxenite and gabbro inclusions in alkali basalts (Table 1, nos. 2–7). The Mg in the clinopyroxenes is regularly replaced by the Fe^{2+} during fractionation. At a later stage hedenbergite is crystallized from the magma after ferroaugite. Although the composition of clinopyroxene richest in Fe^{2+} among those analyzed by the author, is $Ca_{43}Mg_{18}Fe_{39}$, Hattori and Katada (1963)

TABLE 1. CHEMICAL ANALYSES OF THE CLINOPYROXENES FROM ALKALIC ROCKS OF JAPAN

| | Ultramafic and mafic inclusions | | | | | | |
	1	2	3	4	5	6	7
SiO_2	51.41	48.84	48.42	48.07	48.43	48.11	47.46
TiO_2	0.33	1.05	1.33	1.48	1.15	1.14	1.67
Al_2O_3	4.69	7.65	7.49	7.93	8.02	7.26	8.19
Fe_2O_3	0.69	2.59	2.50	2.66	2.68	3.13	3.14
Cr_2O_3	1.03	0.08	0.13	0.11	0.10		0.05
FeO	2.64	4.09	4.50	4.51	4.78	4.86	4.76
MnO	0.11	0.14	0.15	0.15	0.15	0.11	0.17
MgO	16.32	14.18	14.05	14.22	13.60	14.04	13.58
CaO	21.63	20.46	20.35	20.15	20.46	20.46	19.90
Na_2O	0.72	0.83	0.65	0.61	0.84	0.66	0.74
K_2O	0.04	0.04	0.05	0.02	0.04	0.04	0.03
H_2O^+						0.33	
	0.11		0.31				0.21
H_2O^-						0.10	
Total	99.81[1]	99.95	99.93	99.91	100.25	100.24	99.90
Analyst	M. D. Foster	K. Aoki	K. Aoki	K. Aoki	K. Aoki	K. Aoki	K. Aoki
β		1.697–1.699	1.699	1.700	1.701	1.700–1.701	1.699–1.704
$2Vz$						51°–53°	53°
Atomic per cent							
Ca	45.9	45.1	44.8	44.2	45.3	44.3	44.3
Mg	48.6	43.7	43.3	43.7	42.1	42.6	42.3
Fe	5.5	11.2	11.9	12.0	12.6	13.1	13.4
Na	1.9	6.2	4.9	4.4	6.4	4.8	5.4
Mg	89.7	79.6	78.5	78.6	77.0	76.5	76.0
Fe	8.4	14.2	16.6	17.2	16.6	18.7	18.6

| | Phenocryst | | | | | |
	8	9	10	11	12	13
SiO_2	52.30	49.57	49.87	46.58	49.19	46.93
TiO_2	0.51	1.04	1.43	2.11	0.91	2.06
Al_2O_3	2.29	5.17	5.83	8.22	3.39	8.08
Fe_2O_3	2.19	1.41	2.28	2.98	3.86	3.60
Cr_2O_3						
FeO	3.73	5.87	4.82	4.31	4.53	4.51
MnO	0.15	0.17	0.28	0.10	0.17	0.10
MgO	16.35	15.19	14.45	12.98	14.27	13.18
CaO	22.06	21.21	20.53	21.47	22.02	19.85
Na_2O	0.30	0.43	0.42	0.55	0.56	0.64
K_2O	0.03	0.03	0.07	0.05	0.05	0.05
H_2O^+	0.12	0.05		0.25	0.82	
						0.85
H_2O^-	0.54	0.08		0.00	0.61	
Total	100.57	100.22	99.98	99.60	100.43	99.85
Analyst	Y. Oji	Y. Matsuura	K. Aoki	K. Aoki	Y. Kawano	K. Aoki

[1] Includes NiO_2 0.04, V_2O_5 0.05.

TABLE 1—(*continued*)

β	1.684–1.691	1.690–1.704	1.693–1.700	1.705–1.713		1.708–1.715
2Vz	54°–58°	53°–50°			50°–57°	46°–50°
Atomic per cent						
Ca	44.6	44.0	44.3	47.6	45.5	44.7
Mg	46.2	44.2	43.6	40.2	41.3	41.5
Fe	9.2	11.8	12.1	12.2	13.2	13.8
Na	2.1	3.1	3.2	4.6	4.0	4.9
Mg	83.0	81.4	78.4	76.6	75.8	75.1
Fe	14.9	15.4	18.4	18.8	20.2	20.0

	Phenocryst			Groundmass		
	14	15	16	17	18	19
SiO_2	48.86	51.96	49.76	49.68	46.03	48.85
TiO_2	0.95	0.67	1.21	1.70	3.98	2.73
Al_2O_3	4.58	1.91	3.39	4.67	6.65	4.04
Fe_2O_3	3.86	1.77	2.88	1.75	2.39	2.30
Cr_2O_3				0.20	0.03	
FeO	6.44	8.12	8.10	7.19	6.62	8.11
MnO	0.19	0.62	0.36	0.22	0.17	0.24
MgO	14.20	13.93	13.65	13.05	11.60	12.26
CaO	20.39	19.87	19.60	20.65	21.75	20.78
Na_2O	0.55	0.69	0.62	0.63	0.76	0.57
K_2O	0.03	0.17	0.08	0.06	0.28	0.02
H_2O^+	0.26					
H_2O^-	0.04					
Total	100.35	99.71	99.65	99.80	100.26	99.90
Analyst	K. Aoki	K. Aoki	K. Aoki	K. Aoki	K. Aoki	K. Aoki

	14	15	16	17	18	19
β	1.706–1.711	1.696	1.703–1.708	1.704–1.710	1.712–1.727	1.705–1.707
2Vz	45°–54°		49°–54°	50°–53°	41°–53°	49°–54°
Atomic per cent						
Ca	42.4	41.9	41.4	45.0	48.4	45.1
Mg	41.3	41.1	40.4	39.8	36.1	37.3
Fe	16.3	17.0	18.2	15.2	15.4	17.6
Na	3.7	4.5	4.4	4.9	7.2	4.1
Mg	71.7	70.7	69.0	72.3	70.1	67.9
Fe	24.6	24.8	26.6	22.8	22.7	28.0

	Groundmass					
	20	21	22	23	24	25
SiO_2	49.14	47.54	46.04	49.71	48.75	50.23
TiO_2	2.54	2.59	3.29	1.41	1.80	1.16
Al_2O_3	4.79	4.54	5.94	3.19	2.18	3.11
Fe_2O_3	1.35	2.78	3.47	3.34	3.18	1.96
Cr_2O_3						
FeO	8.70	8.18	7.30	9.20	10.00	11.63
MnO	0.27	0.17	0.26	0.15	0.08	0.57
MgO	11.36	12.70	11.90	12.65	12.93	11.55
CaO	20.50	20.79	20.39	19.25	19.36	19.04
Na_2O	0.98	0.53	0.78	1.08	0.63	0.42
K_2O	0.13	0.22	0.06	0.26	0.22	0.02
H_2O^+		0.29	0.53	0.03	0.02	
H_2O^-		0.00	0.00	0.04	0.04	
Total	99.76	100.33	99.96	100.31	100.19	99.69
Analyst	K. Aoki	H. Onuki	K. Aoki	K. Ishibashi	K. Ishibashi	K. Aoki

TABLE 1—(*continued*)

β	1.707–1.716	1.705–1.713	1.704–1.725	1.701–1.704	1.698–1.702	1.705–1.716
$2Vz$	47°–54°	47°–51°	49°–52°	53°–58°	50°–55°	48°–52°
Atomic per cent						
Ca	46.2	44.2	45.0	41.3	40.7	41.3
Mg	35.9	37.9	36.7	38.0	38.1	35.1
Fe	17.9	17.9	18.3	20.6	21.2	23.6
Na	4.0	4.7	5.9	8.5	5.0	2.9
Mg	66.7	69.9	66.7	64.9	64.3	59.8
Fe	29.3	25.5	27.4	26.6	30.7	37.3

