Chemical features of orthopyroxene in peraluminous igneous rocks

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ABSTRACT

Chemical compositions of orthopyroxene from peraluminous igneous rocks (PAl orthopyroxene) are compared with those from metaluminous igneous rocks (MAl orthopyroxene). Most of the PAl and MAl orthopyroxene coexists with garnet or Ca-rich clinopyroxene, respectively. PAl orthopyroxene samples are richer in Al_2O_3 and poorer in CaO than MAl orthopyroxene samples, and these two types of orthopyroxene are clearly separated in an Al-Ca plot. PAl orthopyroxene has Al > 2Ca and MAl orthopyroxene Al < 2Ca; that is, PAl orthopyroxene is corundum normative and MAl orthopyroxene is diopside normative. These compositional differences are understood by the position of orthopyroxene in the ACF diagram, where orthopyroxene is the only ferromagnesian mineral straddling the boundary between the corundum- and diopside-normative fields. Compositional differences between PAl and MAl orthopyroxene samples reflect the magmas from which they crystallized.

INTRODUCTION

Igneous rocks are classified into peraluminous, metaluminous, and peralkaline on the basis of the alumina saturation principle of Shand (1927). Peraluminous igneous rocks, such as those classified as S-type granitoids (Chappell and White, 1974; White and Chappell, 1977), characteristically contain biotite, muscovite, cordierite, garnet, or Al_2SiO_5 minerals (Fig. 1). These minerals have aroused great interest, and their compositional features have been discussed extensively (e.g., Clarke, 1981). Although orthopyroxene is also reported from some peraluminous rocks, published analyses are very limited in number, and compositional features of the orthopyroxene in peraluminous rocks have not been fully understood. Igneous orthopyroxene is also reported from metaluminous rocks.

In this paper, we discuss the chemical features of orthopyroxene found in peraluminous rocks, comparing them with those of orthopyroxene from metaluminous igneous rocks. Although the boundary between peraluminous and metaluminous is located at A/CNK [mole ratio of $Al_2O_3/(CaO + Na_2O + K_2O)$] = 1.0, our usages of "peraluminous" and "metaluminous" in this paper approximate those of S-type and I-type by Chappell and White (1974). Hereafter, we refer to orthopyroxene from peraluminous and metaluminous igneous rocks as PAl orthopyroxene and MAl orthopyroxene, respectively.

DATA SET

Sources of PAl and MAl orthopyroxene analyses examined in this paper are listed in Table 1. Localities of the PAl orthopyroxene samples are rather limited, and 90% of the data are taken from three suites: the Ohmine (Omine), Niikappu, and Nozukadake suites of Japan. Because these three suites are typically peraluminous and classified as S-type igneous rocks, we believe that the data are adequate to serve as the basis of discussion of the chemical features of PAl orthopyroxene.

Most of the PAl orthopyroxene samples studied occur in the granites, tonalites, dacites, rhyodacites, and rhyolites and are accompanied by garnet + biotite or garnet + biotite + cordierite. The Nozukadake orthopyroxene is present in a quartz-bearing norite and is associated

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with Fe-rich olivine + garnet + biotite (Maeda et al., 1985). Maeda et al. (1985) suggested that the Nozukadake norite may be a cumulate from peraluminous rhyodacitic magma.

MAl orthopyroxene samples examined occur in ferro-gabbros, diorites, granites, andesites, dacites, rhyodacites, and rhyolites and are, in general, accompanied by Ca-rich clinopyroxene, biotite, or hornblende. Olivine and pigeonite are also present in some suites (Table 1).

Representative analyses of PAl and MAl orthopyroxene are given in Table 2. We accepted the analyses of both types of orthopyroxene if (1) the sum of oxides in the analysis is ≥ 99.00 and $< 101.00\%$; (2) Si is ≤ 2.000 in the structural formula based on six O atoms; (3) X_{Fe} [$= Fe_{tot}/(Mg + Fe_{tot})$] is ≥ 0.340. Restriction 3 is necessary because all PAl orthopyroxene samples examined have $X_{Fe} \geq 0.340$. We do not use data from the literature for xenocrystic, quenched, or altered orthopyroxene. In the Horobetsu, Ishizuchisan, Niikappu, Nozukadake, Pankenushi, Satsunaigawa, Tottabetsu, and Ohmine suites, Japan, the textures of the orthopyroxene considered indicate a magmatic origin, and xenocrysts or restites are not included. Orthopyroxene from plutonic rocks may have undergone reequilibration during cooling. However, we cannot find any systematic differences in composition between orthopyroxene from plutonic and volcanic rocks, so the distinction is considered insignificant for the purpose of this paper.

COMPOSITIONAL FEATURES OF PAl AND MAl ORTHOPYROXENE

PAl orthopyroxene samples examined range in X_{Fe} from 0.806 to 0.340 (Fig. 2). In X_{Fe}-Al_2O_3 and X_{Fe}-CaO diagrams, notable differences are found between PAl and MAl orthopyroxene samples (Figs. 2 and 3). No significant difference exists between them in X_{Fe}-SiO_2, X_{Fe}-TiO_2, X_{Fe}-FeO (FeO = Fe_{tot}), X_{Fe}-MnO, X_{Fe}-MgO, and X_{Fe}-Na_2O diagrams (not shown). Although we compared Al and Ca contents of PAl orthopyroxene in various mineral assemblages, e.g., with biotite, biotite + garnet, and biotite + garnet + cordierite, we find no systematic differences among them (not shown).

PAl orthopyroxene ranges in Al_2O_3 content from 1.0 wt% up to 4.3%, whereas the Al_2O_3 content of MAl orthopyroxene is lower than 2.0%, mostly less than 1.0% (Fig. 2). PAl orthopyroxene is poorer in CaO than MAl orthopyroxene (Fig. 3). CaO contents of PAl orthopyroxene are mostly lower than 0.5%. MAl orthopyroxene shows a scattered distribution in the X_{Fe}-CaO plot, with CaO contents higher than 0.5%. The Al-rich and Ca-poor nature of PAl orthopyroxene is also observed in orthopyroxene from aluminous pelitic granulites (e.g., Grant, 1981). This suggests the presence of similar equilibrium relations in both kinds of rocks.

About 70% of the PAl orthopyroxene samples have $^{[6]}Al > ^{[4]}Al$ (Fig. 4). In the PAl orthopyroxene samples, Na content is negligible (Table 3), and the jadeite substitution is essentially absent. Therefore, the data showing
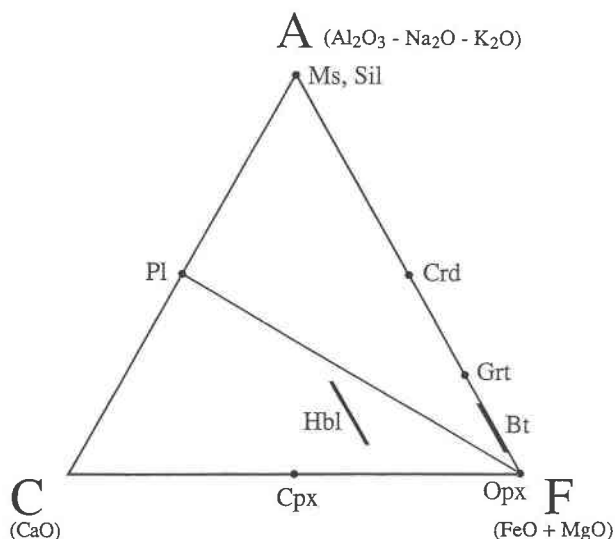

Fig. 1. ACF [$(Al_2O_3-Na_2O-K_2O)$-CaO-(FeO + MgO) in mole ratio] diagram. Representative minerals are plotted. Abbreviations are as follows: Bt, biotite; Cpx, Ca-rich clinopyroxene; Crd, cordierite; Grt, garnet; Hbl, hornblende; Ms, muscovite; Opx, orthopyroxene; Pl, plagioclase; and Sil, sillimanite.

