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Zoisite-clinozoisite relations in low- to medium-grade high-pressure metamorphic rocks and their implications

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SUMMARY. Coexisting zoisite and clinozoisite in seventeen specimens from six localities in Japan have been studied with the electron-probe microanalyser. Zoisite and clinozoisite are commonly zoned, but compositional gaps between them are systematic. Referring to the metamorphic grade of the host rocks, a temporary and schematic phase-diagram for the system $Ca_2Al_3Si_3O_{12}$-(OH)-$Ca_2Al_2Fe^{3+}Si_3O_{12}$(OH) is presented. With increasing temperature, in the range of low- to medium-grade metamorphism, the compositional gap between the two epidote-group minerals shifts towards higher Fe^{3+} compositions.

EPIDOTE-GROUP minerals with the general formula $Ca_2(Al,Fe^{3+})_3Si_3O_{12}(OH)$ have two series of solid solutions, zoisite and clinozoisite-pistacite. The chemical compositions of coexisting zoisite and clinozoisite have been reported by many authors (Banno, 1964; Myer, 1966; Ackermand and Raase, 1973; Hietanen, 1974; Raith, 1976), but their stability relations are insufficiently understood. There are two opposite views on which of zoisite and clinozoisite is the higher-temperature phase. Banno (1964), Holdaway (1972), and Raith (1976) favoured the view that zoisite is the higher-temperature phase and hence the compositional gap between zoisite and clinozoisite shifts towards the Fe^{3+}-rich region with increasing temperature, whereas Ackermand and Raase (1973) considered the opposite to be true. Because of the difficulty of the direct determination of the phase relations by synthetic experiments, petrographic data have to be fully used to solve this problem. We have studied the compositional gap between zoisite and clinozoisite in specimens collected at six localities in Japan (Iratsu, Tonaru, Fujiwara, Nishisonogi, Yoshimi, and Omi). The results mainly based on electron-probe microanalysis of coexisting zoisite and clinozoisite are described below, with our view on the temperature-dependence of the gap in the temperature range of low- to medium-grade metamorphism of high-pressure intermediate type.

Mode of occurrence of coexisting zoisite and clinozoisite

Fig. 1 shows specimens localities. Brief accounts of the geology and petrology of these areas and the mode of occurrence of coexisting zoisite and clinozoisite are described below.

Iratsu and Tonaru epidote-amphibolite masses. The Iratsu and Tonaru masses are metamorphosed layered gabbros that occur in the epidote amphibolite-facies area in central Shikoku (Banno *et al.*, 1976; also for general petrology, cf. Ernst *et al.*, 1970 and Banno *et al.*, 1978). This is the highest metamorphic grade areas in the Sanbagawa metamorphic terrain. Main rock-types are epidote amphibolite, garnet-epidote amphibolite, hornblende eclogite, quartz eclogite, bimineralic eclogite, and zoisite rock. The coexistence of zoisite and clinozoisite is common in these masses, and has been found in three rock-types; leucocratic epidote amphibolite, hornblende eclogite, and zoisite rock. In the following these epidote amphibolites are sometimes referred to as metagabbros, but the samples we have studied do not exhibit the textures and mineralogies of metamorphism other than the Sanbagawa event.

In the leucocratic epidote amphibolite the occurrences of zoisite and clinozoisite are classified into three types by texture. In the first type they occur as subhedral grains measuring 50-500 μm. This is