	Groundmass			Phenocryst	
	26	27	28	A	B
SiO_2	49.27	50.59	48.78	48.58	48.69
TiO_2	0.61	0.57	0.65	0.71	0.86
Al_2O_3	3.00	2.03	2.25	2.06	2.04
Fe_2O_3	1.24	4.38	1.76	5.69	5.60
Cr_2O_3					
FeO	23.16	12.36	19.69	20.15	21.96
MnO	1.02	1.04	1.42	1.31	1.25
MgO	9.05	7.82	5.70	2.67	0.89
CaO	12.39	19.79	18.98	16.93	16.36
Na_2O	0.34	1.29	0.62	2.31	2.86
K_2O	0.09	0.21	0.05	0.09	0.09
H_2O^+					
H_2O^-					
Total	100.17	100.08	99.90	100.50	100.60
Analyst	K. Aoki	K. Aoki	K. Aoki	I. S. E. Carmichael	
β	1.712–1.718	1.704–1.719	1.716–1.723	1.740	1.747
$2Vz$	52°–24°	54°–58°	54°–57°	65°	66°
Atomic per cent					
Ca	27.7	44.7	42.6	40.9	41.2
Mg	28.3	24.8	17.8	8.9	3.1
Fe	44.0	30.5	39.6	50.2	55.7
Na	2.1	10.5	4.5	16.5	16.8
Mg	36.5	44.8	31.1	15.1	5.3
Fe	61.4	44.7	64.4	68.4	78.0

1. Chromian diopside, chromian spinel enstatite chromian diopside olivine nodule in titanaugite olivine trachyandesite, Ichinomegata, northeastern Japan (Ross *et al.*, 1954).
2. Aluminous augite, hercynite bronzite aluminous augite gabbro inclusion in olivine alkali basalt, Komaki Numazu, Iki Island, southwestern Japan.
3. Aluminous titanaugite, olivine pyroxenite inclusion in olivine alkali basalt, Komaki, Numazu, Iki Island.
4. Aluminous titanaugite, hercynite olivine pyroxenite inclusion in olivine alkali basalt, Komaki, Numazu, Iki Island.
5. Aluminous titanaugite, olivine pyroxenite inclusion in hypersthene bearing titanaugite olivine kaersutite trachyandesite, Yokouchi, Numazu, Iki Island.
6. Aluminous titanaugite, aluminous titanaugite peridotite inclusion in olivine alkali basalt, Komaki, Numazu, Iki Island.

TABLE 2. FORMULAS OF PYROXENES OF TABLE 1 ON THE BASIS OF 6 OXYGENS

	1	2	3	4	5	6	7
Si	1.877	1.794	1.788	1.771	1.781	1.782	1.758
Al	0.123	0.206	0.212	0.229	0.219	0.218	0.242
Ti							
Al	0.079	0.125	0.113	0.114	0.128	0.099	0.115
Ti	0.009	0.029	0.037	0.041	0.032	0.032	0.046
Fe^{3+}	0.019	0.071	0.069	0.073	0.074	0.087	0.087
Cr	0.029	0.002	0.004	0.003	0.003		0.001
Fe^{2+}	0.080	0.125	0.139	0.138	0.147	0.150	0.147
Mn	0.003	0.004	0.005	0.005	0.003	0.003	0.005
Mg	0.894	0.781	0.778	0.786	0.750	0.775	0.755
Ca	0.846	0.805	0.805	0.795	0.806	0.812	0.790
Na	0.051	0.059	0.047	0.043	0.060	0.047	0.053
K	0.002	0.002	0.002	0.001	0.002	0.002	0.001
Z	2.000	2.000	2.000	2.000	2.000	2.000	2.000
WXY	2.014	2.003	1.999	1.999	2.005	2.007	2.000
$CaAl_2SiO_6$[1] (mol%)	8.8	13.8	11.8	11.8	13.6	10.7	11.7

[1] Ca-Tschermak's mol was calculated by Kushiro's method (Kushiro, 1962).

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7. Aluminous titanaugite, hercynite bronzite aluminous titanaugite gabbro inclusion in olivine alkali basalt, Komaki, Numazu, Iki Island.
8. Augite, augite olivine alkali basalt, Horikoshi, Abu, San-in, southwestern Japan (Oji, 1961).
9. Augite, olivine augite alkali basalt, Hirase, Mishima Island, San-in. (Matsuura and Oji, 1962).
10. Titanaugite, titanaugite olivine picrite basalt, Takenoyama, Iki Island.
11. Aluminous titanaugite, aluminous titanaugite olivine oxykaersutite trachyandesite, Tsunokami-yama, Iki Island.
12. Augite, augite olivine alkali dolerite, Nemuro, Hokkaido (Kawano, 1942).
13. Aluminous titanaugite, olivine aluminous titanaugite kaersutite trachybasalt, Takenotsuji, Iki Island.
14. Augite, augite olivine alkali basalt, Keyano-oto, Kyushu, southwestern Japan (Matsuura and Oji, 1962).
15. Augite, olivine augite mugearite-trachyte, Suribachi-yama, Iwo Island, western Pacific.
16. Titanaugite, olivine titanaugite mugearite, Madarashima Island near Iki Island.
17. Titanaugite, olivine alkali basalt, Hatsuyama, Iki Island.
18. Titanaugite, olivine alkali basalt, west of Kainei, Korea.
19. Titanaugite, olivine mugearite, Matsushima Island near Iki Island.
20. Titanaugite, olivine mugearite, Shobu-toge, Yobuko, Kyushu.
21. Titanaugite, olivine alkali dolerite, Oga peninsula, northeastern Japan (Aoki, 1962b).
22. Titanaugite, titanaugite kaersutite teschenite, Yaizu, central Japan.
23. Titanaugite, olivine alkali basalt, Kirigo, Kyushu (Ishibashi, 1962).
24. Titanaugite, olivine alkali basalt, Kirigo, Kyushu (Ishibashi, 1962).
25. Titanaugite, mugearite, Madarashima Island.
26. Subcalcic ferroaugite, hortonolite trachyte, Kakarashima Island near Iki Island.
27. Ferroaugite, ferrohortonolite trachyte, Utsuryo Island, Korea.
28. Ferroaugite, fayalite ferroaugite trachyte, Matsushima Island.
A. Sodic ferrohedenbergite, obsidian, Pantelleria (Carmichael, 1962).
B. Sodic ferrohedenbergite, obsidian, Pantelleria (Carmichael, 1962).