$^{[6]}Al > ^{[4]}Al$ are not easily explained. If the presence of substantial amounts of Fe^{3+} is assumed, the values of Si and of other cations in the formula are decreased. Thus, incorporation of Fe^{3+} may make $^{[6]}Al$ less than $^{[4]}Al$. However, peraluminous (or S-type) magmas are, in general, rather reduced (e.g., Clemens and Wall, 1988). For example, Phillips et al. (1981) calculated the f_{O_2} of the Strathbogie granite to be approximately an order of magnitude below that of QFM. Therefore, participation of Fe^{3+} is assumed to be unlikely.

The apparent site occupancy of Al is critically dependent on the accuracy of the analysis, especially that of Si. When we select superior analyses with $3.985 \leq$ total cations ≤ 4.004 (43% of the examined PAl orthopyroxene), $^{[6]}Al/^{[4]}Al$ is nearly unity (Fig. 4). Therefore, Al substitution in PAl orthopyroxene is explained in terms of Tschermak components. Although not all analyses of PAl orthopyroxene that we have used satisfy the total cations criterion for accuracy, we think this does not have a serious influence on the discussion of the chemical features of PAl orthopyroxene.

DISCUSSION

Al and Ca contents of orthopyroxene

Contents of Al and Ca of orthopyroxene are controlled by the composition of magma, pressure, and temperature during crystallization (e.g., Deer et al., 1978). Because most PAl and MAl orthopyroxene examined coexists with garnet or Ca-rich clinopyroxene, respectively (Table 1), orthopyroxene-garnet and orthopyroxene-Ca-rich clinopyroxene phase relations are useful for interpretation. Many experimental and theoretical studies of these relations indicate that the Ca content of orthopyroxene co-

TABLE 1. Data list of orthopyroxene samples examined in this paper

Locality	Rock type*	Paragenesis**	n	Reference
		PAI orthopyroxene		
Canterbury	Rd	Grt	1	Wood (1974)
Goobarragandra	Dc	Bt + Crd	1	Wyborn et al. (1981)
Hawkins	Dc	Bt + Grt + Crd	1	Wyborn et al. (1981)
Horobetsu	Gr	Bt + Grt ± Crd	17	Bamba (1985)
Lake Mountain†	Rd	Bt + Crd ± Sil	1	Birch et al. (1977)
Niikappu	Gr	Bt ± Grt ± Crd	60	Shimura (unpublished data)
Nozukadake	Gb	Bt + Grt + Ol	20	Maeda et al. (1985, unpublished data)
Ohmine (Omine)	Gr	Bt ± Grt + Crd	99	Kawasaki (1980), Murata (1982b)
Osuzuyama	Rd	Bt + Crd (Xc: Grt + Sil)	2	Nakada (1983)
Taima	Gr	Bt ± Grt ± Crd	1	Fang et al. (1985)
Violet Town	Rd-Gr	Bt + Grt + Crd	4	Clemens and Wall (1984)
		(Sum	207)	
		MAI orthopyroxene		
Bandelier	Rd	Cpx ± Ol	2	Warshaw and Smith (1988)
Bear Mountain	Di-Md	Cpx + Bt ± Hbl	2	Snoke et al. (1981)
Bishop	Rd	Cpx	1	Hildreth (1979)
Bushveld	Gb	Cpx ± Pgt	7	Gruenewaldt and Weber-Diefenbach (1977), Buchanan (1979)
Clear Lake	Ad	Ol + Cpx	5	Stimac et al. (1990)
Fongen-Hyllingen	Gb	Ol + Cpx ± Hbl	6	Wilson et al. (1981)
Hikimi	Dc	Cpx + Hbl + Bt	7	Imaoka and Murakami (1979)
Ibaragi	Qd	Cpx + Hbl + Bt	1	Tainosho (1984)
Iritono	Gb	Ol + Cpx	1	Ikeda (1976)
Ishizuchisan	Ad	Cpx + Bt	2	Murata (unpublished data)
Kimpokusan	Dc	Cpx + Hbl	1	Shimazu and Toyama (1982)
Koyama	Gb	Cpx + Pgt	3	Yamaguchi et al. (1974)
La Perouse	Gb	Cpx ± Pgt ± Hbl	6	Loney and Himmelberg (1983)
Makido	Gb	Cpx + Bt ± Hbl	4	Kamiya and Harayama (1982)
Motegi	Dc	Ol + Cpx + Pgt	2	Shiramizu et al. (1983)
Mount Mazama	Rd	Cpx + Hbl	1	Druitt and Bacon (1989)
Niikappu	Gr	Hbl + Bt ± Cpx	24	Shimura (unpublished data)
Novarupta	Ad-Rd	Cpx	9	Hildreth (1983)
Ohmine (Omine)	Gr	Ol + Cpx + Hbl + Bt	3	Kawasaki (1980)
Pankenushi	Gb	Ol + Cpx + Hbl ± Bt	19	Maeda (1981)
Rancho Virulento	Rd	Cpx + Bt	1	Moll (1981)
Satsunaigawa	Di	Cpx + Hbl + Bt	3	Suetake (1986)
Shikotsu	Dc	Cpx ± Hbl	5	Kasugai et al. (1980)
Tarumai	Ad-Dc	Cpx ± Ol	5	Soya and Satoh (1980)
Thessaloniki	Gb	Ol + Cpx	1	Sapountzis (1979)
Tigalak	Di	Cpx + Bt	2	Wiebe and Wild (1983)
Tonomura	Rd	Cpx + Bt ± Hbl	4	Kasahara and Harayama (1981)
Tottabetsu	Gb	Cpx + Hbl + Bt ± Ol	27	Suetake (1986)
Tsugawa	Rd	Cpx	2	Shimazu and Takano (1977), Yoshimura et al. (1984)
Tsuwazaki	Dc	Cpx + Bt	2	Kawahara et al. (1984)
Twin Peaks	Rd	Cpx ± Hbl ± Bt	3	Crecraft et al. (1981)
Ugetsuzawa	Rd		1	Ikeda and Mukoyama (1983)
Whangarei	Di	Cpx + Pgt	3	Brothers and Yokoyama (1990)
Weiselberg	Ad	Cpx + Pgt	5	Nakamura and Kushiro (1970)
Wooley Creek	Gb-Gr	Cpx ± Hbl ± Bt	4	Barnes (1983, 1987)
		(Sum	174)	

