Rhodonite, spessartine and manganoan amphiboles from the Ryoke metamorphic rock at Wakagashi, Osaka Prefecture, Japan

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(with 2 Tables, 5 Figures and 2 Plates)

Introduction

The specimen used in this study was collected from the Ryoke metamorphic rock at Wakagashi by one (S.M.) of the authors during the summer of 1975. It containes rhodonite, spessartine, manganoan cummingtonite and manganoan actinolite as main constituent minerals. These minerals outside of manganoan actinolite are common in manganese ore deposits in Japan, but their compositions were magnesium rich in comparison with those reported up to now. These manganese silicates have been very rarely reported from the metamorphic rock in the central part of the Ryoke belt (SUWA, 1961; HIROWATARI, 1968). We are very interested in their constituent minerals and their modes of occurrances.

Rhodonite occurs as one of the important and abundant manganese ore minerals from various types of manganese deposits, such as metamorphosed bedded manganese ore body, hydrothermal polymetallic vein type deposits and pegmatite. Rhodonite also occur in one of rock-forming minerals with contact-metamorphosed calc-silicate rocks. Spessartine is rather less common than many of the garnet species. Although the spessartine molecule is often present in significant amount in almamdine from granites and from metamorphic rocks, especially those of contact aureoles, it is rarely dominant in such environments. Garnet in which spessartine is the principal molecule are found in some skarn deposits and frequently occur in manganese-rich assembleges, with rhodonite, pyroxmangite, tephroite, etc., of metasomatic origin associated either with adjecent igneous intrusives or with a more wide spread regional metasomatism. Rhodonite and spessartine occur in various kinds of geological environments as described above. It is well known that they do not show pure $MnSiO_3$ and $Mn_3Al_2Si_3O_{12}$ respectively, and always contain in a varying amount of Ca^{2+}, Fe^{2+} and Mg^{2+} substituted for Mn^{2+}. The changes of mineralogical properties due to cationic substitution have been well studied. However, the relationship between the compositions and the conditions of formation of these two minerals has not been so well studied.

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On the other hand, manganese-rich amphiboles occur in relatively restricted environments. Manganoan cummingtonite is present in some amphibolities of regionally metamorphosed manganiferous sediments, and also in the eulysites and in the contact metamorphosed manganese deposits. The modes of occurrences from many localities in Japan are restricted to "Yakeno Type" manganese deposits intimately associated with the Ryoke belt and "Kaso Type" (YOSHIMURA & MOMOI, 1961). Both types named and classified by YOSHIMURA (1967), are considered to be manganese deposits formed at a high temperature and under a "high pressure", which may be up to 4–5 Kbar. Manganoan actinolite containing more than 5 wt% MnO is very rare. DEER et al. (1963) pointed out that high contents of manganese are rare particularly in magnesium-rich members of tremolite-actinolite series, and manganoan tremolite, hexagonite, containing about 1 wt% MnO occurs in some metamorphosed calcareous rocks. YOSHIMURA (1939) and TANIDA et al. (1978) reported manganoan actinolite containing more than 5 wt% MnO from the Kaso mine and the Nodatamagawa mine respectively. These two occurrences are from "Kaso Type" manganese deposits in either case.

In this study, the authors will clarify the mineralogical properties of these manganese minerals, and discuss the condition and the process of formation from genetical point of view.

Outline of geology and petrography

The Wakagashi area is situated in the Ryoke metamorphic belt in Osaka Prefecture, being south of the Izumi city. Fig. 1 shows a geological sketch map of the Wakagashi area and the locality of the specimen. The Ryoke belt in this area has been studied in detail by MASAOKA and the Research Group for the Ryoke belt (1978) and YAMADA et al. (1979). According to them, the Ryoke granitic rocks in this area divided into two facies, Takijiri adamellite and Konoyama gneissose granodiorite. Takijiri intrusive exposed in the southern part of this area is the younger granite, and shows massive or slightly gneissose texture and scarcely shows a evidence for mylonitization. On the other hand, Konoyama intrusive exposed in the northern part is the older granite and shows a strongly gneissose texture and often shows a evidence for mylonitization. The metamorphic rock which has been considered to be derived from chert and sandstone shows occurrence such as a roof pendant of Konoyama intrusive. The constituent minerals of this gneiss are quartz, plagiolase, biotite, spessartine-almandine garnet and graphite. It is not clear whether this gneiss was formed with a regional metamorphism, or with a contact metamorphism due to the younger granite intrusive and or with the influence of both metamorphism. Garnet in gneiss shows a characteristic chemical zoning which is similar to those from the Takato and Hazu areas (ONO, 1976). Judging from the chemical nature of garnet alone in gneiss, this gneiss may be formed with a regional metamorphism. Under the microscope, quartz in gneiss and in rock containing four manganese minerals shows a strong undulatory extinction, but recrystallized texture was not observed. These facts may show that this gneiss had not been subjected to the influence of a contact metamorphism due to the younger granite.
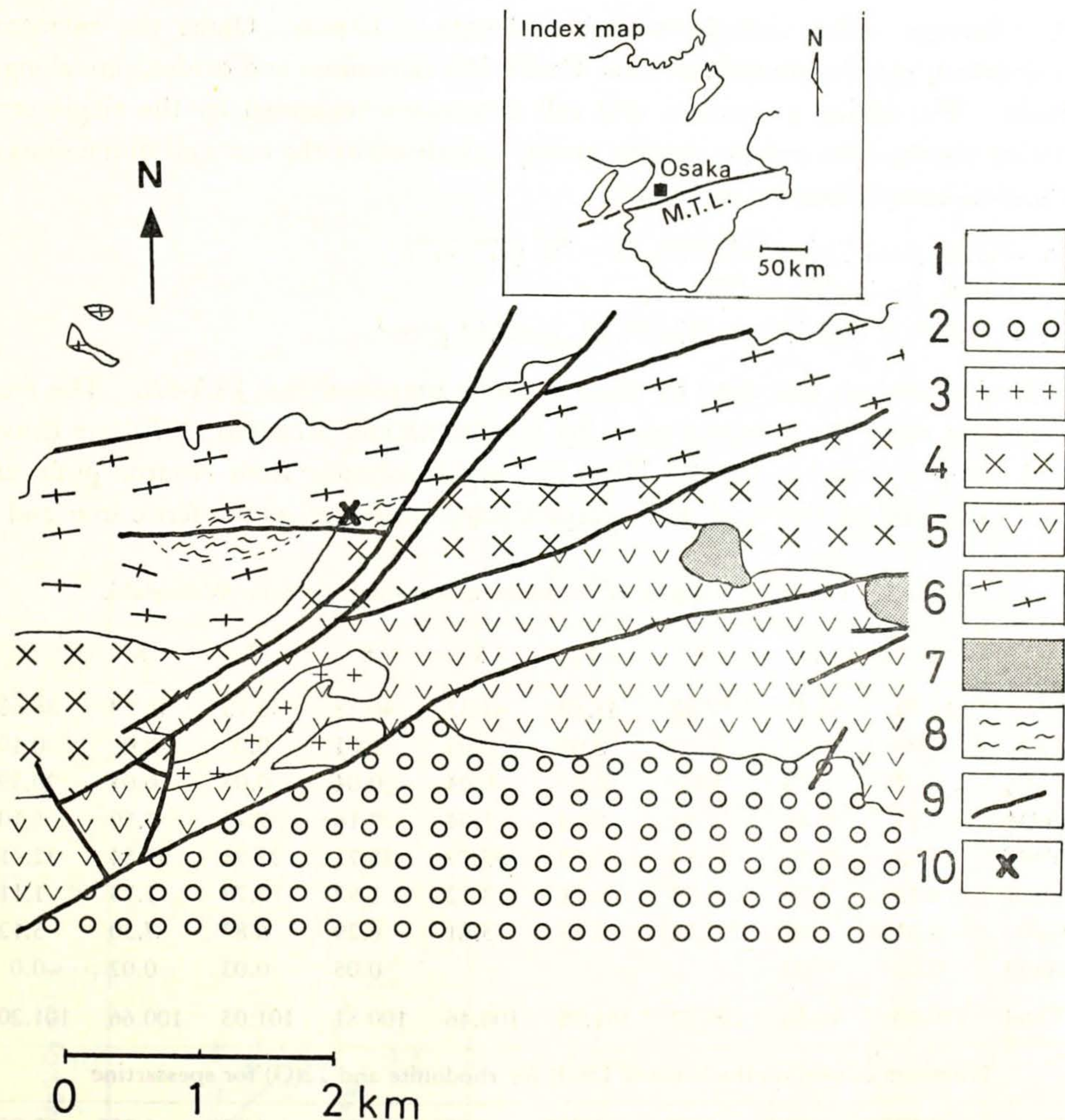
Fig. 1.   A geological sketch map of the Wakagashi area, Osaka Prefecture.
1: Plio-Pleiostcene and Osaka group. 2: Izumi group. 3: Medium-grained biotite adamellite.
4: Takijiri adamellite. 5: Sennan group and granite porphyry. 6: Konoyama gneissose
granodiorite. 7: Phyllite and hornfels. 8: Gneiss. 9: Fault. 10: Locality of the specimen.

