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GARNET ZONING AND POLYMETAMORPHISM IN THE ECLOGITIC ROCKS OF ISLA DE MARGARITA, VENEZUELA

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Abstract

The eclogitic rocks of Isla de Margarita have been produced during two stages — the latter at a lower P/T — producing a continuous series of rock types from eclogite through amphibole eclogite and garnet amphibolite to diablastic amphibolite. Microprobe studies of the garnets of these rocks show two stages of garnet growth separated by a hiatus which generally included garnet resorption and a reversal of zoning patterns. All garnet growth took place during the formation of the eclogites and the second stage of growth exhibits a significant increase in pyrope/almandine. From experimental considerations, this indicates higher temperature conditions in the second stage. Garnet was resorbed during amphibolitization of the eclogites and the effect on chemical zoning was dependent on the reaction product.

Sommaire

Les roches éclogitiques de l'île de Marguerite ont produit au cours des deux étapes — la dernière à un P/T plus bas — une série continue de types de roches variant de l'éclogite à l'éclogite amphibole et de l'amphibolite à grenat à l'amphibolite diablastique. Des analyses à la microsonde des grenats de ces roches démontrent qu'ils correspondent à deux étapes de croissance séparées par un arrèt qui correspond généralement à une résorption du grenat et à une renversement des modèles de zonation. Toute la croissance de grenat a eu lieu pendant la formation des éclogites et on note une forte augmentation de pyrope/almandin pendant la deuxième étape de croissance. D'après les expériences, ceci indique une température plus élevée pendant la deuxième étape. Le grenat s'est résorbé pendant l'amphibolitisation des éclogites et l'effet sur la zonation chimique dépendait du produit de la réaction.

(Traduit par la Rédaction)

Introduction

The use of garnet as a petrogenetic indicator has proved to be invaluable for the interpretation of metamorphic processes and events. Bearth (1952), for example, noted the presence of garnets from the metamorphic zone of Monte Rosa with inclusion-rich cores surrounded by inclusion-free outer zones. He interpreted the cores to represent garnets grown during the older metamorphic event, probably antealpine, whereas the outer zones represent new garnet growth during alpine metamorphism. This interpretation has been corroborated by de Béthune *et al.* (1968) who described the chemical zoning of similar garnets from the same area. These authors noted that the inner core exhibits a "normal" zoning pattern, as has been described by Hollister (1966) and others, with Mn and Ca decreasing outwards from the center. However, they found an obvious discontinuity in the chemical zoning at the boundary between the inner and outer petrographic zones. This was interpreted as a resorption stage which followed the growth of the core. The growth of the outer zone is again accompanied by chemical zoning according to a fractionation scheme. Finally, there is a narrow zone at the outermost edge where there is a rapid increase in Mn accompanied by a decrease in Mg. This latter effect has been noted by several authors, notably Grant & Weiblen (1971), and most likely represents the effect of exchange reactions with other ferromagnesian minerals under retrograde conditions.

It is thus obvious that much information on metamorphic history may be gained by the detailed inspection of garnets from complex metamorphic terrains and this paper reports the results of a similar study on an eclogite sequence from Venezuela. The eclogitic rocks described are on Margarita Island (Fig. 1), which is one of the few islands on the continental shelf north of Venezuela. The island lies along the southwestern extension of the active Antilles volcanic island arc and the positive gravity anomaly associated with the arc tereminates at this point (Talwani 1966).

The bulk of the metamorphic rocks of the re-

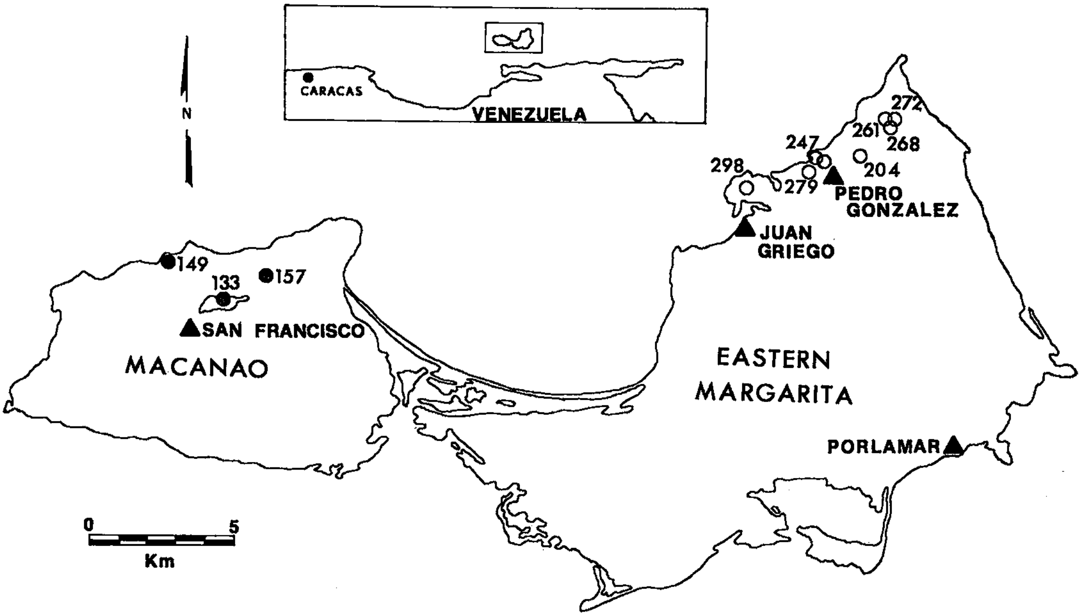


FIG. 1. Map of Isla de Margarita showing areas of eclogitic rocks and sample locations. Pedro Gonzalez-type rocks are shown as open circles. Macanao-type rocks are shown as closed circles.

