MINERALOGICAL MAGAZINE, SEPTEMBER 1976, VOL. 40, PP. 773–9

Compositional range of $P2/n$ omphacite from the eclogitic rocks of central Shikoku, Japan

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SUMMARY. The lattice types of omphacite–diopside series clinopyroxenes were determined for 9 Japanese, 2 Norwegian, and 1 South African samples. The boundary between the compositional ranges of *P* and *C* lattice clinopyroxenes lies at about 14·5 wt. % CaO in Japanese and Norwegian samples, and the compositional gap between them is very small, if it exists. The South African omphacite has *C*-lattice in the compositional range of *P* lattice omphacite in metamorphic eclogites. These data combined with the reported electron microscope studies suggest that the omphacite–diopside series clinopyroxene has a *C* lattice structure above 3 to 400 °C, and very slow cooling after regional metamorphism is responsible for the transition to the ordered structure with *P* lattice symmetry.

SINCE the finding by Clark and Papike (1966) that Californian omphacite has primitive lattice symmetry, *P*-lattice omphacites have been described from Venezuela, Colombia, Norway, New Caledonia, Japan, and East Papua (Clark and Papike, 1968; Clerk *et al.*, 1969; Black, 1969; Matsumoto and Banno, 1970; Kanazawa and Matsumoto, 1971). The symmetry of this omphacite was first considered to be $P2$, but Matsumoto and Banno (1970) and Matsumoto *et al.* (1975) have shown that there are $P2/n$ omphacites. We believe that the majority of *P*-lattice omphacite is $P2/n$, but in the experiments on which the following discussion is based, we did not confirm the space group on individual specimens, but only determined the lattice type, and hence probable $P2/n$ omphacites will be called *P* lattice omphacites and probable $C2/c$ pyroxenes will be called *C* lattice pyroxenes.

Recently, transmission electron microscopy of Californian omphacites has revealed the presence of anti-phase domains that are probably the result of redistribution of cations from disordered $C2/c$ to ordered $P2/n$ structures (Champness, 1973; Phakey and Ghose, 1973). This suggests that continuous solid solution between omphacite and diopside, with $C2/c$ symmetry, exists at the temperature of eclogite formation.

During our petrographic work on the eclogitic rocks of the Sanbagawa metamorphic belt in central Shikoku(Sikoku), Japan, we have determined the compositional range of *P* and *C* lattice clinopyroxenes that were formed under isophysical conditions. It has also been found that the compositional range of *P* and *C* lattice clinopyroxenes is essentially the same for the Japanese and Norwegian eclogite associations that were formed at different temperatures. Relevant mineralogical data are described below along with their petrological implications.

Source of samples. The Japanese clinopyroxene samples were collected from the peridotite–epidote-amphibolite complex in the Sanbagawa metamorphic belt in central Shikoku. This complex includes the Mt. Higashi-Akaishi (Higasi-Akaisi) peridotite and the Iratsu(Iratu) epidote amphibolite, the latter being a metamorphosed gabbro. Detailed geological and petrographical studies of this complex are still in progress, but progress reports are available in Mori and Banno (1973), Yokoyama and Mori (1975), Yokoyama (1975), and Banno *et al.* (1976).

In brief, the peridotite–gabbro complex was formed by the crystallization differentiation of basaltic magma at high pressures, 12 to 18 kb, and later metamorphosed in the high-pressure granulite facies. During the Sanbagawa metamorphism, the granulite facies peridotite–metagabbro complex was metamorphosed again in the epidote amphibolite facies. The eclogitic rocks in the complex are the product of the Sanbagawa metamorphism, and not of the granulite facies metamorphism. This fact is established by means of the Fe–Mg partitioning between garnet and clinopyroxene and the content of Ca-Tschermak's component in clinopyroxene. The garnet–clinopyroxene assemblage of the Sanbagawa metamorphism occurs in three modes: Garnet-clinopyroxenite lenses in the Mt. Higashi-Akaishi peridotite; hornblende eclogites in the epidote amphibolite and in the peridotite masses; and quartz eclogite in the epidote amphibolite mass.

Three other omphacitic clinopyroxenes, one from a South African kimberlite and two from Norwegian eclogites, were also studied.