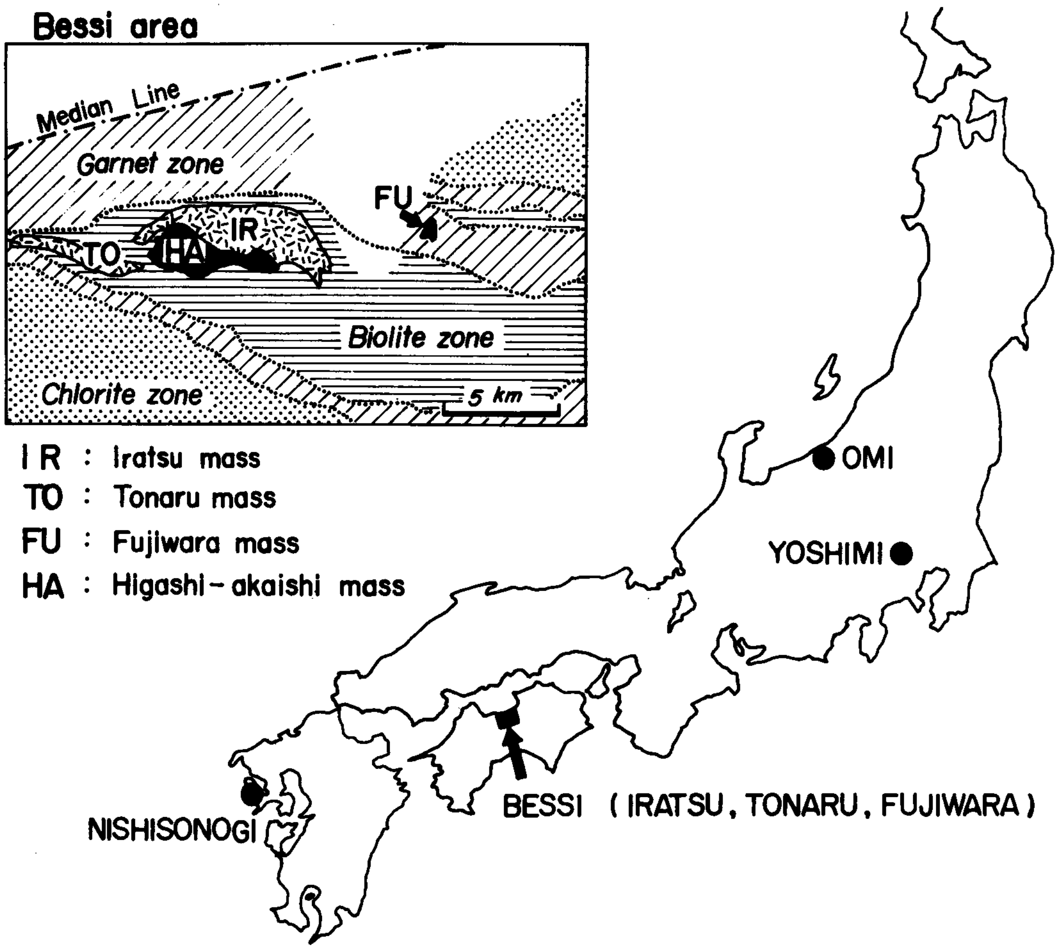

FIG. 1. Localities of the samples investigated in this paper. A metamorphic zone map of the Bessi district is shown in the upper-left of the figure.

the commonest among the zoisite + clinozoisite-bearing specimens we have dealt with. The second type consists of an aggregate of fine-grained (about 20–50 μm), subhedral zoisite and clinozoisite (specimen *ME75042501*). The third type is the intergrowth of zoisite and clinozoisite in a single grain (specimen *ST7055a*).

In hornblende eclogite, clinozoisite is fine-grained (50–100 μm) and subhedral, and occurs in the interstices of large subhedral grains (0.5–1.0 mm) of zoisite.

Zoisite rock is metamorphosed anorthosite, originally forming layers in gabbro, and consists of zoisite-rich leucocratic bands intercalated with hornblende-rich ones. Zoisite is rare in the hornblende-rich band, whereas clinozoisite is rare in the zoisite-rich one, but they coexist at the boundary of two layers, where the zoisite + clinozoisite + hornblende + paragonite + muscovite + quartz assemblage occurs. Paragonite and muscovite are subordinate in amount. In this rock-type, zoisite and clinozoisite are fine-grained, measuring about 40–200 μm. The zoisite and clinozoisite in this rock-type are not in mutual contact but their chemical relation is the same as those found in mutual contact in other specimens.

Fujiwara albite-epidote amphibolite mass. The Fujiwara mass is a complex of ultrabasic and basic rocks (Onuki *et al.*, 1978; Enami, in press). It occurs in the garnet zone of Higashino *et al.* (1977) and Banno *et al.* (1978) of the Sanbagawa terrain in central Shikoku, and is situated about 8 km east of the Iratsu mass, probably belonging to the lower albite-epidote amphibolite facies. Yokoyama

(1976) estimated the equilibration temperature of the mass to be about 350–450 °C on the basis of the antigorite + brucite and epidote + actinolite assemblages.

The coexistence of zoisite and clinozoisite was found in a thin section containing hornblende + clinopyroxene + chlorite + muscovite + zoisite + clinozoisite + albite. Clinopyroxene is a relic from pre-metamorphic assemblage. The clinozoisite is subhedral, is surrounded by aggregates of prismatic zoisite, and is optically homogeneous. Most of the zoisites show sector zoning (Enami, 1977), but some optically homogeneous grains do occur and were used in the analyses.

Metasomatized metagabbro in the Nishisonogi area. The Nishisonogi area is a high-pressure metamorphic terrain located in the western part of the Nagasaki Prefecture, Kyushu. Metagabbros of this area mainly consist of actinolite, chlorite, omphacite, zoisite, clinozoisite, muscovite, paragonite, and albite. Jadeite (but not with quartz) and Na-amphiboles also occur. The associated rocks are inferred to belong to the garnet zone of the Sanbagawa belt, on the basis of common presence of garnet in pelitic schists (Nishiyama, 1978; Nishiyama, pers. comm. 1978).

The coexisting zoisite and clinozoisite were found in banded metagabbros consisting of amphibole-rich and zoisite-rich bands. Their mineral parageneses are tremolite + omphacite + chlorite + muscovite + clinozoisite and zoisite + clinozoisite + chlorite + muscovite + albite, respectively. The zoisite and clinozoisite in the zoisite-rich unit are in mutual contact. Grain sizes are variable ranging from 100 μm to 2 mm.