Mineral description

The rock specimen collected from the gneiss consists of quartz, rhodonite, spes-
sartine, sphene and minor amount of apatite as primary crystallized minerals, and also
contains manganoan cummingtonite, manganoan actinolite, (Mn, Ca, Fe) carbonates and
oxides and minor amount of Fe-sulfide as alteration products (see Plate 1 and 2).   In
this section, we will describe the mineralogical properties of rhodonite, spessartine,
manganoan cummingtonite and manganoan actinolite in detail.

Rhodonite

The mineral is abundant and forming the greater proportion of the specimen.   It is
light-pink to brownish-pink in colour, and has distinct cleavages parallel to (100) and

(010).   Cleavage surface sometimes attains a length of 10 mm.   Under the microscope, it is colourless, and the altered minerals, Ca-Fe-Mn carbonates and oxides, are along the cleavages. The optical properties, unit cell dimensions measured by the single crystal precession photographs and the specific gravity calculated by the unit cell dimnesions and the chemical composition are as follow;

$\alpha = 1.720$, $\beta = 1.724$, $\gamma = 1.7338$, $2V = 70°$ $(67°-72°)$,
$a = 6.67Å$, $b = 7.66Å$, $c = 12.21Å$,
$\alpha = 111.60°$, $\beta = 85.57°$, $\gamma = 93.65°$, $D_{calc} = 3.61$ g/cm^3.

The chemical analysis was done by electron probe microanalyser, JXA-5A.   The results calculated by using the α-factors given by Nakamura and Kushiro (1970) are listed in Table 1 and are plotted in Fig. 2. Total iron and manganese from electron probe analysis are calculated as Fe^{2+} and Mn^{2+} respectively.   However, as the ferric iron and the

Table 1.   Chemical analyses of rhodonite and spessartine from Wakagashi.

	1	2	3	4	5	6	7	8	9
SiO$_2$	47.30	46.43	47.42	47.50	47.33	46.58	46.73	46.53	36.68
TiO$_2$	0.02	0.02	0.02	0.03	0.03	0.01	0.0	0.0	0.19
Al$_2$O$_3$	0.07	0.04	0.0	0.0	0.04	0.04	0.03	0.04	20.59
FeO*	8.07	8.16	7.94	8.02	7.94	7.16	7.70	7.50	5.10
MnO**	34.33	35.21	36.10	36.03	35.79	38.71	37.91	37.54	32.41
MgO	4.48	3.86	3.73	3.71	3.52	1.97	1.78	1.73	1.11
CaO	6.01	5.82	5.72	5.89	5.81	6.29	6.87	7.30	5.12
Na$_2$O	0.02	0.02				0.05	0.03	0.02	0.0
Total	100.30	99.56	100.93	101.18	100.46	100.81	101.05	100.66	101.20

Numbers of ions on the basis of 15(O) for rhodonite and 12(O) for spessartine

Si	4.937	4.919	4.946	4.944	4.958	4.928	4.929	4.933	2.956
Al	0.008	0.005			0.006	0.006	0.006	0.004	1.956
Ti	0.002	0.001	0.002	0.002	0.002	0.0	0.001	0.001	0.012
Fe^{+2}	0.704	0.723	0.693	0.698	0.696	0.664	0.634	0.680	0.343
Mn^{+2}	3.035	3.159	3.190	3.176	3.176	3.367	3.469	3.389	2.212
Mg	0.697	0.610	0.581	0.576	0.505	0.273	0.310	0.281	0.133
Ca	0.673	0.661	0.639	0.657	0.652	0.829	0.713	0.777	0.442
Na	0.005	0.004				0.005	0.011	0.007	

Molecular ratio MnO : CaO : FeO : MgO

MnO	59.4	61.3	62.5	62.2	62.6	67.7	66.1	65.6	70.7
CaO	13.2	12.8	12.5	12.9	12.9	13.9	15.1	16.1	14.1
FeO	13.8	14.0	13.6	13.7	13.7	12.4	13.3	12.9	10.9
MgO	13.6	11.8	11.4	11.3	10.8	6.0	5.5	5.3	4.2

Analyses 1–8, rhodonite; 9, spessartine. *: Total Fe as FeO, **: Total Mn as MnO,
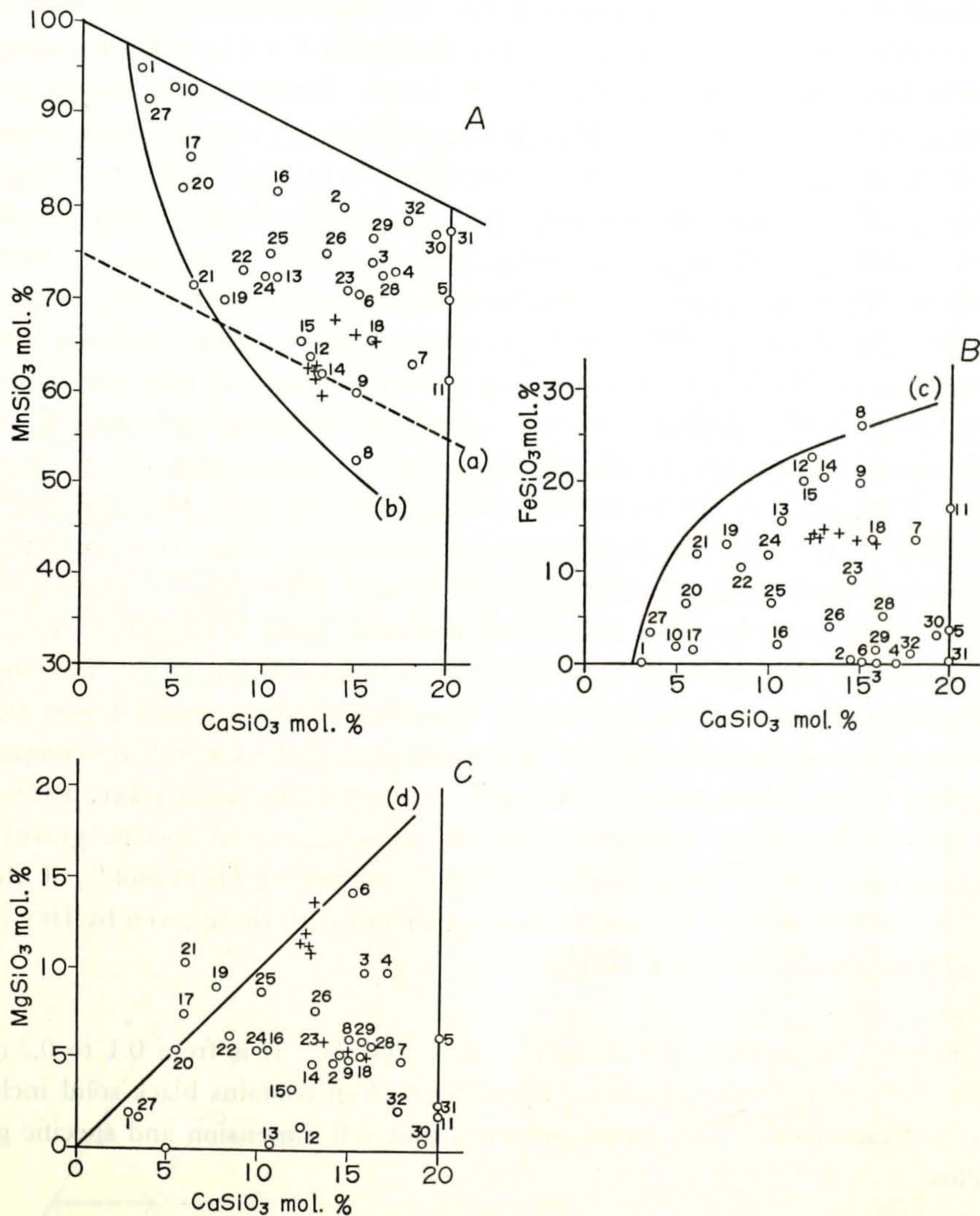——: Not determined.

Fig. 2. Relations between $MnSiO_3$ and $CaSiO_3$ (A), between $FeSiO_3$ and $CaSiO_3$ (B) and between $MgSiO_3$ and $CaSiO_3$ (C) in natural rhodonites respectively. (a) shows $(Fe, Mg) SiO_3 = 25$ mol.%. (b) and (c) show the compositional boundary between rhodonite (marked area) and pyroxmangite in the diagrams of $CaSiO_3–MnSiO_3$ and $CaSiO_3–FeSiO_3$ respectively (after Momoi, 1964). (d) shows $Ca:Mg=1:1$.

Rhodonites cited from the literatures. 1–8, Sundius (1931a); 9–10, Bilgrami (1955); 11–12, Henderson and Glass (1929); 13, Mason (1973); 14–17, Nambu (1978); 18, Russel (1946); 19–20, Hietanen (1938); 21–22, Yoshimura (1939); 23–27, Momoi (1964); 28, Olrov (1935); 29, Harada (1933); 30, Yoshimura and Momoi (1960); 31, Yoshimura (1952); 32, Kitahara (1948); +, present study.

trivalent manganese contents are usually low, they are negligible for all rhodonite.