Table 1. Chemical and Modal Analyses of the Eclogitic Rocks

	Eclogite				Amphibole eclogite						Garnet Amphibolite
Sample	157*	298	149*	247A	249	279	261	133*	268	204	272
SiO_2	47.5	47.8	47.1	46.9	53.4	48.3	50.6	47.3	48.4	48.1	45.8
Al_2O_3	16.2	12.1	13.2	17.0	14.4	14.8	16.1	13.0	15.2	14.6	10.6
TiO_2	0.5	2.66	1.60	0.76	0.60	1.30	0.76	2.24	1.80	1.80	0.86
Fe_2O_3	6.40	8.40	9.40	6.30	9.40	11.40	8.70	7.63	8.10	7.60	11.00
FeO	2.90	5.50	2.67	3.65	2.90	5.20	3.50	6.60	5.74	4.60	5.60
MgO	6.70	6.40	6.50	5.90	3.20	4.50	5.12	6.63	5.00	6.20	12.03
MnO	0.20	0.16	0.22	0.10	0.23	0.32	0.20	0.22	0.21	0.17	0.29
CaO	9.50	8.18	11.49	10.50	9.58	7.70	10.10	10.64	7.30	8.51	9.17
Na_2O	4.50	4.60	4.80	3.60	2.49	3.00	2.76	2.50	3.88	4.15	2.00
K_2O	0.02	0.60	0.02	0.06	0.02	0.01	0.17	0.03	0.15	0.10	0.08
L.O.I.	2.50	1.90	2.65	2.50	2.15	2.25	1.85	1.60	1.55	1.80	2.40
Total	96.98	98.30	99.65	97.28	98.37	98.78	99.86	98.39	97.25	97.63	99.83
Omphacite	40	50	60	59	24	25	10	5	20	30	-
Garnet	20	35	35	20	25	15	20	30	10	10	20
Sub-calcic amphibole	-	-	-	-	25	25	20	43	35	30	80
Clinozoisite	-	6	-	15	15	-	-	20	15	12	-
Epidote	-	-	-	-	-	15	20	-	-	-	-
Zoisite	20	-	-	-	-	-	-	-	-	-	-
Paragonite	5	1	3	Tr	5	4	5	-	5	10	-
Kyanite	8	-	-	-	-	-	-	-	-	-	-
Quartz	5	5	-	5	5	15	24	2	10	5	-
Sodic Plagioclase	-	-	-	-	-	-	-	-	5	1	-
Rutile	2	3	1	1	1	1	1	-	-	2	-
Others	-	-	1	-	-	-	-	-	-	-	-

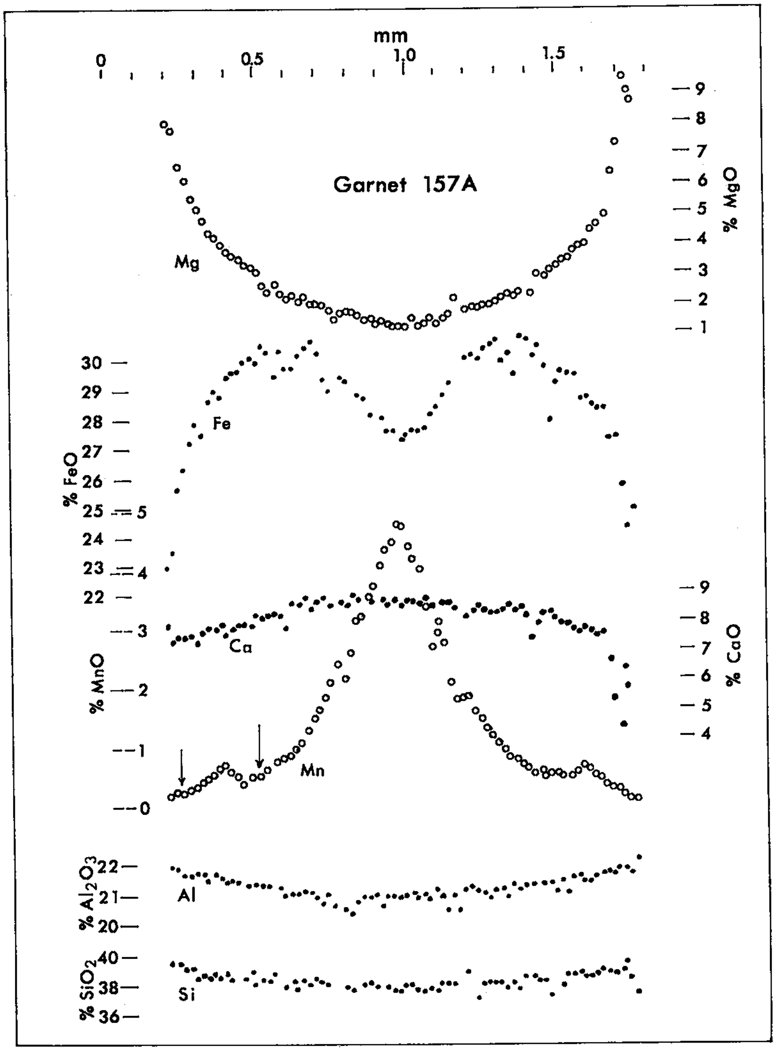
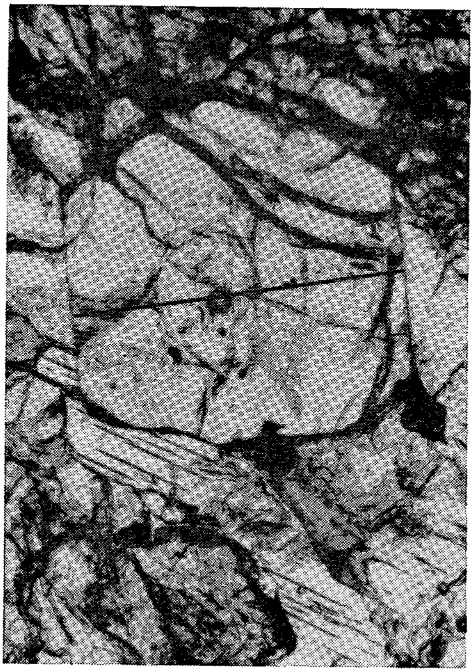


