

PIGEONITE-BEARING ANDESITE AND ASSOCIATED DACITE FROM ASIO, JAPAN

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ABSTRACT. Andesite and dacite dikes near Asio represent late stage members of the pigeonitic rock series, some of which have unusually high $\text{FeO} + \text{Fe}_2\text{O}_3 : \text{MgO}$. Orthopyroxene, Ca-rich and Ca-poor clinopyroxenes, and olivine, all having Fe:Mg higher than 50:50, occur as phenocrysts. Orthopyroxene is richer in Ca than orthopyroxene coexisting with hornblende, biotite, and garnet from other areas, possibly because of the high temperature of crystallization. Orthopyroxene and Ca-poor clinopyroxene are lower in Fe:Mg than the coexisting olivine. The latter mineral bears no reaction relation to the pyroxenes. The mafic silicate assemblages in the Asio rocks resemble in some way those of the late stage of fractionation in the Skaergaard intrusion.

INTRODUCTION

Although the crystallization of ferromagnesian silicate minerals in the early stage of basalt magma fractionation has been well studied, little is known about their crystallization in the late stage. This is partly because of the great variety of ferromagnesian silicate minerals appearing in the late stage. Various combinations of olivine, Ca-rich and Ca-poor clinopyroxenes, and orthopyroxenes, all high in Fe:Mg, together with amphibole and biotite, appear in granophyres in gabbro and dolerite intrusions and as phenocrysts in andesite, dacite, rhyolite, and trachyte. Sometimes almandine garnet may occur as phenocrysts.

Iron-rich silicate mineral assemblages are described from Skaergaard and some other gabbro and dolerite intrusions, but these are mostly Ca-rich clinopyroxene-olivine assemblages. Similar assemblages were also described from acid volcanic rocks from Britain and Iceland (Carmichael, 1960). Rather unique examples of the Ca-poor pyroxene-olivine assemblage are found in andesite and dacite from the Asio district, 100 km north-northwest of Tokyo. The present paper provides some mineralogical data on these rocks, and a comparison is made with similar assemblages in volcanic rocks of the Sidara district, southwest of Tokyo.

Compositions of some of the minerals were determined by the microprobe of the Shimadzu-ARL type. Chemically analyzed, homogeneous crystals of orthopyroxenes (hypersthene in dacite from Suruga-Oyama, ferrohypersthene in hornfels from Yu-hsi-kou, and eulite in eulysite from Wang-chang-tzu), clinopyroxenes (diopside in skarn from St. Lawrence, ferrosalite in skarn from St. Lawrence, hedenbergite in skarn from Herault, and pigeonite in dolerite from New Jersey), and olivines (forsterite in marble from Antarctica, forsterite in peridotite nodule from Antarctica, chrysolite in basalt from Hatizyō-zima, ferrohortonolite in dacite druse from Sirobori) were used as standards for the respective minerals. These analyzed minerals cover wide ranges of FeO (total iron recalculated as FeO), MgO, CaO, and Al_2O_3 . Based on these standards, calibration curves for microprobe counts versus weight percent of each of the above oxides were drawn. The weight percents of these oxides in

pyroxenes and olivine from the Asio rocks were obtained by plotting the counts on these curves.

Because of a slight deviation of individual points for the standard minerals from the calibration curve and also from the variability of composition in different crystals as well as in different parts of a single crystal as shown in table 5, it is difficult to evaluate the range of errors involved in the microprobe analyses. However, the average values of the microprobe analyses on the pyroxenes (table 5) are close to the results of the wet analyses on the same minerals (table 4). Some discrepancy between the results of the two different methods appears to be due largely to inhomogeneity of the pyroxenes, which is commonly observed in minerals of volcanic rocks.

PETROGRAPHY

Paleozoic slate and Cretaceous (?) quartz diorite, occurring to the north and north-northwest of the town of Asio, are traversed by numerous dikes of pyroxene andesite and dacite, probably Miocene or Pliocene in age (Kawata, 1955). Three of the dikes containing iron-rich pyroxene and olivine phenocrysts are described below.