Metagabbro of the Yoshimi area. This area is located to the east of the Kanto mountains, where a small isolated faulted block of metamorphosed basic and ultrabasic complexes is exposed in an area of Tertiary sediments. Main rock-types are garnet amphibolite, schistose amphibolite, hornblendite, pyroxenite, two-mica gneiss, and serpentinite (Murai, 1968). Yokoyama (1976) has distinguished two stages of recrystallization in this complex, garnet amphibolite and greenschist stages. The constituent minerals formed in the garnet amphibolite stage are hornblende, garnet, clinopyroxene, and plagioclase, and those of the greenschist stage are actinolite, chlorite, zoisite, clinozoisite, and albite.

Zoisite and clinozoisite coexist in garnet amphibolite. The plagioclase, once equilibrated with the garnet and hornblende, now consists of albite and subordinate amounts of fine-grained (about 20–30 μm) zoisite and clinozoisite, which are in mutual contact. The zoisite + clinozoisite assemblage was stable in the second, lower-grade stage.

Metagabbro of the Omi area. The Omi area is located in the southern part of the Niigata Prefecture and is a glaucophanitic metamorphic terrain (Banno, 1958). The coexisting zoisite and clinozoisite are found in a metagabbro which occurs as a tectonic block in the albite-epidote amphibolite facies area (Maruyama, pers. comm. 1978).

The specimen studied has hornblende + zoisite + clinozoisite + albite. Prehnite occurs in veins. Subhedral clinozoisite is in contact with zoisite, forming an aggregate of fine (20–30 μm) subhedral grains.

Chemistry of coexisting zoisite and clinozoisite

Zoisite and clinozoisite were analysed by an electron-probe microanalyser, Hitachi Model XMA 5A, with accelerating voltage of 15 kV, specimen current 0.02 μA, and beam diameter 5 μm.

Chemical analyses were performed on 8 specimens from the Iratsu mass, 3 from the Tonaru mass, 1 from the Fujiwara mass, 2 from the Nishisonogi area, 2 from the Yoshimi area, and 1 from the Omi area. Table I lists the analyses.

The coexistence of zoisite and clinozoisite was confirmed on four specimens by X-ray powder patterns of magnetic and less-magnetic fractions of epidote concentrates following the criteria of Seki (1959) as well as on three samples by a single-crystal method using an automated four-circle X-ray diffractometer. In all these specimens clinozoisite is distinctly richer in Fe^{3+} than zoisite, and they may be identified by the difference of interference colour that clinozoisite is yellow to lavendar-blue whereas zoisite is grey or bluish grey.

Zonal structure. Many of the clinozoisites examined are optically heterogeneous, but the zoisites appear to be homogeneous optically, although compositional variation was found by microanalysis. Three types of zoning patterns were recognized in the clinozoisites. In the first type observed in a specimen from the Tonaru mass (specimen HK901C), the Fe^{3+} content, being measured in terms of $X_{ps}^{cz} = Fe^{3+}/(Fe^{3+} + Al)$ hereafter (suffixes zo and cz stand for zoisite and clinozoisite respectively), decreases from the core towards the rim, with minor fluctuations, but it again increases at the very margin. In this specimen the zoisite composition shows minor fluctuations ($X_{ps}^{zo} = 0.036$–0.046), but X_{ps}^{zo} invariably increases at the very margin, thereby giving nearly the same X_{ps}^{zo} and X_{ps}^{cz} at the zoisite–clinozoisite interface, respectively. Fig. 2 shows the compositional profile across such an interface in this specimen.

In the second type, X_{ps}^{cz} increases more or less continuously from the core to the rim, and X_{ps}^{zo} increases from the core to the rim as well. This