FIG. 2. Profiles of Mg, Fe, Ca, Mn, Al, and Si across garnet A from kyanite eclogite 157 (Macanao-type). Analysis points are at 20 μm intervals.

gion belong to a metasedimentary sequence which was originally divided into two main units: the Juan Griego Group and the younger Los Robles Group (Hess & Maxwell 1949). A series of intrusions of granitic to tonalitic composition and irregular elongate masses of serpentinized ultramafic rocks associated with metagabbros are also found within the metasedimentary sequence.

The Juan Griego Group consists of a thick sequence of occasionally garnetiferous, quartz-mica schists, graphitic schists, banded quartzites, lenses of marble and mafic gneisses of Lower Cretaceous to Jurassic age. As originally described by Hess & Maxwell (1949), the Group is divided into a quartzose division and a greenstone division. Taylor (1960) shows that the greenstone division is the older. Within the greenstone division, the predominant mafic gneisses, which might also be called banded amphibolites, represent several lithological types. It is within this group that rocks of eclogitic type have formed. These are massive rocks with abundant patches of green omphacite, garnet porphyroblasts, and randomly oriented porphyroblasts of paragonite. The rocks occur generally as tabular masses conformable to mafic schists and greenstones, and are restricted to the northern part of eastern Margarita where they grade laterally into amphibolite. These rocks will be referred to as "Pedro Gonzalez eclogitic rocks" since their major area of exposure is located near the town of Pedro Gonzalez (Fig. 1).

Locally within the rocks of the quartzose division of the Juan Griego Group, however, small bodies of eclogitic rocks are also found. These occur as recognizable boudins or as totally isolated blocks in the schists and gneisses at various stratigraphic levels within the quartzose division. Mineralogically and texturally, these eclogitic rocks are somewhat different from the Pedro Gonzalez type. Typically, they are massive and show no metacrystic paragonite. Their occurrence is not restricted to any region of the island but they are especially abundant in the western part which is called Macanao.


3A

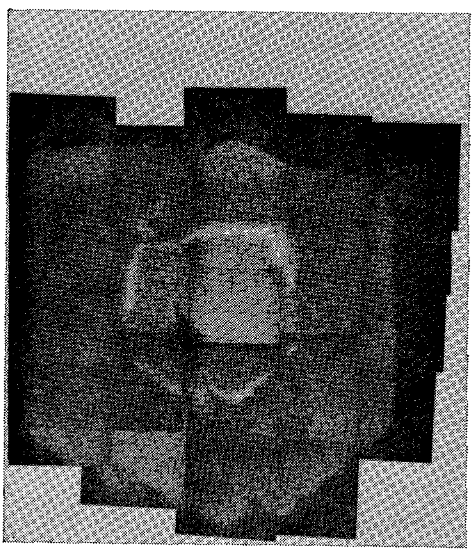

3B

FIG. 3. (A): Photomicrograph of garnet A from eclogite 247A (Pedro Gonzalez-type) showing the microprobe traverse. Note the inclusion-rich core. Plane polarized light. Field is 1.13 × 0.88 mm. Traverse of Figure 4 is from left to right. (B): X-ray image of manganese (Mn$K\alpha$) of garnet 247A. The mosaic is made up of several oscilloscope images of 200×200 microns.