Ferrohypersthene andesite with ferropigeonite and ferroaugite phenocrysts (tables 1, 2, and 3, columns 1 and 1a).—The rock occurs as a dike only 10 cm thick cutting through the quartz diorite. It contains phenocrysts of zoned plagioclase (An_{33-36}), ferrohypersthene (column 5, table 4, $\gamma = 1.740-1.744$, average $Mg:Fe = 38:62$), ferropigeonite, ferroaugite, magnetite, and apatite in a glassy groundmass. The results of microprobe analysis of the pyroxenes are given in table 5. Ferrohypersthene is zoned with increase of iron toward the margin of crystals. The two kinds of clinopyroxenes usually occur in irregular intergrowth. Numerous acicular crystals of clinopyroxene and a small amount of plagioclase prisms are scattered in the brown glass.

The material used for the chemical analysis of ferrohypersthene contains some clinopyroxenes as impurity. The true CaO content of this mineral as determined by the microprobe is probably close to 2.3 instead of 2.94. For the other oxides, the average of the three microprobe determinations is very close to that of the chemical analysis, in spite of the heterogeneity of composition in different grains and in different portions of a single crystal.

Ferropigeonite-ferrohortonolite andesite (tables 1, 2, and 3, columns 2a, b, c, and d). The rock occurs as a dike 1.3 m thick cutting through the slate. It has glassy selvages 5 to 20 cm thick at the contact with the slate. The phenocrysts are unzoned plagioclase (An_{84}), ferrohortonolite, ferropigeonite (column 6, table 4), magnetite, and apatite. The composition of ferrohortonolite was determined by the microprobe (table 5). That of ferropigeonite as inferred from its optical properties (table 6) is very close to the chemical analysis. Ferrohortonolite has sharp crystal outlines, whereas ferropigeonite usually has rounded or irregular terminations. For this reason, it is not possible to decide whether this pyroxene

originally crystallized in the monoclinic or orthorhombic form (protopyroxene). Twinning on 100 is rather rare, and there is no indication of inversion from protopyroxene. From this negative evidence, it has been suggested that the ferropigeonite originally crystallized in the monoclinic form ("high clinopyroxene", Kuno, 1966). Morimoto and others (1960) have made a detailed X-ray study of this pyroxene and determined its crystal structure and unit cell dimensions. Morimoto (oral commun., 1968) recently found that the pyroxene contains a small amount of exsolution lamellae of Ca-rich clinopyroxene parallel to 001, suggesting its crystallization in the monoclinic form.

Both ferrohortonolite and ferropigeonite are apparently unzoned. Angular xenoliths of unmetamorphosed slate and chert are rarely present.

TABLE 1

Chemical compositions of pigeonite-bearing andesites and associated dacite from Asio

	1	2a	2b	2c	3	4a	4b	4c
SiO ₂	58.97	59.62	59.80	59.71	63.82	64.84	65.01	64.93
Al ₂ O ₃	15.14	13.96	15.62	14.79	14.66	14.06	14.67	14.36
Fe ₂ O ₃	0.50	1.45	1.94	1.69	2.08	1.29	1.72	1.51
FeO	7.07	7.72	6.70	7.21	2.54	2.72	2.02	2.37
MgO	1.46	0.45	0.44	0.45	0.36	0.05	0.04	0.04
CaO	6.87	6.26	6.21	6.24	4.60	4.66	4.72	4.69
Na ₂ O	2.62	3.19	3.13	3.16	2.63	2.79	2.90	2.84
K ₂ O	0.89	0.96	0.87	0.91	0.92	1.24	1.16	1.20
H ₂ O ⁺	4.27	3.40	3.51	3.46	4.20	6.43	6.52	6.48
H ₂ O ⁻	1.34	1.37	0.84	1.10	3.94	1.45	1.28	1.36
TiO ₂	0.90	1.01	0.70	0.86	0.29	0.37	0.23	0.30
P ₂ O ₅	0.32	0.27	0.35	0.31	0.14	0.12	0.15	0.14
MnO	0.16	0.15	0.14	0.14	0.09	0.06	0.05	0.05
Total	100.51	99.81	100.25	100.03	100.27	100.08	100.47	100.27

1. Ferrohypersthene andesite with ferropigeonite and ferroaugite phenocrysts (HK50093003). Analyst, H. Haramura. A cliff on the northern bank of the river Matuki-zawa at the confluence of Suzuuti-zawa, 4 km north-northwest of the town of Asio.