Table 1. Representative analyses of coexisting *zoisite and clinozoisite.*

Locality	IRATSU								NISHISONOGI		YOSHIMI			TONARU				FUJIWARA		OMI		
Sample No.	ST309A		ME75050106		ME75042501		ST7055A		NI-01		YS-3B			HK901C		ME76031706		ME76032101		OM-01		
	Cz	Zo	Cz	Zo	Cz	Zo	Cz	Zo	Cz	Zo	Cz	Zo	Cz***	Cz	Zo	Cz	Zo	Cz	Zo	Cz	Zo	
SiO_2	39.1	39.6	38.9	39.5	39.6	40.1	38.6	39.7	38.4	39.2	38.8	40.0	38.3	39.5	40.0	38.1	38.1	39.2	39.9	38.0	39.0	SiO_2
TiO_2	0.09	0.07	0.00	0.03	0.16	0.01	0.06	0.01	0.13	0.10	0.00	0.00	0.07	0.16	0.01	0.09	0.00	0.18	0.01	0.11	0.03	TiO_2
Al_2O_3	27.8	31.0	28.2	31.5	29.5	32.4	26.4	31.4	28.3	32.0	29.5	32.8	26.7	29.1	32.1	27.6	31.4	29.5	32.4	28.3	31.7	Al_2O_3
Fe_2O_3*	6.92	2.70	7.47	2.65	5.58	2.00	9.24	2.21	5.89	1.55	4.93	0.75	8.83	6.10	1.80	6.74	2.05	5.38	1.67	5.89	2.32	Fe_2O_3*
MnO	0.10	0.03	0.03	0.00	0.18	0.04	0.11	0.03	0.11	0.06	0.18	0.06	0.17	0.18	0.05	0.19	0.14	0.14	0.03	0.09	0.06	MnO
MgO	0.13	0.15	0.30	0.21	----	----	0.03	0.04	----	----	0.00	0.00	0.00	----	----	0.11	0.12	----	----	----	----	MgO
CaO	24.9	25.1	23.9	24.4	23.7	24.2	23.5	24.2	23.2	23.8	23.4	23.8	23.6	23.7	24.1	23.9	24.6	24.1	24.5	23.4	24.2	CaO
Na_2O	0.00	0.00	0.03	0.03	----	----	0.00	0.02	----	----	0.28	0.23	0.23	----	----	0.00	0.00	----	----	----	----	Na_2O
K_2O	0.00	0.00	0.00	0.00	----	----	0.00	0.00	----	----	0.07	0.05	0.06	----	----	0.00	0.00	----	----	----	----	K_2O
Total	99.04	98.65	98.83	98.32	98.72	98.75	97.94	97.61	96.03	96.71	97.16	97.69	97.96	98.74	98.06	96.73	96.41	98.50	98.51	95.79	97.31	Total
Si	3.032	3.029	3.000	3.008	3.027	3.024	3.022	3.033	3.029	3.017	3.020	3.042	3.003	3.030	3.038	3.003	2.968	3.011	3.016	3.007	3.026	Si
Al	2.533	2.792	2.564	2.831	2.658	2.882	2.433	2.832	2.625	2.903	2.706	2.937	2.471	2.627	2.868	2.562	2.879	2.666	2.890	2.638	2.848	Al
Ti	0.005	0.004	0.000	0.002	0.009	0.001	0.004	0.001	0.008	0.005	0.000	0.000	0.004	0.009	0.001	0.005	0.000	0.011	0.001	0.007	0.001	Ti
Fe^{3+}	0.403	0.155	0.433	0.152	0.322	0.113	0.544	0.127	0.349	0.090	0.288	0.043	0.521	0.352	0.103	0.400	0.120	0.311	0.095	0.351	0.133	Fe^{3+}
Mn	0.007	0.002	0.002	0.000	0.012	0.003	0.008	0.002	0.007	0.004	0.012	0.004	0.011	0.012	0.003	0.013	0.009	0.009	0.002	0.006	0.004	Mn
Mg	0.015	0.017	0.034	0.023	-----	-----	0.004	0.005	-----	-----	0.000	0.000	0.000	-----	-----	0.013	0.014	-----	-----	-----	-----	Mg
Ca	2.064	2.058	1.973	1.987	1.945	1.956	1.973	1.984	1.958	1.962	1.951	1.936	1.982	1.941	1.963	2.021	2.050	1.983	1.986	1.982	1.971	Ca
Na	0.000	0.000	0.004	0.004	-----	-----	0.000	0.004	-----	-----	0.042	0.034	0.035	-----	-----	0.000	0.000	-----	-----	-----	-----	Na
K	0.000	0.000	0.000	0.000	-----	-----	0.000	0.000	-----	-----	0.007	0.005	0.006	-----	-----	0.000	0.000	-----	-----	-----	-----	K
X_{Ps}**	0.140	0.053	0.145	0.051	0.109	0.039	0.183	0.040	0.107	0.033	0.093	0.025	0.159	0.118	0.035	0.139	0.043	0.109	0.035	0.116	0.043	X_{Ps}
$\pm\sigma$	0.005	0.002	0.005	0.003	0.006	0.003	0.018	0.007	0.012	0.003	0.004	0.012	0.030	0.007	0.003	0.005	0.004	0.006	0.008	0.002	0.004	$\pm\sigma$

* total Fe as Fe_2O_3

** average X_{Ps} in a thin section

*** clinozoisite not contact with zoisite

Abbreviations for minerals: Cz: clinozoisite, Zo: zoisite.

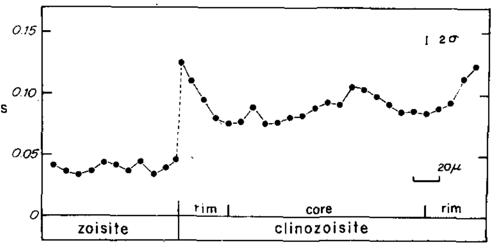

FIG. 2. Compositional profile of a zoisite-clinozoisite interface of sample HK901C from the Tonaru mass of the Bessi district.

zoning type is common in the specimens from the Iratsu mass and is not uncommon in those from the Nishisonogi area, but is absent in others.