Lattice types and their compositional range. The Japanese clinopyroxene samples were treated as follows: the pyroxenes from the garnet–clinopyroxene assemblage were separated from their host rocks. Twenty-one pyroxene concentrates were prepared and their unit cell parameters were determined by the X-ray powder method to determine their approximate compositions in order to select eighteen samples, which were mounted in epoxy resin for electron-probe microanalysis. From each concentrate, 10 to 30 grains were analysed for Na_2O, CaO, and FeO (total Fe), and then several grains were analysed for SiO_2, TiO_2, Al_2O_3, FeO, MgO, CaO, and Na_2O. Table I lists the average of analysed grains from each specimen. An electron-probe microanalyser was used following the procedure of Albee and Ray (1970). For partial analyses, the correction factors for the average compositions of each specimen were used.

The analyses of the pyroxenes are shown in figs. 1A and 1B, the former showing the heterogeneity of the pyroxene in one hand specimen, and the latter showing the whole compositional range of the analysed pyroxenes of this area. The lattice type of 9 clinopyroxene grains was determined by Weissenberg photographs, and then the grains were mounted in epoxy for analysis, but we failed to analyse 4 grains for which unit cell parameters were determined by automatic four circle goniometer (specimen 185-3 and 14-A-7), and average compositions of concentrates (specimen Go-1 and Go-2) were used to estimate the compositions. Fig. 2 shows the relationships between the average unit cell parameters and average compositions of the concentrates from which the compositions of X-rayed grain of specimen 185-3 and 14-A-7 were determined. The analyses of X-rayed grains are shown in Table II. The relationships between the lattice type and the composition are seen in fig. 2.

Discussion. The relationships between the composition of pyroxene and the lattice types are shown in fig. 3. For the Japanese pyroxenes, the boundary between *P* and *C* lattice types is located in the compositional range of apparent continuity of fig. 2.

TABLE I. *Average compositions of omphacite–diopsides of the Iratsu Complex*

Sample	13-A-17	70102102	70101813	185	MGME	14-A-7	14-A-10	Go-5	7001-A
SiO_2	54·95	53·87	55·22	54·69	53·58	53·74	55·18	53·86	53·83
TiO_2	0·14	0·26	0·25	0·26	0·33	0·27	0·17	0·30	0·31
Al_2O_3	11·90	11·08	10·41	10·06	8·67	9·59	7·91	8·91	7·28
FeO	7·97	7·93	7·07	5·90	8·37	6·95	6·99	6·44	7·25
MgO	6·70	6·90	7·38	8·63	9·11	9·67	9·63	9·27	10·31
CaO	11·10	12·10	12·30	14·00	14·40	14·90	15·70	15·70	16·10
Na_2O	7·22	6·93	6·92	5·68	5·49	5·01	4·65	4·69	4·57
Total	99·98	99·07	99·55	99·22	99·95	100·13	100·23	99·17	99·65

Sample	14-A-19	Go-1	B-8	Gi-A	7002	317	305	319	7-B-9
SiO_2	53·50	53·07	53·05	53·74	54·03	55·10	54·17	54·32	54·22
TiO_2	0·52	0·51	0·27	0·39	0·22	0·17	0·28	0·15	0·33
Al_2O_3	6·41	6·14	5·71	3·81	2·62	2·68	3·19	2·17	3·16
FeO	5·97	5·18	5·31	4·89	5·68	5·45	3·94	2·50	3·49
MgO	11·53	13·27	12·91	14·06	14·89	14·57	15·37	16·77	15·65
CaO	19·00	20·60	21·00	21·60	21·70	22·00	22·70	22·80	23·30
Na_2O	3·20	2·04	2·22	1·66	1·61	1·35	1·15	1·17	0·65
Total	100·13	100·81	100·47	100·15	100·75	101·32	100·80	99·88	100·80

To confirm the compositional ranges of the *P* and *C* lattice type clinopyroxenes, two clinopyroxenes from Norwegian eclogites, specimens Nr. 4B and 5B of Brynhi *et al.* (1969), and one from a South African eclogite, specimen No. 1 of Kushiro and Aoki (1968), were also examined. These specimens are designated respectively as Nos. 2, 3, and 1 in fig. 3. The temperature of eclogite formation in the figure is estimated from the Fe–Mg partitioning between garnet and clinopyroxene (Banno, 1970; Mori and Banno, 1973; Råheim and Green, 1974; etc). The compositional boundary between the two lattice types is essentially the same for the Japanese and Norwegian pyroxenes, and the Californian and other omphacites from low-temperature metamorphic rocks have a *P* lattice in the range of *P* lattice pyroxenes of Japanese and Norwegian pyroxenes. On the other hand, the South African omphacite has a *C* lattice although its composition lies within the *P* lattice omphacites from regionally metamorphosed eclogites.