Note: The complete data set may be obtained on request to J.M.
* This does not indicate the compositions coexisting with pyroxene but types of pyroxene-bearing rocks. Abbreviations: Ad, andesite; Dc, dacite; Di, diorite; Gb, gabbro; Gr, granite; Md, monzodiorite; Qd, quartz diorite; and Rd, rhyodacite and rhyolite.
** Abbreviations: Bt, biotite; Cpx, Ca-rich clinopyroxene; Crd, cordierite; Grt, garnet; Hbl, hornblende; Ol, olivine; Pgt, pigeonite; Sil, sillimanite; and Xc, xenocryst. Quartz, plagioclase, potassium feldspar, and accessory minerals are not shown.
† Partial analysis.

existing with Ca-rich clinopyroxene increases with increasing temperature and X_{Fe} of orthopyroxene but decreases with increasing pressure (Deer et al., 1978; Huebner, 1980; Lindsley, 1980, 1983). Compared with the effect of temperature, those of pressure and X_{Fe} of orthopyroxene are not significant (Lindsley, 1983). On the other hand, the Al content of orthopyroxene coexisting with garnet increases with temperature and decreases with pressure and X_{Fe} of orthopyroxene (Wood and Banno, 1973; Harley and Green, 1982; Harley, 1984; Lee and Ganguly, 1988). Pressure conditions during crystalliza-

tion of the suites examined are shown in Table 3, as far as given in the literature. Taking the pressure determinations in the literature, it is evident that most of the orthopyroxene-bearing igneous rocks have crystallized at 5 ± 2 kbar, although the overall pressure range is from less than 1 kbar to more than 10 kbar. Considering that pressure has a smaller effect on Al and Ca contents of orthopyroxene than does temperature in this pressure range (Deer et al., 1978), we assume here that all orthopyroxene samples in our compilation formed at essentially the same pressure.

TABLE 2. Representative analyses of orthopyroxene samples

PAI orthopyroxene

Loc.*	HRBT 106/2	NKP 1564	NKP 333	NKP 1045	NZK NZSTD	NZK NZ1/9	NZK NZ151	OMN MRT72	OMN MRT33	OMN MRT89
SiO₂	49.99	52.57	52.16	48.96	48.91	47.64	47.73	51.87	50.41	49.55
TiO₂	0.09	0.21	0.21	0.15	0.16	0.21	0.00	0.21	0.22	0.20
Al₂O₃	3.33	2.97	2.69	3.15	2.15	1.61	1.17	1.56	1.52	2.59
Cr₂O₃	0.00	0.09	0.06	0.04	0.01	0.00	0.00	0.19	0.00	0.00
FeO**	29.11	21.04	23.98	31.46	34.25	41.18	44.03	27.72	31.44	34.83
MnO	0.64	0.46	0.88	0.40	0.89	0.65	0.73	0.68	0.90	1.11
MgO	16.31	22.89	20.36	14.92	12.69	7.67	5.95	18.13	15.23	12.35
CaO	0.15	0.21	0.15	0.12	0.40	0.63	0.28	0.19	0.23	0.19
Na₂O	0.10	0.00	0.00	0.06	0.00	0.20	0.00	0.00	0.00	0.00
K₂O	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.72	100.44	100.49	99.28	99.45	99.79	99.89	100.55	99.95	100.82
					Formula based on six O atoms					
Si	1.929	1.933	1.947	1.922	1.949	1.961	1.987	1.970	1.966	1.948
[4]Al	0.071	0.067	0.053	0.078	0.051	0.039	0.013	0.030	0.034	0.052
[6]Al	0.081	0.062	0.065	0.068	0.049	0.040	0.044	0.039	0.036	0.068
Cr	0.000	0.003	0.002	0.001	0.000	0.000	0.000	0.006	0.000	0.000
Ti	0.003	0.006	0.006	0.004	0.005	0.007	0.000	0.006	0.006	0.006
Fe	0.940	0.647	0.748	1.033	1.141	1.418	1.533	0.880	1.025	1.145
Mn	0.021	0.014	0.028	0.013	0.030	0.023	0.026	0.022	0.030	0.037
Mg	0.938	1.256	1.133	0.873	0.753	0.471	0.369	1.027	0.885	0.723
Ca	0.006	0.008	0.006	0.005	0.017	0.028	0.012	0.008	0.010	0.008
Na	0.007	0.000	0.000	0.005	0.000	0.016	0.000	0.000	0.000	0.000
K	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000
Total	3.996	3.996	3.988	4.003	3.996	4.001	3.984	3.988	3.992	3.987
X_{Fe}†	0.500	0.340	0.398	0.542	0.602	0.751	0.806	0.461	0.537	0.613
Wo‡	0.3	0.4	0.3	0.3	0.9	1.5	0.7	0.4	0.5	0.4
En‡	49.8	65.7	60.0	45.7	39.4	24.6	19.3	53.6	46.1	38.6
Fs‡	49.9	33.9	39.7	54.0	59.7	74.0	80.1	46.0	53.4	61.0

MAI orthopyroxene

Loc.*	NKP 931	PNK M/25	PNK M/29	PNK M/42	STNG S/43	TTBT S/21	TTBT S/28	TTBT S/36	TTBT S/18	TTBT S/20
SiO₂	52.02	53.26	51.46	50.65	53.43	52.84	52.42	51.09	49.85	47.96
TiO₂	0.11	0.08	0.08	0.13	0.10	0.30	0.16	0.41	0.15	0.15
Al₂O₃	0.77	0.77	0.59	0.37	0.50	0.81	0.43	0.41	0.46	0.30
Cr₂O₃	0.00	0.03	0.06	0.00	0.04	0.06	0.06	0.05	0.07	0.00
FeO**	28.50	22.21	28.18	33.50	24.72	21.45	27.89	31.63	35.73	43.53
MnO	0.56	0.49	0.65	0.63	0.65	0.48	0.74	0.78	1.06	0.98
MgO	18.00	22.34	18.16	13.63	20.67	22.26	17.88	14.95	12.24	6.42
CaO	0.88	0.95	0.94	1.27	0.61	0.95	1.10	1.06	0.92	1.01
Na₂O	0.00	0.01	0.00	0.04	0.05	0.01	0.04	0.04	0.00	0.06
K₂O	0.00	0.01	0.03	0.00	0.05	0.06	0.04	0.04	0.00	0.03
Total	100.84	100.15	100.15	100.22	100.82	99.22	100.76	100.46	100.48	100.44
					Formula based on six O atoms					
Si	1.980	1.980	1.975	1.994	1.995	1.979	1.994	1.988	1.983	1.990
[4]Al	0.020	0.020	0.025	0.006	0.005	0.021	0.006	0.012	0.017	0.010
[6]Al	0.014	0.014	0.001	0.011	0.017	0.015	0.013	0.007	0.005	0.004
Cr	0.000	0.001	0.002	0.000	0.001	0.002	0.002	0.002	0.002	0.000
Ti	0.003	0.002	0.002	0.004	0.003	0.008	0.005	0.012	0.004	0.005
Fe	0.907	0.691	0.904	1.103	0.772	0.672	0.887	1.029	1.189	1.510
Mn	0.018	0.015	0.021	0.021	0.021	0.015	0.024	0.026	0.036	0.034
Mg	1.021	1.238	1.039	0.800	1.150	1.243	1.014	0.867	0.726	0.397
Ca	0.036	0.038	0.039	0.054	0.024	0.038	0.045	0.044	0.039	0.045
Na	0.000	0.001	0.000	0.003	0.004	0.001	0.003	0.003	0.000	0.005
K	0.000	0.000	0.001	0.000	0.002	0.003	0.002	0.002	0.000	0.002
Total	4.000	4.001	4.010	3.995	3.994	3.996	3.994	3.992	4.001	4.002
X_{Fe}†	0.470	0.358	0.465	0.580	0.402	0.351	0.467	0.543	0.621	0.792
Wo‡	1.8	1.9	1.9	2.7	1.3	2.0	2.3	2.3	2.0	2.3
En‡	52.0	63.0	52.4	40.9	59.1	63.6	52.1	44.7	37.2	20.3
Fs‡	46.2	35.1	45.6	56.4	39.6	34.4	45.6	53.0	60.8	77.4

* Abbreviations: HRBT, Horobetsu; NKP, Niikappu; NZK, Nozukadake; OMN, Ohmine; PNK, Pankenushi; STNG, Satsunaigawa; and TTBT, Tottabetsu.