The third type of zoning also shows the continuous variations of X_{ps}, but X_{ps}^{cz} decreases from the core to the rim. In the associated zoisite, X_{ps}^{zo} decreases from the core to the rim as well. This type occurs in the Nishisonogi area.

Choice of equilibrium pair. Fig. 3 shows the frequency distribution of X_{ps}^{cz} at the core and rim of the type 1 clinozoisite. The X_{ps}^{cz} at the core has a wide variation ranging from 0.079 to 0.120 even in a single thin section, but the rim in contact with zoisite has fairly constant X_{ps}^{cz}, ranging from 0.110 to 0.130. The precision of microanalysis is $\sigma = 0.002$ X_{ps}^{cz} in count statistics, and hence the observed variation of X_{ps}^{cz} at the interface exceeds the analytical errors. The presence of such a variation may be due partly to the difference of equilibration temperatures from one interface to another, but may also be due to the difficulty of determining X_{ps}^{cz} at the rim of zoned clinozoisite. As is seen in fig. 2, the change of X_{ps}^{cz} for 0.01 takes place over a short distance of 10 μm. At all the interfaces of coexisting pairs examined in this specimen, the pattern of the zoning, so far as it exists, is the same. Therefore, we consider that the interfaces were equilibrated at the same stage of recrystallization, even if the temperature or exact time of equilibration may differ from place to place to some extent, giving rise to slight variation of X_{ps}^{cz} at the interfaces. In this specimen the compositional variation of the zoisite at the interface is 0.032 to 0.046, and is much smaller than that of the clinozoisite.

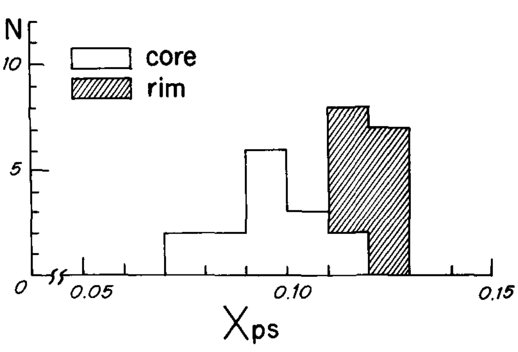

FIG. 3. Frequency distribution of the values of X_{ps}^{cz} for sample HK901C.

The variation of X_{ps}^{cz} at the interfaces in other specimens differs in different specimens, but is smaller than that shown in the above example (cf. Table I).

In the specimens of the Iratsu and Tonaru masses of the Bassi area and those of the Omi area, the rims of clinozoisites that are not in contact with zoisite have the same composition as those in contact with zoisite. In the specimens from the Yoshimi area, however, the former type of clinozoisite has a Fe^{3+}-richer composition than the other type as shown in Table I. This shows that chemical equilibrium was satisfied only in small domains in the specimens from the Yoshimi area. To avoid possible mix-up of various equilibrium domains, only the compositions at the interface of coexisting zoisite and clinozoisite will be treated in the following discussion, even for the specimens from the Bessi and Omi areas.

In the zoisite-clinozoisite composite grain from the Iratsu mass (specimen *ST7055a*), the compositional gap at the interface is quite different from those at the interfaces of independent zoisite and clinozoisite grains. In this particular composite grain $X_{ps}^{zo} = 0.040 \pm 0.007$ and is fairly constant, but X_{ps}^{cz} ranges from 0.145 to 0.198. In other specimens from the same mass the coexisting zoisite and clinozoisite have $X_{ps}^{zo} = 0.051 \pm 0.004$ and $X_{ps}^{cz} = 0.140 \pm 0.006$ at the interfaces. The fact that X_{ps}^{cz} varies between different faces within the composite grain as well as differing significantly from values at the faces of isolated grains suggest that the interfaces of the composite grain were not in chemical equilibrium.

Based upon the above discussion, we proceed assuming that the interfaces of independent zoisite and clinozoisite were in chemical equilibrium, even if this was not attained at exactly the same temperature in each specimen. The deviation from equilibrium may be measured in terms of the standard deviation of X_{ps}^{cz}, which is smaller than 0.01 X_{ps}^{cz} in each specimen.

The relationships between X_{ps}^{zo} and X_{ps}^{cz} at the interfaces of all the studied specimens are shown in fig. 4. The cross at the upper right of the figure shows the average variation of X_{ps} of zoisite and clinozoisite within a single thin section. There is a distinct correlation between X_{ps}^{zo} and X_{ps}^{cz} over the specimens studied, although the variation of the trend exceeds slightly that in an individual thin section.

In the binary system the compositions of the coexisting phases plotted in a diagram like fig. 4 should define a line determined by the transitional loop in the phase diagram.

