

Chemical composition of clinopyroxenes associated with the gehlenite skarn from the Hirata outcrop, Kushiro, Tojo-Cho, Hiroshima Prefecture, Japan

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The clinopyroxenes of the hybrid rocks from the Hirata outcrop, Kushiro, Hiroshima Prefecture, Japan are grouped into (1) diopside, (2) aegirine, and (3) zoned pyroxene. The diopside occurs as isolated crystals enclosed in feldspars. The aegirine occurs along with late hydrous minerals in pore spaces. The zoned pyroxenes occur as discrete crystals with wide rims growing interstitially between feldspar laths and show a continuous compositional trend from diopside through hedenbergite and aegirine-augite to aegirine or titanian aegirine. The pyroxenes enclosed in feldspars and the cores of the zoned crystals have nearly same chemical composition. The late stage pyroxenes are characterized by extreme enrichment of sodium and sometimes titanium. The titanian aegirines studied here are characterized by the predominance of the $\text{Na}(\text{Fe}^{2+}, \text{Mg})_{0.5}\text{Ti}_{0.5}\text{Si}_2\text{O}_6$ component over other Ti-bearing pyroxene components.

The compositional trend of clinopyroxenes from the Hirata hybrid rocks follows a typical trend of peralkaline rocks. The peralkaline nature of the Hirata samples is a result of compositional change of magma accompanied by the metasomatic skarn formation.

Keywords: aegirine, aegirine-augite, diopside, pyroxene, hybrid rock, skarn

I. Introduction

Clinopyroxenes occur in a wide variety of igneous rocks and show variety of igneous rocks and show various compositional trend that reflect the physicochemical conditions of magmas from which they crystallized. The compositional trends of clinopyroxenes from alkaline rocks generally show a gradual enrichment of the aegirine component as crystallization proceeds. Such compositional trends were commonly noted in the clinopyroxene crystallization sequences differentiated alkaline rock suits, as studied by Yagi (1953), Aoki (1964), Narsh and Wilkinson (1970), Jones and Peckett (1980), Platt and Woolley (1986) and others, and less commonly in a pyroxene crystal, as studied by Neuman (1976), Larsen (1976), Powell (1978), Ferguson (1978) and others.

Hybrid (or contaminated) rocks commonly occur at the localities of high-temperature skarn such as Crestmore, California (Burnham, 1959), Carneal, Northern Ireland (Sabine, 1975) Fuka, Okayama (Kusachi, 1976), Christmas Mountains, Texas (Joesten,

1977) and Tokatoka, New Zealand (Baker and Black, 1980).

The hybrid rocks from Kushiro are associated with gehlenite-superrite skarns and consist mainly of feldspars and clinopyroxenes (Numano, 1979). The feldspars of these hybrid rocks are extremely varied in the chemical compositions and the Al-Si ordering states; i.e., among those found to occur are included such feldspars as plagioclase, low albite, orthoclase, intermediate microcline and maximum microcline. Most of pyroxenes belong to the diopside-hedenbergite series. Some of the clinopyroxenes show an extensive compositional zoning from calcium-rich pyroxene at the core to aegirine at the rim.

In the present paper, the compositional variations and crystal chemistry of pyroxenes from the hybrid rock sampled at Hirata outcrop are described in detail and their genetic significance in relation to the development of gehlenite skarns is discussed. The clinopyroxenes from the hybrid rock are compared with those from various rocks studied previously by other conditions of the magma from which each of them precipitated.

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II. Samples and their occurrence

The gehlenite skarns from the Hirata outcrop have been reported by Henmi *et al.* (1971), Numano (1979) and others. The hybrid rocks from narrow zones (three meters width) between the intrusive igneous rocks and skarns, and occasionally from these main zones branch off into skarns with sharp boundaries. The hybrid rocks in general consist mainly of feldspars and pyroxenes and occasionally contain accessory amounts of amphibole, mica, quartz, calcite and others. The bulk compositions of various hybrid rocks from Kushiro have been given by Numano (1979) and some representative analyses are cited in the last four columns of Table 1. Depending

Table 1. Wet chemical analyses of the hybrid rocks from Hirata outcrop, Kushiro, Hiroshima Prefecture.