2a. Ferropigeonite-ferrohortonolite andesite (HK51081501a) chilled selvage of dike. Analyst, H. Asari. A cliff on the northeastern bank of the river Aso-zawa, 10 m from the confluence of Kuzô-zawa, 4 km north of the town of Asio.

2b. Same specimen as 2a. Analyst, T. Arikai.

2c. Average of 2a and 2b.

3. Fayalite dacite (pitchstone) with phenocrysts of eulite and subcalcic ferroaugite (HK48091001). Analyst, H. Haramura. Locality same as that of 1.

4a. Another specimen (HK51070901b) from the same dike as 3. Analyst, H. Asari.

4b. Same specimen as 4a. Analyst, T. Arikai.

4c. Average of 4a and 4b.

TABLE 2

Chemical compositions of pigeonite-bearing andesites and
associated dacite from Asio, recalculated as water free

	1a	2d	3a	4d
SiO ₂	62.14	62.54	69.27	70.25
Al ₂ O ₃	15.95	15.49	15.91	15.54
Fe ₂ O ₃	0.53	1.77	2.26	1.63
FeO	7.45	7.55	2.76	2.56
MgO	1.54	0.47	0.39	0.04
CaO	7.24	6.54	4.99	5.07
Na ₂ O	2.76	3.31	2.85	3.07
K ₂ O	0.94	0.95	1.00	1.30
TiO ₂	0.95	0.90	0.31	0.32
P ₂ O ₅	0.34	0.32	0.15	0.15
MnO	0.17	0.15	0.10	0.05
Total	100.01	99.99	99.99	99.98

1a. Same as 1 of table 1.

2d. Same as 2c of table 1.

3a. Same as 3 of table 1.

4d. Same as 4c of table 1.

TABLE 3

Norms calculated from the analyses of table 2

		1a	2d	3a	4d
F	Q	21.35	22.01	36.74	35.64
	or	5.57	5.62	5.90	7.68
	ab	23.33	28.00	24.12	25.95
	an	28.37	24.62	23.73	24.11
Hy	en	3.26	0.92	0.97	0.10
	fs	10.22	8.82	2.86	2.92
Di	wo	2.22	2.37	...	...
	en	0.57	0.25	...	...
	fs	1.77	2.36	...	...
	Mt	0.76	2.57	3.29	2.36
	Il	1.81	1.71	0.59	0.61
	Ap	0.81	0.77	0.37	0.37
	C	...	...	1.45	0.24

The interior of the dike has a holocrystalline groundmass consisting of andesine, clinopyroxene, olivine, magnetite, ilmenite, tridymite (or cristobalite ?), quartz, alkali feldspar, and zeolite (?). Olivine is not surrounded by a rim of clinopyroxene.

TABLE 4

Chemical compositions of ferrohypersthene, ferropigeonite,
and hemoilmenite from Asio

	5	6	7
SiO ₂	49.45	48.36	...
Al ₂ O ₃	1.53	0.41	3.44
Fe ₂ O ₃	2.59	1.36	8.63
FeO	30.31	32.86	26.28
MgO	12.01	11.34	2.39
CaO	2.94	4.58	0.91
Na ₂ O	0.13	tr.	...
K ₂ O	0.27	tr.	...
H ₂ O ⁺	0.24	0.15	...
H ₂ O ⁻	0.05	tr.	...
TiO ₂	0.35	0.39	34.75
P ₂ O ₅	0.04	0.04	...
MnO	0.69	0.84	...
Total	100.60	100.33	76.40

Atomic proportion based on six oxygens

Si	1.945	} 2.000	1.940	} 2.000
Al	0.055		0.019	
Al	0.016	} 1.976	...	} 2.017
Fe ⁺³	0.076		0.041	
Ti	0.012	} 1.976	0.012	} 2.017
Fe ⁺²	0.994		1.102	
Mn	0.024	} 1.976	0.028	} 2.017
Mg	0.708		0.678	
Ca	0.123	} 1.976	0.197	} 2.017
Na	0.009		...	
K	0.014	} 1.976	...	} 2.017
			...	
Ca	7		10	
Mg	37		33	
Fe ⁺² + Fe ⁺³	56		57	

5. Ferrohypersthene phenocrysts from andesite (HK51070901a).
Analyst, H. Haramura. The analyzed material contains several percent ferroaugite and ferropigeonite. The host rock is from the same dike as column 1, table 1.