Champness (1973) has proposed a schematic diagram to explain the stability of *C* and *P* lattice pyroxenes. If the lattice types of the pyroxenes in the omphacite–diopside (+hedenbergite) series are quenched at the temperature of initial crystallization, a phase diagram of Champness' scheme with the apex at about 1000 °C can explain the

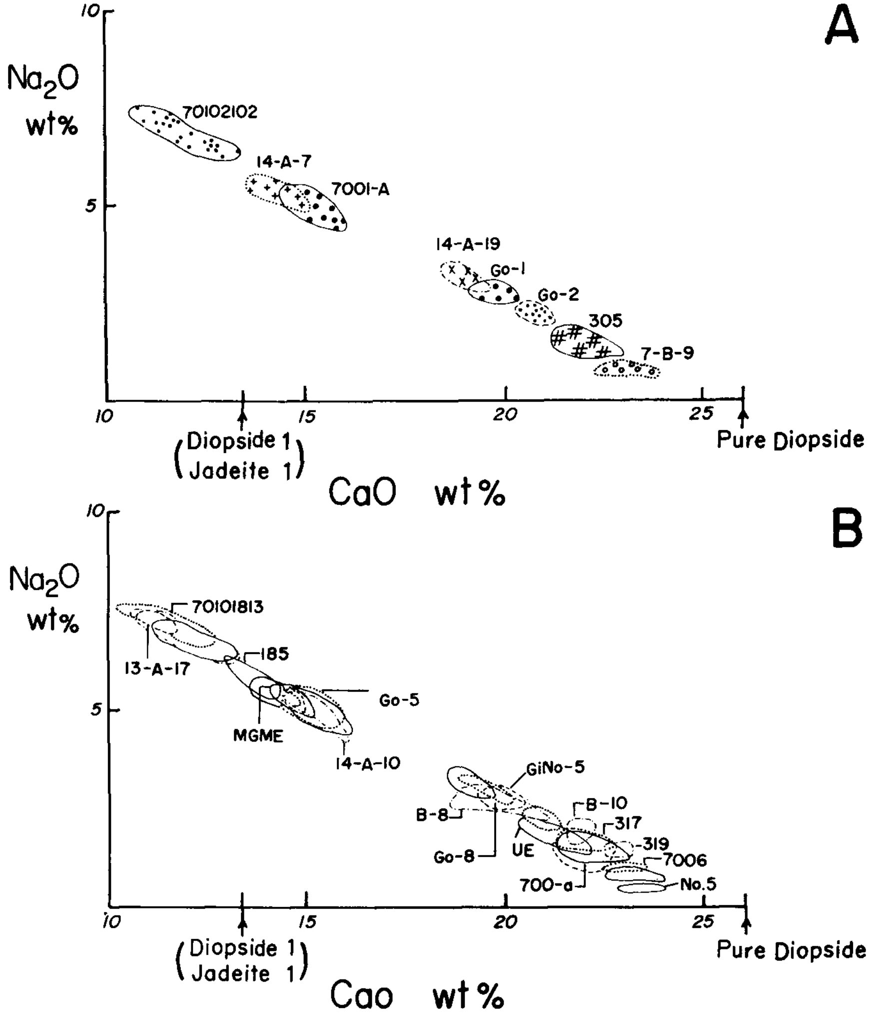

Fig. 1. Compositional range of omphacite–diopside series clinopyroxenes from the Mt. Higashi-Akaishi peridotite and Iratsu epidote-amphibolite masses. A: Compositional ranges of clinopyroxene in several hand specimens. Each point corresponds to an individual point analysis. B: Compositional range of clinopyroxene in the surveyed area (nearly pure diopsides as described by Mori and Banno, 1973, are excluded). Each area corresponds to the compositional range in one hand specimen. The areas of the samples shown in fig. 1A are shown without specimen number.