Rhodonite is divided into two sreies with respect to the composition. One of two series contains about 5–6 mol.% of $MgSiO_3$, and the other contains about 11–14 mol.%, but both series of rhodonites contain the same amount of $FeSiO_3$, and the former contains slightly larger amount of $CaSiO_3$ than the latter. However, the former is rather rare and consists of small grain enclosed in quartz and does not associate with spessartine, as far as we are aware. Among the natural rhodonite, so far studied, the maximum contents of Ca^{2+}, Fe^{2+} and Mg^{2+} are about 20 mol.% as $CaSiO_3$, about 26 mol.% as $FeSiO_3$ and about 15 mol.% as $MgSiO_3$ respectively (MOMOI, 1964). However, the maximum content of $(Fe, Mg)SiO_3$ component is not more than 25 mol.% except for the rhodonite from Langban by SUNDIUS (1931a), and Mn-poor rhodonite which contains less than about 70 mol.% of $MnSiO_3$ is generally iron-rhodonite, and the rhodonite containing more than 10 mol.% of $MgSiO_3$ is very rare. Mn-poor rhodonites and some of common rhodonites reported until now are illustrated in Fig. 2 together with the rhodonites in this study. Although it is well known that varing amount of Ca^{2+}, Fe^{2+} and Mg^{2+} substitute for Mn^{2+} in the rhodonite structure as described above, it has never been reported such rhodonite as from Wakagashi which contains from 11 to 14 mol.% of $CaSiO_3$, $FeSiO_3$ and $MgSiO_3$ respectively (see Fig. 2). Thus, rhodonite from Wakagashi is very infrequent, and contains Mg equivalent to the magnesium rhodonite intergrown with diposide from Langban by SUNDIUS (1931a). On the other hand, it is generally saying that the physical properties of rhodonite depend on the amounts of the Ca and Mg components, but the effect of the substitution of Mn by Fe appears to be slight (HEY, 1929, many other studies). The optical properties, unit cell dimensions and specific gravity were measured and calculated by using the rhodonite grain containing 11–14 mol.% of $MgSiO_3$. The results obtained in this study are in good agreement with those given by HEY (1929), SUNDIUS (1931a) and NAMBU et al. (1978).

Spessartine

The mineral is abundant and forms euhedral crystals. It is from 0.1 to 0.3 mm in diameter. The colour is pale- yellow. Spessartine often contains black solid inclusions which are not identified. The optical property, unit cell dimension and specific gravity are as follow;

$$n_d = 1.805, \quad a = 11.641 \pm 0.003 \text{ Å}, \quad D_{calc} = 4.08 \text{ g/cm}^3.$$

As the compositions of garnets analysed are nearly equal, one of the compositions is given in Table 1 together with rhodonites. Compositional changes of garnet crystal could not be detected by electron probe scan. Although total iron and manganese from electron microprobe analysis are calculated as Fe^{2+} and Mn^{2+} respectively, the amounts of Fe^{3+} and Mn^{3+} in garnet can be estimated fairly well from the deficiency of trivalent elements after Al has been considered. There is virtually no Fe^{3+} and Mn^{3+} substituting for Al, and so the andradite and blythite component are regardless as negligible for garnet. The pyrope component is usually low in spessartine garnet, and is contained baout 4 mol.%

in the Wakagashi spessartine. The compositions of spessartine from Wakagashi is similar to those from the "Yakeno Type" spessartine, but is clearly different from those of the "Kaso Type" spessartine containing a considerable amount of the andradite component (YOSHIMURA, 1967).

Manganoan cummingtonite

The occurrences of manganoan cummingtonite are two types. Manganoan cummingtonite in rhodonite occurs as an alteration product after a part of rhodonite, and has a certain orientational relationship with rhodonite (see Plate 2). On the other hand, it occurs as a fibrous aggregate associated with mangnoan actinolite around the rhodonite and spessartine mass. Manganoan cummingtonite in rhodonite is from 0.01 to 0.1 mm in length, and has a short prismatic shape. It in a fibrous aggregate is about 10 mm in length and its colour is light-pink or pale-green, but pale-green fibrous crystal may be manganoan actinolite described later. The optical properties, unit cell dimensions of manganoan cummingtonite intergrown with rhodonite by the single crystal precession method and specific gravity are as follow;

$\alpha=1.647$, $\beta=$not determined, $\gamma=1.669$, $2V=78°$,
$a=9.87Å$, $b=18.22Å$, $c=5.31Å$, $\beta=102.83°$
$D_{calc}=3.15$ g/cm³.

The chemical compositions are listed in Table 2 and are plotted in Fig. 3. The composition of manganoan cummingtonite from Wakagashi is one of the richest for the Mg content among the many analysed manganoan cummingtonites in the past (Rabbitt,
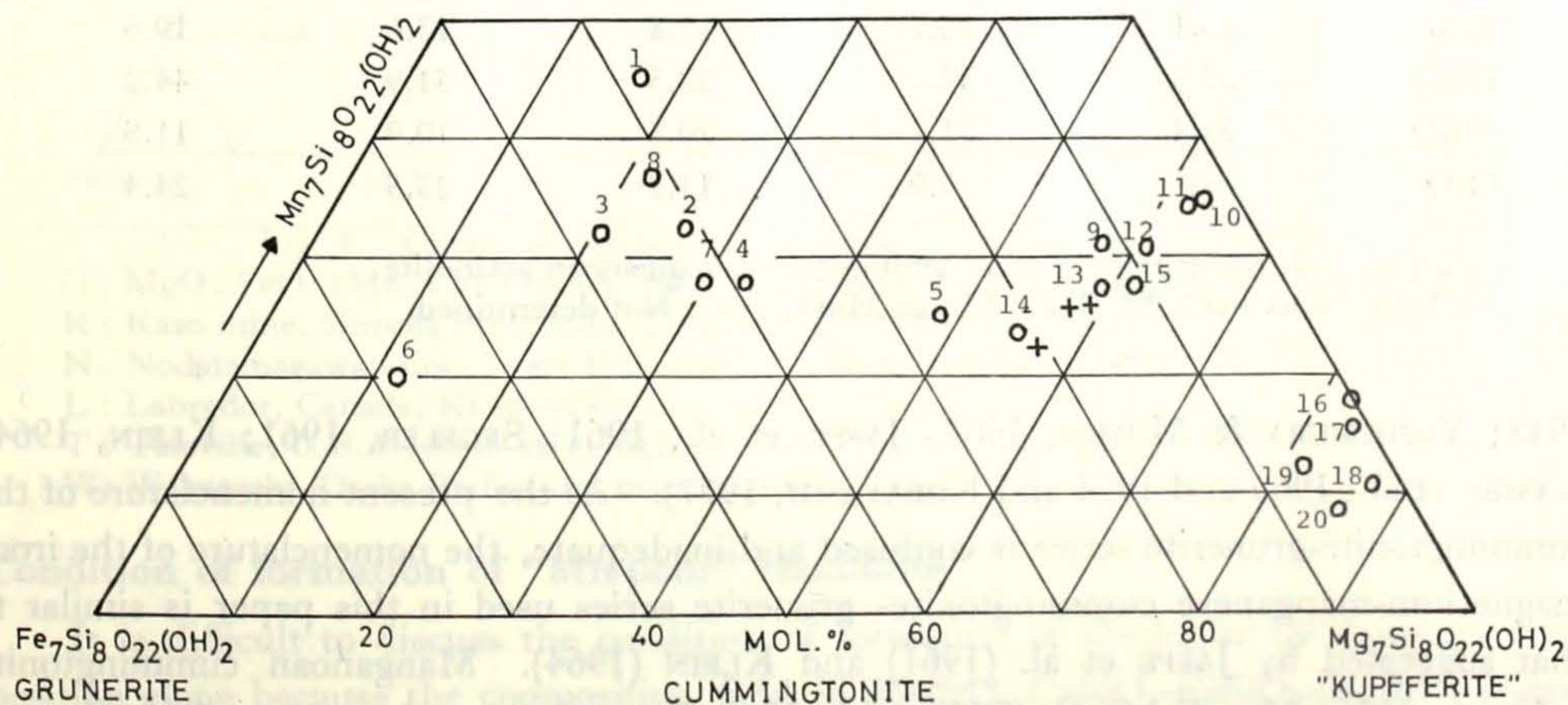

Fig. 3. Chemical composition of manganoan grunerite-cummingtonite. The given data are selected menbers containing more than 20 mol. % of Mn-compornent and magnesium-rich members.
Manganoan grunerite-cummingtonite cited from the literatures. 1-4, YOSHI-MURA (1952); 5, YOSHIMURA and MOMOI (1961); 6, SUNDIUS (1924); 7, BAUR and BERMAN (1930); 8, NAMBU et al. (1973); 9, NAMBU et al. (1969); 10, JAFFE et al. (1961); 11, KOBAYASHI (1977); 12-14, KLEIN (1964); 15, RABBITT (1948); 16-17, SEGELER (1961); 18-20, BILGRAMI (1956); +, present study.

Table 2.　Chemical analyses of manganoan cummingtonite and manganoan actinolite from Wakagashi.