6. Ferropigeonite phenocrysts from andesite (HK51081501d).
Analyst, H. Haramura. The host rock is from the same dike as column 2, table 1.

7. Hemoilmenite phenocrysts from dacite (HK51070901b). Analyst, T. Katsura. The analyzed material contains nearly 20 percent eulite, which was corrected by assuming that all SiO₂ is due to this mineral. The host rock is from the same dike as column 4, table 1.

TABLE 5
Microprobe analyses of minerals

Ferrohypersthene andesite (HK51070901a)					
	Al ₂ O ₃	FeO*	MgO	CaO	Ca:Mg:Fe**
<u>Ferrohypersthene</u>					
Crystal A, core	1.0	36.0	11.0	2.4	
Crystal B, core	2.4	31.1	14.6	2.0	
Crystal B, margin	1.2	37.0	10.7	2.5	
Average	1.5	34.7	12.1	2.3	5:36:59
<u>Ferropigeonite</u>					
Four different portions of a crystal	1.0	31.5	11.1	4.5	
	1.1	29.8	10.5	4.4	
	1.3	31.5	11.2	5.2	
	1.1	31.5	11.4	4.6	
Average	1.1	31.1	11.0	4.7	11:34:55
<u>Ferroaugite</u>					
Three different portions of a crystal	2.5	21.4	9.7	16.6	
	2.6	21.3	9.5	16.6	
	2.4	22.5	9.7	16.2	
Average	2.5	21.7	9.6	16.5	35:29:36
Ferropigeonite-ferrohortonolite andesite (HK51081501a)					
		FeO*	MgO	Mg:Fe**	
<u>Ferrohortonolite</u>					
Average of six determinations†		56.5	11.0	26:74	

*Total iron as FeO.

**Fe⁺² + Fe⁺³.

†Determined on core and margin of three different crystals that gave a uniform composition.

Fayalite dacite pitchstone with phenocrysts of eulite and subcalcic ferroaugite (tables 1, 2, and 3, columns 3, 3a, 4a, b, c and d).—The rock occurs as a dike 50 cm thick cutting through the quartz diorite at a point only 1 m away from the ferrohypersthene andesite dike. It contains phenocrysts of zoned plagioclase (An_{35-45}), fayalite, eulite, subcalcic ferroaugite, magnetite, hemoilmenite (column 7, table 4), apatite, and zircon. The optical properties, unit cell dimensions, and inferred compositions of some of these minerals are given in table 6. Fayalite has sharp crystal outlines and is completely fresh, whereas eulite is replaced largely by an amorphous, pale-green mineral, though its orthorhombic outline is distinctly preserved. Because of its small size and amount, it is impossible to determine whether the subcalcic ferroaugite consists of a single phase or of a submicroscopic intergrowth of more than one phase produced by unmixing of a single phase. It is also uncertain whether original homogeneous crystals were formed as a stable or metastable phase. It is possible, if not proved, that the solvus between the Ca-rich and Ca-poor clinopyroxene series narrows in such iron-rich compositions, and a single-phase subcalcic ferroaugite can form as a stable phase.

Pink almandine (table 6) is often observed as irregular-shaped crystals surrounded by a reaction rim of plagioclase. Some of such rimmed crystals are completely enclosed in eulite. Almandine may have crystallized at some deeper level and may have reacted with the magma to form plagioclase when eulite crystallized at a shallower level. It is also possible that the mineral was captured from some country rock which is not exposed in the vicinity.

The groundmass is largely made up of pale-brown to colorless glass with irregular patches of pale-green amorphous material. Very small crystals of clinopyroxene, olivine, oligoclase, and an iron oxide mineral are disseminated in the glass.

INTERPRETATION OF THE RESULTS

The analyses given in table 2 are plotted in figure 1 which shows that the rocks fall either within the field of the pigeonitic rock series (Kuno, 1968) or outside this field toward the MgO-poor side. The rocks may be interpreted as having been formed from late-stage magmas of this series with an unusually high concentration of $FeO + Fe_2O_3$ relative to MgO. In the ordinary late-stage members of this series, the mafic mineral assemblage is either augite-hypersthene or augite-hypersthene-pigeonite with varying Fe:Mg as in the ferrohypersthene andesite of Asio (point 1, fig. 1). The unusually high $FeO + Fe_2O_3$:MgO in the other two rocks of Asio (points 2, 3, and 4, fig. 1) probably favored the formation of iron-rich olivine and iron-rich pyroxenes.