data summarized in fig. 3. However, the electron-microscopy of Californian omphacites by Champness herself and by Phakey and Ghose (1973) has revealed the presence of anti-phase domains, which indicates the transition from *C* to *P* lattice. Champness then considered that metastable crystallization of *C* lattice omphacite during regional metamorphism was followed by the transition from *C* to *P* lattices. In this view, any

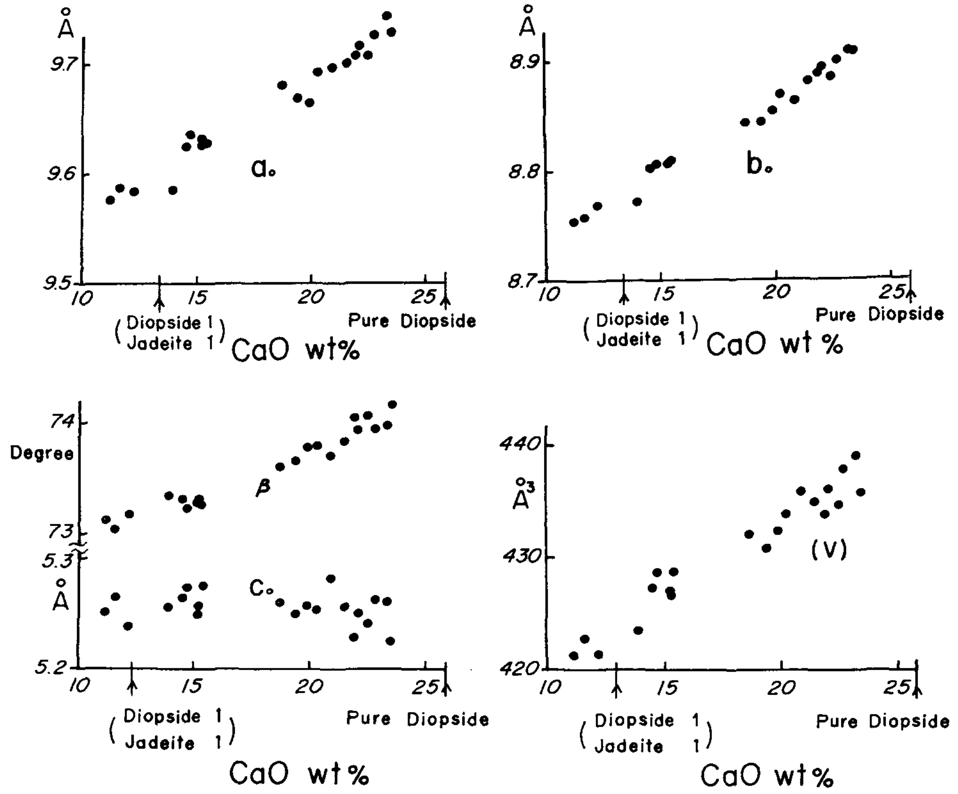

FIG. 2. The relationships between unit-cell parameters and the CaO content of the clinopyroxenes. The data are the average of concentrates.

TABLE II. *Chemical compositions of omphacite grains used in single crystal studies*

Sample	Go5	14-A-10	181_1	185_2	70102102	Sample	Go5	14-A-10	181_1	185_2	70102102
Lattice	C	C	P	P	P	Lattice	C	C	P	P	P
SiO_2	52·94	54·00	54·89	54·30	54·50	Si	1·940	1·959	1·981	1·960	1·975
TiO_2	0·39	0·26	0·33	0·29	0·28	Ti	0·011	0·008	0·009	0·008	0·008
Al_2O_3	8·58	8·11	9·45	10·65	10·77	Al	0·369	0·347	0·401	0·452	0·459
FeO	6·86	7·22	5·86	5·63	6·87	Fe	0·213	0·222	0·180	0·171	0·211
MgO	9·87	10·23	8·89	8·63	7·85	Mg	0·538	0·553	0·478	0·464	0·424
CaO	16·26	15·60	14·60	14·01	12·50	Ca	0·637	0·607	0·565	0·542	0·485
NaO_2	4·38	4·68	5·66	5·99	6·44	Na	0·312	0·327	0·394	0·420	0·452
Total	99·28	100·10	99·68	99·50	99·21	ΣM	4·020	4·023	4·008	4·017	4·014