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TABLE 2—(*continued*)

	8	9	10	11	12	13
Si	1.910	1.832	1.834	1.737	1.832	1.751
Al	0.081	0.168	0.166	0.263	0.148	0.249
Ti					0.020	
Al	0.018	0.057	0.086	0.098		0.106
Ti	0.014	0.029	0.040	0.059	0.033	0.058
Fe^{3+}	0.060	0.039	0.063	0.083	0.108	0.101
Cr						
Fe^{2+}	0.114	0.181	0.148	0.134	0.141	0.140
Mn	0.005	0.005	0.009	0.003	0.005	0.003
Mg	0.900	0.842	0.797	0.726	0.797	0.738
Ca	0.867	0.840	0.809	0.858	0.879	0.794
Na	0.021	0.031	0.030	0.040	0.040	0.046
K	0.001	0.001	0.003	0.002	0.002	0.002
Z	2.000	2.000	2.000	2.000	2.000	2.000
WXY	2.000	2.025	1.985	2.003	2.005	1.988
$CaAl_2SiO_6$ (Mol.%)	1.7	7.8	7.2	10.1	0.0	9.4

	14	15	16	17	18	19
Si	1.823	1.942	1.869	1.853	1.729	1.835
Al	0.177	0.058	0.131	0.147	0.271	0.165
Ti						
Al	0.024	0.026	0.019	0.058	0.023	0.014
Ti	0.027	0.019	0.034	0.047	0.112	0.077
Fe^{3+}	0.108	0.050	0.081	0.049	0.067	0.065
Cr				0.006	0.001	
Fe^{2+}	0.200	0.253	0.254	0.224	0.207	0.254
Mn	0.006	0.020	0.011	0.007	0.005	0.008
Mg	0.795	0.781	0.769	0.730	0.653	0.691
Ca	0.815	0.795	0.789	0.825	0.875	0.836
Na	0.040	0.050	0.045	0.046	0.055	0.041
K	0.001	0.008	0.004	0.003	0.014	0.001
Z	2.000	2.000	2.000	2.000	2.000	2.000
WXY	2.016	2.002	2.006	1.996	2.012	1.987
$CaAl_2SiO_6$ (mol.%)	3.9	1.6	2.5	5.9	3.5	0.1

TABLE 2—(*continued*)

	20	21	22	23	24	25
Si	1.848	1.793	1.746	1.870	1.864	1.905
Al	0.152	0.201	0.254	0.130	0.098	0.095
Ti		0.006			0.038	
Al	0.060		0.011	0.011		0.044
Ti	0.072	0.067	0.094	0.040	0.014	0.033
Fe^{3+}	0.038	0.079	0.099	0.094	0.091	0.056
Cr						
Fe^{2+}	0.273	0.257	0.231	0.288	0.318	0.368
Mn	0.009	0.005	0.008	0.005	0.003	0.018
Mg	0.641	0.719	0.677	0.714	0.741	0.657
Ca	0.826	0.840	0.829	0.776	0.793	0.774
Na	0.071	0.038	0.057	0.079	0.047	0.031
K	0.006	0.010	0.003	0.013	0.011	0.001
Z	2.000	2.000	2.000	2.000	2.000	2.000
WXY	1.996	2.015	2.009	2.020	2.018	1.982
$CaAl_2SiO_6$ (Mol.%)	1.5	0.6	1.9	2.9	0.0	2.5

|	26	27	28	A	B
Si	1.926	1.945	1.930	1.934	1.950
Al	0.074	0.055	0.070	0.066	0.050
Ti					
Al	0.054	0.037	0.035	0.030	0.046
Ti	0.018	0.016	0.019	0.021	0.026
Fe^{3+}	0.036	0.126	0.052	0.172	0.168
Cr					
Fe^{2+}	0.754	0.396	0.649	0.670	0.737
Mn	0.034	0.034	0.047	0.043	0.043
Mg	0.530	0.451	0.338	0.158	0.053
Ca	0.519	0.815	0.805	0.723	0.703
Na	0.026	0.096	0.047	0.177	0.221
K	0.005	0.010	0.002	0.005	0.005
Z	2.000	2.000	2.000	2.000	2.000
WXY	1.986	1.982	1.994	1.999	2.002
$CaAl_2SiO_6$ (Mol.%)	4.4	0.6	3.2	2.7	0.0
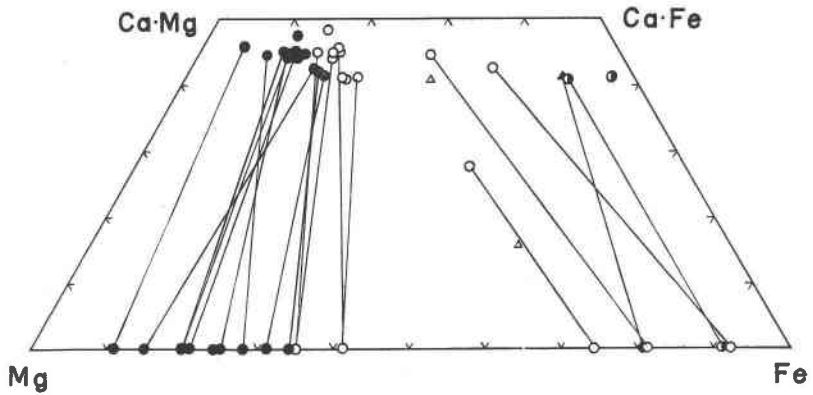
FIG. 1. Composition of clinopyroxenes and olivines from alkaline rocks of Japan.
Clinopyroxenes:

● chemical analyses of ultramafic and mafic inclusions and phenocrysts.
○ chemical analyses of groundmass.
▲ composition of phenocryst estimated from optical determination (Hattori and
    Katada, 1963).
△ composition of groundmass estimated from optical determination.
◐ phenocrysts from pantellerite, Pantelleria (Carmichael, 1962).

Olivines:

● ultramafic and mafic inclusions and phenocrysts.
○ groundmass.
◐ phenocrysts from pantellerite, Pantelleria (Carmichael, 1962).
    Composition of olivines determined from optical properties.
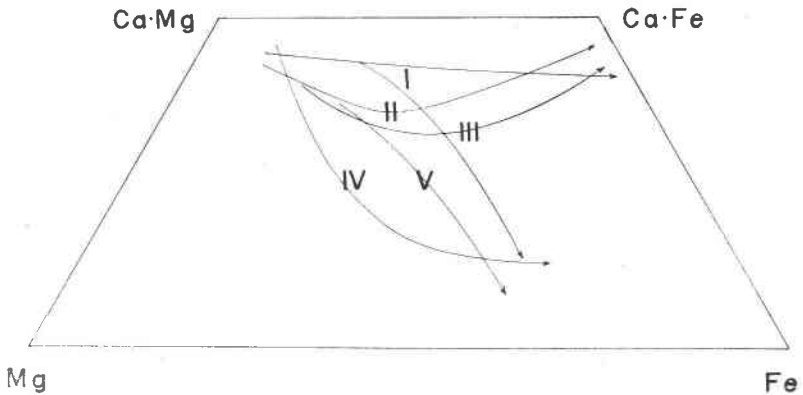
FIG. 2. Crystallization trends of clinopyroxenes. I. Japanese alkaline basalt series, II.
Skaergaard intrusion (Brown, 1957; Brown and Vincent, 1963), III. Tasmanian dolerite
(McDougal, 1961), IV. Japanese tholeiite series (Kuno, 1955), V. Otaki dolerite, Japan
(Aoki, 1962a).

reported phenocrystic hedenbergite from trachytes near Daisen, south-western Japan, as $Ca_{41}Mg_9Fe_{50}$ according to optical determinations.

In order to include the complete course of crystallization of clinopyroxenes from alkali basalt magmas, the composition of the sodic hedenbergites from Pantelleria is also plotted in Fig. 1. When the compositions of all the clinopyroxenes plotted in Fig. 1 are traced, the clinopyroxenes lead from diopside through augite and ferroaugite to hedenbergite. On the other hand the ratio $Ca/Ca+Mg+Fe$ in all clinopyroxenes remains between 40 and 48, and no remarkable change in Ca is apparent; the trend line is nearly parallel to the diopside-hedenbergite join.

The compositions of subcalcic ferroaugites from the Kakarashima trachyte were determined by optical properties to be $Ca_{41}Mg_{27}Fe_{32}$ (cores) to $Ca_{16}Mg_{27}Fe_{56}$ (rims). A chemical analysis gave $Ca_{27.7}Mg_{28.3}$-$Fe_{44.0}$, about midway between the optically determined values. In this case, the compositions determined by optical properties clearly show that Mg is almost constant, while Ca is replaced by Fe^{2+}. The Mg-Fe^{2+} substitution found in other clinopyroxenes does not occur.