	H-1*	H-2*	HN-4**	HE-3**	HE-2**	HB-1**
SiO ₂	57.12	57.63	58.70	53.55	53.24	52.54
TiO ₂	0.52	0.56	0.55	1.07	0.90	0.46
Al ₂ O ₃	13.63	13.50	13.03	15.59	17.63	12.82
Fe ₂ O ₃	2.85	2.89	3.46	3.40	4.44	1.67
FeO	0.97	0.91	0.96	2.73	2.85	4.39
MnO	0.04	0.03	0.04	0.11	0.12	0.19
MgO	0.68	0.76	0.70	2.86	3.50	5.16
CaO	6.96	6.37	5.30	8.53	6.94	15.17
Na ₂ O	0.90	1.60	0.86	0.61	4.84	3.09
K ₂ O	11.86	12.35	13.13	9.40	3.90	1.73
P ₂ O ₅	0.04	0.04	0.04	0.03	0.05	0.07
CO ₂	0.74	0.66				
B ₂ O ₃	0.04	0.01		1.44	1.36	2.00
F	0.13	0.14				
H ₂ O(+)	2.56	2.24				
H ₂ O(-)	0.75	0.79	0.25	0.19	0.29	0.59
O=F	0.05	0.06				
Total	99.74	99.88	99.82	99.51	100.06	99.88
Q	0.13	0.00	1.96	0.00	0.00	0.00
or	70.06	70.34	71.12	55.53	23.04	10.22
ab	4.09	0.00	0.00	0.35	29.72	21.36
an	0.00	0.00	0.00	12.04	14.87	16.01
lc	0.00	2.05	0.00	0.00	0.00	0.00
ne	0.00	0.38	0.00	2.60	6.08	2.59
ac	3.10	7.29	6.40	0.00	0.00	0.00
ks	0.00	0.00	1.79	0.00	0.00	0.00
wo	10.00	8.29	8.84	3.75	0.00	4.15
di	1.96	2.63	2.02	8.80	8.03	20.39
en	1.69	1.89	1.75	7.12	6.76	12.85
fs	0.00	0.50	0.00	0.64	0.23	6.27
fo	0.00	0.00	0.00	0.00	1.37	0.00
ol	0.00	0.00	0.00	0.00	0.05	0.00
fa	1.75	0.54	1.64	4.93	6.44	2.42
mt	0.57	0.00	0.11	0.00	0.00	0.00
hm	0.99	1.06	1.05	2.03	1.71	0.87
il	0.09	0.09	0.10	0.07	0.12	0.17
ap	0.27	0.29	—	—	—	—
fr	1.68	1.50	—	—	—	—
cc	—	—	—	—	—	—

* present study.

** Numano (1979).

upon proportions of hybrid rocks vary widely in the CaO and K₂O contents but less widely in the SiO₂, FeO, MgO and Na₂O contents. Most of the hybrid rocks are nepheline-normative and few contain a small amount of normative quartz.

The hybrid rocks examined in the present study was sampled at the Hirata outcrop. It contains abundant K-feldspar and a relatively small amount of pyroxenes with euhedral titanite and slender apatite prisms as accessories. Apophyllite, rosenhahnite, datolite, pectolite, calcite and pyrrhotite fill interstices of the feldspar and pyroxene

primocrysts. The feldspar is maximum microcline with composition close to the orthoclase end-member. New analyses for two different parts of the hybrid rock are given in Table 1. Because of the high modal K-feldspar contents, they are extremely enriched in K₂O and are similar in composition to the sample HN-4 reported by Numano (1979). The new analyses resemble each other in composition but one of them is quartz-normative and the other contains small amounts of normative nepheline and leucite.

The pyroxenes can be classified into to the following three groups based on their microscopic and compositional characteristics; (1) diopside, (2) aegirine and (3) zoned pyroxene. The diopside (group 1) is colorless in thin section and occurs as somewhat rounded prisms with dimensions of 0.3 x 0.3 x 0.7 mm and are always completely enclosed in feldspar crystals. The aegirines (group 2) are light grass green or light brown and occur as needles and short prisms (ca. 0.5 mm long) in the interstices between euhedral feldspar crystals. The cores in the zoned pyroxenes (group 3) are compositionally homogeneous and have the same composition as the pyroxenes of group 1. The rims with thickness of up to 1.5 mm range from green aegirine-augite to green or light brown aegirine. It is indicated that the diopside enclosed in feldspars and the cores of the zoned pyroxenes crystallized first and then were followed by crystallization of the aegirine rims of the zoned crystals and discrete aegirines.

III. Chemistry of pyroxenes

Selected microprobe analyses of the pyroxenes from the hybrid rocks are presented in Table 2. The Fe₂O₃ and FeO contents were estimated from total iron contents and pyroxene stoichiometry (i.e., 4 cations and 6 oxygens per formula unit). The clinopyroxenes investigated are characterized by their low Mn and Al contents. The pyroxene analyses are plotted in the Ca - Mg - (Fe²⁺+Fe³⁺+Mn) triangular diagram (Fig. 1) and the Na - Mg - (Fe²⁺+Mn) diagram (Fig. 2). The compositional trend is from diopside through aegirine-augite to aegirine.