** Fe_tot as FeO.

† Fe/(Mg + Fe).

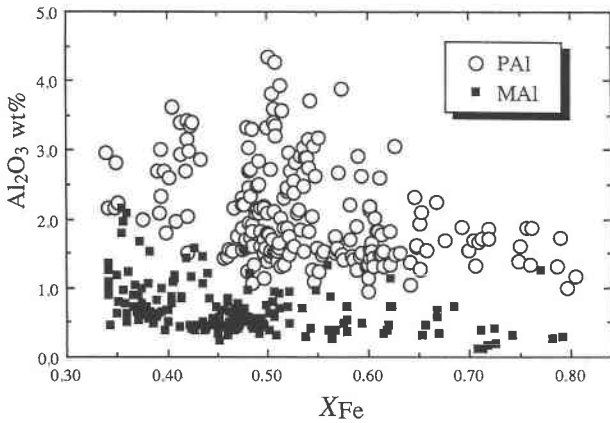‡ Wo = Ca/(Ca + Mg + Fe) × 100; En = Mg/(Ca + Mg + Fe) × 100; Fs = Fe/(Ca + Mg + Fe) × 100.

Fig. 2. PAl and MAl orthopyroxene plotted on X_{Fe}-Al_2O_3 (wt%). Data sources are given in Table 1.

Representative Al and Ca contents of PAl and MAl orthopyroxene samples examined are plotted against temperature in Figure 5. Equilibrium temperatures were estimated by the orthopyroxene-Ca-rich clinopyroxene geothermometer of Wood and Banno (1973) for the MAl orthopyroxene and by the orthopyroxene-garnet geothermometer of Lee and Ganguly (1988) for PAl orthopyroxene. The Al contents of orthopyroxene coexisting with garnet and Ca contents of orthopyroxene coexisting with Ca-rich clinopyroxene increase with temperature. Figure 5 also indicates that differences in Al and Ca contents between the two types of orthopyroxene, which crystallized in the same temperature range, should be attributed to differences in magma compositions.

The relationship between Ca and Al contents of PAl and MAl orthopyroxene is shown in Figure 6. PAl orthopyroxene samples plot at Al > 2Ca and MAl orthopyroxene samples at Al < 2Ca. Because the orthopyroxene samples examined contain negligible amounts of Na and K, this relationship indicates that PAl orthopyroxene is corundum normative and MAl orthopyroxene is diopside normative. As stated above, most PAl and MAl ortho-
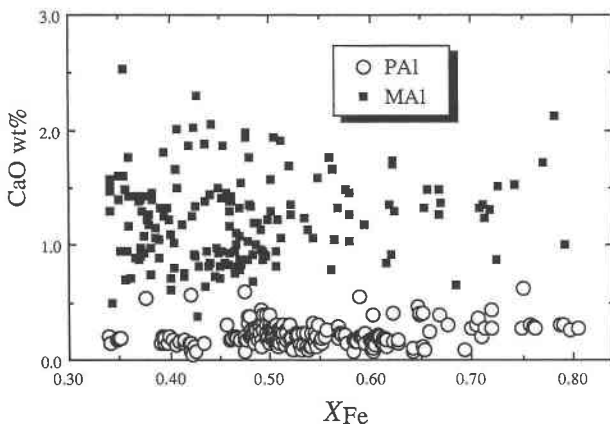
Fig. 3. PAl and MAl orthopyroxene plotted on X_{Fe}-CaO (wt%). Data sources in Table 1.
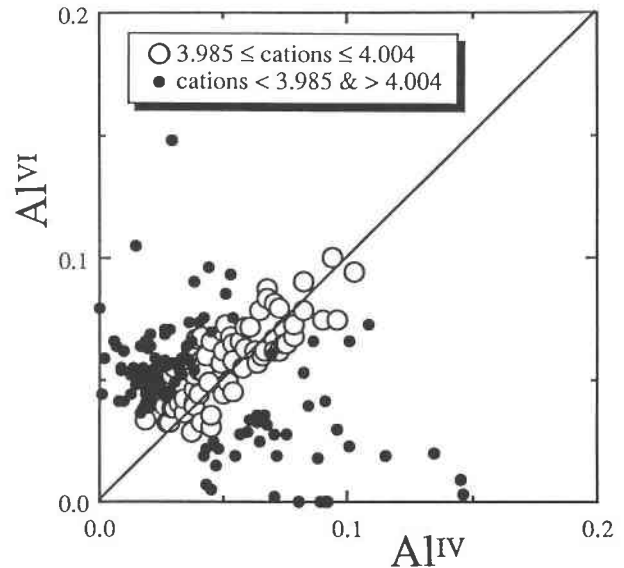
Fig. 4. Diagram of $^{[6]}Al$-$^{[4]}Al$ (O = 6) for PAl orthopyroxene.

pyroxene coexists with garnet or Ca-rich clinopyroxene, respectively. Moreover, in the ACF [(Al_2O_3-Na_2O-K_2O)-CaO-(FeO + MgO) in mole ratio] diagram, orthopyroxene is the only ferromagnesian mineral straddling the boundary between the corundum- and diopside-normative fields (Fig. 1). Accordingly, it is reasonable that PAl orthopyroxene is corundum normative and MAl orthopyroxene is diopside normative.