Discussion

Temperature-dependence of the compositional gap. Among the six localities studied in detail, obvious difference of metamorphic grade is recognized between the Iratsu and Tonaru masses of the Bessi area on the one hand, and the Nishisonogi area on the other; the former belonging to the epidote amphibolite facies and the latter to the epidote-glaucophane schist facies. Both of them belong to the high-pressure intermediate facies series. The compositional gaps observed on the specimens from the Iratsu and Tonaru masses scatter rather widely in fig. 4, but if we combine them into three subgroups based upon the mode of occurrence, the scatter in each of them becomes significantly reduced to be more or less comparable with that of the Nishisonogi specimens. The three groups are the central and marginal parts of the Iratsu mass and the Tonaru mass. As the thermal history of these masses is complex, it is possible that the final temperature of equilibration could have been slightly different between these masses and even in different parts of the masses. All three subgroups of metagabbros of the Bessi area belong to the epidote amphibolite facies and they were equilibrated at higher temperatures than the Nishisonogi specimens. Thus it follows from fig. 4 that the compositions of coexisting zoisite and clinozoisite become Fe^{3+}-richer with increasing temperature, or zoisite solid-solution is the higher temperature phase.

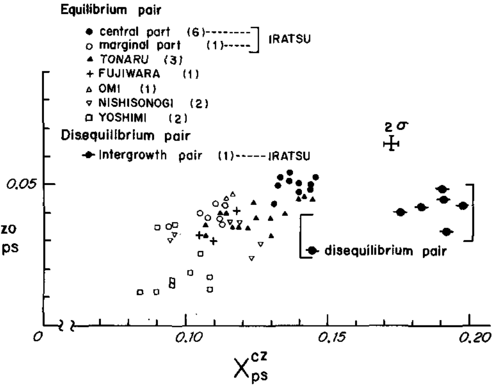

FIG. 4. Compositions of coexisting zoisite and clinozoisite at their interfaces. Numbers in parenthesis show the number of samples studied in detail. (For the disequilibrium pairs, see the text.)

Epidote-group minerals contain Mn^{3+}, Fe^{2+}, and Mg^{2+}, but the contents of MnO (total Mn as MnO, but probably mostly in the trivalent state) and MgO determined in this study are so low that they may hardly affect the phase relations in regard to Fe^{3+}-Al substitution. Some Fe^{2+} may be contained in zoisite. The Fe^{2+}/Fe^{3+} ratio in some zoisites analysed by wet chemistry approaches 1, including a zoisite from the Tonaru mass described by Banno (1964). The possible variation of the Fe^{2+}/Fe^{3+} ratio of zoisite may partly be responsible for the scatter of points in fig. 4.

However, the general tendency for the compositions of the coexisting zoisite and clinozoisite to become Fe^{3+}-richer with increasing temperature is strong enough to ignore, at least in the studied specimens, the effect of Fe^{2+}. The effect of pressure among the Japanese specimens, except on the Yoshimi pair, which are from the high-pressure intermediate type metamorphism may be very small, in view of the fact that the unit cell volumes of zoisite and clinozoisite (1/2 unit cell volume for zoisite) extrapolated to the same composition are quite similar as shown by Seki (1959) and later confirmed by Myer (1966) and Dollase (1968). Accordingly, we conclude that the compositional gap between zoisite and clinozoisite shifts towards Fe^{3+}-richer side as the temperature increases. In the following, the phase relations between zoisite and clinozoisite in other areas will be examined in order to test the validity of our conclusion.

In the epidote amphibolite of the Omi area the compositional gap is between 0.043 ± 0.004 and 0.116 ± 0.002 X_{ps}, which is comparable to those of the specimens from the Iratsu and Tonaru masses. The Fujiwara mass is situated in the lowest-grade area of the albite-epidote amphibolite facies; that is, its metamorphic grade is intermediate between those of the Bessi and Nishisonogi areas. The X_{ps} values of zoisite and clinozoisite in the specimen from this mass are also between those of the Bessi and Nishisonogi areas. The coexisting zoisite and clinozoisite of the specimens from the Yoshimi area probably represent the lowest temperature among the studied areas. This conclusion is not positively proved by independent mineralogical data, but is compatible with the occurrence of albite + chlorite + epidote + actinolite in some of the associated rocks. Therefore, the relative temperatures of equilibration of the five localities (excluding Yoshimi) being studied in this work, as estimated by the compositional gaps, are not contradictory with the paragenesis of associated minerals and metamorphic grade of the associated rocks. Fig. 5 shows the inferred phase diagram of the zoisite–clinozoisite–

pistacite system at the temperatures of low- to medium-grade metamorphism. The temperature scale cannot be calibrated quantitatively. The diagram is part of a transitional loop, but we cannot extrapolate the observed relations to higher temperature unless we know more about the mixing properties of the epidote-group minerals.

