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ELECTRON MICROPROBE ANALYSES OF GARNET IN GLAUCOPHANE SCHISTS AND ASSOCIATED ECLOGITES

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ABSTRACT

Analyses of zoned garnet in 15 different rock types from the Franciscan assemblage of California are reported. Specimen localities include the Tiburon Peninsula, Occidental, Ward Creek near Cazadero, and Santa Catalina Island, Garnet in glaucophane schists from Shubin, U.S.S.R. and Loh oelo, Java is compositionally similar to Franciscan samples.

Oscillatory zoning of garnet porphyroblasts is observed in rocks containing fine-grained monomineralic garnet bands.

Comparison of microprobe analyses of the present study with conventional analyses of garnets from the same outcrops indicates that the latter are most representative of inclusion-free outer zones of individual crystals.

Preliminary data for coexisting garnet, pyroxene and amphiboles shows similar fractionation of Mg and Fe in Franciscan eclogites and regionally metamorphosed glaucophane eclogites in the southern Urals.

INTRODUCTION

Coleman *et al.* (1965) and Chesnokov (1959) reported wet chemical analyses for garnet in eclogites associated with glaucophane schists in California and the southern Urals. Their analyses have recently been used by several workers calculating distribution coefficients for Mg and Fe in coexisting pyroxene and garnet in eclogites (Banno and Matsui, 1965; Perchuk, 1967; Saxena, 1968). Evans (1965) showed that garnets in eclogites of glaucophane schist terranes are compositionally zoned as are garnets of other metamorphic environments such as the greenschist (Brown, 1967), epidote amphibolite (Banno, 1965) and amphibolite facies (Hollister, 1966). The present paper reports the extent of inhomogeneity in Mg, Fe, Ca and Mn observed in garnets from several of the same localities studied by Coleman and Chesnokov: Tiburon, Occidental and Cazadero in California, and Shubin, U.S.S.R. In addition, analyses are presented for garnets of associated glaucophane schists, hornblende schists and other rocks of these localities as well as Santa Catalina Island, California and southern Java.

GEOLOGIC SETTING

Most samples of the present study are from the Franciscan assemblage of California (Bailey *et al.*, 1964) and in particular from the Tiburon Peninsula, Marin County, the type locality of lawsonite (Ransome, 1894). Garnet bearing rocks at Tiburon crop out as isolated blocks resting in soil developed on graywackes and shales or on incipiently recrystallized metasediments containing jadeite and/or lawsonite. Many blocks are coated with rinds of chlorite-actinolite schist and are interpreted by the author as tectonic inclusions which have been eroded out of associated serpentinite masses. All the Franciscan garnets of this study are from blocks which are out of place with the exception of sample 665-C-59 which is from a glaucophane schist sequence continuously exposed for 330 meters in Ward Creek (Coleman and Lee, 1963).

Glaucophane schists mapped as Franciscan and containing lawsonite and aragonite crop out on Santa Catalina Island west of the San Andreas fault near Los Angeles. Bailey (1941) mapped higher grade assemblages containing occasional kyanite as an older "Olas Series" thrust over the Franciscan. The Catalina samples of this study are assigned to the Franciscan by Essene (1967) but the presence of kyanite, tan hornblende and relatively pyrope-rich garnet distinguish them from Franciscan rocks of northern California.

Two specimens from Shubin near Mednogorsk in the southern Urals were kindly provided by Drs. B. V. Chesnokov and D. P. Grigoriev. Lawsonite has been found in the area, and eclogites similar to those of the northern California Coast Ranges crop out apparently in place in a regionally metamorphosed sequence of glaucophane-quartz schists (Chesnokov, 1959, 1961, 1963). The eclogites form boudinaged lenses up to several hundred meters long and tens of meters thick (Lennikh, 1963).

Sample 198–9 in the Berkeley collection is from the Loh oelo River near Banjoemas in south central Java. Associated rock types at this locality include glaucophane schist, aegirine-augite bearing quartzite, and garnet-blue-green hornblende schist (Niethammer, 1909).