The pyroxenes in feldspar (group 1) are characterized by high Ca contents and are plotted closely to the diopside-hedenbergite join in Fig. 1. The discrete aegirines (group 2) have more than 0.845 atoms of Na per formula unit and sometimes contain up to 0.133 atoms of Ti per formula unit. The zoned pyroxenes (group 3) show a

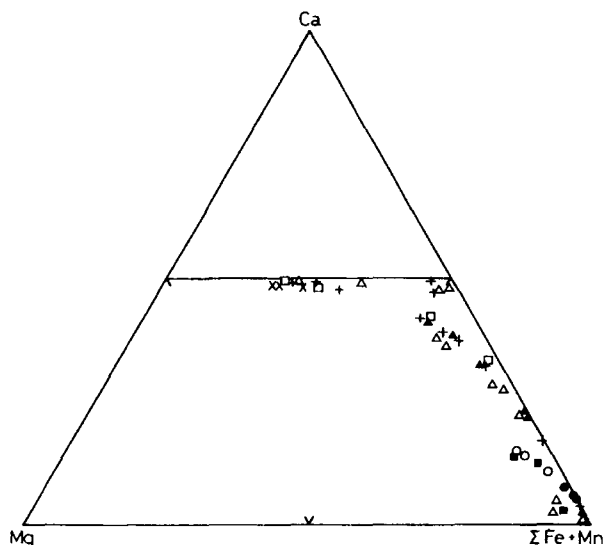


Fig. 1. Pyroxene analyses plotted on the triangular diagram Ca-Mg-(Fe²⁺+Fe³⁺+Mn) (atomic per cent). The analyses shown with the same symbol represent those obtained different points of one singly crystal.

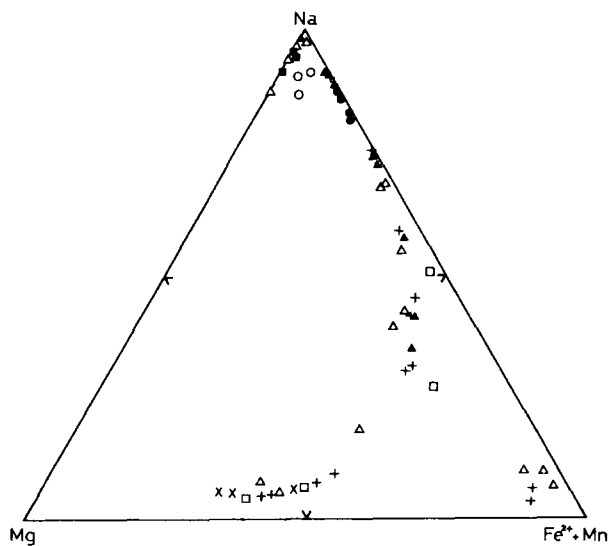


Fig. 2. Pyroxene analyses plotted of the triangular diagram Na-Mg-(Fe²⁺+Mn) (atomic per cent). The symbols are the same as those in Fig. 1.

continuous compositional variation and the trend is characterized by the ionic substitution of Fe²⁺ for Mg at the early stages of crystallization and then by the coupled substitution of Na + Fe³⁺ for Ca + Mg followed by that of Na + Fe³⁺ for Ca + Fe²⁺. The chemical variation in zoned pyroxene grains are shown in Fig. 3. It is reveals that zoned crystals have homogeneous core with diopside composition and their compositions change gradually to aegirine toward the rim. The analyses, listed in Table 2, show that the core of the zoned pyroxene and its aegirine rim are identical in composition with the group 1 diopsides and with group 2 aegirines, respectively. The

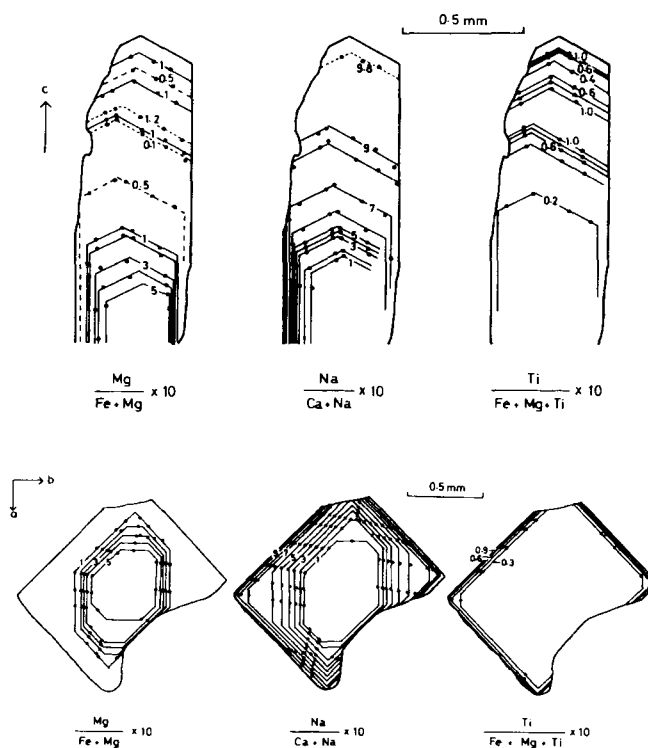


Fig. 3. Compositional variations in zoned pyroxene crystals (a) parallel to c-axis (b)parallel to a- and b-axes.

aegirine rim is sometimes enriched in titanium and is similar in composition to the group 2 titanian aegirines. Fig. 4 shows the variation between the Ti and Na contents in pyroxenes. The pyroxenes rich in titanium are always rich in sodium, but those rich in sodium are not always rich in titanium.