The compositions of the silicate minerals given in tables 4, 5, and 6 are plotted in figure 2 in which points for the coexisting minerals are connected by tie lines.

The two orthopyroxenes (A-1 and A-3, fig. 2) have high Ca contents ($Ca \times 100 / Ca + Mg + Fe \geq 5$) as compared with iron-rich orthopyroxenes

from some dacites ($\text{Ca} \times 100 / \text{Ca} + \text{Mg} + \text{Fe} \leq 3$) whose analyses are given in table 7 and plotted also in figure 2. The latter orthopyroxenes are from the rocks of the hypersthene rock series and have probably crystallized at temperatures lower than those for the Asio rocks. These orthopyroxene phenocrysts are not associated with those of augite but coexist with phenocrysts of hornblende, biotite, or garnet. The high Ca is possibly due to the high temperature of crystallization or the difference in mineral assemblage. The CaO contents in the Asio orthopyroxenes represent the maximum value of solubility of this component as seen from the statistical study of orthopyroxene analyses (Kuno, 1966, fig. 4).

TABLE 6

Optical properties and unit-cell dimensions of minerals

Ferropigeonite-ferrohortonolite andesite (HK51081501a)

Ferropigeonite

$\alpha = 1.715-1.732$ (+) $2V = 16^\circ-5^\circ$
 $\beta = 1.715-1.732$ in 010 plane
 $\gamma = 1.740 \pm 1.757$ $\rho < v$ strong
 $c/\wedge z = 40^\circ$
 $\text{Ca:Mg:Fe} = 12:31:57$ (after Muir, 1951)

Fayalite dacite (HK48091001)

Fayalite

$\alpha(\text{min}) = 1.804$ (-) $2V = 56^\circ-52^\circ$
 $\rho > v$ distinct
 $\text{Mg:Fe} = 10:90$ (from $2V = 54^\circ$, after Deer, Howie, and Zussman, 1962)

Eulite

$\gamma = 1.767-1.774$ (rarely 1.738) (-) $2V$ (avg) = 87°
 $\rho < v$ about X

Distinctly pleochroic with X, smoky brown; Y, pale brown; Z, smoky green

$\text{Mg:Fe} = 17:83$ (after Kuno, 1954)

Unit-cell dimensions

$a = 18.429 \text{ \AA}$ $b = 9.016 \text{ \AA}$ $c = 5.249 \text{ \AA}$

Subcalcic ferroaugite

$\beta = 1.740$ (+) $2V = 32^\circ-27^\circ$
 (avg 30°)
 in 010 plane

$\text{Ca:Mg:Fe} = 17:18:65$ (after Muir, 1951)

Almandine

$n = 1.807$

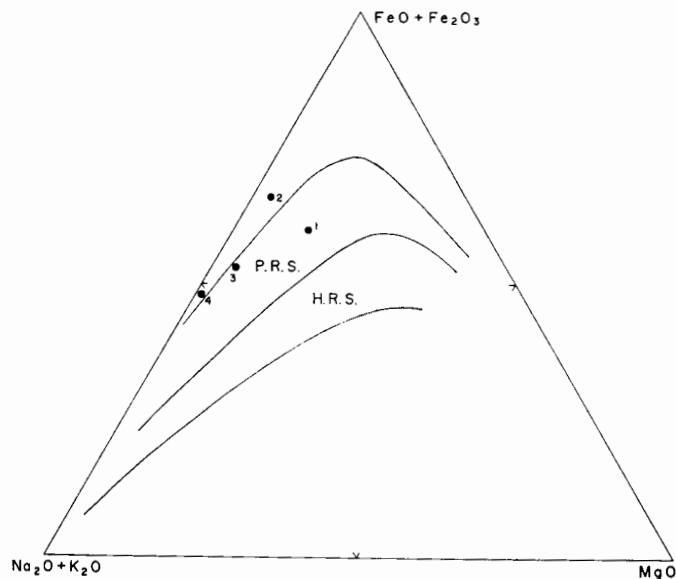


Fig. 1. M-F-A plot of andesites and dacite from Asio. Numbers 1, 2, 3, and 4 refer to columns 1a, 2d, 3a, and 4d respectively of table 2. P.R.S. and H.R.S. are the fields of the pigeonitic and hypersthene rock series respectively as established by aphyric rocks of the Izu-Hakone region.