Thus, the compositional differences between PAl and MAl orthopyroxene can be explained in terms of the paragenesis of orthopyroxene, i.e., whether it is accompanied by garnet or Ca-rich clinopyroxene. Of course, in

TABLE 3. Pressure conditions of orthopyroxene samples examined in this paper

Locality	Pressure (kbar)	Reference
PAl orthopyroxene		
Canterbury	10–15	Wood (1974)
Hawkins	5.5	Wyborn et al. (1981)
Horobetsu	6–8	Bamba (1985)
Niikappu	5–6	Shimura et al. (1990)
Nozukadake	4–5	Maeda et al. (1985)
Ohmine (Omine)	5	Murata (1984)
Taima	0.5	Fang et al. (1985)
Violet Town	4	Clemens and Wall (1984)
MAl orthopyroxene		
Bushveld	2.7	Buchanan et al. (1980)
Fongen-Hyllingen	5–6	Wilson et al. (1981)
La Perouse	5.4	Loney and Himmelberg (1983)
Niikappu	5–6	Shimura et al. (1990)
Ohmine (Omine)	5	Murata (1984)
Pankenushi	6–7	Maeda (1981)
Tigalak	3	Wiebe and Wild (1983)
Wooley Creek	3–6.5	Barnes (1987)

Note: Most of the orthopyroxene, except for the Canterbury and Taima suites, crystallized under the pressure condition of 5 ± 2 kbar. Using the Newton and Perkins' (1982) geobarometer, the crystallizing pressures are calculated as 7 kbar for the Canterbury rhyolite and 2 kbar for the Taima granite.
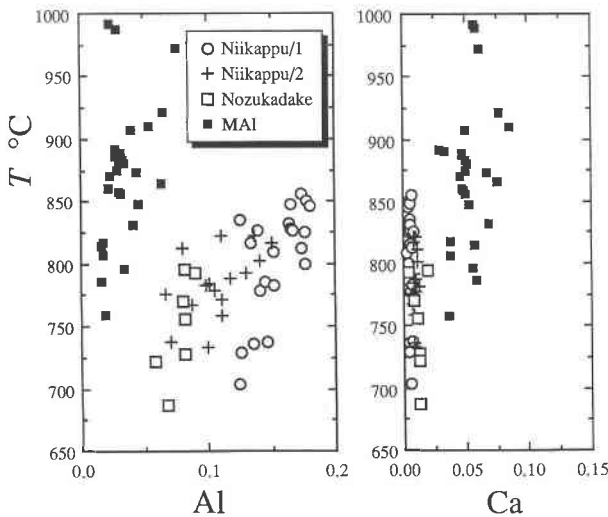
Fig. 5. Al and Ca contents of orthopyroxene samples plotted against temperature. The Niikappu/2 and Nozukadake orthopyroxenes are accompanied by biotite + garnet, and Niikappu/1 orthopyroxenes by biotite + garnet + cordierite. Their pressure conditions are similar, i.e., 5 ± 1 kbar (Table 2).

our data from peraluminous suites, garnet is not xenocrystic or restitic but is of magmatic origin, as judged from textural and compositional comparisons with garnet from nearby metasedimentary rocks (e.g., Maeda et al., 1985). Also, there is no evidence indicating disequilibrium between PAl orthopyroxene and garnet.

Relationship between compositions of orthopyroxene and magma

The mineral paragenesis should be controlled by magma composition. We need to compare the compositions
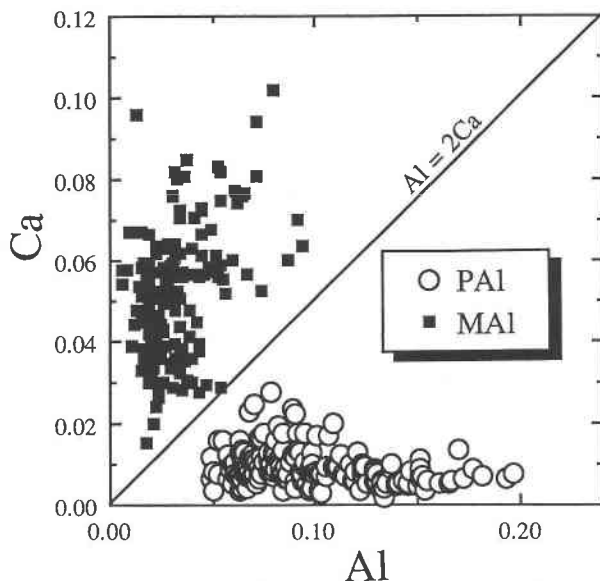
Fig. 6. Al-Ca (O = 6) diagram plotting PAl and MAl orthopyroxene. The line Al = 2Ca is the boundary between corundum- and diopside-normative fields.
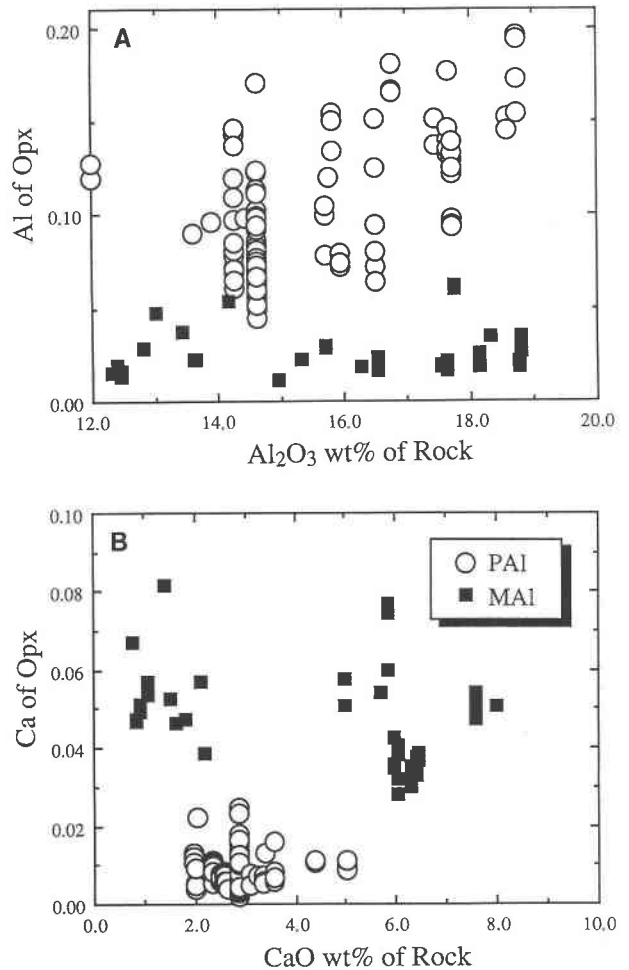
Fig. 7. Al and Ca contents (O = 6) of orthopyroxenes plotted against Al_2O_3 (A) and CaO (B) (wt%) of the orthopyroxene-bearing rocks. The rock analyses are recalculated on an anhydrous basis. Data are from Clear Lake (Stimac et al., 1990), Goobarragandra and Hawkins (Wyborn et al., 1981), Horobetsu (Bamba, 1985), Ibaragi (Tainosho, 1984), Mount Mazama (Bacon and Druitt, 1988; Druitt and Bacon, 1989), Niikappu (Shimura, unpublished data), Novarupta (Hildreth, 1983), Ohmine (Murata, 1982a, 1982b), Rancho Virulento (Moll, 1981), Taima (Fang et al., 1985), Tsugawa (Yoshimura et al., 1984), Twin Peaks (Crecraft et al., 1981), Violet Town (Clemens and Wall, 1984), and Whangarei (Brothers and Yokoyama, 1990). Glass compositions are used with the Clear Lake pyroxene analyses, and in the other suites bulk rock compositions are used for comparison.

of orthopyroxene with those of coexisting liquids. However, the comparison is not easy because few literature sources include both compositions of orthopyroxene and orthopyroxene-bearing rock. Furthermore, the bulk compositions of these rocks may not be identical to those of liquids coexisting with orthopyroxene, although data for known cumulates are not included. In fact, there are considerable variations in Al and Ca contents of orthopyroxene in a single rock (Figs. 7 and 8). Although it is preferred that glasses rather than bulk rocks are used for