	1	2	3	4	5
SiO_2	52.71	54.21	54.49	54.41	54.45
TiO_2	0.04	0.04	0.04	0.04	
Al_2O_3	0.14	0.14	0.12	0.15	0.14
FeO*	9.24	8.94	9.75	7.64	11.22
MnO**	13.25	12.23	11.14	6.05	6.66
MgO	17.13	16.82	15.55	16.28	14.15
CaO	3.17	4.40	4.78	10.25	10.86
Na_2O					0.04
Total	95.68	96.78	95.87	94.82	97.52
Numbers of ions on the basis of 22(O)					
Si	7.893	7.975	8.079	8.027	7.980
Al	0.024	0.025	0.021	0.026	0.024
Ti	0.004	0.004	0.004	0.005	
Fe^{+2}	1.157	1.100	1.209	0.942	1.375
Mn^+	1.681	1.523	1.398	0.755	0.827
Mg	3.822	3.688	3.437	3.580	3.091
Ca	0.509	0.693	0.759	1.620	1.705
Na					0.012
Molecular ratio FeO: MgO: MnO: CaO					
FeO	16.1	15.7	17.8	13.6	19.6
MgO	53.3	52.7	50.5	51.9	44.2
MnO	23.4	31.7	20.5	10.9	11.8
CaO	7.1	9.9	11.2	23.5	24.4

Analyses 1–3, manganoan cummingtonite; 4–5, manganoan actinolite.
*: Total Fe as FeO, **: Total Mn as MnO, ——: Not determined.

1948; YOSHIMURA & MOMOI, 1961; JAFFE et al., 1961; SEGELER, 1961; KLEIN, 1964; NAMBU et al., 1969 and 1974 and KOBAYASHI, 1977).　As the present nomenclature of the cummingtonite-grunerite series is confused and inadequate, the nomenclature of the iron-magnesium-manganese cummingtonite- grunerite series used in this paper is similar to that suggested by JAFFE et al. (1961) and KLEIN (1964).　Manganoan cummingtonite refers to $(Mg, Mn, Fe)_7Si_8O_{22}(OH)_2$ with $Mg > Fe$ and more than 10 mol.% of manganoan component.　Cummingtonite is usually low in the content of CaO, however, manganoan cummingtonite from Wakagashi contains various and considerable amount of CaO.

Manganoan actinolite

Manganoan actinolite occurs as a fibrous aggregate, and may be an alteration product

of rhodonite. Its colour is pale-green and the fibrous crystal is about 10 mm in length. Unit cell dimensions and specific gravity could not be obtained because of the fibrous aggregate intimately associated with manganoan cummingtonite. The optical properties are as follow;

$$\alpha=1.6440, \; \beta=\text{not determined}, \; \gamma=1.6643, \; 2V=84°(82°-86°).$$

The chemical compositions are listed in Table 2, and shown in Fig. 4 together with those reported by YOSHIMURA (1939), TANIDA et al. (1968), KLEIN (1966) and SEGELER (1961). Manganoan actinolite from Wakagashi is the richest in the Mg content. Manganoan actinolite from the high grade metamorphosed manganiferous sediment at Labrador by KLEIN (1966) is slightly richer in the Mg content than that of Wakagashi, but is far less in the Mn content than the latter (see Fig. 4). This fact may show that manganoan actinolite containing more than 5 wt.% of MnO from Wakagashi is the richest member in the Mg content for the tremolite-actinolite series.
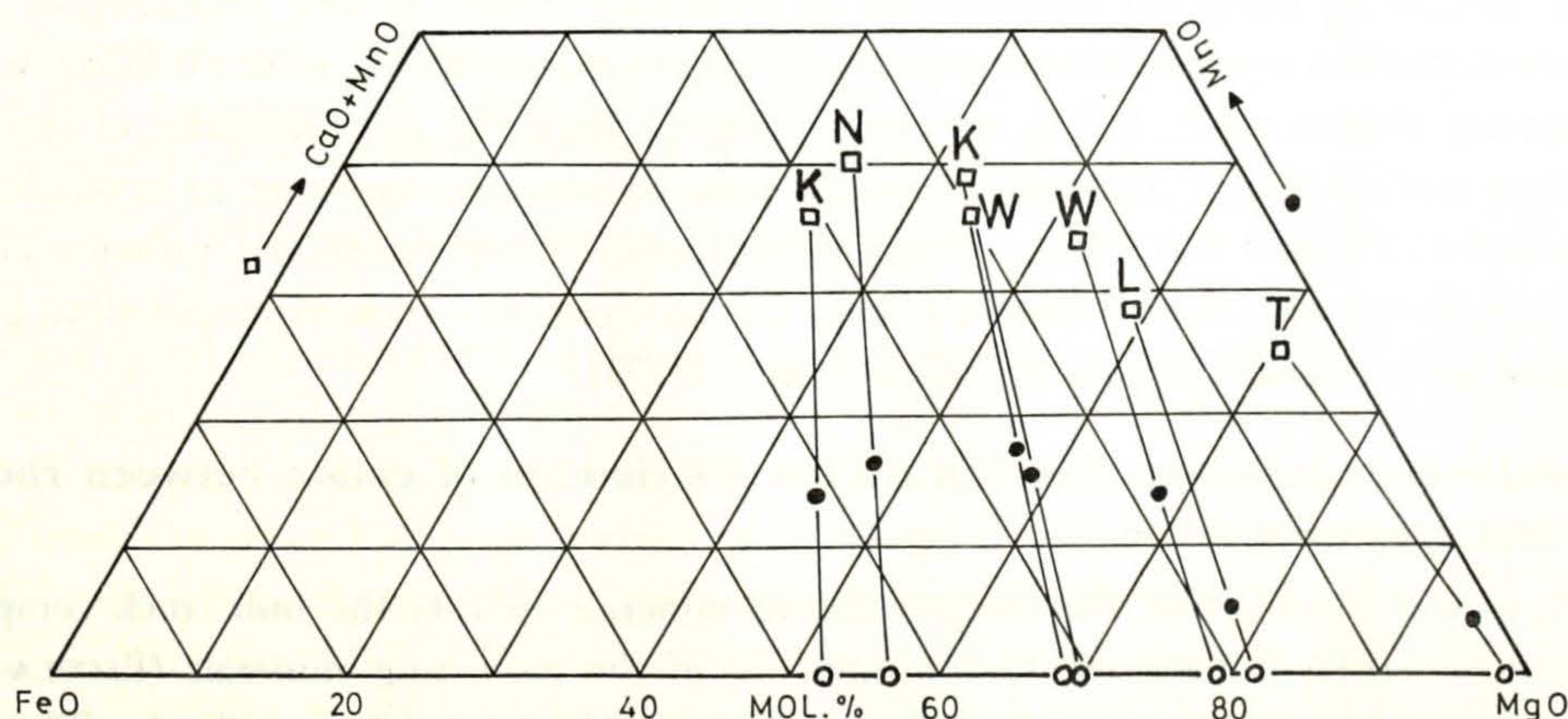

Fig. 4. Chemical composition of manganoan tremolite-actinolite.
□ ; MgO: FeO: (Mn, Ca)O ratios. ● ; MgO: FeO: MnO ratios. ○ ; Mg/(Fe+Mg).
K : Kaso mine, Gunma Prefecture, YOSHIMURA (1939).
N : Nodatamagawa mine, Iwate Prefecture, TANIDA et al. (1978).
L : Labrador, Canada, KLEIN (1966).
T : Talcville, U.S.A., SEGELER (1961).
W: Wakagashi, Osaka Prefecture, present study.

Condition of formation of "Mn-poor" rhodonite

It is difficult to discuss the condition of formation of rhodonite by using its composition alone because the composition field in $MnSiO_3$-$CaSiO_3$-$FeSiO_3$-$MgSiO_3$ system is considerably large (MOMOI, 1964). However, among a number of studies of the Mn-poor rhodonite in the past, those reports by SUNDIUS (1931a), HENDERSON and GLASS (1936), HIETANEN (1938), RUSSEL (1946), BILGRAMI (1956) and MASON (1973) suggest that the Mn-poor rhodonite formed at a high temperature and under a high pressure. The reports by YOSHIMURA (1938), MOMOI (1964), NAMBU et al. (1978), etc. in Japan also indicate that the Mn-poor rhodonite formed at a high temperature and under a "high

pressure". These facts are supported by the synthetic expriments in the system $CaSiO_3$-$MnSiO_3$-$FeSiO_3$-$MgSiO_3$ (ITO, 1972a and b; MOMOI, 1973; RIBOUD and MUAN, 9164). According to the results of their experiments, rhodonite-pyroxmangite-clinopyroxene-olivine-quartz-Mn-cummingtonite-talc appear depending on the temperature and with decreasing order of Mn content, and rhodonite stable region expanded toward Fe^{2+} and Mg^{2+} side with rising temperature. The Wakagashi rhodonite contains about 11–14 mol.% of $MgSiO_3$ which is near the maximum content of $MgSiO_3$, and it also contains about 25 mol.% or more of $(Fe,Mg)SiO_3$ which is the maximum content in natural rhodonite (see Fig. 2). MOMOI (1973) discussed the Mg content of the natural rhodonite and pyroxmangite. Pyroxmangite is generally regarded as a low temperature polymorph of rhodonite, and its structure favours Fe^{2+} and Mg^{2+} in comparison with the rhodonite structure. According to MOMOI (1973), pyroxmangite containing about 11–12 mol.% of $MgSiO_3$ from the Taguchi mine and from the Kinko mine formed at more than 550°C and under 2 Kbar. Mason also discussed the crystallization of the Broken Hill manganese silicate by using the composition of coexisting bustamite and hebenbergite, and estimated that the equilibrium temperature is approximately 650°C under 6 Kbar, which is arbitrary chosen value, but is reasonable judging from the characteristics of the surrounding rocks. The Wakagashi rhodonite may be strongly surmised to crystallize at about 550–650°C and 2–6 Kbar. These crystallization temperature and pressure are in good agreement with those estimated from the metamorphic rock of amphibolite grade by using garnet-cordierite pair at Takato (ONO, 1977a).