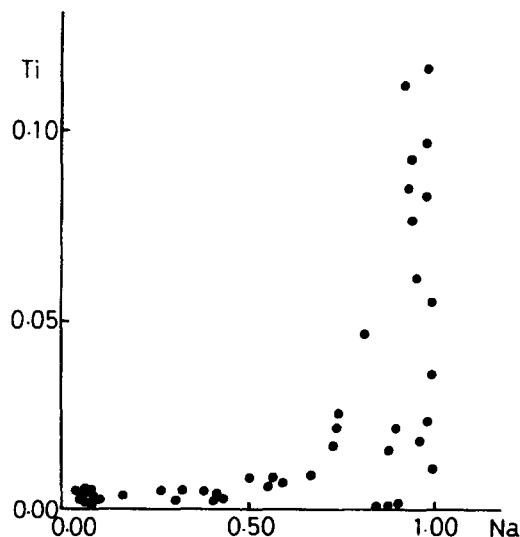


Fig. 4. Relation between Ti and Na (atoms per formula unit) in the Hirata pyroxenes.

Table 2. Selected microprobe analyses, number of ions and pyroxene components of the Hirata pyroxenes. The pyroxene components are NAT: $\text{Na}(\text{Mg}, \text{Fe}^{2+})_{0.5}\text{Ti}_{0.5}\text{Si}_2\text{O}_6$, Ae-Jd: $\text{Na}(\text{Fe}^{3+}, \text{Al})\text{Si}_2\text{O}_6$, Ca-Ti-Ts: $\text{CaTi}(\text{Al}, \text{Fe}^{3+})\text{SiO}_6$, Ca-Ts: $\text{Ca}(\text{Al}, \text{Fe}^{3+})_2\text{SiO}_6$, Di-Hd: $\text{Ca}(\text{Mg}, \text{Fe}^{2+})\text{Si}_2\text{O}_6$, Wo: $\text{Ca}_2\text{Si}_2\text{O}_6$ and Opx: $(\text{Mg}, \text{Fe}^{2+})_2\text{Si}_2\text{O}_6$.

	diopside		aegirine			titaniferous aegirine		
	525	263	522	213	211	225	356	635
SiO ₂	51.67	52.23	52.14	51.39	51.66	51.99	51.93	52.96
TiO ₂	0.11	0.17	0.52	0.01	0.01	2.21	4.08	4.72
Al ₂ O ₃	0.06	0.07	0.04	0.06	0.03	0.01	0.00	0.05
Fe ₂ O ₃ *	2.67	2.33	29.03	30.30	30.33	27.98	25.84	24.38
FeO*	11.54	10.13	0.32	0.78	0.58	4.00	3.79	0.86
MnO	0.30	0.34	0.69	0.51	0.87	0.14	0.11	0.17
MgO	9.50	10.70	1.53	1.38	1.05	0.04	0.02	2.63
CaO	23.58	23.27	3.60	4.11	3.85	1.59	0.75	1.00
Na ₂ O	0.62	0.70	11.74	11.31	11.53	12.48	13.14	13.06
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01
Total	100.28	99.94	99.61	99.85	99.91	100.45	99.66	100.01
Si	1.980	1.986	2.002	1.981	1.990	1.997	1.997	1.997
Al	0.003	0.003	0.002	0.003	0.001	0.000	0.000	0.002
Ti	0.003	0.005	0.015	0.000	0.000	0.063	0.118	0.133
Fe ³⁺	0.077	0.067	0.839	0.880	0.879	0.809	0.748	0.692
Fe ²⁺	0.370	0.322	0.010	0.025	0.019	0.129	0.122	0.026
Mn	0.010	0.011	0.022	0.017	0.029	0.005	0.004	0.006
Mg	0.543	0.607	0.087	0.080	0.060	0.002	0.001	0.147
Ca	0.968	0.948	0.148	0.170	0.159	0.065	0.031	0.040
Na	0.046	0.052	0.874	0.845	0.862	0.929	0.980	0.955
K	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001
NAT [Mg]	0.4	0.6	2.2	0.0	0.0	0.2	0.2	21.8
NAT [Fe]	0.2	0.4	0.8	0.0	0.0	12.4	23.4	4.8
Ae-Jd [Ae]	4.0	4.2	84.2	84.5	86.1	80.4	74.4	69.1
Ae-Jd [Jd]	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0
CaTi-Ts [Ca]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CaTi-Ts [FeAl]	0.3	0.3	0.0	0.3	0.1	0.0	0.0	0.2
Ca-Ts [Al]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ca-Ts [Fe]	1.6	1.2	0.0	1.5	0.7	0.2	0.2	0.0
Di-Hd [Di]	54.2	60.4	7.6	8.0	6.0	0.1	0.0	3.1
Di-Hd [Hd]	37.0	33.0	2.8	4.2	5.0	6.2	0.9	0.7
Wo	2.2	0.0	2.2	1.5	2.1	0.0	0.0	0.0
Opx [En]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2
Opx [Fs]	0.0	0.0	0.0	0.0	0.0	0.5	0.9	0.1