PETROGRAPHY

Most garnet, except that in metacherts and garnetites, forms euhedral to subhedral porphyroblasts 0.5 to 2.0 mm in diameter. Metacherts have thin pink bands of fresh, euhedral garnet which is 0.01 to 0.05 mm in diameter and lacks inclusions. Some hornblende schists and occasional glaucophane schists and eclogites at Tiburon contain monomineralic garnetite bands up to 3 cm in width composed of anhedral grains 10 to 20 μm in diameter. Coarse-grained garnetites at Santa Catalina form boulders 6 m across (Essene, 1967) and contain interstitial quartz and tan hornblende; sample 665-Cat-8 contains garnet 5 mm in diameter. Garnetites associated with glaucophane schists have been reported from the North Berkeley Hills (Brothers, 1954), New Caledonia (Lacroix, 1942, p. 42), the southern Urals (Chesnokov, 1963) and the Pennine Alps (Bearth, 1959, p. 271).

Retrogressive replacement of garnet by other minerals has occurred in

FIG. 1. Electron beam scanning photograph of pyroxene vein in Tiburon hornblende schist 665-T-12. Na Kα radiation. Pyroxene invades blue-green hornblende along cleavages and cuts euhedral garnet (dark). Scale 400×400μm.

some of the coarse-grained Franciscan schists. At Tiburon, retrograde alteration of garnet is mainly accompanied by the growth of chlorite and white mica and less commonly by pumpellyite, lawsonite, aragonite (*cf.* Brown *et al.*, 1962), glaucophane and sodic pyroxene. Veins of sodic pyroxene cut garnet and blue-green hornblende in some hornblende schists (Fig. 1). Replacement of garnet by epidote was not observed. Other rocks show no retrograde effects; fresh garnet coexists with glaucophane (677–318), sodic pyroxene (292–4) and rarely lawsonite (665-C-59). Rims of accessory kyanite are altered to paragonite in 665-Cat-3 (Essene, 1967).

All garnets except those of the metachert 677–556 contain inclusions of other minerals, usually concentrated in the cores. Sphene and epidote are the most abundant inclusions and present a problem of calcium contamination in analysis. In some schists with no quartz in the groundmass, garnets contain quartz inclusions (677–707).

Sample 677–D from the southern Urals is composed of omphacite, garnet and actinolite with subordinate glaucophane and quartz. The actinolite optically resembles blue-green hornblende but is low in Al_2O_3 (3.6%: Klein, 1969, No. 3–3). Omphacite is concentrated in a green band. This rock resembles Tiburon sample 677–1417 from a single block exhibiting bands of hornblende eclogite, epidote hornblende schist, quartz-epidote eclogite and glaucophane-white mica-quartz schist (677–1351).

TABLE 1. REPRESENTATIVE GARNET ANALYSES[a]

	Urals 677		Tiburon eclogite 677-702		Cazadero "Type III" metabasalt 665-C-59		Occidental zoisite eclogite M169		Tiburon glauco-schist 677-707	Santa Catalina garnetite 665-Cat-8
	D	E	Core	Rim	Core	Rim	Core	Rim		
SiO_2	38.3	38.5	38.1	37.9	38.6	38.7	38.5	37.9	38.3	38.9
Al_2O_3	21.2	21.1	20.4	20.2	21.6	21.7	19.5	21.8	21.3	21.9
FeO	27.4	27.9	26.0	28.8	14.8	22.2	23.7	24.4	29.0	26.0
CaO	9.5	10.4	10.8	9.0	11.6	10.4	12.7	12.6	3.5	5.2
MnO	2.0	1.8	5.1	0.6	14.6	7.1	3.7	0.5	3.6	2.2
MgO	2.5	1.6	1.2	2.6	0.7	1.1	1.1	2.2	4.6	6.3
Total	100.9	101.3	101.6	99.0	101.9	101.5	99.2	99.4	100.3	100.5
	Numbers of ions on the basis of 12 (0)									
Si	3.01	3.02	3.02	3.04	3.02	3.02	3.09	2.99	3.02	3.01
Al	1.96	1.96	1.90	1.91	1.99	1.98	1.85	2.03	1.98	2.00
Fe	1.81	1.83	1.72	1.93	0.96	1.43	1.59	1.61	1.91	1.68
Ca	0.80	0.87	0.91	0.78	0.97	0.86	1.09	1.07	0.30	0.43
Mn	0.13	0.12	0.34	0.04	0.96	0.46	0.25	0.04	0.24	0.14
Mg	0.29	0.19	0.14	0.29	0.08	0.17	0.13	0.26	0.54	0.73

[a] Samples described in Key to Figure 2.