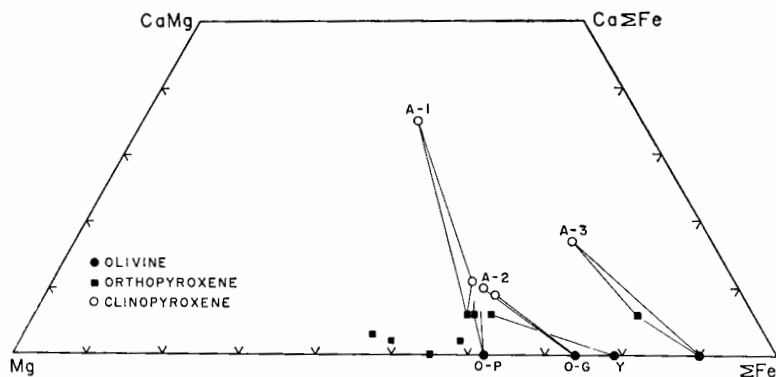


Fig. 2. Compositions of coexisting pyroxenes and olivines from Asio and Sidara and those of the orthopyroxenes of table 7 (black squares without marks). A-1, A-2, and A-3 represent minerals of the rocks of columns 1, 2a, and 3 respectively of table 1. O-P and O-G represent phenocrysts and groundmass minerals, respectively, of ferroaugite-ferrohypersthene-hortonolite andesite dike (HK39082103) from near Orimoto-tôge, north of Kami-Tugu, northern Sidara district. Y represents phenocrysts of ferrohypersthene-ferrohortonolite glassy dacite dike (HK48080703) near Yosimura, north of Nagasino, southern Sidara district. The compositions of the minerals in the Sidara rocks are inferred from their optical properties. The Ca-contents of the two Sidara orthopyroxenes are assumed to be similar to those of the Asio orthopyroxenes. They may be a little lower than these assumed values. Clinopyroxene O-G is very close in composition to clinopyroxene A-2, and the coexisting olivines have the identical composition.

In the ferrohypersthene andesite (A-1, fig. 2), the compositional relation between the coexisting orthopyroxene and Ca-poor and Ca-rich clinopyroxenes is similar to that found in many other rocks having the same pyroxene assemblage: Fe:Mg is the lowest in the Ca-rich clinopyroxene and highest in the Ca-poor clinopyroxene, and the latter mineral has a higher Ca content than the orthopyroxene (Kuno, 1966, fig. 5).

In the other two rocks of Asio (A-2 and A-3, fig. 2) in which Ca-poor pyroxenes and olivines are associated, the pyroxenes are lower in Fe:Mg than the olivines. This compositional relation is obtained in the iron-rich pyroxene-olivine assemblages in the system MgO-FeO-SiO_2 (Bowen and Schairer, 1935) and also in some natural rocks (Ramberg and DeVore, 1951).

Volcanic rocks with similar iron-rich pyroxene-olivine assemblages are found in the Sidara district, Aiti Prefecture, southwest of Tokyo. One is an andesite dike containing phenocrysts of ferroaugite, ferrohypersthene, and hortonolite (O-P in fig. 2) and ferropigeonite and ferrohortonolite in the groundmass (O-G). The other is a glassy dacite dike containing phenocrysts of ferrohypersthene and ferrohortonolite (Y) and clinopyroxene and olivine in the groundmass. In these assemblages, the Ca-poor pyroxenes are also lower in Fe:Mg than the associated olivines.

It should be noted that both in the Asio and Sidara rocks, olivine occurs as phenocrysts as well as in the groundmass and is not surrounded by a reaction rim of pyroxene. This indicates that olivine does not bear a reaction relation to pyroxene in such iron-rich compositions.