Crystallo-chemical consideration on the distribution of cation between rhodonite and spessartine

It is well known that the composition of minerals reflects the bulk rock composition, and is strongly subjected to the influence of the coexisting minerals (ESCOLA and KERVINEN, 1936; MIYASHIRO, 1953; KRETZ, 1978 and many other studies). There is spessartine as a primary mineral associated with rhodonite at Wakagashi. The partition of the cations, i.e. Ca^{2+}, Mn^{2+}, Fe^{2+} and Mg^{2+} between rhodonite and spessartine is of interest. Especially, MIYASHIRO (1953) discussed the distribution of Mn^{2+}, Fe^{2+} and Mg^{2+} in garnet (pyralspite) and associated minerals on the basis of the crystal chemistry. Each of the Mn^{2+}, Fe^{2+} and Mg^{2+} ion in pyralspite is surrounding by eight O^{2-} ions. An eight coordination position in the crystal structure may be appropriate for such large ions as Ca^{2+} and Mn^{2+} to enter, but is less appropriate for such smaller ions as Fe^{2+} and especially Mg^{2+}. The ordinary coordination number of Fe^{2+} and Mg^{2+} ions is six. Thus, the concentration of Mn^{2+} and also Ca^{2+} in pyralspite is a strong tendency in all case. It suggests that the pyralspite structure favours Mn^{2+} and also Ca^{2+} in comparison with Fe^{2+} and Mg^{2+} for the crystallo-chemical consideration. On the other hand, there are one seven-coordination position and four six-coordination positions in the rhodonite structure (PEACOR and NIIZEKI, 1963). Therefore, Fe^{2+} and especially Mg^{2+} may preferentially enter into the rhodonite structure, and Ca^{2+} favours with spessartine, but also favours with rhodonite on the basis of crystallo-chemical reason. MASON (1973)
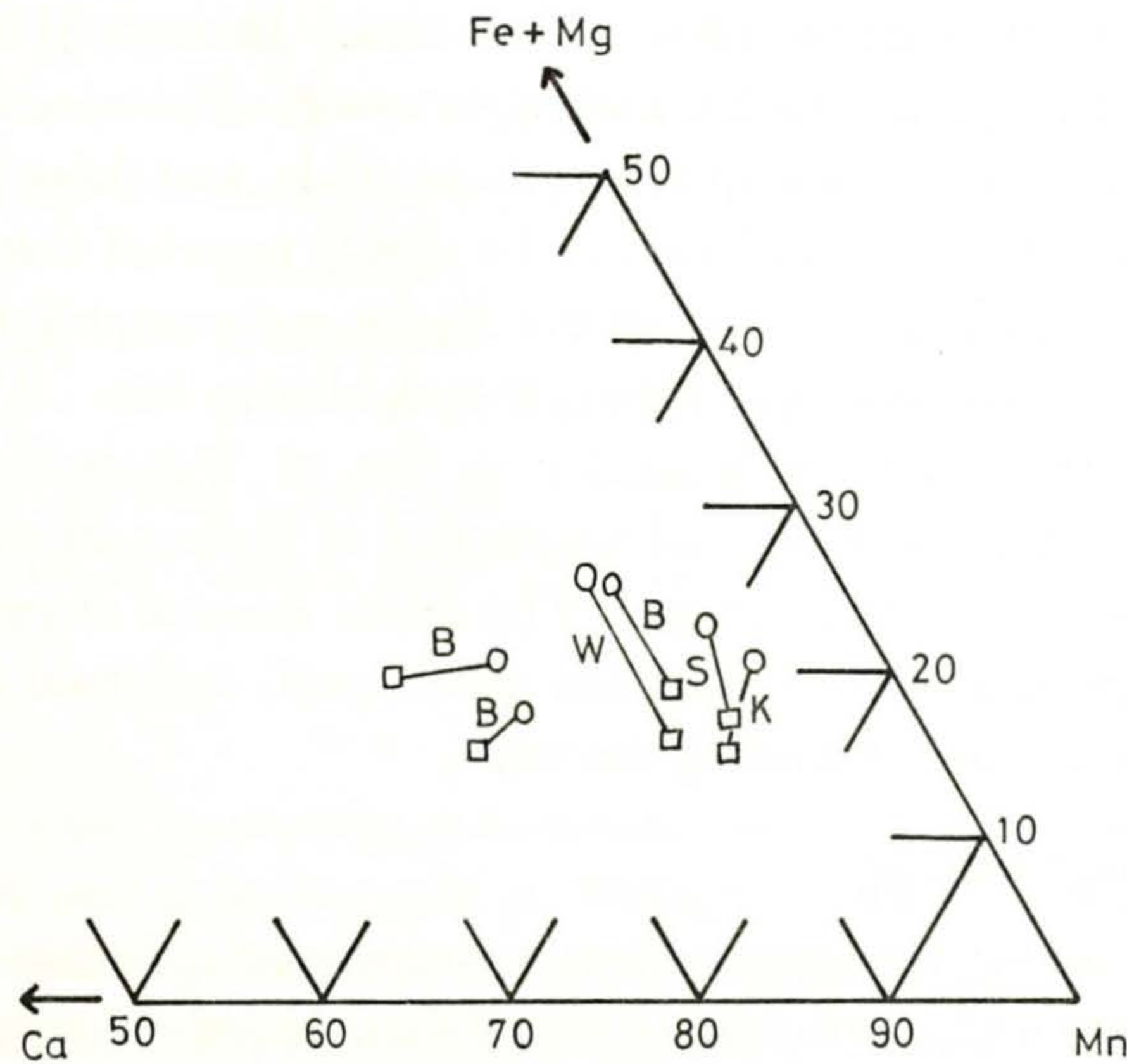
Fig. 5. Ca: (Fe+Mg): Mn ratios (atomic) in coexisting garnet (□) and rhodonite (○).
   B : Broken Hill, Australia, MASON (1973).
   S : Simsio, Finland, HIETANEN (1938).
   K : Kaso mine, Gunma Prefecture, YOSHIMURA (1939).
   W: Wakagashi, Osaka Prefecture, present study.

suggested that the spessartine in equilibrium with rhodonite has similar Ca : Mn : Fe ratios. The compositions of the coexisting rhodonite and spessartine from four localities are plotted in Fig. 5. The compositions from Wakagashi can not be directly compared with those from the other loaclitites because of the large different amount of Mg. Mg^{2+} is smaller ionic radius, therefore it will play a similar crystallo-chemical role with Fe^{2+} which is also smaller than Mn^{2+}. The tie lines between rhodonite and spessartine locate similar positions in the Ca-Mn-(Fe, Mg) diagram except for the Ca content. The difference of the length of tie lines mainly depends on the concentration of Fe and especially of Mg in rhodonite. These facts concerning the distribution of Ca^{2+}, Mn^{2+}, Fe^{2+} and Mg^{2+} show in good agreement with the requirment from the crystallo-chemical reason. Therefore, the result may show that the rhodonite and spessartine of Wakagashi have crystallized in equilibrium.

Stability of spessartine

The compositional field of pyralspite may become larger from compositional rich in Mn^{2+}, to those rich in Fe^{2+} and further to those rich in Mg^{2+}, with increase in pressure. Especially MnO content of garnet is considered to be sensitive to change in pressure (MIYASHIRO, 1953). However, TILLEY (1938) and HIETANEN (1967 and 1943) suggested that the almamdine and spessartine garnets may crystallize from suitable composition of rock at high grade. BLOXAM (1959) and JUNNER (1927) reported that spessartine as a stable mineral has formed in metachert associated with gloucophene schists and in manganiferous rock associated with kyanite schists respectively, and those spessartines contain

about 5 mol.% of pyrope component in eithre case. HUTTON (1957) and HIETANEN (1938) also reported that spessartine has formed in manganiferous schist and in manganiferous part associated with schistose quartzite respectively, and those pyrope components were about 1 mol.%. On the other hand, SUWA (1961) reported that the rhodonite and spessartine from the highest grade part of the Ryoke metamorphic rock in the Mitsue area, Nara Prefecture, occur only in psammitic rock rich in Mn. The mode of occurrence from Mitsue seems to be very similar to that of Wakagashi. These examples strongly suggested that the rhodonite and spessartine of Wakagashi stably occur in manganiferous part in the surrounding gneiss. The minor amount of pyrope component in spessartine of Wakagashi and other localities can be well explained by the distribution of cations between garnet and coexisting minerals.
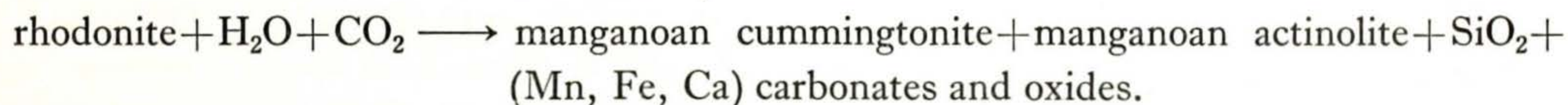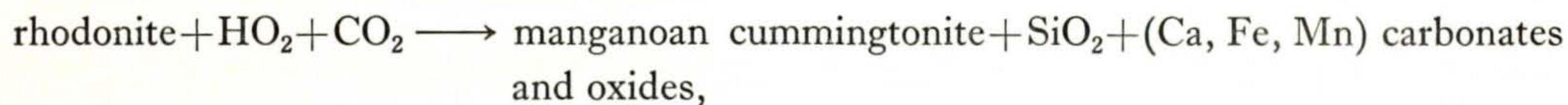
Absence of chemical zoning