In neither rock is there textural evidence of replacement of amphiboles by omphacite (as there is in Tiburon hornblende schist 677–1403). Glaucophane partially replaces a few omphacite grains in 677–1417, and Lennikh (1963) reports replacement of omphacite by glaucophane in rocks of the Shubin area.

In Urals sample 677-E, pale glaucophane and sphene form a fine-grained matrix in which are embedded garnet porphyroblasts 6 mm in diameter containing quartz, epidote, rutile and sphene inclusions. Lenses

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M 169: Zoisite eclogite, Occidental. Collected by R. Rose. Microprobe analysis of pyroxene: jadeite 43, acmite 1, augire 56 mol percent (Essene and Fyfe, 1967, Table 1, No. 17).

Lee 113-RGC-58: Wet analysis of garnet in clinozoisite eclogite from same locality as M 169 (Lee *et al*, 1963).

677-318: Garnet-epidote-glaucophane schist, Tiburon.

Pabst 1955: Analysis of garnet in glaucophane schist from same locality as 677-318 (Pabst, 1931, 1955, Sample "B.")

677-736: Garnet-glaucophane-actinolite-epidote schist, Tiburon.

677–522: Garnet-epidote-omphacite schist, Tiburon.

677-707: Garnet-white mica-glaucophane schist, Tiburon.

677-C: Garnet-hornblende schist with garnetite bands, Tiburon. Collected by S. Rice. Hornblende and glaucophane analysed by Klein (1969, No. 4-2).

677-T-12: Epidote-garnet-hornblende schist, Tiburon. Collected by E. Essene. Veined by pyroxene: partial microprobe analysis: jadeite 20, acmite 27, augite 43 mole percent (Essene, 1967).

677-1403: Garnet-hornblende schist, Tiburon. Veined by pyroxene: jadeite 31± 7, acmite 30± 7 mole percent.

Samples collected on Santa Catalina Island by E. Essene and W. S. Fyfe:

665-Cat-3: Garnet-zoisite-tremolite-albite (an 7) rock with accessory kyanite and paragonite (Essene, 1967).

665-Cat-8: Garnetite with interstitial quartz.

665-Cat-34: Garnet-zoisite-hornblende schist.

665-Cat-37: Garnetite with interstitial tan hornblende. Occurs as bands in hornblende schist.

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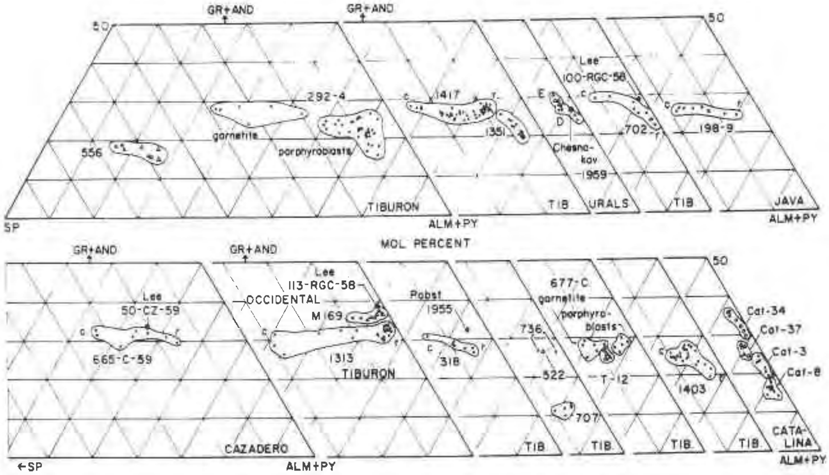

FIG. 2. Garnet analyses.[1] Compositions plotted in the lower portion of triangles representing spessartine, almandine+pyrope, and grossular+andradite mole percent. For probe analyses, all Fe calculated as almandine. c = core, r = rim.

Approximate jadeite and acmite content of coexisting pyroxenes estimated by method of Essene and Fyfe (1967) using 221 spacing and β refractive index.