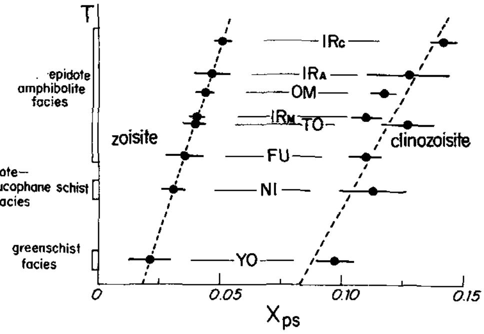

FIG. 5. Speculative temperature-composition relations for the zoisite–clinozoisite series. The transition loop is approximated by straight lines, and the relative formative temperatures were inferred from X^{zo}_{ps}. Abbreviations. OM: Omi, TO: Tonaru mass of the Bessi district, FU: Fujiwara mass, NI: Nishisonogi metagabbro, YO: Yoshimi metagabbro, IR: Iratsu mass of the Bessi district. Subscripts C, M, and A denote the central part, marginal part, and average of the Iratsu mass, respectively.

Data from other metamorphic terrains. In the literature, there are several groups of data which are apparently contradictory with the temperature dependence proposed here. Ernst (1977) reported optically identified clinozoisite with $X_{ps} = 0.025$–0.029 from eclogitic rocks of the Alpe Arami mass in the assemblage garnet + clinopyroxene + hornblende + plagioclase (An = 15–37) ± biotite ± quartz. With the courtesy of Professor Ernst, we obtained the Alpe Arami specimens described by him and their epidote-group minerals were re-examined by automated four-circle diffractometer. The epidote-group mineral in specimen *F-16f* was found to be zoisite with possible space groups *Pnma* if centric and *Pn2₁a* if acentric. The unit cell dimensions are $a_0 = 16.202(1)$, $b_0 = 5.554(1)$, and $c_0 = 10.033(1)$ Å, respectively, in which the number in the parenthesis is the standard error in the last digit. These values agree well with those given by Dollase (1968). If the Alpe Arami epidote is actually zoisite, it is consistent with our proposed phase relations. Hietanen (1974) described clinozoisite with $X^{cz}_{ps} = 0.044$–0.094 coexisting with zoisite and epidote in the amphibolite-facies area of the contact aureole of northern Sierra Nevada. However, the coexistence of three epidote-group minerals of essentially binary system, zoisite, clinozoisite, and epidote in one thin section makes it difficult to evaluate the significance of the observed paragenesis. Tanner (1976) reported that clinozoisite with $X^{cz}_{ps} = 0.130$–0.160 coexists with zoisite in his zones 2 and 3 of the Moine schists, in which plagioclase (An = 33–97) occurs. If zoisite with $X^{zo}_{ps} = 0.04$ coexists with clinozoisite $X^{cz}_{ps} = 0.160$, it is not contradictory with our view, but if it coexists with the one with $X^{cz}_{ps} = 0.13$ in equilibrium, our view has to be modified. Further consideration may be fruitless until more detailed descriptions of the chemical heterogeneity of clinozoisite from this area are available. Ackermand and Raase (1973) showed that the compositional gap between zoisite and clinozoisite in plagioclase-bearing specimen from Hohe Tauern is about 0.04–0.10 X_{ps}. This compositional range corresponds to that of the lower albite-epidote amphibolite-facies conditions similar to those of the Fujiwara mass. It is not evident whether or not the zoisite + clinozoisite assemblage coexists stably with plagioclase, because Miller (1977) has shown that, in the associated eclogitic rocks of Hohe Tauern, this assemblage was not in equilibrium with plagioclase (4–10% An) but postdated it. The X_{ps} values of coexisting zoisite and clinozoisite from Trollheim, Norway, as described by Myer (1966) are estimated to be 0.04 and 0.12, respectively, that again correspond to the albite-epidote amphibolite facies. The mineral facies of the Norwegian specimen is considered to be the middle almandine amphibolite facies.

In these examples the compositional gap gives a lower temperature than that estimated by the mineral paragenesis, if we accept the phase relations obtained on Japanese rocks. In this connection it is possibly significant that the phase relations in fig. 5 were constructed from data on high-pressure metamorphic rocks. Pressure may hardly affect the zoisite–clinozoisite relations, but it may affect the temperature range of mineral facies, especially of the epidote amphibolite facies, bringing its higher temperature limit to higher temperature with increasing pressure (Miyashiro, 1961). It is, therefore, possible that the epidote amphibolite facies in high-pressure terrains represents a similar temperature to the middle of the almandine amphibolite facies of medium-pressure type of metamorphism.

Frey (1978) has reported that biotite schists of the Helvetic zone of the Alps have zoisite with $X^{zo}_{ps} = 0.03$ (Fe_2O_3 = 1.7 wt%) coexisting with zoned epidotes with clinozoisite rims with $X_{ps} =$ 0.09. The grade is lower than the staurolite isograd and associated plagioclase is oligoclase or andesine. The associated rocks commonly contain margarite + quartz. The paragenesis of calc-alumino silicates of this area indicates lower temperatures than the metagabbros of the Bessi area (Tonaru and Iratsu masses) that contain kyanite + zoisite + quartz, in harmony with what is expected from zoisite–clinozoisite relations.