The composition of groundmass clinopyroxenes from Japansee tholeiite magmas at the earliest stage of differentiation is about $Ca_{25}Mg_{48}Fe_{27}$ (Kuno, 1955; Aoki, 1963a), and that of Ca-rich clinopyroxene phenocrysts crystallized from the magma at the same stage is considerably more calcic and poorer in iron (about $Ca_{46}Mg_{42}Fe_{12}$). In the Skaergaard and Tasmanian pyroxenes (Brown, 1957; Brown and Vincent, 1963; Mc-Dougal, 1961), some Ca and Mg is replaced by the Fe^{2+} during early and middle stages; $Ca/Ca+Mg+Fe$ decreases progressively to about 35, and then increases again during the middle and later stages. Therefore, the trend line of the clinopyroxenes is nearly parallel to the diopside-hedenbergite join but is slightly convex toward the Mg-Fe join (Fig. 2). The crystallization trend of Japanese tholeiite pyroxenes, however, proceeds from diopside to ferropigeonite (Kuno, 1955; Aoki, 1962) by the Ca-Fe^{2+} substitution.

From these relations a difference is recognized between pyroxenes of most Japanese alkali basalts and tholeiites; a) clinopyroxene phenocrysts crystallized at early stages in both series are similar, but clinopyroxenes from the groundmass are remarkably different, b) the trend line of alkali basalt pyroxene parallels the diopside-hedenbergite join without showing the downward sag of the tholeiite pyroxenes. An exception to these generalizations is found in the clinopyroxenes from the Kakarashima trachyte which have the same ion substitution as Japanese tholeiite pyroxenes.

The alkali contents of the clinopyroxenes from these Japanese areas reach values as high as 0.1, but usually range from 0.03 to 0.06, and they

almost remain unchanged from the early to the later stages. The Na content of the sodic ferrohedenbergite from Pantelleria is slightly higher, (about 0.2) but is still lower than Ca. On the other hand, clinopyroxenes from the teschenite-syenite series of Morotu (Yagi, 1953) are progressively enriched in Na and Fe^{3+} and change from augite through soda-augite and aegirine augite to aegirine.

Published chemical analyses of iron-rich clinopyroxenes from alkaline rocks are compiled in Tables 3 to 5, and the compositions are plotted in a Na-Mg-Fe diagram (Fig. 3). The composition of the clinopyroxenes was calculated by a modification of Carmichael's method (1963). In the calculation of the atomic ratio, Na was combined with Fe^{3+} to form the Ac molecule, and Na which forms the Jd molecule with Al was excluded. The Fe included Fe^{2+}, Mn, and the excess Fe^{3+}, if any, remaining after the
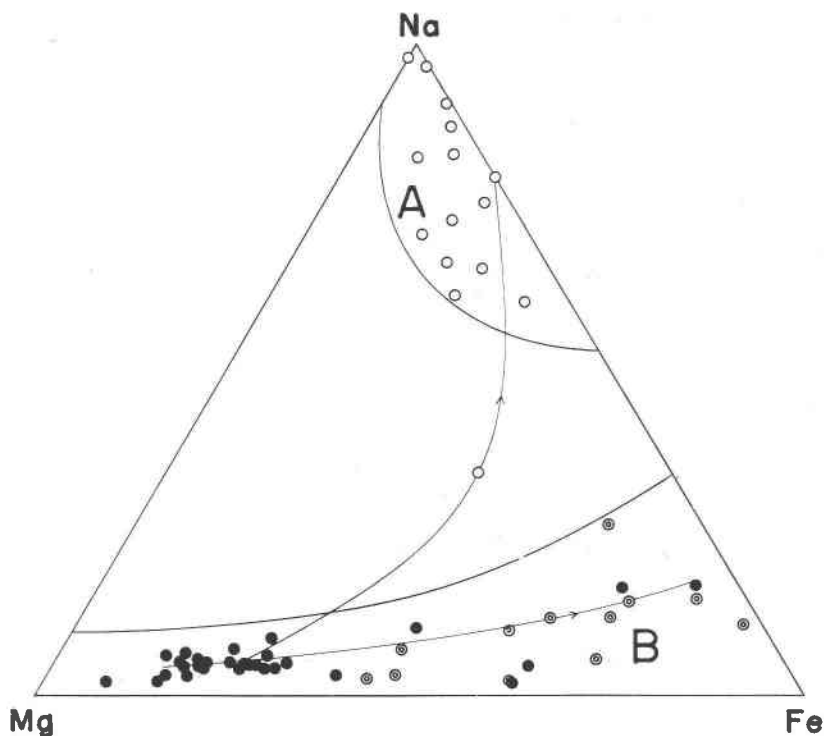

FIG. 3. Composition of Ca-rich and Na-rich clinopyroxenes from alkaline rocks in the world. A; field of Na-rich clinopyroxenes, ○ Na-rich clinopyroxenes shown in Tables 4 and 5, B; field of Ca-rich clinopyroxenes, ● Japanese and Pantellerian Ca-rich clinopyroxenes shown in Table 1, ⊙ Ca-rich clinopyroxenes shown in Table 3. lines; crystallization trends of diopside-aegirine series and diopside-hedenbergite series.

TABLE 3. COMPOSITION OF Ca-Fe^{2+} CLINOPYROXENES FROM ALKALINE ROCKS PLOTTED ON FIG. 2

	Fe_2O_3	FeO	MnO	MgO	Na_2O	K_2O	Na	Fe	Mg	Rock name	Locality	Reference
1	3.96	27.02	0.76	0.32	1.51	0.14	11.1	87.0	1.9	quartz syenite	Ausbole Forks, U.S.A.	Hess, 1949
2	5.88	21.02	0.84	1.57	1.86	0.05	14.9	78.9	6.2	nepheline syenite	Haliburton, Canada	Tilley and Gittins, 1961
3	5.55	20.66	0.62	4.56	2.17	0.53	14.3	70.6	15.1	theralitic canadite	Haliburton, Canada	Tilley and Gittins, 1961
4	2.48	23.27	0.66	4.56	0.83	tr	5.6	70.2	24.1	vein in dolerite	Antrim, England	Murray, 1954
5	8.77	18.73	0.67	3.91	1.52	0.46	12.1	69.0	18.9	theralitic canadite	Haliburton, Canada	Tilley and Gittins, 1961
6	8.79	18.23	0.25	1.98	3.79	nil	26.3	61.8	11.9	alkali granite	Camas Malag, England	Tilley, 1949
7	3.33	15.83	nd	3.80	2.21	0.75	11.8	61.6	26.6	trachyte	Gough Is., Atlantic	Le Maitre, 1962
8	0.90	20.18	1.11	7.27	1.04	0.27	2.2	60.8	37.0	syenite	Okonjeje, S.W. Africa	Simpson, 1954
9	3.19	16.19	0.45	5.46	1.81	0.09	9.7	56.8	32.9	mugearite	Scrogg's Hill, New Zealand	Muir and Tilley, 1961
10	1.32	15.05	0.67	9.90	0.92	0.17	3.3	45.5	51.2	mugearite-trachyte	Totardor, Skye, England	Muir and Tilley, 1961
11	2.22	12.67	0.46	7.90	1.70	0.31	6.8	44.7	48.5	mugearite	Mull, England	Muir and Tilley, 1961
12	1.50	13.97	0.25	10.26	0.31	tr	2.1	42.6	55.2	crinanite	Garbh Eilean, England	Murray, 1954