Fig. 9. Al/Ca of orthopyroxene plotted against A/C of the orthopyroxene-bearing rocks. Data sources as in Figure 7.
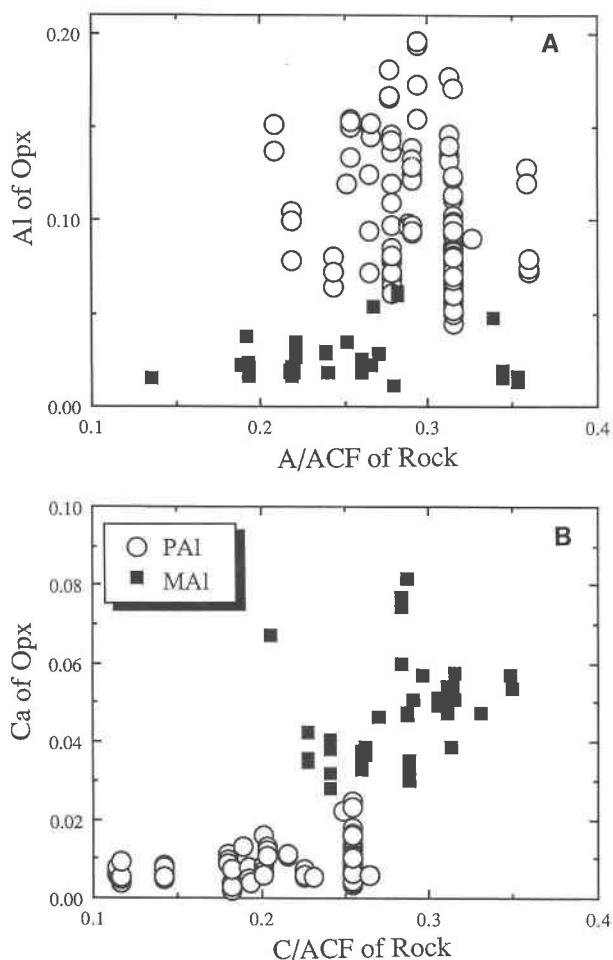

Fig. 8. Al and Ca contents (O = 6) of orthopyroxenes plotted against A/ACF [A/(A + C + F)] (A) and C/ACF [C/(A + C + F)] (B) of the orthopyroxene-bearing rocks. In this figure, F is calculated using Fe_{tot} as FeO rather than reported FeO, because it is doubtful that Fe^{2+}/Fe^{3+} ratios of the bulk rocks are magmatic values and because fairly reducing conditions prevail in comparatively Fe-rich orthopyroxene-bearing rocks. Data sources as in Figure 7.

comparison, published data on coexisting orthopyroxene and glass compositions are rare. It is uncertain whether Fe^{2+}/Fe^{3+} ratios of the bulk rocks represent those during magmatic crystallization; this is especially important for Figure 8. The following discussion based on comparison of orthopyroxene compositions with those of bulk rocks is not necessarily precise but offers the only practical approach at present.

Figure 7 shows that the Al and Ca contents of orthopyroxene are not directly controlled by the concentration of Al_2O_3 and CaO in the rocks. Al contents of PAl orthopyroxene increase with increasing Al_2O_3 of the bulk rocks. However, Al and Ca contents of MAl orthopyroxene are distinctly lower and higher, respectively, than those of PAl orthopyroxene in the same range of Al_2O_3 and CaO contents of the bulk rocks.
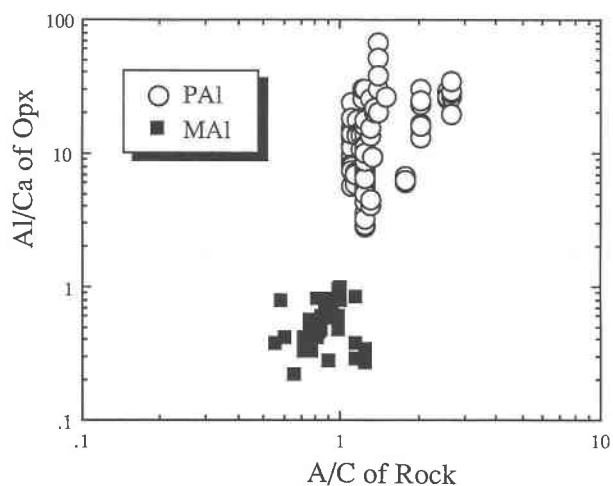
Nielsen and Drake (1979) discussed the equilibrium between orthopyroxene and liquid. They suggested that the activities of SiO_2, $AlO_{1.5}$, CaO, etc. in the liquid are not expressed by the simple oxide-ideal mixing model and proposed a model modified from Bottinga and Weill (1972). In Nielsen and Drake's model, the activities of $AlO_{1.5}$ and CaO in the liquid are expressed as follows:

$$a_{AlO_{1.5}}^l = X_{AlO_{1.5}}^{NM} = (X_{AlO_{1.5}}^l - X_{NaO_{0.5}}^l - X_{KO_{0.5}}^l)/X_{NM}^l$$

$$a_{CaO}^l = X_{CaO}^{NM} = X_{CaO}^l/X_{NM}^l$$

$$X_{NM}^l = X_{FeO}^l + X_{MgO}^l + X_{CaO}^l + X_{TiO_2}^l + X_{CrO_{1.5}}^l$$

$$+ (X_{AlO_{1.5}}^l - X_{NaO_{0.5}}^l - X_{KO_{0.5}}^l)$$

where a_B^A and X_B^A are activity and mole fraction of B in phase A, and l and NM are liquid and network-modifying components. Because concentrations of TiO_2 and $CrO_{1.5}$ in magmas are low, especially in felsic ones, the activities of $AlO_{1.5}$ and CaO in the above equations are nearly identical to the components A and C in the ACF diagram. Figure 8 shows the relationships between Al and Ca contents of orthopyroxene and A/ACF [A/(A + C + F)] and C/ACF [C/(A + C + F)] of the bulk rocks. In this figure, F is calculated from FeO as Fe_{tot}. Ca contents of orthopyroxene increase from PAl to MAl, with increasing C/ACF of bulk rocks. This rather good correlation supports the validity of the model of Nielsen and Drake (1979). On the other hand, there is no clear correlation between Al contents of orthopyroxene and A/ACF of bulk rocks. This lack of correlation may be due to subtle effects of pressure and temperature during crystallization or inappropriate comparison between the compositions of orthopyroxene and bulk rocks, as mentioned above. At any rate, Figure 8 does not explain the critical difference in Al/Ca between PAl and MAl orthopyroxene shown in Figure 6. This difference is related to Shand's degree of alumina saturation; that is, a meaningful factor in this

case is not A or C but A/C of rocks. This relation is clearly illustrated in Figure 9, which shows the positive correlation between A/C of rocks and Al/Ca of orthopyroxene from MAl to PAl.