Garnets in the surrounding gneiss show a characteristic chemical zoning similar to those from the Takato and Hazu areas (ONO, 1976). However, spessartine associated with rhodonite does not show compositional changes. Why was compositional change absent, nevertheless spessartine would have formed under the same condition with the surrounding gneiss? It may be explained by the bulk rock composition and crystallo-chemical consideration. The distribution of elements between rhodonite and spessartine would be controlled by the crystallo-chemical rule. In the manganiferous part in which spassartine has formed, the manganese supply would be sufficient during the growth. Therefore, spessartine may imply the maximum content of Mn^{2+} under a certain physical condition. The relatively small amount of Ca^{2+}, Fe^{2+} and Mg^{2+} will distribute between rhodonite and spessartine in conformity with the crystallo-chemical rule as has been stated, and may not exert a strong influence upon the chemical zoning. Furthermore, the period of the garnet growth may be short because of the small crystal size and the somewhat rounded crystal surface. Therefore the change of physical condition may be small. It is surmised that these things stated above result in the absence of chemical zoning in spessartine.

The formation of manganoan amphiboles

Under the microscope, it is clear that manganoan cummingtonite and manganoan actinolite formed after the crystallization of the rhodonite and spessartine. However, among the number of studies, those reports by SUNDIUS (1924, 1931b), YOSHIMURA (1938), YOSHIMURA and MOMOI (1961), KLEIN (1964, 1966) and KOBAYASHI (1977) suggest that manganoan amphiboles especially manganoan cummingtonite intimately intergrown with rhodonite is considered to form at a high temperature during theretrograde metamorphism or the high temperature contact metamorphism due to the younger granite. Judging from the character of quartz in gneiss and in rock containing manganese minerals, manganese amphiboles from Wakagashi are considered to be formed by the action of water during the retrograde metamorphism. They would be formed by the following reaction

for the formation of manganoan cummingtonite intergrown with rhodonite and of manganoan amphiboles occurred as fibrous aggregate respectively,

$$rhodonite + HO_2 + CO_2 \longrightarrow manganoan\ cummingtonite + SiO_2 + (Ca, Fe, Mn)\ carbonates$$
$$and\ oxides,$$

$$rhodonite + H_2O + CO_2 \longrightarrow manganoan\ cummingtonite + manganoan\ actinolite + SiO_2 +$$
$$(Mn, Fe, Ca)\ carbonates\ and\ oxides.$$

where (Ca, Fe, Mn) carbonates and oxides and (Mn, Fe, Ca) carbonates and oxides were qualitatively confirmed by electron probe microanalyser.

Summary

We found rhodonite, spessartine, manganoan cummingtonite and manganoan actinolite from the Ryoke metamorphic rock at Wakagashi, Osaka Prefecture. The optical properties, unit cell dimensions and specific gravity were measured and calculated. Chemical analysis of these four minerals have been made by means of electron probe microanalyser. Each of minerals except for spessartine is magnesium rich member. Rhodonite from Wakagashi contains from 11 to 14 mol.% of $MgSiO_3$ equivalent to magnesium rhodonite from Langban (SUNDIUS, 1931), and the contents of Mg and $(Fe, Mg)SiO_3$ are virtually maximum in the natural rhodonite. Manganoan actinolite containing 5 wt.% MnO is the richest member in the Mg content among the tremolite-actinolite series. Special attention is drown to some clue to the genesis of rhodonite and spessartine as a primary mineral in the manganese rich part in gneiss. It was clarified that the rhodonite and spessartine had formed in equilibrium and under the same physical condition with the surrounding gneiss on the basis of the Mg and also (Fe, Mg) contents in rhodonite and of the partition of Ca^{2+}, Mn^{2+}, Fe^{2+} and Mg^{2+} between rhodonite and spessartine. Spessartine stably occurs at high grade metamorphism when the bulk rock composition and coexisting minerals are suitable. The absence of chemical zoning in spessartine associated with rhodonite was explained by the crystallo-chemical reason and by the sufficient supply of manganese during the growth. Manganoan amphiboles would be formed in replacement of a part of rhodonite during retrograde metamorphism after the crystallization of rhodonite and spessartine.

Acknowledgements

References

Bauer, L.H. and Berman, H. (1930):   Note on some Franklin minerals. *Amer. Mineral.*, **15**, p. 340–348.

Bilgrami, S.A. (1955):   Manganese amphiboles from Chikla, Bhandara district, India. *Min. Mag.*, **30**, p. 633–644.

Bilgrami, S.A. (1956):   Manganese silicate minerals from Chikla, Bhandara district, India. *Min. Mag.*, **31**, p. 236–244.

Bloxam, T.W. (1959):   Glaucophene-schists and associated rocks near Valley Ford, California. *Amer. Jour. Sci.*, **257**, p. 95–112.

Deer, W.A., R.A. Howie and J. Zussmann (1963):   *Rock forming minerals.* Vol. 2, *Chain silicates.* Longmanns.

Dunn, J.A. and P.C. Roy (1938):   Tirodite, a new mineral. *Rec. Geol. Surv. India,* **73**, p. 295–298.

Escola, P. and T. Kervinen (1936):   A paragenesis of gedrite and cummingtonite from Isopää in Kolvala, Finland. *Compt. Rendu Soc. Geol. de Finlande.* no. 9 p. 475. cited from Tilley (1938)

Harada, J. (1933):   Some minerals of Japan. (2) Rhodonite (in Japanese). *Jour. Geol. Soc. Japan,* **40**, p. 342–343.

Henderson, E.P. and Glass, J.J. (1936):   Pyroxmangite, new locality: identity of sobralite and pyroxmangite. *Amer. Mineral.*, **21**, p. 273–294.

Hey, M.H. (1929):   The variation of optical properties with chemical composition in the rhodonite-bustamite series. *Min. Mag.*, **22**, p. 193–205.

Hietanen, A. (1938):   On the petrology of Finnish quartzite. *Bull. Comm. Géol. Finlande,* **21**, no. 122.

Hietanen, A. (1943):   Über das Grundgebirge des Kalantigebietes im südwestlichen Finnland. *Acad. Sci. Fennicae Annales,* ser. A, III, Geol., **6**, p. 1–105.

Hietanen, A. (1967):   On the facies in various types of metamorphism. *Jour. Geol.,* **75**, p. 187–214.

Hirowatari, F. (1968):   Distribution of the manganese ore deposits in Paleozoic Formation of Japan. *Mem. Geol. Soc. Japan,* **1**, p. 33–40.

Hutton, C.O. (1957):   Contributions of the mineralogy of New Zealand, Part IV. *Trans. Roy. Soc. New Zealand,* **84**, p. 182.

Jaffe, H.W., W.O.J.G. Meijer and D.H. Selchow (1961):   Manganoan cummingtonite from Nsuta, Ghana. *Amer. Mineral.*, **46**, p. 642–653.

Junner, N.R. (1927):   *Trans. Amer. Mining Metall. Engin.,* **75**, p. 385–395. cited from Miyashiro (1953).

Ito, J. (1972a):   Synthesis and crystal chemistry of Li-hydro-pyroxenoids. *Mineral. J.* (Tokyo), **7**, p. 45–65.

Ito, J. (1972b):   Rhodonite-pyroxmangite pelitectic along the join $MnSiO_3$–$MgSiO_3$ in air. *Amer. Mineral.*, **57**, p. 865–876.

Kitahara, J. (1948):   Mineralization of manganese in the Hamayokohama mine, Nagano Prefecture (in Japanese). *Jour. Geol. Soc. Japan,* **54**, p. 181–183.

Klein, C. (1964):   Cummingtonite-grunerite series: A chemical, optical and x-ray study. *Amer. Mineral.*, **49**, p. 963–982.

Klein, C. (1966):   Mineralogy and petrology of the metamorphosed Wabush Iron Formation, southwestern Labrador. *Jour. Petrol.,* **7**, p. 246–305.

Kobayashi, H. (1977):   Kanoite (Mn^{2+}, Mg) $[Si_2O_6]$, a new clinopyroxene in the metamorphic rock from Tatehira, Oshima Peninsula, Hokkaido, Japan. *Jour. Geol. Soc. Japan,* **83**, p. 537–542.

Kretz, R. (1978):   Distribution of Mg, Fe^{2+}, and Mn in some calcic pyroxene-hornblende-biotite-garnet gneisses and amphobolites from the Grenville Province *Jour. Geol.,* **86**, p. 599–619.