TABLE 4. COMPOSITION OF Na-Fe^{3+} CLINOPYROXENES FROM ALKALINE ROCKS PLOTTED ON FIG. 2

	Fe$_2$O$_3$	FeO	MnO	MgO	Na$_2$O	K$_2$O	Na	Fe	Mg	Rock name	Locality	Reference
1	28.12	3.01	0.00	0.04	11.48	0.32	89.0	11.0	0.0	syenite	Morotu, Sakhalin	Yagi, 1953
2	28.70	3.07	0.29	0.34	12.63	0.36	86.6	11.3	2.1	nepheline syenite	Kangerdluarsuk, Greenland	Washington and Merwin, 1927
3	25.43	3.70	0.18	0.58	11.65	0.14	82.3	14.0	3.7	nepheline syenite	Sutherland, England	Sabine, 1950
4	26.14	2.38	0.21	1.41	11.28	0.34	82.1	9.1	8.8	nepheline syenite pegmatite	Bearpaw Mountain, U.S.A.	Pecoa, 1942
5	23.42	5.26	0.10	1.48	9.84	0.24	72.5	18.4	9.1	nepheline syenite	Magnet Cove, U.S.A.	Washington and Merwin, 1927
6	22.72	4.30	0.26	2.27	9.36	0.08	70.3	15.6	14.1	nepheline syenite	Magnet Cove, U.S.A.	Washington and Merwin, 1927
7	22.69	7.45	0.68	1.48	8.25	0.52	65.0	26.0	9.0	syenite	Morotu, Sakhalin	Yagi, 1953
8	19.20	6.87	0.05	2.28	8.01	0.15	61.0	24.5	14.5	nepheline syenite pegmatite	Laven Island, Norway	Washington and Merwin, 1927
9	22.36	10.58	0.00	0.94	7.78	0.16	60.0	35.0	6.0	syenite	Morotu, Sakhalin	Yagi, 1953
10	15.48	11.53	0.70	4.10	3.76	0.85	34.0	25.0	41.0	syenite	Morotu, Sakhalin	Yagi, 1953

proper amount was added to Na+K for acmite. Na combined with Al is excluded, because according to Kushiro (1962), the Jd molecule is not included in igneous clinopyroxenes, and the Na and Al probably result from small impurities of alkali feldspar. When clinopyroxene analyses including feldspar impurities are calculated by Carmichael's method, alkali feldspars are calculated as Jd molecule.

TABLE 5. CHEMICAL ANALYSES OF AEGIRINES

	1	2	3	4
SiO_2	51.22	51.30	51.92	50.17
TiO_2	0.83	0.72	0.77	0.57
Al_2O_3	1.13	3.08	1.85	0.93
Fe_2O_3	32.45	24.32	31.44	31.13
FeO	0.79	6.18	0.75	2.27
MnO	0.24	0.08		0.58
MgO	0.08	0.57		0.19
CaO	0.41	3.08		1.24
Na_2O	12.67	9.25	12.86	12.07
K_2O	0.00	0.18	0.19	tr
H_2O^+			0.19	0.52
H_2O^-		0.78		
Total	99.82	99.54	99.95	99.67
Analyst	K. Aoki	K. Yagi	F. A. Gonyer	J. Ito

1. Aegirine riebeckite granite-pegmatite, Quincy, Mass., U. S. A.
2. Arfvedsonite aegirine syenite, Morotu River, Morotu, Sakhalin (Yagi, 1953).
3. Riebeckite aegirine granite, south Kigom Hills, Nigeria (Greenwood, 1951).
4. Aegirine riebeckite quartz syenite, Kogan-zan, Korea (Ito, 1955).

FRACTIONATION TRENDS

The following three crystallization trends of clinopyroxenes from the alkaline rocks are clearly distinguishable.

    1) diopsidic augite–augite–ferroaugite–hedenbergite
    2) diopsidic augite–augite–ferropigeonite
    3) diopsidic augite–soda augite–aegirine–augite–aegirine

They are illustrated by the following examples.

    1) Japanese alkali basalt-trachyte series, Pantelleria alkali basalt-pantellerite series (Carmichael, 1962), Garbh Eilean picrite-crinanite series (Murray, 1954), Otago mugearite series (Muir and Tilley, 1961), Okonjeje gabbro-syenite series (Simpson, 1954) and Gough Island trachybasalt-trachyte series (LeMaitre, 1962).
    2) Kakarashima, northwestern Japan mugearite-trachyte series.
    3) Morotu and Nayoshi, Sakhalin, teschenite-syenite series (Yagi, 1953; Iwao, 1939).

The fields of Na and Ca pyroxenes are separated by a wide region of immiscibility under igneous conditions. The aegirine augite from Morotu is plotted near the center of the Na-Mg-Fe diagram (Fig. 2), but in this pyroxene, aegirine forms discrete rims around cores of soda augite and total composition is a mixture of the two (Yagi, 1953). The average clinopyroxene composition of the Morotu liquid changes continuously from augite to aegirine, but the clinopyroxenes crystallized from the magma are either Ca-rich or Na-rich and Ca-Na clinopyroxenes are not crystallized.

Below solidus temperatures diopside and acmite form a complete solid solution series (Yagi, 1962), but at higher temperatures, hematite crystallizes from the Na-rich liquid as a primary phase; at lower temperatures the hematite reacts with the liquid to form acmite. From this it can be concluded that under magmatic conditions, there is a compositional gap between Ca-rich and Na-rich clinopyroxenes and a very limited range of solid solution.

The mafic minerals coexisting with the clinopyroxenes of trends (1), (2) and (3) show completely different mineral assemblages in late stages of the magmatic differentiation. These will be discussed in a later section.

VARIATIONS OF AL AND TI

The Z group of the clinopyroxenes is occupied chiefly by Si and a deficiency of Si would be made up by Al and Ti. The Z group of almost all Japanese clinopyroxenes is filled only by Si and Al, but the proportions of Al in this group are variable. The role of Al and Ti in the Z group of the igneous clinopyroxenes has been discussed in detail by Kushiro (1960), and LeBas (1962). They have shown that clinopyroxenes of the alkaline rock series have higher Al proportions in the Z group than those of the tholeiite series. It is also shown that the proportion of Al in the Z group decreases during magmatic fractionation.

When Si-Al and Al-Ti relations of the clinopyroxenes from Japan are plotted (Figs. 4 and 5), most fall in Kushiro's (1960) alkaline rock clinopyroxene field but clinopyroxenes crystallized at late stages of fractionation do not. The proportions of Al and Ti in the Z group tend to decrease with fractionation. The phenocrystic and groundmass clinopyroxenes fall near the $Si + Al = 2$ and $2Al = Ti$ lines. On the other hand, the clinopyroxenes from peridotite, pyroxenite and gabbro inclusions in basaltic rocks and kaersutite-bearing rocks are plotted far from these lines, suggesting that these pyroxenes are rich in the Ca-Tschermak's molecule.

Diopside or augite sometimes contains large amounts of $CaAl_2SiO_6$, and the concentration of the Ca-Tschermak's molecule may be related to physico-chemical conditions. When the $CaAl_2SiO_6$ component in Japa-

nese clinopyroxenes is calculated by Kushiro's (1962) method clinopyroxenes from ultramafic and mafic inclusions contain 14–15%, those of the kaersutite-bearing rocks contain 9–10%, and others 0–8%. The average for the rock in Table 2 is about 2.7%. But, according to Kushiro (1962),
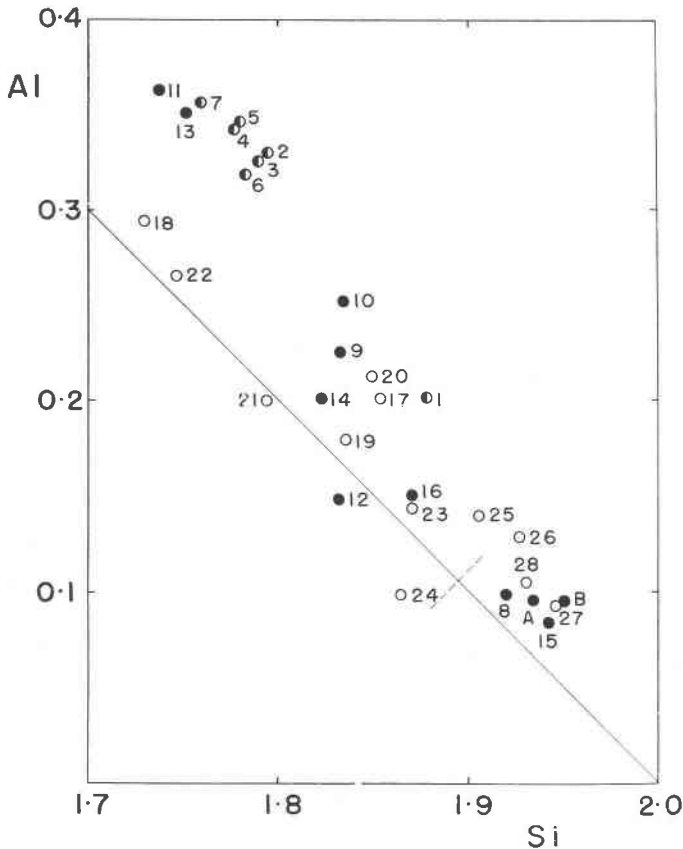