A complete report on the petrogenesis of the eclogitic rocks of Margarita is in preparation and only a brief summary is presented here. From chemical evidence, the eclogites can be considered as having originated from basaltic lavas of spilitic affinity which were emplaced during the early orogenic, geosynclinal volcanism. Navarro (1974), from a study of the petrography of these rocks and the chemistry of mineral separates, has developed a three-stage process for the production of the eclogitic rocks and their subsequent amphibolitization. This process is chronologically in agreement with the regional deformation scheme proposed by Vignali (1972). Navarro (1974) proposed that an initial stage of high-pressure – low-temperature metamorphism transformed the proto-rock basalts into eclogites typical of the blueschist facies. He speculated that a second stage of metamorphism took place under conditions of higher temperature, with little or no increase of pressure, producing eclogites more typical of the amphibolite facies. This stage was accompanied by the growth of more pyropic garnet and a second generation of omphacite. Clinozoisite was typically produced at this juncture.

Finally, in a third stage, Navarro (1974) proposed an amphibolitization under conditions of lower temperature and possibly lower pressure. Garnet-clinopyroxene assemblages are in various stages of transformation from eclogites through amphibole eclogites and garnet amphibolites to garnet-free diablastic amphibolites.

Chemical Zoning in the Garnets

To more closely examine the effect of the polymetamorphic scheme on the chemistry of the garnets, samples representative of all stages were selected. Chemical and modal analyses of these rocks are given in Table 1. Samples 157, 298, 149, and 247A are true eclogites. Samples 249, 279, 261, 133, 268, and 204 are amphibole eclogites, whereas sample 272 is a garnet amphibolite.

Generally, the microprobe determinations were made in accordance with the method described by de Béthune *et al.* (1968). An ARL Model AMX Electron Microanalyzer was used with 20 kV operating voltage. Counting was normalized to integrated probe current (Martin *et al.* 1972) and raw X-ray data were reduced to compositional data using EMPADR VII (Rucklidge & Gasparrini 1969). Beam diameter was generally 4 microns and step-scanning was made using either 10 or 20-micron intervals. The counting error for all elements reported as oxides for each point is within 2 percent of 100 percent.

Results

The results of semi-quantitative and quantitative step-scanning traverses will be described in some detail. However, certain generalizations may be made. For example, Mn typically decreases from garnet centers to edges in a manner similar to that described by other authors. Similarly, Mg generally increases toward a garnet edge. Some Fe and Ca zoning, although reminiscent of the zoning patterns illustrated by Hollister (1966, 1969), is oscillatory. The zoning reversals at garnet edges noted by many authors (see Grant & Weiblen 1971; de Béthune *et al.* 1968) are well-developed in several of the garnets considered in this study. Typically, these reversals involve an increase in Mn and Mg coupled with a decrease in Fe. The behavior of Ca is variable.

Garnets from eclogites. The zoning exhibited by the eclogite samples studied by microprobe techniques is complex, but generally shows two growth stages separated by a stage of reaction and/or resorption as discussed by de Béthune *et al.* (1968). For example, garnets from eclogites 157 (Macanao type) and 247A (Pedro Gonzalez type) show two growth stages separated by a resorption layer. Garnet 157A (Fig. 2) shows an inner core with normal chemical zoning (Mn and Ca decreasing, Fe and Mg increasing). There is an inflection in the zoning pattern, at approximately 0.45 mm from center, where Fe and Ca decrease rapidly. Further growth is accompanied by decreasing Fe and Ca, increasing Mg, and no obvious change in the Mn fractionation pattern. A discontinuity occurs at a radial distance of approximately 0.65 mm from center where an increase in Mn and Ca is evident and accompanied by a rapid decrease in Fe. An outer growth zone then shows decreasing Ca and Mn whereas Fe decreases and Mg increases more rapidly. No obvious retrograde border zones are evident in garnets from this rock. Furthermore, all the garnets are euhedral and show no obvious corrosion.

A garnet typical of eclogite 247A is shown in Figure 3A where an inner core rich in quartz inclusions is surrounded by an inclusion-free outer growth zone. The zoning pattern for this garnet (Fig. 4) is complex and shows an inner core with increased Ca, decreased Mn and Mg, and relatively constant Fe. A rapid increase in Ca and Mn at about 75 microns from center marks the boundary between the inner and outer growth zones. The rise in Mn at this corroded boundary is conspicuous on the X-ray image presented as Figure 3B. Further growth is accompanied by increased Mg and Fe and decreased Ca and Mn. There is, however, a wide border reaction zone of increased Mn and Mg coupled with decreased Fe and Ca.

Garnets from eclogites 298 and 149 support the two-stage growth phenomena described above. The inner cores of these garnets are typically rich in included material whereas the outer zones are relatively inclusion-free. In the inner core, Mn decreases outward, Mg increases regularly, and Fe increases in an irregular fashion. Ca is relatively constant but typically increases outward. The boundary between the inner and outer zones is marked by a decrease in Fe and Ca, and growth in the outer zone is typified by