* The Fe₂O₃ and FeO contents were calculated from total iron and pyroxene stoichiometry of 4 cations and 6 oxygens.

	zoned crystal					
	diopside		aegirine-augite			aegirine
	316	314	321	322	324	333
SiO ₂	51.40	51.18	49.98	50.49	50.91	52.62
TiO ₂	0.18	0.15	0.15	0.28	0.32	1.90
Al ₂ O ₃	0.08	0.05	0.02	0.04	0.02	0.01
Fe ₂ O ₃ *	4.39	3.17	13.50	15.89	21.92	30.38
FeO*	10.11	11.76	12.56	14.63	9.31	0.22
MnO	0.35	0.44	0.36	0.32	0.19	0.07
MgO	9.50	9.01	2.45	0.45	0.41	1.02
CaO	23.04	23.28	15.54	11.48	8.13	0.58
Na ₂ O	1.02	0.69	4.89	6.52	8.72	13.32
K ₂ O	0.01	0.02	0.02	0.02	0.02	0.01
Total	100.08	99.75	99.46	100.12	99.95	100.13
Si	1.967	1.975	1.982	2.003	1.999	2.002
Al	0.004	0.002	0.001	0.002	0.001	0.000
Ti	0.005	0.004	0.005	0.009	0.009	0.055
Fe ³⁺	0.126	0.092	0.403	0.474	0.647	0.870
Fe ²⁺	0.324	0.379	0.416	0.485	0.306	0.007
Mn	0.011	0.014	0.012	0.011	0.007	0.002
Mg	0.542	0.518	0.145	0.027	0.024	0.058
Ca	0.945	0.963	0.660	0.488	0.342	0.023
Na	0.075	0.052	0.376	0.501	0.664	0.983
K	0.000	0.001	0.001	0.001	0.001	0.001
NAT [Mg]	0.6	0.4	0.3	0.1	0.1	9.5
NAT [Fe]	0.4	0.4	0.7	1.7	1.7	1.5
Ae-Jd [Ae]	6.5	4.5	36.7	47.6	64.7	87.2
Ae-Jd [Jd]	0.0	0.0	0.0	0.2	0.0	0.0
CaTi-Ts [Ca]	0.0	0.0	0.0	0.0	0.0	0.0
CaTi-Ts [FeAl]	0.4	0.2	0.1	0.0	0.0	0.0
Ca-Ts [Al]	0.0	0.0	0.0	0.0	0.0	0.0
Ca-Ts [Fe]	2.8	2.2	1.7	0.0	0.0	0.0
Di-Hd [Di]	53.9	51.6	14.4	2.7	2.3	1.0
Di-Hd [Hd]	33.3	39.1	42.4	46.3	30.5	0.2
Wo	2.1	1.6	3.7	0.0	0.7	0.6
Opx [En]	0.0	0.0	0.0	0.1	0.0	0.0
Opx [Fs]	0.0	0.0	0.0	1.2	0.0	0.0

IV. Discussion

Coupled substitutions of pyroxenes in the standard chemical formula $\text{M}2^{2+}\text{M}1^{2+}\text{Z}^{4+}_2\text{O}_6$ are given by Morimoto *et al.* (1988). As shown in Fig 5, some of pyroxenes from Hirata do not contain enough Si + Al to fill up the Z-positions of pyroxene structure. There may be substitution of 2Fe^{3+} in both M1- and Z-positions,

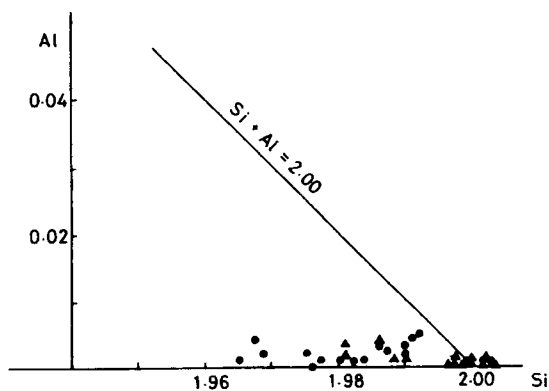


Fig. 5. Relation between Al and Si (atoms per formula unit) in the Hirata pyroxenes. Triangles indicate aegirines and circles indicate the other pyroxenes.

reading to the $\text{CaFe}^{3+}_2\text{SiO}_6$ component.