Alternative model of temperature dependence. Our foregoing discussion leading to fig. 5 is essentially based upon the assumption that the equilibrium temperature of interface pairs of the metagabbros, at Bessi, Nishisonogi, and Yoshimi areas, decreases in this order. If we accept the opposite temperature dependence that clinozoisite is the higher-temperature modification, we must consider that the temperature increases in that order. As the parageneses of the host and associated rocks of these pairs show that the temperature decreases in that order, we must consider that the Bessi interfaces were produced by retrograde metamorphism in which material exchange and growth of zoisite continued to much lower temperatures than in the other areas. In this model the core of clinozoisite from the Bessi metagabbro ($X_{\text{ps}} = 0.08–0.12$) represents the epidote amphibolite-facies. This possibility cannot be fully rejected as we know little about the rate of cooling, kinetic effects on recrystallization, etc. that affect the temperature of freezing the local equilibration. To examine the alternative model further, we consider epidote in basic schists of the Sanbagawa belt. At low-grade, X_{ps} of epidote generally decreases with the grade, as pointed out by Miyashiro and Seki (1958), but at grades higher than the breakdown of pumpellyite, X_{ps} is largely determined by the bulk rock chemistry (Nakajima *et al.*, 1977). The frequency distribution of $X_{\text{ps}}^{\text{cz}}$ of clinozoisite in specimen *AS-78B* from the Asemi-river route in central Shikoku, which was donated by Mr T. Nakajima, is shown in fig. 6A. The host rock contains albite + clinozoisite + chlorite + aluminous actinolite (Al_2O_3 = 2 wt %), but not zoisite. The grade of the rock is slightly higher than the disappearance of pumpellyite, and since associated pelitic schists contain garnet with MnO = 5–7 wt % (Kurata and Banno, 1974; Higashino, 1975; Nakajima, pers. comm.). Thus it is slightly lower than the epidote amphibolite facies. The clinozoisite is zoned with an Fe^{3+}-poor core ($X_{\text{ps}}^{\text{cz}} = 0.12$) and Fe^{3+}-rich rim ($X_{\text{ps}}^{\text{cx}} = 0.17$). Nakajima (pers. comm.) interprets this zoning by the selective decomposition of the Al-end member of epidote solid-solution with progressive metamorphism. This view as shown in fig. 6B is consistent with our proposed temperature dependence. On the other hand, if we accept the opposite temperature dependence, as shown in fig. 6C, we have to consider that the rock reached the albite–epidote amphibolite facies before the final equilibration. The latter view is hardly consistent with the general petrology of the Sanbagawa schists in Shikoku.

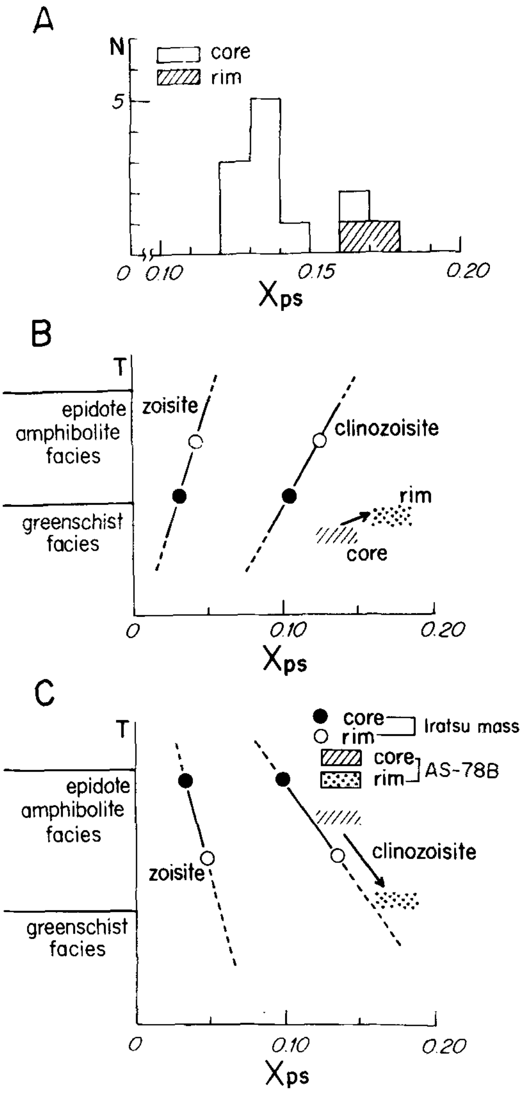

FIG. 6A. Frequency distribution of $X_{\text{ps}}^{\text{cz}}$ in a greenschist of central Shikoku (sample AS-78B). The rock is from the garnet zone of pelitic schists, and of lower grade than the first appearance of biotite in pelitic schists. B. Proposed temperature variation of the sample AS-78B. Legend is shown in Fig. 6C. C. Alternative model of temperature variation of the same greenschist. In this model the schist had to be in the epidote amphibolite facies when the core of the clinozoisite was formed.

For these reasons, so far as the first-hand data we have and the general petrology of the Sanbagawa belt are concerned, we prefer the model shown in fig. 5.

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