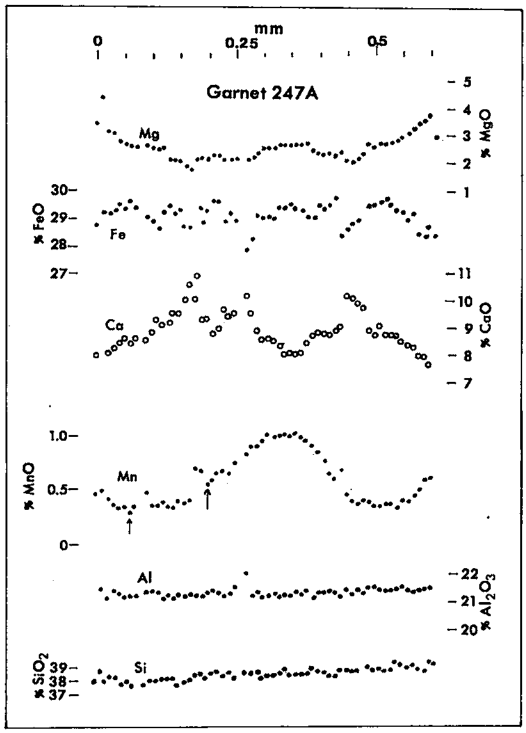


FIG. 4. Electron microprobe profile across garnet 247A. Analytical spot interval is 10 μm.

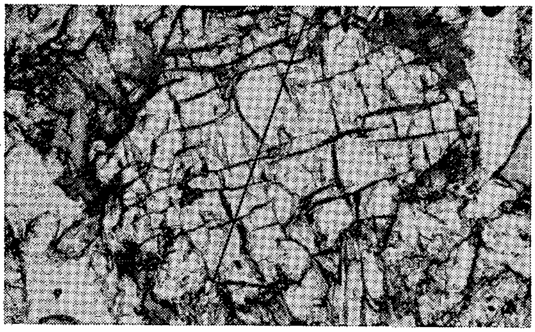


FIG. 5. Photomicrograph of garnet B from amphibole eclogite 249 showing microprobe traverse. Plane polarized light. Field size is 1.80×1.28 mm.

enriched Mg and depleted Fe and Ca. A zoning reversal within 50 microns of the garnet edge is marked by an increase in Mn. Fe decreases and Mg increases in this border zone but the magnitudes are different between the two edges examined. Since the border pattern is probably due to exchange reactions, the nature of the materials taking part in the exchange is important in resolving asymmetrical profiles.

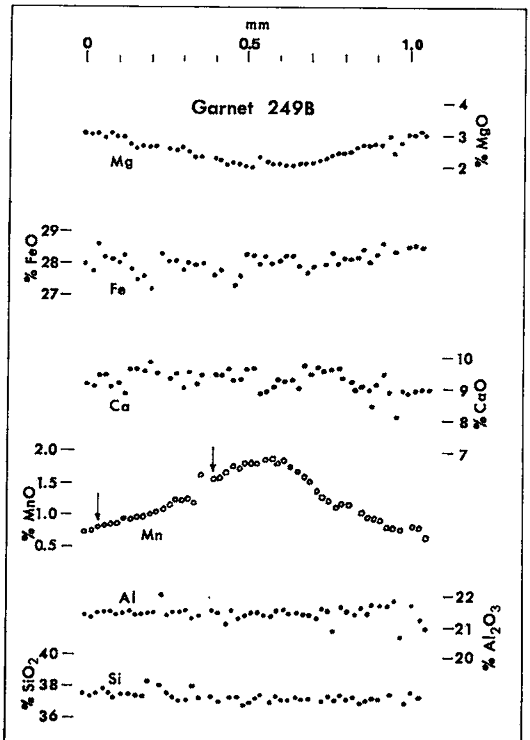


FIG. 6. Electron microprobe profile across garnet 249B. Analytical spot interval is 20 μm.

Garnets from amphibole eclogites. Fifteen garnets from the amphibole eclogites of Margarita Island were studied by electron microprobe techniques. The bulk of the resultant zoning patterns is much the same. Thus, the discussion which follows is based on representative garnets for which there are quantitative data.

All of the garnets examined show two stages of growth separated by a resorption layer as described by de Béthune *et al.* (1968, 1975). Garnet 249B (Figs. 5 & 6) is representative of this group. An inner growth zone is typified by increased Mg, decreased Mn, and oscillatory Fe and Ca. At 250 microns from center, there is a rapid rise in Mn followed by a second growth zone which exhibits a normal depletion pattern. A zoning reversal at the extreme outer edge is not obvious. Due to the anhedral nature of garnet grains in this sample, one cannot be sure that a profile traverses the true grain center. The largest grain in the section was chosen to minimize this problem.

Zoning profiles for two garnets from sample 261 are shown in Figure 7. Generally, the zoning in the inner growth zone is similar to that exhibited by Garnet 249B, described above, with increasing Mg and Fe, a bell-shaped depletion curve for Mn, and oscillatory but rising Ca. The break between the inner and outer zones of growth is marked by a rapid rise in Mn and Ca and a decrease in Fe and Mg. The increase in Mn is particularly obvious in the X-ray scanning photo (Fig. 8). In the outer rim, Mn decreases steadily to the grain boundary. Garnets in this rock are generally euhedral and show little or no corrosion of outer edges. Furthermore, they typically have few inclusions in either inner or outer growth zones.