KEY TO ANALYSES

Left to right, upper row:

677-556: Metachert, Tiburon.

292-4: Eclogite with contorted garnetite bands Collected at Tiburon by R. Holway (1906). Pyroxene: jadeite 33 ± 7, acmite 20 ± 7 mole percent.

677-1417: Epidote-garnet-hornblende-omphacite schist, Tiburon. Pyroxene: jadeite 31-34 ± 7, acmite 17 ± 7 mole percent.

677-1351: Garnet-glaucophane-quartz schist interbanded with 677-1417, Tiburon.

677-D: Garnet-actinolite-omphacite schist, Shubin, U.S.S.R. Donated by B. V. Chesnokov. Pyroxene: jadeite 35 ± 7, acmite 17 ± 7 mol percent. Actinolite and glaucophane analysed by Klein (1969, No. 3-3).

677-E: Garnet-glaucophane schist, Shubin, U.S.S.R. Donated by B V. Chesnokov.

Chesnokov 1959: Wet analysis of garnet in glaucophane eclogite containing "anomalous glaucophane" and actinolite, Shubin, U S.S R. (Chesnokov, 1959).

677-702: Eclogite, Tiburon.

Lee 100-RGC-58: Wet analysis of garnet in eclogite from same locality as 677-702 (Lee *et al.*, 1963).

198-9: Omphacite-actinolite-glaucophane schist, Loh oelo River, Java. Partial microprobe analysis of pyroxene: jadeite 34, acmite 14, augite 52 mole percent (Essene, 1967).

From left to right, lower row:

665-C-59: Omphacite-garnet-glaucophane schist with aragonite and lawsonite, "Type III", Ward Creek (Coleman and Lee, 1963). Collected by E. Essene. Microprobe analysis of pyroxene: jadeite 42, acmite 4, augite 56 mole percent (Essene and Fyfe, 1967, Table 1, No. 5).

Lee 50-CZ-59: Wet analysis of garnet in Type III metabasalt (glaucophane-quartz-aragonite-clinozoisite-pumpellyite), Ward Creek (Lee *et al.*, 1963).

677-1313: Zoisite eclogite, Tiburon. Pyroxene: jadeite 35 ± 7, acmite 14 ± 7 mole percent.

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[1] To obtain a copy of analyses corresponding to points plotted in Figure 2 together with tabulated mineralogy of analyzed samples, order NAPS Document #00478 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting in advance $1.00 for microfiche or $3.00 for photocopies, payable to ASIS NAPS.

of green sodic pyroxene are present in the matrix. Pleochroic haloes surrounding tiny inclusions, possibly zircon, are abundant in the amphiboles of both Russian samples. Such haloes were not observed in the Franciscan rocks.

ANALYTICAL TECHNIQUE

All analyses were made with an Applied Research Laboratories EMX electron probe using an accelerating potential of 15 kilovolts and sample currents of 0.05 to 0.06 microamperes. Beam diameter was approximately one micron. Integration time was 20 seconds for all elements. Three elements were measured simultaneously during each traverse of a crystal: Ca, Mn and Mg followed by Fe, Si and Al. For the major elements, line intensity was greater than 1000 counts per second. Accuracy is estimated at about 2 percent of the amount present for major elements and 5 to 10 percent for minor elements.

Several standards were used in all runs, but for consistency, two garnets were used for all the calculations presented in this paper: almandine-pyrope No. 423 (SiO_2 39.50, Al_2O_3 21.53, FeO 20.91, Fe_2O_3 1.05, CaO 8.34, MgO 7.85 weight percent; Knorring and Kennedy, 1958) and almandine-spessartine Ely (MnO 11.96 weight percent; Pabst, 1938). These standards and all analysed samples are on file in the Department of Geology and Geophysics, University of California, Berkeley.

Analyses were calculated by a computer program written by Dr. W. Chinn. The program includes a linear correction for instrument drift (runs in which drift exceeded 3 percent were discarded), a background correction, and the unmodified Philibert correction for absorption.