FIG. 4. Relation between the atomic proportions of Si and Al in the clinopyroxenes. ◐ ultra mafic and mafic inclusions, ● phenocrysts, ○ groundmass. Straight line is Si+Al = 2. The numbers refer to analyses in Table 1. (Atomic proportions are calculated on the basis of six oxygen atoms).

$CaAl_2SiO_6$ in clinopyroxenes from basaltic rocks from throughout the world is 1.7%, but in clinopyroxenes from olivine nodules in basaltic rocks it is about 8.3%. (The latter also contain 4.1% of $NaAlSi_2O_6$.) Therefore, phenocrystic and groundmass clinopyroxenes from Japan have much more Ca-Tschermak's molecule than those of average basaltic rocks of the world. Clinopyroxenes from ultramafic and mafic inclusions also con-

tain more $CaAl_2SiO_6$ than do those of olivine nodules, but the former do not contain the high pressure component, $NaAlSi_2O_6$. Kushiro (1962) suggests that as pressure increases, the $CaAl_2SiO_6$ component of clino-pyroxenes also increases. Kuno has shown (unpublished data quoted by

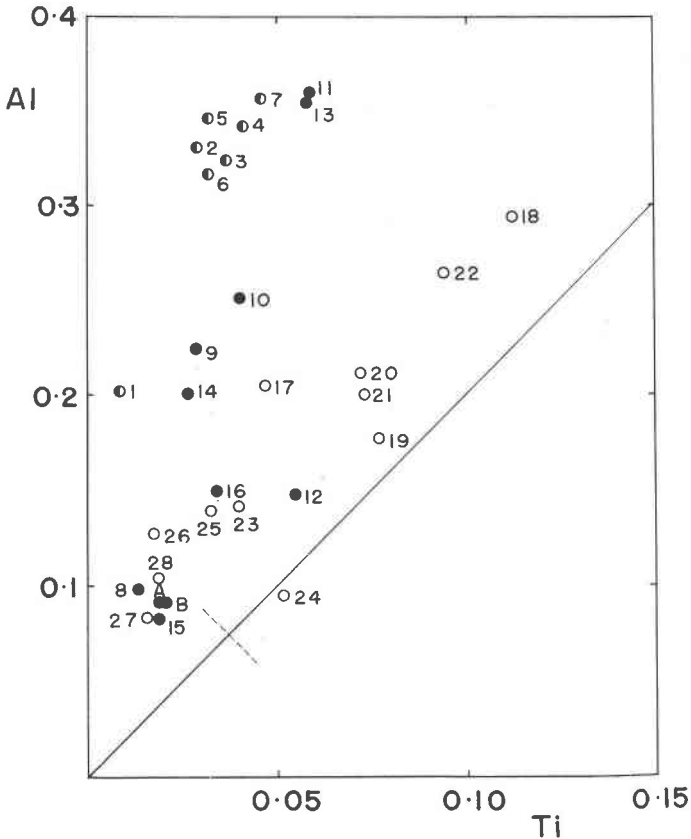

Fig. 5. Relation between the atomic proportions of Al and Ti in the clinopyroxenes. Marks and numbers are same as those in Fig. 4. Straight line is 2Al=Ti.

Kushiro, 1962, p. 215) that augite occurring as large phenocrysts in the alkali basalts of Takashima Island near Iki Island has about 18 mol per cent of $CaAl_2SiO_6$, and he believes that the Takashima augite has crystal-lized from the alkali basalt magma under high pressure. His conclusions are in agreement with the experimental work of Clark, *et al.* (1962). Per-haps peridotite, pyroxenite and gabbro inclusions from the Iki Islands were also produced by crystallization from the alkali basalt magma under

high-pressure conditions. The genesis of these inclusions is a separate problem that will be considered in detail elsewhere.

Phenocrystic clinopyroxenes from kaersutite-bearing rocks are rich in the $CaAl_2SiO_6$ component and coexisting kaersutite and iron ore also have much Al. It is believed that these clinopyroxenes crystallized at higher pressure and lower temperature conditions than those of the alkali basalts-mugearite series.

Mafic Silicates Coexisting with Clinopyroxenes

Optical properties and compositions of olivines coexisting with clinopyroxenes from alkaline rocks of Japan are given in Table 6 and are plotted in Fig. 1. All rocks of the alkali basalt-trachyte series have olivine and clinopyroxene both as phenocrysts and in the groundmass, but hydrous mafic components are not considered essential minerals. The Fe^{+2} content of olivine is low at the early stage of fractionation, but it increases toward the acidic end of the series. Initially the enrichment of Fe^{+2} is relatively gradual, but it becomes extremely rapid in the later stages. The tie line of clinopyroxenes and olivines crystallized during early and middle stages is almost parallel to the Ca-Mg line, but that of the later stage is parallel to the Ca-Fe line, and Fe^{+2} is markedly concentrated in the olivines at the expense of the clinopyroxenes in the later stage. Examples

TABLE 6. OPTICAL PROPERTIES OF OLIVINES ASSOCIATED
WITH CLINOPYROXENES OF TABLE 1

	1	2	3	7	8	10
2Vx					88°–85°	
β		1.693	1.693	1.695		1.704
Fa mol.%	11*	20	20	21	26–32	25

	13	14	15	16	17	19
2Vx	86°–84°			82°	81°–75°	80°–78°
		1.671–	1.700			
β		1.699				
Fa mol.%	22–26	13–23	34	31	32–44	33–38
		15[1]				

	20	25	26	27	28	
2Vx	78°–76°	81°–72°	61°–60°	57°	53°–51°	
β						
Fa mol.%	38–43	31–50	73–75	81	90–94	

[1] Determined by chemical analysis.

of iron-enrichment in olivines in the later stages of differentiation are found in the alkali basalt-trachyte series from Gough Island (Le Maitre, 1962), the picrite-crinanite series of Garbh Eilean, England (Johnston, 1953) and the alkali basalt-pantellerite series of Pantelleria (Carmichael, 1962).