All of the amphibole eclogites examined in this study were of the Pedro Gonzalez type except for sample 133 which, however, shows two-stage growth as exhibited in Figure 9 where an inclusion-rich inner core is surrounded by a relatively inclusion-free rim. This petrographic feature is common in these rocks but may be most easily compared to garnets from eclogites 247A (Pedro Gonzalez type) and 298 (Macanao type). Microprobe scans on garnets from sample 133 are typical of the amphibole eclogite garnets described above, but with a distinct zoning reversal evident at the extreme outer edge.

Garnet from garnet amphibolite. Two garnets from sample 272, a typical garnet amphibolite, were examined by microprobe techniques. The zoning for both was quite similar and showed normal Rayleigh depletion profiles for a single growth stage. The profile for garnet 272B (Fig.

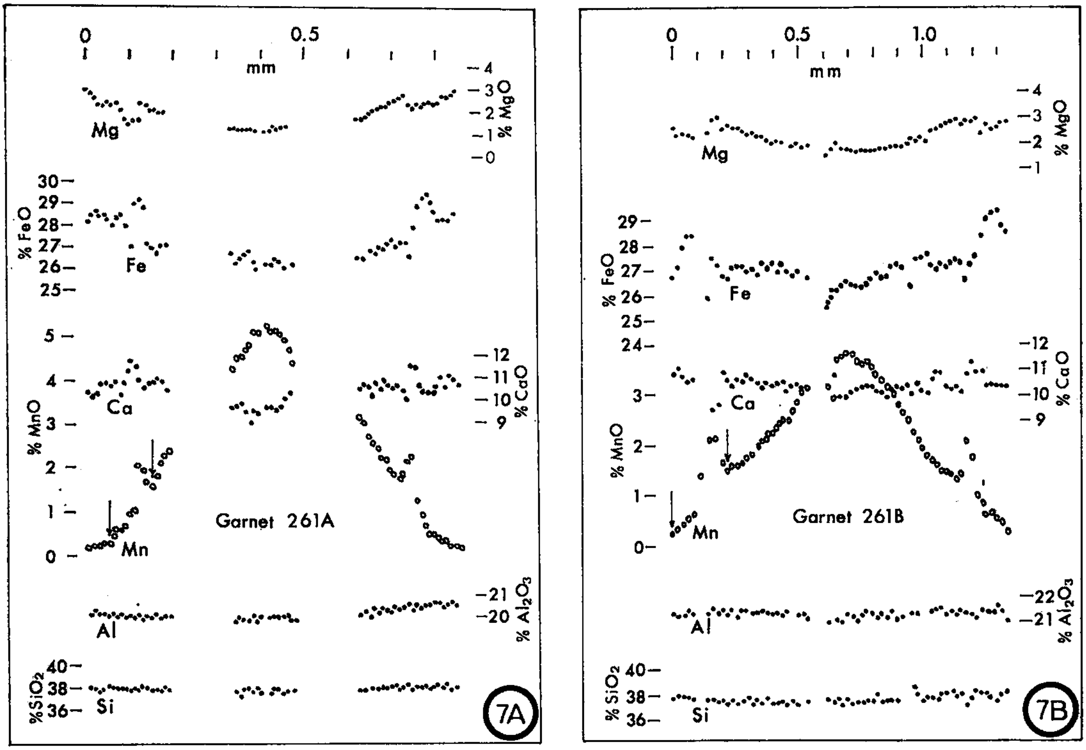


FIG. 7. (A): Microprobe profile across garnet A from amphibole eclogite 261. Step scanning at 10 μm intervals was done on three linear traverses. (B): Profile across garnet B from amphibole eclogite 261. Analytical spot interval is 20 μm.

10) is typical: Mn and Ca decrease toward the grain edge with concomitant increase in Fe and Mg. There is, however, a reversal of the zoning patterns for Fe and Ca within 150 microns of the garnet edge. This may be due to resorption at a retrograde stage or growth under conditions of a changing mineral assemblage.

DISCUSSION

As described in earlier sections, most of the garnets from the eclogitic rocks of Margarita Island have chemical profiles which indicate two stages of growth. This conclusion is corroborated in several cases by petrographic evidence of garnets with inclusion-rich inner cores rimmed by inclusion-free outer growth zones. The difference in chemical fractionation patterns between the initial growth and the second growth generally involves a sharp increase in MgO/FeO. Furthermore, where two growth stages are observed, the inner zone or core generally exhibits increasing Ca from center to rim whereas the outer zone generally has decreasing CaO.

Petrographic evidence of corroded grain boundaries and late-stage zoning-profile reversals lead the authors to believe that the amphibolitization of the rocks involved no production of garnet. Garnets typical of the assemblages produced by amphibolitization of eclogite show corroded edges and reaction rims of symplectitic

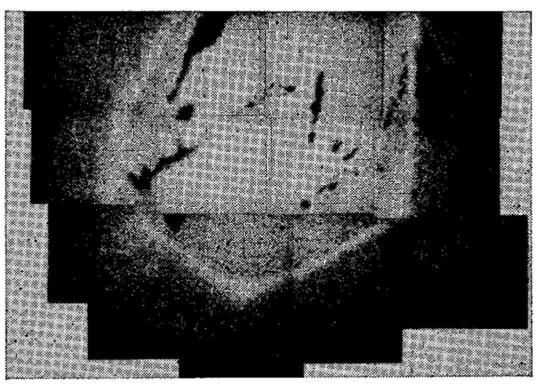


FIG. 8. X-ray image of manganese (Mn$K\alpha$) of part of garnet 261B. The mosaic is made up of several oscilloscope images of 200×200 microns.