A marked difference is to be noted between the mafic silicate mineral assemblages here described and those in the later stages of the hypersthene rock series or calc-alkali rock series, the latter being characterized by orthopyroxene usually less ferriferous than $\text{En}_{10}\text{Fs}_{90}$, hornblende, and biotite (Kuno, 1968). The latter assemblage is probably due to the higher water pressure of the magmas and also to the higher oxygen pressure by which part of the Fe^{+2} in the magma is converted to Fe^{+3} , resulting in less ferriferous composition of the orthopyroxene.

The mafic mineral assemblages of the Asio rocks resemble in some way those in the later stages of fractionation of the Skaergaard magma (Muir, 1951; Brown, 1957; Wager, 1960), probably due to the similarity in $\text{FeO} + \text{Fe}_2\text{O}_3:\text{MgO}$ ratio of the magmas (see fig. 1). Those in the ferrohypersthene andesite, ferropigeonite-ferrohortonolite andesite, and fayalite dacite are comparable to those in the middle zone, the earliest stage of the upper zone, and the middle to late stages of the upper zone of Skaergaard, respectively (see fig. 25 in Kuno, 1968).

However, there are some differences in the assemblages. For example, in the middle zone, orthopyroxene is lacking, and augite and pigeonite are less ferriferous than those of the ferrohypersthene andesite. This difference may be ascribed to the lower temperature of the Asio magma where the orthopyroxene-pigeonite inversion took place at a more iron-rich composition.

TABLE 7

Chemical compositions of iron-rich orthopyroxene phenocrysts from some dacites

	8	9	10	11
SiO ₂	51.07	51.00	49.24	48.95
Al ₂ O ₃	1.30	1.47	0.49	0.24
Fe ₂ O ₃	3.28	1.23	2.03	3.93
FeO	24.52	27.96	31.16	30.66
MgO	16.65	16.29	15.24	13.28
CaO	1.31	0.67	0.17	0.85
Na ₂ O	0.16	0.00	0.12	0.11
K ₂ O	0.03	0.00	0.00	0.03
H ₂ O ⁺	0.18	0.11	0.12	0.08
H ₂ O ⁻	0.02	0.01	0.00	0.16
TiO ₂	0.00	0.10	0.00	0.75
P ₂ O ₅	0.00	0.00	0.02	n.d.
MnO	1.48	1.16	0.90	0.93
Total	100.00	100.00	99.49	99.97

Atomic proportion based on six oxygens

Si	1.957	2.000	1.964	2.000	1.952	2.000	1.943	2.000
Al	0.043		0.036		0.023		0.011	
Al	0.017	1.970	0.033	1.973	...	2.011	...	1.972
Fe ⁺³	0.097		0.037		0.025		0.046	
Fe ⁺³	...	1.970	...	1.973	0.035		0.071	1.972
Ti	...		0.002		...		0.022	
Fe ⁺²	0.784	1.970	0.896	1.973	1.030	2.011	1.017	1.972
Mn	0.048		0.037		0.030		0.031	
Mg	0.957	1.970	0.940	1.973	0.900		0.785	1.972
Ca	0.053		0.028		0.007		0.036	
Na	0.014	1.970	...	1.973	0.009		0.009	1.972
K	...		...		...		0.001	
Ca	3		2		0		2	
Mg	51		49		45		40	
Fe ⁺² + Fe ⁺³	46		49		55		58	

Analyst, H. Haramura.

8. Hypersthene phenocrysts from brown hornblende-bearing hypersthene dacite (HK53051602). Light-gray welded tuff at a quarry 500 m northwest of Kogasira, 8 km northwest of Kagosima City, south Kyusyu. The analysis was corrected for 0.61 percent ilmenite and 0.34 percent apatite impurity.

9. Hypersthene phenocrysts ($\gamma = 1.722$ -1.731, average Mg:Fe = 50:50) from hypersthene-quartz dacite (HK53051501). Unwelded pumice flow deposit (Ito pyroclastic flow, Aramaki and Ui, 1966) at Sin-Kamibasi in the western part of Kagosima City, south Kyusyu. The analysis was corrected for 0.3 percent ilmenite and 0.34 percent apatite impurity.

10. Ferrohypersthene phenocrysts from biotite-ferrohypersthene-quartz dacite (pitchstone) (HK56071001). A lava exposed just behind the temple of Hōrai-ji, Sidara district, Aiti Prefecture, central Japan. All TiO₂ (0.42 percent) in the original analysis was subtracted as ilmenite impurity.