In most of the titanian aegirines, the Z-positions are essentially saturated with silicon. Consequently, it is dif-

ficult to consider that these titanian aegirines contain the undersaturated components such as NaTiAlSiO_6 , $\text{NaTiFe}^{3+}\text{SiO}_6$ and $\text{CaTiFe}^{3+}_2\text{O}_6$ which were described by Ronsbo *et al.* (1977) and Nielsen (1979). The amount of Na - ($\text{Fe}^{3+} + \text{Al}$) represents approximately the excess Na ions left after the formation of aegirine and jadeite com-

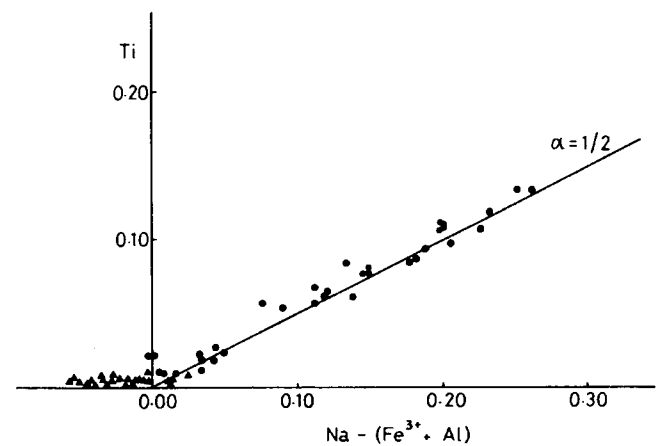


Fig. 6. Relation between Ti and Na - ($\text{Fe}^{3+} + \text{Al}$) (atoms per formula unit) in the Hirata pyroxenes. The latter represents approximately excess Na ions left after the formation of aegirine and jadeite components. The reference line is drawn with the slope of $1/2$. Circles indicate aegirines and triangles indicate the other pyroxenes.

ponents. Fig. 6 shows the relation between Ti and Na - ($\text{Fe}^{3+} + \text{Al}$) in the pyroxenes. The titanian aegirines are all

plotted on or close to the reference line with a slope of 1/2, suggesting that the excess sodium is combined with titanium in the proportion of 2:1. The component $\text{Na}(\text{Fe}^{2+}, \text{Mg})_{0.5}\text{Ti}_{0.5}\text{Si}_2\text{O}_6$ can be regarded as the only Ti-bearing pyroxene component in the pyroxenes studied here and is contained up to 27 mole percent. This titanian component is also the essential component in the titanian aegirines reported by Pederson *et al.* (1975), Larsen (1976), Ronsbo *et al.* (1977) and Nielsen (1979).

The pyroxenes of the hybrid rocks from Hirata exhibit a complete and successive variation in composition from Ca-rich pyroxene through aegirine-augite to aegirine. The compositional trend is observed within the single

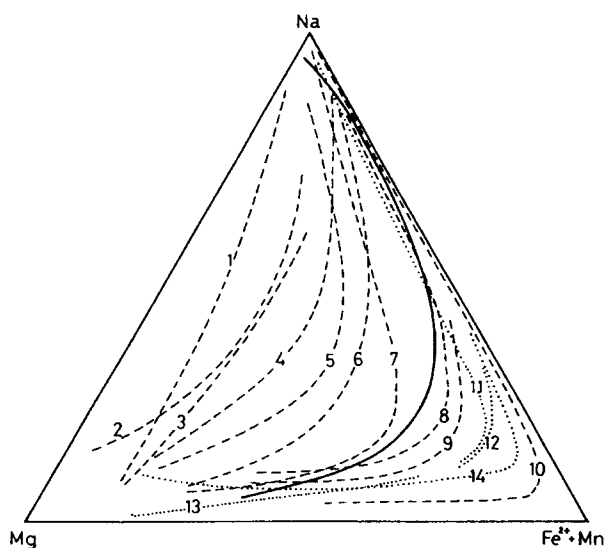


Fig. 7. A comparison of compositional trend for alkali pyroxenes in the Na-Mg-(Fe²⁺+Mn) diagram (atomic per cent). This figure is largely based on Larsen (1976) with additional data published subsequently. The solid lines indicates the trend of the Hirata pyroxenes (present work).