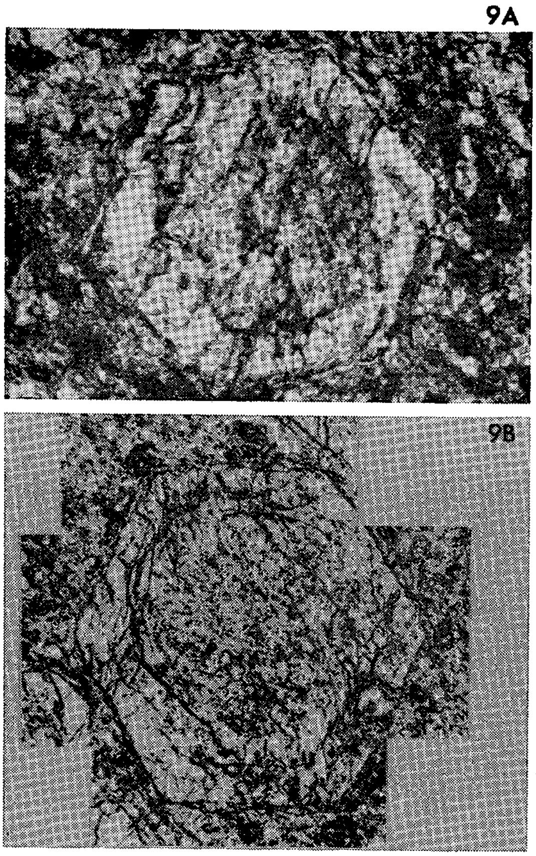


FIG. 9. Photomicrographs of two garnets from amphibole eclogite 133. Note the inclusion-rich cores with inclusion-free outer growth zones. The garnet in photomicrograph A has a diameter of 0.9 mm; that in micrograph mosaic B has a diameter of 1.7 mm.

plagioclase and amphibole. Generally, edges of these garnets have zoning reversals accompanied by a sharp decrease in Fe coupled with a rapid rise in Mg. Ca may increase or decrease, the particular case probably being dependent on the nature of the reaction products and their ability to accept the Ca released during garnet corrosion. de Béthune *et al.* (1975) show a striking example of CaO increase in garnet due to non-acceptance of this element by retrograde chlorite.

Late-stage manganese zoning is complicated and somewhat unpredictable. In many of the amphibolitized samples, Mn shows an increase near the border, similar to that noted by other authors. This situation is probably indicative of the limited diffusion of Mn (and sometimes Ca) in garnet during retrograde reactions which involve products unable to accept Mn. On the other hand, several garnets in amphibolitized rocks such as 272, 261, and 249 show no border enrichment of Mn. In these cases, the zoning reversals for the other elements may be due to continued growth in a changing assemblage or, more likely since the garnets in question all show some corrosion of the grain edges, released Mn is accepted into the reaction product (amphibole). On this topic, it should be noted that garnets from eclogites 298 and 247A show rather strong zoning-profile changes for Mn, Ca, Fe, and Mg near grain edges. Since amphibolitization is not evident in these samples and, indeed, no other retrograde products are observed, one might speculate that the zoning reversals are due to continued growth in a changing assemblage.

The two growth stages exhibited by the garnets in the eclogitic rocks probably correspond to the two metamorphic events proposed for eclogite formation. The first, a high P/T stage, developed garnets with relatively high almandine content and is represented by the lower MgO/FeO cores of many of the garnets of this study.

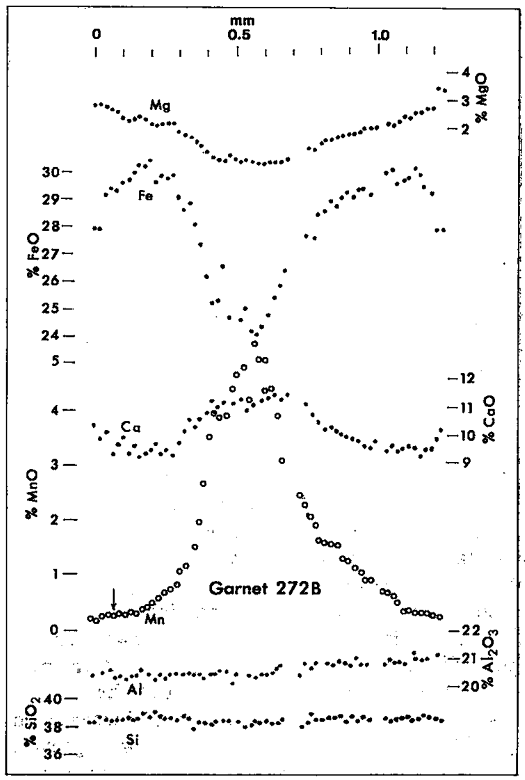


FIG. 10. Microprobe profile across garnet B from garnet amphibolite 272. Analyses are at 20 µm intervals.