CONCLUSIONS

Most PAl orthopyroxene coexists with garnet, and MAl orthopyroxene coexists with Ca-rich clinopyroxene. PAl orthopyroxene, ranging in X_{Fe} from 0.806 to 0.340, is richer in Al and poorer in Ca than MAl orthopyroxene. PAl orthopyroxene has Al > 2Ca and MAl orthopyroxene has Al < 2Ca. Thus, PAl orthopyroxene coexisting with garnet is corundum normative, and MAl orthopyroxene coexisting with Ca-rich clinopyroxene is diopside normative. This relationship is in harmony with the ACF diagram, in which orthopyroxene is the only ferromagnesian mineral straddling the boundary (Al = 2Ca) between corundum-normative and diopside-normative fields. The above compositional differences in Al and Ca between PAl and MAl orthopyroxene are not due to the differences in pressure or temperature during the crystallization of magma but to the compositional difference between two types of magma.

REFERENCES CITED

Bacon, C.R., and Druitt, T.H. (1988) Compositional evolution of the zoned calcalkaline magma chamber of Mount Mazama, Crater Lake, Oregon. Contributions to Mineralogy and Petrology, 98, 224–256.

Bamba, M. (1985) Metamorphism of the Main zone of the Hidaka metamorphic belt, 554 p. M.S. thesis, Niigata University, Niigata, Japan (in Japanese).

Barnes, C.G. (1983) Petrology and upward zonation of the Wooley Creek batholith, Klamath Mountains, California. Journal of Petrology, 24, 495–537.

——— (1987) Mineralogy of the Wooley Creek batholith, Slinkard pluton, and related dikes, Klamath Mountains, northern California. American Mineralogist, 72, 879–901.

Birch, W.D., Clemens, J.D., and Phillips, G.N. (1977) Devonian acid igneous complexes in Central Victoria. Guide to Excursion "C," 27 p. Second Australian Geological Convention, National Museum of Victoria, Melbourne, Australia.

Bottinga, Y., and Weill, D.F. (1972) The viscosity of magmatic silicate liquids: A model for calculation. American Journal of Science, 272, 438–475.

Brothers, R.N., and Yokoyama, K. (1990) Fe-rich pyroxenes from a microdiorite dike, Whangarei, New Zealand. American Mineralogist, 75, 620–630.

Buchanan, D.L. (1979) A combined transmission electron microscope and electron microprobe study of Bushveld pyroxenes from the Bethal area. Journal of Petrology, 20, 327–354.

Buchanan, D.L., Nolan, J., and Viljoen, E.A. (1980) Determination of

silica activity in Bushveld rocks. Contributions to Mineralogy and Petrology, 73, 311–319.

Chappell, B.W., and White, A.J.R. (1974) Two contrasting granite types. Pacific Geology, 8, 173–174.

Clarke, D.B. (1981) The mineralogy of peraluminous granites: A review. Canadian Mineralogist, 19, 3–17.

Clemens, J.D., and Wall, V.J. (1984) Origin and evolution of a peraluminous silicic ignimbrite suite: The Violet Town volcanics. Contributions to Mineralogy and Petrology, 88, 354–371.

——— (1988) Controls on the mineralogy of S-type volcanic and plutonic rocks. Lithos, 21, 53–66.

Crecraft, H.R., Nash, W.P., and Evans, S.H., Jr. (1981) Late Cenozoic volcanism at Twin Peaks, Utah: Geology and petrology. Journal of Geophysical Research, 86, 10303–10320.

Deer, W.A., Howie, R.A., and Zussman, J. (1978) Rock-forming minerals, vol. 2A: Single-chain silicates (2nd edition), 668 p. Longman, London.

Druitt, T.H., and Bacon, C.R. (1989) Petrology of the zoned calcalkaline magma chamber of Mount Mazama, Crater Lake, Oregon. Contributions to Mineralogy and Petrology, 101, 245–259.

Fang, Q., Feng, J., and He, L. (1985) Characteristics and genesis of Taima S-type super-hypabyssal hypersthene granite-porphyry. In L. Wu, T. Yang, K. Yuan, J. Didier, J.K. Greenberg, G.R. Lowell, H. Xia, S. Yu, S.S. Augustithis, Eds., The crust—the significance of granites, gneisses in the lithosphere, p. 399–419. Theophrastus, Athens.

Grant, J.A. (1981) Orthoamphibole and orthopyroxene relations in high-grade metamorphism of pelitic rocks. American Journal of Science, 281, 1127–1143.

Harley, S.L. (1984) The content of alumina in orthopyroxene coexisting with garnet in FeO-MgO-Al$_2$O$_3$-SiO$_2$ and CaO-FeO-MgO-Al$_2$O$_3$-SiO$_2$. Journal of Petrology, 25, 665–696.

Harley, S.L., and Green, D.H. (1982) Garnet-orthopyroxene barometry for granulites and peridotites. Nature, 300, 697–701.

Hildreth, W. (1979) The Bishop tuff: Evidence for the origin of compositional zonation in silicic magma chambers. Geological Society of America Special Paper, 180, 43–75.

——— (1983) The compositionally zoned eruption of 1912 in the Valley of Ten Thousand Smokes, Katmai National Park, Alaska. Journal of Volcanology and Geothermal Research, 18, 1–56.

Huebner, J.S. (1980) Pyroxene phase equilibria at low pressure. In Mineralogical Society of America Reviews in Mineralogy, 7, 213–288.

Ikeda, Y. (1976) Petrology and mineralogy of the Iritono basic intrusive rocks, Central Abukuma plateau. Journal of Faculty of Science, University of Tokyo, Section III, 19, 227–251.

Ikeda, Y., and Mukoyama, S. (1983) Stratigraphy and correlation of the pyroclastic flow deposits in the Furano-Asahikawa area, Central Hokkaido, Japan. Journal of the Geological Society of Japan, 89, 163–172 (in Japanese with English abstract).

Imaoka, T., and Murakami, N. (1979) Petrochemistry of late Mesozoic to early Tertiary volcanic rocks in West Chugoku, Southwest Japan. Memoirs of the Geological Society of Japan, 17, 259–272 (in Japanese with English abstract).

Kamiya, K., and Harayama, S. (1982) Geology and petrology of the Makido mafic complex, Shokawa-mura, Gifu Prefecture, Central Japan. Journal of the Geological Society of Japan, 88, 249–269 (in Japanese with English abstract).

Kasahara, Y., and Harayama, S. (1981) Note on the Tonomura welded tuff, Central Japan—a study of the latest Cretaceous pyroclastic flow magma. Bulletin of the Gifu Prefectural Museum, 2, 29–43 (in Japanese with English abstract).

Kasugai, A., Fujita, A., Hosokawa, K., Okamura, S., Satoh, H., and Yano, M. (1980) Late Pleistocene tephras in the southern Ishikari low-land, Hokkaido—a comparative study of the relation between refractive indices and Mg-Fe ratios of orthopyroxene. Journal of the Association for the Geological Collaboration in Japan, 34, 1–15 (in Japanese with English abstract).

Kawahara, K., Tsukahara, S., Tajima, T., and Kamogawa, N. (1984) The late Miocene volcanism in Nakadori-jima, Goto Islands, Nagasaki Prefecture, Japan. Memoirs of the Geological Society of Japan, 24, 77–92 (in Japanese with English abstract).

Kawasaki, M. (1980) Omine acid rocks, Kii Peninsula—mineralogy. Jour-

nal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists, 75, 146–159.

Lee, H. Y., and Ganguly, J. (1988) Equilibrium compositions of coexisting garnet and orthopyroxene: Experimental determinations in the system FeO-MgO-Al₂O₃-SiO₂, and applications. Journal of Petrology, 29, 93–113.