The trachyte magmas from these areas precipitate small amounts of a

TABLE 7. CHEMICAL ANALYSES OF ASSOCIATED HORNBLENDES
WITH CLINOPYROXENES

	1	2	3
SiO_2	40.73	40.27	43.06
TiO_2	8.47	7.23	3.34
Al_2O_3	10.62	10.70	11.83
Fe_2O_3	1.39	1.82	4.22
FeO	11.91	12.45	5.99
MnO	0.25	0.24	0.29
MgO	10.46	10.73	14.90
CaO	10.40	11.85	11.22
Na_2O	2.92	2.40	2.47
K_2O	1.33	0.69	0.28
H_2O^+	1.97	1.46	1.72
H_2O^-	0.23	0.03	0.34
Total	100.68	99.87	99.71
Analyst	K. Yagi	K. Aoki	K. Aoki

1. Kaersutite, titanbiotite titaniferous soda augite kaersutite monzonite, Tyaki, Tiyo Village, Morotu, Sakhalin (Yagi, 1953).
2. Kaersutite, titanaugite kaersutite teschenite, Takakusa-yama, Yaizu, Japan (Aoki, 1963b).
3. Hornblende, titanaugite hornblende trachyandesite, Otsurumizu, Saganoseki, Kyushu, Japan.

hastingsitic amphibole in the final stage, but they do not produce other amphiboles. The pantellertic liquid from Pantelleria (Carmichael, 1962) crystallizes aenigmatite (cossyrite) with sodic ferrohedenbergite and fayalite. The presence of aenigmatite in pantellerites has an important petrogenetic significance.

In the trachybasalt-alkali rhyolite series (kaersutite-bearing rock type), trachybasalts and trachyandesites have olivine as phenocrystic and groundmass minerals. But more silica-rich rocks do not contain clinopyroxenes or olivine, because the olivines or clinopyroxenes form kaersutite by discontinuous reaction with the magma (Aoki, 1959). This series is not a normal crystallization product of alkali basalt magma. The mafic

mineral assemblages at the middle and later stages of the teschenite-syenite series from the Nayoshi and Morotu district, Sakhaline (Iwao, 1939; Yagi, 1953) differ completely from the alkali basalt-trachyte series mentioned above. The only mafic silicate coexisting with the clinopyroxenes in early stages of fractionation is olivine, but after the middle stage, calciferous amphiboles, alkali amphiboles and titanian biotites crystallize from the magma, and olivines do not occur. Kaersutite crystallizes in the middle stage from the Nayoshi and Morotu magmas (monzonitic composition); its composition is shown in Table 7, no. 1. The host rocks of the amphiboles of Table 7, nos. 2 and 3 show almost the same degree of fractionation as the Morotu magma. Iwao (1939) and Yagi (1953) have shown that the evolution of the calciferous amphiboles was barkevikite-kaersutite-hastingsite, but their chemical analyses (Table 7) suggest that it was actually Ti- and Mg-rich hornblende-kaersutite-hastingsite. These calciferous amphiboles belong to the pargasite-ferropargasite series.

In late stages hastingsite changes discontinuously to arfvedsonite, and titanian biotite also crystallizes. In the Fukushin-zan district, Korea (Miyashiro and Miyashiro, 1956), and Quincy, Massachusetts, U.S.A. (Ernst, 1962) aegirine and arfvedsonite crystallized from the magmas in the later stages, and riebeckite crystallized during the last (pegmatitic) stage. Chemical compositions of the arfvedsonite and riebeckite coexisting with aegirines are shown in Table 8.

The order of crystallization and the mafic assemblages of the alkaline series mentioned above are summarized into Fig.6.

Conclusions

As is shown in Fig. 6, the order of crystallization and mineral assemblages of the alkali basalt-pantellerite series and teschenite-syenite series in the middle and later stages are completely different. The former is characterized by Fe^{+2}-rich anhydrous minerals such as hedenbergite, fayalite and ferropigeonite, the latter by various hydrous ferromagnesian silicates, such as calciferous and alkali amphiboles and biotite, Na-Fe^{3+}-clinopyroxenes, and the absence of Fe^{2+}-rich clinopyroxenes and olivine. The magma of the alkali basalt-pantellerite series is low in volatiles (chiefly water), while in the teschenite-syenite series volatile components play an important role. Stability relations of riebeckite and riebeckite-arfvedsonite solid solutions have recently been studied by Ernst (1962). The mineral assemblages of trachytes and pantellerites agree with that of the system $Na_2O \cdot 5FeO_2 \cdot 8SiO_2 +$ excess H_2O in the range of oxygen partial pressure and high temperature which he studied, but the assemblages of monzonites and syenites accord with those expected under higher oxygen partial pressure and lower temperature.

Ferroaugite and hedenbergite from trachytes and pantellerites are di-

TABLE 8. CHEMICAL ANALYSES OF ASSOCIATED ARFVEDSONITES
AND RIEBECKITES WITH AEGIRINES

	1	2	3	4	5	6	7
SiO_2	48.51	47.54	48.41	50.79	52.41	50.25	51.3
TiO_2	1.10	1.18	1.32	1.21	0.45	0.80	1.9
Al_2O_3	1.08	2.36	1.81	1.19	0.61	0.26	2.7
Fe_2O_3	17.53	9.50	11.25	15.15	14.37	13.95	14.2
FeO	14.31	23.21	23.81	20.56	14.82	17.09	18.5
MnO	0.66	1.22	0.75	0.83	1.46	0.62	0.9
MgO	1.31	2.37	0.06	0.48	5.07	0.04	
CaO	5.43	3.82	1.18	0.63	1.33	0.20	1.1
Na_2O	7.87	5.36	7.37	6.10	4.94	8.80	6.0
K_2O	1.48	1.59	1.52	1.26	2.10	2.20	1.4
H_2O^+	1.48	1.90	0.94	1.93	2.02	0.4	1.9
H_2O^-	0.17	0.00	0.13	0.07	0.10	0.09	0.1
F			2.95		0.30	3.31	0.3
Cl						0.18	
Less O = F, Cl			1.24		0.13	1.43	0.1
Total	100.93	100.05	100.26	100.20	99.85	100.79[1]	100.2
Analyst	K. Yagi	K. Aoki	W. A. Deer	K. Aoki	T. Miyashiro	G. D. Borley	C. H. Harvey

[1] Includes ZrO_2 0.56, Li_2O 2.20, ZnO 0.93, PbO 0.18, P_2O_5 0.16.

1. Arfvedsonite, aegirine arfvedsonite syenite, Morotu River, Morotu, Sakhalin (Yagi, 1953).

2. Arfvedsonite, aegirine arfvedsonite quartz syenite, Tohenri, Korea.

3. Arfvedsonite, arfvedsonite aegirine syenite, Kap Boswell, Kangerdlugssuaq, east Greenland (Deer *et al.*, 1963).

4. Riebeckite, aegirine riebeckite granite pegmatite, Quincy, Mass., U.S.A.

5. Riebeckite, aegirine riebeckite quartz syenite, Kogan-zan, Korea (Miyashiro and Miyashiro, 1956).

6. Riebeckite, aegirine riebeckite granite, Kaffo Valley, Kiruei Complex, Nigeria (Borley, 1963).

7. Riebeckite, aegirine riebeckite felsite, Shetland, Scotland (Phemister *et al.*, 1950).

FIG. 6. Order of crystallization of the mafic minerals in the alkaline rock series.

rectly crystallized from the magma and do not show the inversion phenomena from wollastonite solid solutions. The Fe^{2+}-rich clinopyroxene ($Di_{24}Hd_{76}$-Hd_{100}) in the join diopside-hedenbergite inverts to wollastonite solid solution at high temperatures before melting (Turnock, 1962). Therefore, these pyroxenes are produced from the magma at temperatures of 1000° C. or less. Ion substitutit of the diopside-ferropigeonite series of the Japanese tholeiite magmas were studied in detail by Kuno who concluded that the clinopyroxene series of the tholeiite series favor Ca-Fe^{2+} substitution under conditions of high temperature and rapid cooling. It is concluded, therefore, that the augite-ferropigeonite series from Kakarashima is produced at high temperatures.