Analytical totals in excess of 100 percent were obtained for the Mn rich cores of some strongly zoned garnets. Enhancement of observed intensity of Mn Kα radiation by fluorescence of Mn by Fe Kβ characteristic radiation is estimated to contribute an excess of no more than 3 to 4 percent of the amount of Mn present. Since this is insufficient to account for the high totals, the difficulty may be in Mn calibration or in imprecise repetition of analytical spots during the second traverse.

ZONATION

All the garnets studied are zoned to some extent. Analyses reported are for individual spots in crystals and are not averages. They do not necessarily represent maximum variation present in any sample since sections were not precisely cut to pass through the exact centers of porphyroblasts. Most of the crystals of the present study show the same pattern of zonation as that previously reported for metamorphic garnets (*e.g.* Hollister, 1966). Mn and Ca are preferentially enriched in the core, while Mg and Fe are enriched near the rim (Fig. 3). Samples 677–C, 318, 736 and 1403 show reverse zoning in Mn near the rims; such zoning is especially characteristic of garnet porphyroblasts in rocks containing fine-grained garnetite bands or veins. Porphyroblasts in the hornblende schist 677-C have Mn rich rims and are immersed in fine-grained garnet richer in Mn than the rims (Table 2). Oscillatory zoning in garnet of eclogite 292–4 is shown by two Mn-rich bands near the rim in eight porphyroblasts of the section that were examined (Fig. 4 a, b). Garnet in the associated fine-

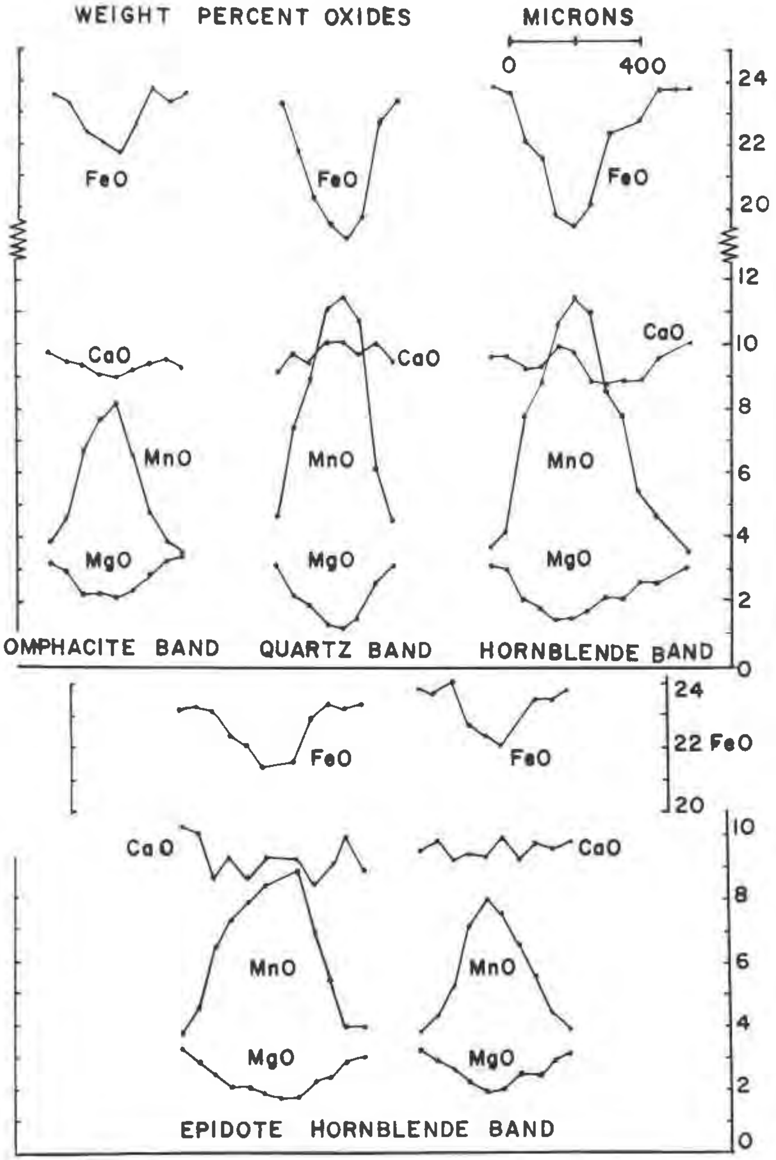

FIG. 3. Microprobe traverses of garnets in several bands of Tiburon sample 677–1417. Variation is not necessarily the maximum present in each crystal since section does not pass precisely through all crystal cores.