11. Ferrohypersthene ($\gamma = 1.735$ -1.738, 2V about $X = 55^\circ$, average Mg:Fe = 42:58) from ferrohypersthene dacite with sporadic phenocrysts of garnet (HK52110301). A thick lava exposed near Nagae, 3 km northeast of the town of Taguti, Sidara district, Aiti Prefecture, central Japan. The analysis was corrected for 1.1 percent ilmenite impurity.

In the earliest stage of the upper zone, Ca-rich clinopyroxene is present together with pigeonite and hortonolite, whereas in the ferro-pigeonite-ferrohortonolite andesite, Ca-rich clinopyroxene is absent. In the middle to late stages of the upper zone, Ca-rich clinopyroxene is associated with fayalite whereas subcalcic ferroaugite and eulite are associated with fayalite in the Asio dacite. These differences may have been caused by the low CaO content in the mafic silicate components in the Asio magmas, as seen by the low CaO content in the norms (table 3).

ACKNOWLEDGMENTS

I am very much obliged to the late G. Asano and also to K. Kawata of the Geological Survey, who called my attention to the rocks described here and supplied some of the samples used in this study. Chemical analyses by H. Haramura of the University of Tokyo and by H. Asari and T. Ariki of the Japan Analytical Chemistry Research Institute, and also assistance by H. Soejima of the Shimadzu Research Laboratory and by T. Ui of the University of Tokyo for the microprobe analyses are greatly appreciated. My thanks are due to T. Kusanagi and T. Osuga of the Furukawa Mining Co. for the hospitality during my field work in the Asio district, and also to K. Yagi of the Hokkaido University and S. Banno of the Kanazawa University for reviewing this paper. A part of the cost of this study was defrayed by a Grant from the Japanese Government Fund for Scientific Research.

REFERENCES

- Aramaki, S. and Ui, T., 1966, Aira and Ata pyroclastic flows and related caldera and depressions in southern Kyushu, Japan: *Bull. volcanologique*, v. 29, p. 29-50.
- Bowen, N. L., and Schairer, J. F., 1935, The system MgO-FeO-SiO_2 : *Am. Jour. Sci.*, v. 29, p. 151-217.
- Brown, G. M., 1957, Pyroxenes from the early and middle stages of fractionation of the Skaergaard intrusion, East Greenland: *Mineralog. Mag.*, v. 31, p. 511-543.
- Carmichael, I. S. E., 1960, The pyroxenes and olivines from some Tertiary acid glasses: *Jour. Petrology*, v. 1, p. 309-336.
- Deer, W. A., Howie, R. A., and Zussman, J., 1962, *Rock-forming minerals*, v. 1, Ortho- and ring silicates: London, Longmans, Green and Co. Ltd., 333 p.
- Kawata, K., 1955, Explanatory text of the geological map of Japan, "Nantaizan": Tokyo, Japan, Geol. Survey, p. 1-43.
- Kuno, H., 1954, Study of orthopyroxenes from volcanic rocks: *Am. Mineralogist*, v. 39, p. 30-46.
- , 1966, Review of pyroxene relations in terrestrial rocks in the light of recent experimental works: *Mineralog. Jour.*, v. 5, p. 21-43.
- , 1968, Differentiation of basalt magmas, in Hess, H. H., and Poldervaart, Arie, *Basalt: The Poldervaart treatise on rocks of basaltic composition*, v. 2: New York, John Wiley and Sons, Inc., p. 623-688.
- Morimoto, N., Appleman, D. E., and Evans, H. T., Jr., 1960, The crystal structures of clinoenstatite and pigeonite: *Zeitschr. Kristallographie*, v. 114, p. 120-147.
- Muir, I. D., 1951, The clinopyroxenes of the Skaergaard intrusion, eastern Greenland: *Mineralog. Mag.*, v. 29, p. 690-714.
- Ramberg, H., and De Vore, G., 1951, The distribution of Fe^{++} and Mg^{++} in coexisting olivines and pyroxenes: *Jour. Geology*, v. 59, p. 193-210.
- Wager, L. R., 1960, The major element variation of the layered series of the Skaergaard intrusion and a re-estimation of the composition of the hidden layered series and of the successive residual magmas: *Jour. Petrology*, v. 1, p. 364-398.