From the studies of clinopyroxenes from the alkaline rock series of Japan, Pantelleria and Morotu, Sakhalin and data on the synthesis and stability fields of riebeckite and riebeckite-arvedsonite solid solutions, it is concluded that the following three crystallization trends of the clinopyroxenes can be traced: 1) diopside-ferropigeonite, 2) diopside-hedenbergite, and 3) diopside-aegirine, and these trends are controlled by temperature and oxygen partial pressure of the alkali basalt magmas. The first corresponds to the highest temperatures and low oxygen partial pressure, the second to intermediate temperatures and low oxygen partial pressure, and the third to low temperatures and high oxygen partial pressure. The first trend is rare; the second and third are the commonest in alkaline rocks.

REFERENCES

Aoki, K. (1959) Petrology of alkali rocks of the Iki Islands and Higashimatsuura District, Japan. *Sci. Rep. Tohoku Univ. Ser. III*, **6**, 261–310.

——— (1962a) The clinopyroxenes of the Otaki dolerite sill. *Jour. Japan. Assoc. Mineral. Pet. Econ. Geol.* **47**, 41–45 (in Japanese).

——— (1962b) Petrology of alkali-dolerite of Oga peninsula, Akita Prefecture. *Jour. Japan. Assoc. Mineral. Pet. Econ. Geol.* **47**, 155–160 (in Japanese).

——— (1963a) Chemical composition of the clinopyroxenes from the Funagata volcano. *Jour. Japan. Assoc. Mineral. Pet. Econ. Geol.* **49**, 163 (in Japanese).

——— (1963b) The kaersutites and oxykaersutites from alkalic rocks of Japan and surrounding areas. *Jour. Petrol.* **4**, 198–210.

BORLEY, G. D. (1963) Amphiboles from the Younger granites of Nigeria. Part 1. Chemical classification. *Mineral. Mag.* **33,** 358–376.

BROWN, G. M. (1957) Pyroxenes from the early and middle stages of fractionation of the Skaergaard intrusion, East Greenland. *Mineral. Mag.* **31,** 511–543.

———— AND E. A. VINCENT (1963) Pyroxenes from the late stages of fractionation of the Skaergaard intrusion, East Greenland. *Jour. Petrol.* **4,** 175–197.

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

CLARK, S. F., J. F. SCHAIRER AND J. NEUFVILLE (1962) Phase relations in the system $CaMgSi_2O_6$–$CaAl_2SiO_6$–SiO_2 at low and high pressure. *Carnegie Inst. Washington, Year Book,* **61,** 59–68.

DEER, W. A., R. A. HOWIE AND J. ZUSSMAN (1963) *Rock-forming Minerals,* vol. 2, *Chain Silicates.* Longmans, London.

ERNST, W. G. (1962) Synthesis, stability relations and occurrence of riebeckite and riebeckite-arfvedsonite solid solutions. *Jour. Geol.* **70,** 689–736.

GREENWOOD, R. (1951) Younger intrusive rocks of Plateau province, Nigeria, compared with the alkalic rocks of New England. *Bull. Geol. Soc. Am.* **62,** 1151–1178.

HATTORI, H. AND M. KATADA (1963) Trachytic rocks near Mt. Daisen, Tottori Pref., western Japan. *Jour. Japan. Assoc. Mineral. Pet. Econ. Geol.* **50** (in press).

HESS, H. H. (1949) Chemical composition and optical properties of common clinopyroxenes. Part 1. *Am. Mineral.* **34,** 621–666.

ISHIBASHI, K. (1962) Alkali-pyroxene in doleritic basalt flow from the Higashi-matsuura District, Saga Prefecture. *Jour. Japan. Assoc. Mineral. Pet. Econ. Geol.* **47,** 213–222 (in Japanese).

ITO, J. (1955) Recueil Mineralogique (III), (5) Aegirine from Hoansan, in the Fukushin-san District, Korea. *Jour. Mineral. Scoc. Japan,* **1,** 252–254 (in Japanese).

IWAO, S. (1939) Petrology of the alkaline rocks of the Nayoshi District, Sakjalin, Japan. *Japan. Jour. Geol. Geogr.* **16,** 155–204.

JOHNSTON, R. (1953) The olivines of the Garbh Eilean sill, Shiant Isles. *Geol. Mag.* **90,** 161–171.

KAWANO, Y. (1942) Chemical studies of common augite from the beach of Nemuro. *Geogr. Soc. Tokyo Jour.* **54,** 251–254.

KUNO, H. (1955) Ion substitution in the diopside-ferropigeonite series of clinopyroxenes. *Am. Mineral.* **40,** 70–93.

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

———— (1962) Clinopyroxene solid solutions. Part 1. The $CaAl_2SiO_6$ component. *Japan. Jour. Geol. Geogr.* **33,** 213–220.

LE BAS, M. J. (1962) The role of aluminum in igneous clinopyroxenes with relation to their parentage. *Am. Jour. Sci.* **260,** 267–288.

LE MAITRE, R. W. (1962) Petrology of volcanic rocks, Gough Island, South Atlantic. *Bull. Geol. Soc. Am.* **73,** 1309–1340.

MATSUURA, Y. AND Y. OJI (1962) Some rock minerals of the alkali basalts from Inner zone of southwestern Japan. *Bull. Fukuoka Gakugei Univ.* **12** (3), 83–92.

MCDOUGALL, I. (1961) Optical and chemical studies of pyroxenes in a differentiated Tasmanian dolerite. *Am. Mineral.* **46,** 661–687.

MIYASHIRO, A. AND T. MIYASHIRO (1956) Nepheline syenites and associated alkalic rocks of the Fukushin-zan District, Korea. *Jour. Fac. Sci. Univ. Tokyo,* **10** (1), 1–64.

MUIR, I. D. AND C. E. TILLEY (1961) Mugearites and their place in alkali igneous rock series. *Jour. Geol.* **69,** 186–203.

Murray, R. J. (1953) The clinopyroxenes of the Garbh Eilean Sill, Shiant Isles. *Geol. Mag.* **91,** 17–31.

Oji, Y. (1960) On the augite phenocryst in alkali basalts from the Abu District. *Jour. Japan. Assoc. Mineral. Pet. Econ. Geol.* **45,** 66–70 (in Japanese).

Pecora, W. T. (1942) Nepheline syenite pegmatites, Rocky Boy Stock, Bearpaw Mountain, Montana. *Am. Mineral.* **27,** 397.

Phemister, J., C. O. Harvey and P. A. Sabine (1950) The riebeckite-bearing dikes of Shetland. *Mineral Mag.* **29,** 359–373.

Ross, C. S., M. D. Foster and A. T. Myers (1954) Origin of dunites and of olivine-rich inclusion in basaltic rocks. *Am. Mineral.* **39,** 693–737.

Sabine, P. A. (1950) The optical properties and composition of acmitic pyroxenes. *Mineral. Mag.* **29,** 113–125.

Simpson, E. S. W. (1954) The Okonjeje igneous complex, South-West Africa. *Trans. Geol. Soc. South Africa.* **57,** 125–172.

Tilley, C. E. and J. Gittins (1961) Igneous nepheline-bearing rocks of the Haliburton-Bancroft province of Ontario. *Jour. Petrol.* **2,** 38–48.

Tomita, T. (1935) On the chemical compositions of the Cenozoic alkaline suite of the Circum-Japan Sea region. *Shanghai Sci. Inst. Jour. Sect.* **2** (1) 227ff.

Turnock, A. C. (1962) Preliminary results on melting relations of synthetic pyroxenes on the diopside-hedenbergite join. *Carnegie Inst. Washington, Year Book* **61,** 82.

Washington, H. S. and H. E. Merwin (1927) The acmitic pyroxenes. *Am. Mineral.* **12,** 233–252.

Wilkinson, J. F. G. (1956) Clinopyroxenes of alkali olivine basalt magma. *Am. Mineral.* **41,** 724–743.

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

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

Yoder, H. S. Jr. and C. E. Tilley (1962) Origin of basalt magmas: An experimental study of natural and synthetic rock systems. *Jour. Petrol.* **3,** 342–532.