Lindsley, D.H. (1980) Phase equilibria of pyroxenes at pressures > 1 atmosphere. In Mineralogical Society of America Reviews in Mineralogy, 7, 289–307.

———(1983) Pyroxene thermometry. American Mineralogist, 68, 477–493.

Loney, R.A., and Himmelberg, G.R. (1983) Structure and petrology of the La Perouse gabbro intrusion, Fairweather range, southeastern Alaska. Journal of Petrology, 24, 377–423.

Maeda, J. (1981) Petrology of the Pankenushi gabbroic intrusion, Hidaka metamorphic belt, Hokkaido, 144 p. Ph.D. thesis, Hokkaido University, Sapporo, Japan.

Maeda, J., Tsuchiya, N., Arita, K., Osanai, Y., Suetake, S., Ikeda, Y., Bamba, M., and Owada, M. (1985) Finding of olivine- and garnet-bearing biotite quartz norite from the Hidaka metamorphic belt, Hokkaido, Japan. Journal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists, 80, 13–20.

Moll, E.J. (1981) Geochemistry and petrology of mid-Tertiary ash flow tuffs from the Sierra el Virulento area, eastern Chihuahua, Mexico. Journal of Geophysical Research, 86, 10321–10334.

Murata, M. (1982a) S-type and I-type granitic rocks of the Ohmine district, central Kii Peninsula. Journal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists, 77, 267–277 (in Japanese with English abstract).

———(1982b) Petrology of Tertiary granitic rocks in the Ohmine district, central Kii Peninsula, 355 p. Ph.D. thesis, Tohoku University, Sendai, Japan.

———(1984) Petrology of Miocene I-type and S-type granitic rocks in the Ohmine district, central Kii Peninsula. Journal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists, 79, 351–369 (in Japanese with English abstract).

Nakada, S. (1983) Zoned magma chamber of the Osuzuyama acid rocks, Southwest Japan. Journal of Petrology, 24, 471–494.

Nakamura, Y., and Kushiro, I. (1970) Equilibrium relations of hypersthene, pigeonite and augite in crystallizing magmas: Microprobe study of a pigeonite andesite from Weiselberg, Germany. American Mineralogist, 55, 1999–2015.

Newton, R.C., and Perkins, D. (1982) Thermodynamic calibration of geobarometers based on the assemblages garnet-plagioclase-orthopyroxene (clinopyroxene)-quartz. American Mineralogist, 67, 203–222.

Nielsen, R.L., and Drake, M.J. (1979) Pyroxene-melt equilibria. Geochimica et Cosmochimica Acta, 43, 1259–1272.

Phillips, G.N., Wall, V.J., and Clemens, J.D. (1981) Petrology of the Strathbogie batholith: A cordierite-bearing granite. Canadian Mineralogist, 19, 47–63.

Sapountzis, E.S. (1979) The Thessaloniki gabbros. Journal of Petrology, 20, 37–70.

Shand, S.J. (1927) Eruptive rocks, 360 p. Thomas Murby and Co., London.

Shimazu, M., and Takano, M. (1977) Ca-Fe-rich pyroxenes in Miocene perlites from the Tsugawa and Tadami areas, Northeast Japan. Journal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists, 72, 419–427.

Shimazu, M., and Toyama, T. (1982) Neogene volcanic rocks of the Sado Islands. Journal of the Geological Society of Japan, 88, 381–400 (in Japanese with English abstract).

Shimura, T., Iiyama, T., and Hirota, K. (1990) Melting experiment of the garnet-hypersthene tonalite of the Hidaka metamorphic belt. 1990 Annual Meeting of the Mineralogical Society of Japan Abstracts, 68 (in Japanese).

Shiramizu, A., Takahashi, M., and Ikeda, Y. (1983) Pigeonite dacite occurring in Motegi district, Tochigi Prefecture. Journal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists, 78, 255–266 (in Japanese with English abstract).

Snoke, A.W., Quick, J.E., and Bowman, H.R. (1981) Bear Mountain igneous complex, Klamath Mountains, California: An ultrabasic to silicic calc-alkaline suite. Journal of Petrology, 22, 501–552.

Soya, T., and Satoh, H. (1980) Geology of the Chitose district. Quadrangle Series, scale 1:50000. Geological Survey of Japan, 92 p. (in Japanese with English abstract).

Stimac, J.A., Pearce, T.H., Donnelly-Nolan, J.M., and Hearn, B.C., Jr. (1990) The origin and implications of undercooled andesitic inclusions in rhyolites, Clear Lake volcanics, California. Journal of Geophysical Research, 95, 17729–17746.

Suetake, S. (1986) Petrology of the plutonic rocks in the middle stream of Tottabetsu river, the Main zone of the Hidaka metamorphic belt, 183 p. M.S. thesis, Yamaguchi University, Yamaguchi, Japan (in Japanese with English abstract).

Tainosho, Y. (1984) Dark inclusions in the Ibaragi granitic complex of Ibaragi City, Osaka Prefecture, Japan. Journal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists, 79, 133–145 (in Japanese with English abstract).

von Gruenewaldt, G., and Weber-Diefenbach, K. (1977) Coexisting Ca-poor pyroxenes in the Main Zone of the Bushveld complex. Contributions to Mineralogy and Petrology, 65, 11–18.

Warshaw, C.M., and Smith, R.L. (1988) Pyroxenes and fayalites in the Bandelier tuff, New Mexico: Temperatures and comparison with other rhyolites. American Mineralogist, 73, 1025–1037.

White, A.J.R., and Chappell, B.W. (1977) Ultrametamorphism and granitoid genesis. Tectonophysics, 43, 7–22.

Wiebe, R.A., and Wild, T. (1983) Fractional crystallization and magma mixing in the Tigalak layered intrusion, the Nain anorthosite complex, Labrador. Contributions to Mineralogy and Petrology, 84, 327–344.

Wilson, J.R., Esbensen, K.H., and Thy, P. (1981) Igneous petrology of the synorogenic Fongen-Hyllingen layered basic complex, south-central Scandinavian Caledonides. Journal of Petrology, 22, 584–627.

Wood, B.J., and Banno, S. (1973) Garnet-orthopyroxene and orthopyroxene-clinopyroxene relationships in simple and complex systems. Contributions to Mineralogy and Petrology, 42, 109–124.

Wood, C.P. (1974) Petrogenesis of garnet-bearing rhyolites from Canterbury, New Zealand. New Zealand Journal of Geology and Geophysics, 17, 759–787.

Wyborn, D., Chappell, B.W., and Johnston, R.M. (1981) Three S-type volcanic suites from the Lachlan Fold Belt, southeast Australia. Journal of Geophysical Research, 86, 10335–10348.

Yamaguchi, Y., Tomita, K., and Sawada, Y. (1974) Crystallization trend of zoned pyroxenes in quartz gabbro from the Koyama intrusive complex at Mt. Koyama, Yamaguchi Prefecture, Japan. Memoirs of the Geological Society of Japan, 11, 69–82.

Yoshimura, T., Fukasawa, H., and Yahata, M. (1984) Miocene acid volcanic rocks in the Tsugawa area, northeast Japan. Memoirs of the Geological Society of Japan, 24, 145–156 (in Japanese with English abstract).