The broken lines indicate pyroxene trends from undersaturated rock suites as follows: (1) Bardiner, East Greenland (Nielsen, 1979); (2) Auvergne, France (Varet, 1969); (3) Oslo (Neuman, 1976); (4) Itapirapua, Brazil (Gomes *et al.*, 1970); (5) Uganda (Tyler and King, 1967); (6) Norotu, Sakhaline (Yagi, 1966); (7) South Quraq Centre, South Greenland (Stephenson, 1972); (8) Motzfeldt, South Greenland (Jones and Peckett, 1980); (9) Igdlerfigssalik, Greenland (Powell, 1978); and (10) Ilimaussaq, South Greenland (Larsen, 1976).

The dotted lines indicate those from oversaturated rock suites as follows: (11) Gough Island (Ferguson, 1978); (12) Pantellerite trend (Nicholls and Carmichael, 1969); (13) Japanese alkali basalts (Aoki, 1964).

rock specimen as well as within a single crystal and is shown in the Na-Mg-(Fe²⁺+Mn) diagrams (Figs. 7 and 8) with published alkali pyroxene trends in various rock suites and in single crystals. These figures indicate that the trend of the Hirata pyroxenes follows the typical trends of clinopyroxenes from alkaline rock suites and that the compositional zoning in single crystals of the

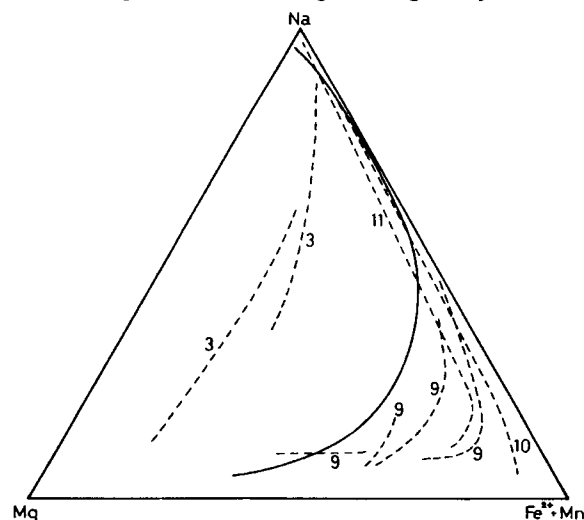


Fig. 8. A comparison of alkali pyroxene trends observed within a single zoned crystal in the Na-Mg-(Fe²⁺+Mn) diagram (atomic per cent). The solid line indicates the Hirata pyroxene (present work). The broken lines are shown for comparison; the numbers to indicate their data sources are the same as in Fig. 7.

Hirata pyroxenes is the most extensive compared to those reported previously.

The peralkaline nature of residual liquid developed at the late stage of crystallization is particularly interesting, because there is no other alkaline rocks and no alkali-containing skarn minerals in this area. It is likely that the hybrid rock is not a simple product of the assimilation or contamination of magma with limestone. During the metasomatism, alkali ions were not transferred to the skarn and remained in the magma.

V. Conclusion

The pyroxene crystallization sequence of the hybrid rocks from Hirata is characterized by diopside at its early stage and aegirine at its late stage. The diopsides occur as isolated crystals enclosed in feldspars and the aegirines as small prismatic or acicular crystals in pore spaces. Some diopside crystals grown in pore spaces are rimmed by Na-rich pyroxenes changing in composition from aegirine-augite to aegirine.

The Hirata hybrid rocks were apparently derived from the magma whose chemical composition was modified due to the metasomatic reaction with the limestone. This reaction led to the formation of skarns and a removal of Si, Al, Fe and Mg ions from the parent magma. The hybrid rocks vary in composition and most of them are nepheline-normative, but a few contain small amount of normative quartz. The hybrid rock studied in the present paper is extensively differentiated and contains aegirine crystallized from residual magma. We can recognize clinopyroxenes formed throughout all stages of crystallization within a single hand specimen. The chemical compositions of each part of the zoned pyroxenes reflect those of each stage of the evolution of magma. In the triangular diagrams, Na-Mg-(Fe²⁺+Mn) (Figs. 7 and 8), the compositional trend of clinopyroxenes from Hirata hybrid rock is similar to those from peralkaline rocks and shows an intermediate degree of hedenbergite enrichment between most of the undersaturated trends and the oversaturated ones. The relative position of the Hirata trend with respect to those of other suites in this triangular diagram is presumed to be related to the approximately saturated compositions of the hybrid rock.