Masaoka, K. and the Research Group for the Ryoke belt (1978):   Geology of the Ryoke belt in the southern part of Osaka Prefecture, Japan (in Japanese). *Geol. Soc. Japan,* Abstracts 85th Ann. Meeting, Tokyo, p. 319.

Mason, B. (1973):   Manganese silicate minerals from Broken Hill, New South Wales. *Jour. Geol. Soc. Australia,* **20**, Pt. 4, p. 397–404.

MIYASHIRO, A. (1953): Calcium-poor garnet in relation to metamorphism. *Geochim. Cosmochim. Acta*, **4**, p. 179–208.

MOMOI, H. (1964): Mineralogical study of rhodonites in Japan, with special reference to contact metamorphism. *Mem. Fac. Sci. Kyushu Univ.* Ser. D, Geol., **15**, p. 39–63.

MOMOI, H. (1973): Some problems of the natural and synthetic proxenoids along the join $MnSiO_2$–$MgSiO_2$ (in Japanese *Mem. Fac. Sci. Kyushu Univ.*, Geol., **11**, p. 251–256.

NAKAMURA, Y. and I. KUSHIRO (1970): Compositional relation of coexisting orthopyroxene, pigeonite and augite in a tholeiitic andesite from Hakone volcano. *Contri. Mineral. Petrol.*, **26**, p. 265–275.

NAMBU, M., K. TANIDA and T. KITAMURA (1969): Mineralogical study of manganese silicate ore in northeasthern Japan. (5) Manganoan cummingtonite from Nodatamagawa mine, Iwate Prefecture (in Japanese with English abstract). *Bull. Res. Inst. Mineral Dress. Metall., Tohoku Univ.*, **25**, p. 21–33.

NAMUBU, M., K. TANIDA and T. KITAMURA (1974): Mineralogical study of manganese silicate ore in northeastern Japan. (16) Manganoan grunerite from Moichi mine, Iwate Prefecture (in Japanese with English abstract). *Bull. Res. Inst. Mineral Dress. Metall., Tohoku Univ.*, **30**, p. 69–78.

NAMBU, M., K. TANIDA and T. KITAMURA (1978): Mineralogical study of manganese silicate ore in northeastern Japan. (20) Rhodonite from Hijikuzu mine, Iwate Prefecture (in Japanese with English abstract). *Bull. Res. Inst. Mineral Dress. Metall., Tohoku Univ.*, **32**, p. 93–108.

ONO, A. (1976): Crystal growth and zoning of garnet from the Ryoke metamorphic rocks of central Japan. *J. Japan Assoc. Min. Petr. Econ. Geol.*, **71**, p. 114–117.

ONO, A. (1977a): Temperature and pressure of the Ryoke gneiss estimated by garnet-cordierite geothermometer. *J. Japar. Assoc. Min. Petr. Econ. Geol.*, **71**, p. 308–325.

ONO, A. (1977b): Petrologic study of the Ryoke metamorphic rocks in the Takato Shiojiri area, central Japan (in Japanese with English abstract). *J. Japan Assoc. Min. Petr. Econ Geol.*, **72**, p. 453–468.

PEACOR, D.R. and N. NIIZEKI (1963): The determination and refinement of the crystal structure of rhodonite, (Mn, Ca) SiO_3. *Z. Kristallogr.*, **119**, p. 98–116.

RABBITT, J.C. (1948): A new study of the anthophyllite series. *Amer. Mineral.*, **33**, p. 263–323.

RIBOUD, P.V. and A. MUAN (1962): Phase equilibrium in a part of the system "FeO"-MnO-SiO_2. *Trans. AIME*, **224**, p. 27–33.

RUSSEL, A. (1946): On rhodonite and tephroite from Treburland manganese mine, Altartum, Cornwall: and on rhodonite from other localities in Cornwall and Devonshire. *Min. Mag.*, **27**, p. 221–235.

SEGELER, C.G. (1961): First U.S. occurrence of manganoan cummingtonite, Tirodite. *Amer. Mineral.*, **46**, p. 637–641.

SUNDIUS, N. (1924): Zur Kenntnis der monoklinen Ca-armen amphibole (Grünerie-Cummingtonite reihe). *Geol. För. Förh Stockholm*, **46**, p. 154–167.

SUNDIUS, N. (1931a): On the triclinic manganiferous pyroxenes. *Amer. Mineral.*, **16**, p. 411–429 and p. 488–518.

SUNDIUS, N. (1931b): The optical properties of manganese-poor grunerites and cummingtonites compared with those of manganiferous menbers. *Amer. Jour. Sci.*, **21**, p. 303–334.

SUWA, K. (1961): Petrogical and geological studies on the Ryoke metamorphic belt. *Jour. Earth Sci. Nagoya Univ.*, **9**, p. 224–303.

TANIDA, K., M. NAMBU and T. KITAMURA (1978): Manganoan amphiboles from Nodatamagawa mine, Iwate Prefecture (abstract in Japanese). *J. Japan Assoc. Min. Petr. Econ. Geol.*, **73**, p. 89–90.

TILLEY, C.E. (1936): Cummingtonite-bearing rocks from the Lewisian. *Geol. Mag.*, **75**, p. 76–81.

YAMADA, T., H. KAGAMI, T. KUTSUKAKE, S. MAENO, K. MASAOKA, Y. HAYAMA and M. YOSHIDA (1979): Geology of the Ryoke belt in the Sennan district, Osaka Prefecture, Japan. (in Japanese with English abstract) Mem. Geol. Soc. Japan, (in press).

YOSHIMURA, T. (1939): Studies on the minerals from the manganese deposit of the Kaso mine, Japan. *Jour. Fac. Sci. Imp. Hokkaido Univ.*, Ser. 4, 4, p. 313–451.

YOSHIMURA, T. (1952): *Manganese ore deposits of Japan* (in Japanese). Shuko-sha Co., p. 567.

YOSHIMURA, T. and H. MOMOI (1961): Dannemorite from Zomeki, Yamaguchi Prefecture, Japan (in Japanese). *Jour. Fac. Sci. Kyushu Univ.*, Ser. D, Geol., 5, p. 99–109.

YOSHIMURA, T. (1967): Manganese ore deposits of Japan (in Japanese). *Sci. Rep. Fac. Sci. Kyushu Univ.*, Geol. 9, Spec. Issue 1, p. 485.

Plate 1

Explanation of Plate 1

Fig. 1. Rhodonite-spessartine-quartz-manganoan amphiboles assemblage. Polirized light.

Fig. 2. Same view in crossed nicols. Note the strong undulatory extinction of quartz.
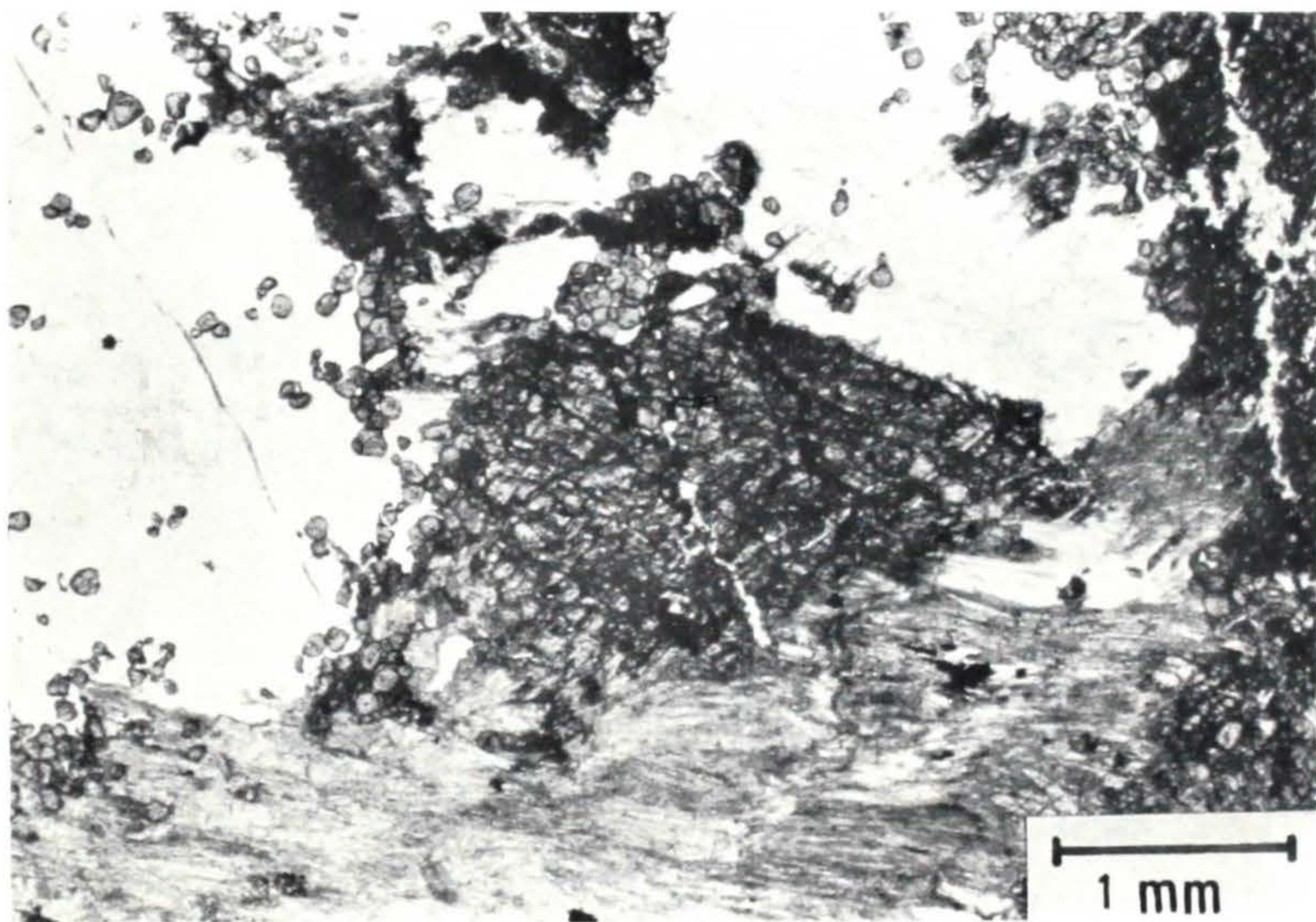
Fig. 1