TABLE 2. COMPOSITION OF GARNETITE BANDS AND ASSOCIATED PORPHYROBLASTS IN HORNBLENDE SCHIST 677-C AND ECLOGITE 292-4, TIBURON PENINSULA

Mole Percent	677-C Porphyroblasts		677-C Garnetite	
	Core	Rim		
Almandine	58.9	53.9	50.7	51.5
Grossular	28.9	26.8	27.0	24.9
Spessartine	2.3	6.1	11.8	13.1
Pyrope	9.9	13.2	10.5	10.4

	292-4					292-4	
Mole Percent	Oscillatory Zoning						
	Core				Rim	Garnetite	
Almandine	52.9	60.5	58.7	49.7	48.6	31.6	33.4
Grossular	24.5	21.4	18.3	25.0	23.6	27.9	28.7
Spessartine	15.4	7.4	9.0	3.9	12.7	37.4	32.8
Pyrope	7.2	10.7	14.0	13.3	15.0	3.1	5.1

grained garnetite band shows only Mn-rich cores with no zoning bands at the rims (Fig. 4c).

DISCUSSION OF ANALYSES

Comparison of the microprobe results with wet analyses of garnets from the same Franciscan outcrops (677–318: Pabst, 1931, 1955, Sample "B"; 677–702, M 169, 655-C-59: Lee et al., 1965, Nos. 100-RGC-58, 113-RGC-58, 50-CZ-59) shows that the latter resemble values obtained for the outer zones of individual crystals (Figure 2). Garnet analyses reported by Chesnokov (1961, Table 3) for Shubin amphibole eclogites and garnet-glaucophane schists are lower in Mn and higher in Mg than cores of garnet crystals 677-D and 677-E, although direct comparison is not warranted since samples may not correspond to the same outcrops. Since inclusions are often concentrated in garnets of this paragenesis, garnet cores are likely to be discarded during separation in preference to purer rim material relatively free of inclusions.

Saxena (1968, Table 1), using the analyses of Lee *et al.* (1963), found that distribution coefficients of Mg and Fe in coexisting garnet and py-

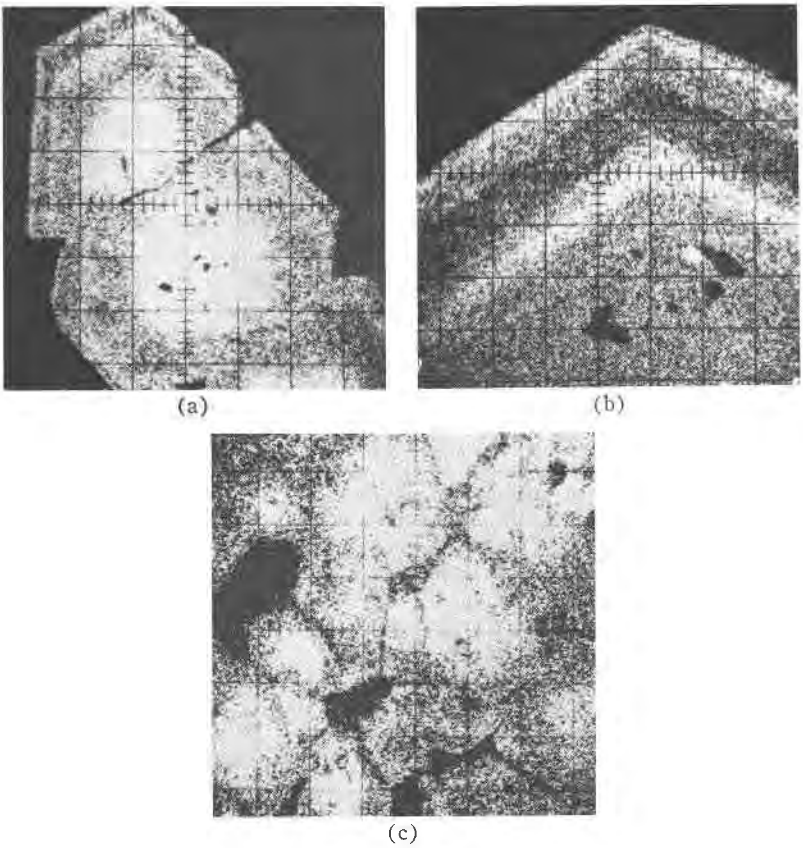
(a) (b) (c)