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References

- Aoki, K. (1964) Clinopyroxenes from alkaline rocks of Japan. *Amer. Miner.*, **49**, 1199-1233.
- Baker, C. K. and Black, P. M. (1980) Assimilation and metamorphism at a basalt-limestone contact, Tokatoka, New Zealand. *Miner. Mag.*, **43**, 797-807.
- Burnham, C. W. (1959) Contact metamorphism of magnesian limestones at Crstmore, California. *Geol. Soc. Amer. Bull.*, **70**, 879-920.
- Ferguson, A. K. (1978) The crystallization of pyroxenes and amphiboles in some alkaline rocks and the presence of pyroxene composition gap. *Contrib. Miner. Petrol.*, **67**, 11-15.
- Gomes, C. de B., Moro, S. L. and Dutra, C. V. (1970) Pyroxenes from the alkaline rocks of Itapirapur, Sao Paulo, Brazil. *Amer. Miner.*, **55**, 224-230.
- Henmi, K., Kusachi, I. and Numano, T. (1971) Contact minerals from Kushiro, Hiroshima Prefecture (1) gehlenite and hydrogrossular. *Journ. Miner. Soc. Japan*, **10**, 160-169.
- Joesten, R. (1977) Mineralogical and chemical evolution of contaminated igneous rocks at a gabbro-limestone contact, Christmas Mountains, Big Bend region, Texas. *Geol. Soc. Amer. Bull.*, **88**, 1515-1529.
- Jones, A. and Peckett, A. (1980) Zirconium-bearing aegirines from Motzfeldt, South Greenland. *Contr. Miner. Petrol.*, **75**, 251-255.
- Kusachi, I. (1976) Occurrence and genesis of skarns at the Fuka north outcrop, the Town of Bitchu, Okayama Prefecture. *Bull. School of Educ. Okayama Univ.*, **43**, 71-105.
- Larsen, L. M. (1976) Clinopyroxenes and coexisting mafic minerals from the alkaline Ilimaussaq intrusion, South Greenland. *Journ. Petrol.*, **17**, 258-290.
- Morimoto, N. (1988) Nomenclature of pyroxenes. *Min. Mag.*, **52**, 535-550.
- Narsh, W. P. and Wilkinson, J. F. G. (1970) Shinkin Sag Laccolith, Montana. 1. Mafic minerals and estimates of temperature, pressure, oxygen fugacity and silica activity. *Contr. Miner. Petrol.*, **25**, 241-269.
- Neuman, E. R. (1976) Compositional relations among pyroxenes, amphiboles and other mafic phases in the Oslo Region plutonic rocks. *Lithos*, **9**, 85-105.
- Nicholls, J. and Carmichael, K. S. E. (1969) Peralkaline acid liquids: A petrological study. *Contr. Miner. Petrol.*, **20**, 268-294.
- Nielsen, E. R. (1979) The occurrence and formation of Ti-aegirines in peralkaline syenites. *Contr. Miner. Petrol.*, **69**, 235-244.
- Numano, T. (1979) Geological and Geochemical studies on gehlenite-spurrite skarns at Kushiro, the Town of Tojo, Hiroshima Prefecture. 2. Occurrence of gehlenite skarns at the Hirata outcrop. *Bull. School of Educ. Okayama Univ.*, **50**, 257-282.
- Pederson, A. K., Engel, J. and Ronsbo, J. P. (1975) Early Tertiary volcanism in the Skagerrak: new chemical evidence from ash-layers in the mo-clay of northern Denmark. *Lithos*, **8**, 255-268.
- Platt, R. G. and Woolley, A. R. (1986) The mafic mineralogy of the peralkaline syenites and granites of the Mulanje complex, Malawi. *Min. Mag.*, **50**, 85-99.
- Powell, M. (1978) The crystallization history of the Igdlertfigssalik nepheline syenite intrusion, Greenland. *Lithos*, **11**, 99-120.
- Ronsbo, J. G., Pederson, A. K. and Engell, (1977) Titanian-aegirine from early Tertiary ash layers in northern Denmark. *Lithos*, **10**, 193-204.
- Sabine, P. A. (1975) Metamorphic processes at high temperature and low pressure: the petrogenesis of the metasomatized and assimilated rocks of Carneal, Co. Antrim. *Roy. Soc. London, Philos. Trans. A*, **280**, 225-269.
- Stephenson, D. (1972) Alkali clinopyroxenes from nepheline syenites of the South Quraq Center, South Greenland. *Lithos*, **5**, 187-201.
- Tyler, R. C. and King, B. C. (1967) The pyroxenes of the alkaline igneous complexes of eastern Uganda. *Min. Mag.*, **36**, 5-21.

- Veret, J. (1969) Les pyroxenes des phonolites du Cantal (Auvergne, France). *Neues Jahrb. Miner. Monatsh.*, **4**, 174-184.
- Yagi, K. (1953) Petrochemical studies of the alkalic rocks of the Norotou District, Sakhalin. *Bull. Geol. Soc. Amer.*, **64**, 769-810.
- Yagi, K. (1966) The system acmite-diopside and its bearing on the stability relations of natural pyroxenes of the acmite-hedenbergite series. *Amer. Miner.*, **51**, 976-1000.