Fig. 2

Plate 2

20

Explanation of Plate 2

Fig. 1. Photomicrograph showing the intimate intergrowth of rhodonite (grey part) and manganoan cummingtonite (light part). Dark interstitial materials are carboneceous and oxidized matters. Crossed nicols.

Fig. 2. Rhodonite-spessartine-sphene assemblage. Polirized light. Note the euhedral spessartine and its rounded crystal surface.
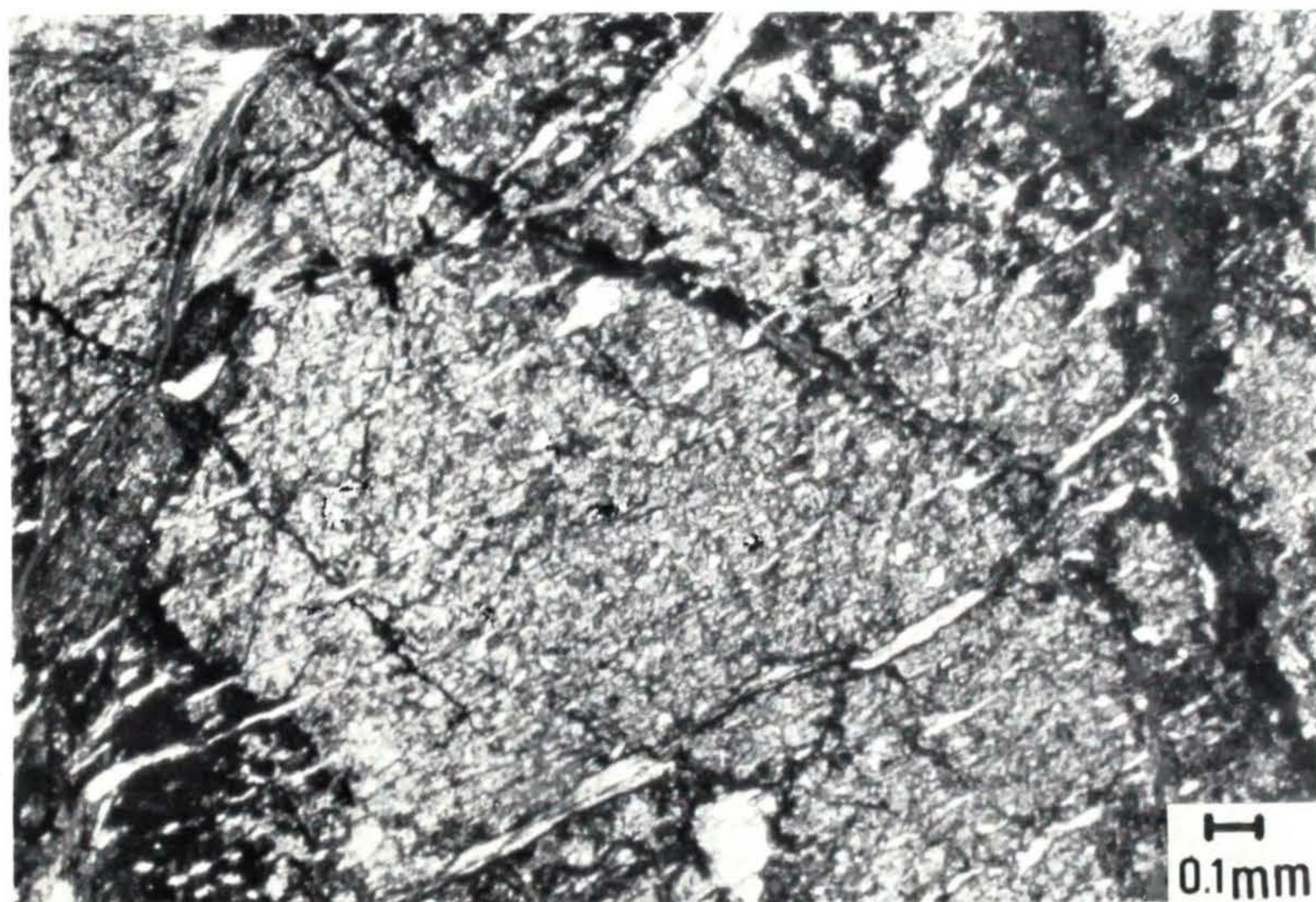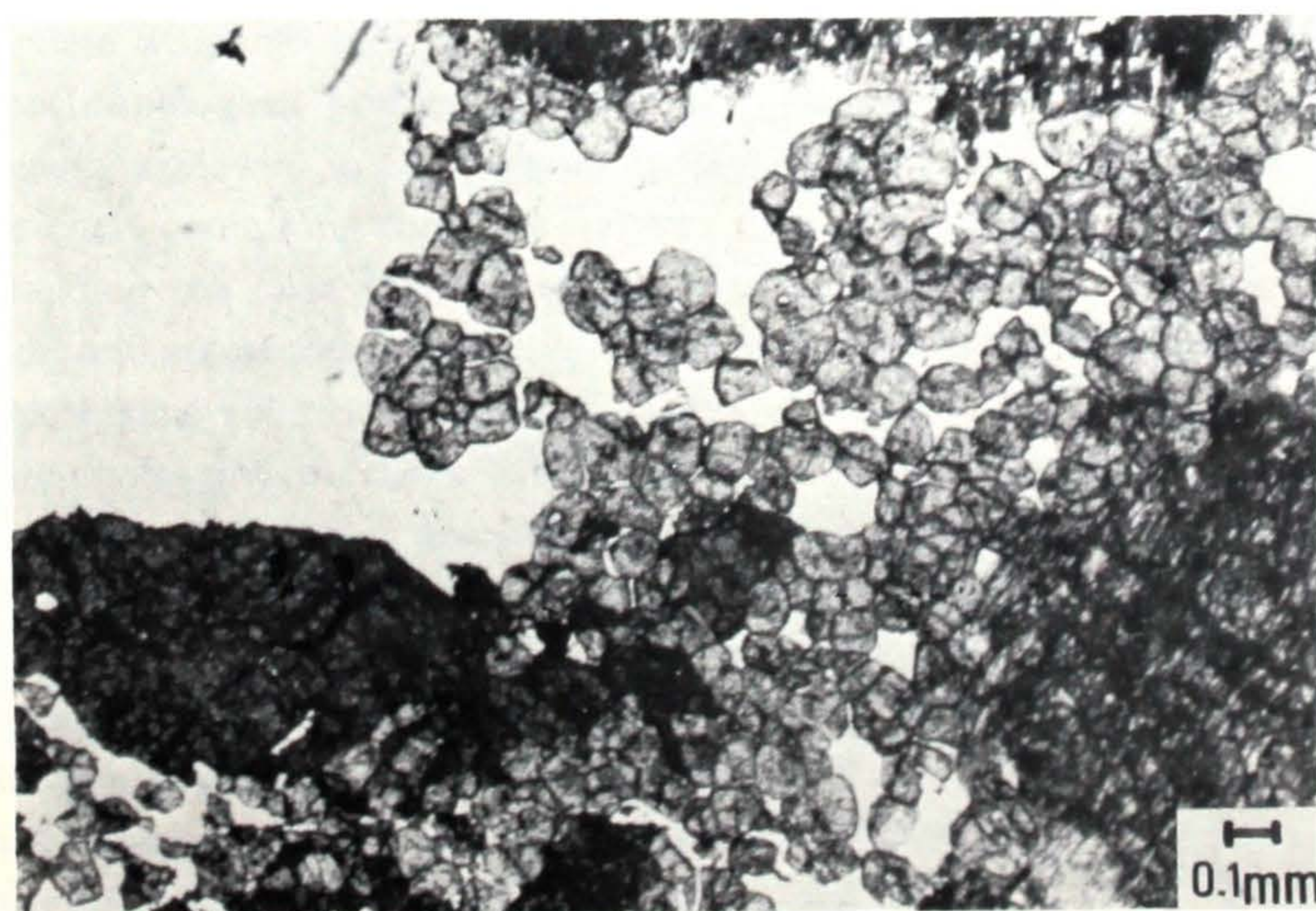
Fig. 1

Fig. 2