FIG. 4. Electron beam scanning photographs of garnet in Tiburon eclogite 292–4. Mn K α radiation. Bright areas represent greatest concentration of manganese. Scale 400×400 μm. (a) and (b) porphyroblasts showing oscillatory zoning at rim; (c) garnetite band in same thin section.

roxene in Franciscan eclogites fall in the range $K_{D(Fe)} = 0.033-0.053$.[1] If the inner portions of the garnets were considered, even lower $K_{D(Fe)}$ values would be obtained, further distinguishing eclogites associated with glaucophane schists from those of gneissic terranes. As an extreme example (for the garnet cores are unlikely to be in exchange equilibrium with the pyroxene of the matrix), $K_{D(Fe)}$ values were calculated for samples M 169 and 665-C-59 using the probe analyses of pyroxenes in the

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[1] $K_{D(Fe)} = \frac{X^{cpx}_{Fe}}{1 - X^{cpx}_{Fe}} \cdot \frac{1 - X^{gar}_{Fe}}{X^{gar}_{Fe}}$ where $X_{Fe} = \frac{Fe^{2+}}{Fe^{2+} + Mg}$.

same thin sections made by Dr. E. Essene (Essene and Fyfe, 1967, Table 1). Garnet cores give $K_{D(Fe)}=0.031$ and 0.027 and rims give 0.063 and 0.039 for M 169 and 665-C-59 respectively. Zoisite eclogite M 169 thus has a high K_D compared to other Franciscan eclogites, as does Occidental clinozoisite eclogite 113-RGC-58 (Coleman *et al.*, 1965; $K_{D(Fe)}=0.053$). Sample 665-C-59, a "Type III" rock from Cazadero in which lawsonite coexists with garnet, has a low K_D. This trend is in agreement with the lower temperature of formation of Type III rocks deduced from oxygen isotope fractionation by Taylor and Coleman (1968; e.g. 270°−280°C. for 50-CZ-59).

Glaucophane bearing eclogites of the southern Urals are of interest since they apparently crop out in place in a regionally metamorphosed sequence of glaucophane-quartz schists, rather than as enigmatic loose blocks which are characteristic of Franciscan terrances. Several lines of evidence show the similarity of rocks of both localities. Pyrope content in garnet and jadeite content in pyroxene of the eclogites is similar. According to the analyses of coexisting garnet (pyrope 8.8 mol percent) and pyroxene (jadeite 26, acmite 18 mole percent) determined by Chesnokov (1959), a Shubin eclogite has a $K_{D(Fe)}=0.024$. Further, Klein's (1969) analyses of coexisting glaucophane and actinolite in Urals sample 677-D shows fractionation of Mg and Fe identical to that in a Cazadero Type IV schist (Lee et al., 1966) and similar to that in Tiburon rocks.[1] Ernst (1968, p. 31) noted that Franciscan actinolite-glaucophane pairs show more pronounced fractionation of Mg and Fe than pairs from Japanese glaucophane schists, in agreement with the lower temperature of formation of Franciscan rocks deduced from mineral assemblages. Sample 677-D falls in the range of Franciscan pairs plotted by Ernst (1968, p. 32, Fig. 15a). Since eclogitic rocks similar to Franciscan types evidently have a regional metamorphic origin in the southern Urals, no support is provided for the contact metamorphic origin of Franciscan eclogites proposed by Essene *et al.* (1965).

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[1] According to Klein's data (1969, Tables 3 and 4):

$$\frac{\dfrac{\text{Mg}}{\text{Mg}+\text{Fe}}\text{glaucophane}}{\dfrac{\text{Mg}}{\text{Mg}+\text{Fe}}\text{ Ca amphibole}} = 0.84 \text{ in Urals 677-D and Cazadero 50-CZ-60 and 0.80 in Tiburon 677-C.}$$

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