diagram having the apex between 300 to 400 °C and 1000 °C can explain the data summarized in the figure. However, this is not the only interpretation just because one accepts a transition below the crystallization temperature for Californian omphacites. As omphacites were formed by regional metamorphism by which the degree of supersaturation was low and crystallization proceeds very slowly, nearly satisfying the requirement of chemical equilibrium, it is natural to assume stable crystallization.

This view necessitates accepting a low-temperature transition from *C* to *P* lattice, however. Which of these two alternatives is correct has to await future study of the kinetics of the transition. We intend here to explain the observations by stable crystallization as it is usually accepted in metamorphic petrogenesis.

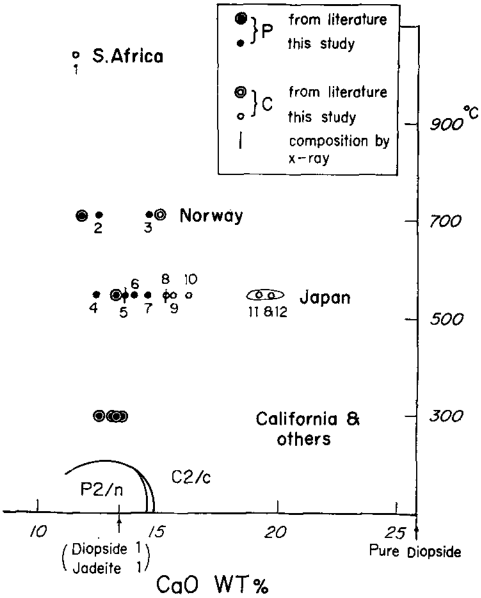

FIG. 3. The relationships between lattice type and composition of clinopyroxene and the probable temperature of equilibration of host eclogitic rocks. Key to specimen numbers. 1, South Africa, No. 1 of Kushiro and Aoki (1969); 2 and 3, Norway, Nr. 4B and Nr. 5B of Bryhni *et al.* (1969); 4 to 12, Japan, 4 = 70102102, 5 = 185-3, 6 = 185-2, 7 = 185-1, 8 = 14-A-7, 9 = 14-A-10, 10 = Go-5, 11 = Go-1, 12 = Go-2. The compositions of Nos. 5 and 8 were determined from cell parameters and those of 11 and 12 from the average compositions of hand specimens. Additional data for Norway and California and other low-temperature eclogites are quoted from Clark *et al.* (1969), and one from Japan from Matsumoto and Banno (1970).

The fact that the omphacite from South Africa does possess *C* lattice symmetry can be explained by the rapid cooling of an eclogitic xenolith captured in the kimberlite. Eclogites from other areas suffered regional metamorphism and cooled down very slowly. The transition of omphacite from *C2/c* to *P2/n* is, then, far more sluggish than that of pigeonite from *C2/c* to *P2₁/c* and this difference can be attributed to the difference in the mechanism of transition whereby that of omphacite is associated with the redistribution of cations, while that of pigeonite is not.

The schematic phase diagram shown in fig. 3 is constructed on these views.

The critical temperature of the transition of omphacite is very low. Hence the nonideality of the jadeite–diopside series clinopyroxene, due to the presence of the *C* to *P* transition, may be small for the temperatures at which synthetic experiments are done. However, the thermodynamics of this pyroxene series at the low temperatures, corresponding to the glaucophane schist and epidote-amphibolite facies, may be affected by the non-ideality, which probably results in a negative deviation from Raoult's law and leads to an underestimation of the pressures determined by the quartz–albite–clinopyroxene equilibrium.

Acknowledgements. Our sincere thanks are due to Professor W. S. MacKenzie, Dr. Y. Matsui, Dr. P. E. Champness, and Dr. M. Tokonami for their critical comments on the manuscript, Dr. I. Bryhni and Professor I. Kuchiro for donating the samples, and Mr. K. Nakamura for drafting.

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[*Manuscript received 24 November 1975*]