The later growth stage, with accompanying higher MgO/FeO, may then be correlated with a higher temperature. This would agree with the experimental results of Råheim & Green (1974), who demonstrated that the Mg/Fe ratio of garnet in association with clinopyroxene increases with increasing temperature at constant pressure. These authors also show, in agreement with Crawford (1976), that garnet growth under increased pressure or decreasing temperature should involve enrichment in grossularite content. This feature is also generally observed for the inner cores of the two-stage garnets of this study. Most outer rims of the garnets of the present work show decreased CaO which could indicate growth accompanying an increase in temperature with little or no increase in pressure (Råheim & Green 1974).

As the physical conditions of metamorphism change, or the relative proportions or types of reactants vary, inflections should be produced in the zoning profiles of the garnets. Inflections of this type are noted especially in the MgO/FeO ratio, which changes radically between growth zones and within some growth zones. It is then interesting to analyze the compositional changes within the garnets in light of the work of Albee (1965) and Hollister (1969), who note a clear inverse relationship of Mn to the Mg/Fe ratio for garnets of medium-grade pelitic schists. This type of analysis involves the imposition of certain constraints in that the garnet compositions should represent limiting compositions as predicted by the phase rule. If this criterion is satisfied, then limiting compositions of garnets at certain stages would correlate by virtue of their production under conditions of similar pressure, temperature, and system reactants.

Points representing limiting compositions which are seemingly unaffected by the retrograde zoning reversals were selected (arrows on zoning profiles) as representative of the conditions under which garnet growth took place. The data are plotted in Figure 11 with weight percent MnO versus the ratio MgO/FeO. Two clear trends emerge, A and B, where B is the more magnesian. If each of the trends represents growth under similar physical conditions and with similar assemblages, then the zones may be grouped as to the metamorphic event. Thus, it is suggested that trend A represents growth under conditions which produced eclogites in the initial high-pressure – low-temperature stage. This trend includes the inner or first growth zones of garnets from eclogites 249, 298 and 247, and amphibole eclogite 261. Trend B includes the outer growth zones of these same

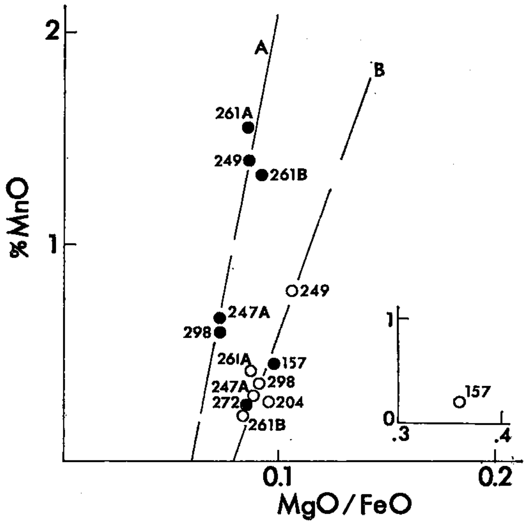


FIG. 11. Plot of MnO versus MgO/FeO for the limiting compositions of garnet growth zones investigated in this study. Solid circles represent inner cores and open circles represent second growth zones. The limiting compositions of the outer growth zone of garnet 157A are shown on an insert with the same ordinates. The compositions used are marked with arrows on the microprobe profile figures.

rocks, plus the inner growth zone of garnet 157A.

Hollister (1969) observed that the MgO/FeO ratios in garnets increase with metamorphic grade and that the limiting composition is sensitive to temperature changes. In this light, it is suggested that Trend A of Figure 11 is representative of the high *P*/*T* conditions of eclogite formation corresponding to the first stage of deformation proposed by Vignali (1972). Trend B of Figure 11 may then represent garnet growth during higher temperature second stage.

Sample 272 is a garnet amphibolite in which the garnets are typically corroded. Garnet 272A has a limiting composition which is representative of Trend B and it is suggested that this garnet grew solely during the second phase of eclogite formation. On the other hand, the garnets from Sample 157 are typically euhedral and all show two distinct growth periods. The inner core of Garnet 157A lies on Trend B and the outer zone is the most observed in this study. Sample 157, however, is atypical even for a Macanao eclogite and may indeed have been subjected to a different set of pressure and temperature conditions than the other rocks of this study.

Zoning reversals are noted at some grain boundaries and at the interface between inner and outer growth zones. de Béthune *et al.* (1968) and Grant & Weiblen (1971) have noted and ascribed similar occurrences to late-stage retrograde reactions between garnet and coexisting ferromagnesian minerals. The present authors believe that the reversals noted at the outer limits of the first growth zone represent reactions during a hiatus in garnet growth, probably between the first and second stages of eclogite formation. The reversals observed at grain edges are thought to have been produced during amphibolitization since there is good petrographic evidence that garnet was being consumed at this stage. It should be noted that the interface between growth stages is always marked by an enrichment of Mn whereas the later grain-boundary corrosion does not necessarily show this effect. In explanation, one must consider the significantly higher concentration of Mn involved in the corrosion reactions which followed the first growth stage, and the non-acceptance of this element by omphacite. On the other hand, Mn levels in garnet edges formed after the second growth stage are very low, and the corrosion product is amphibole which may accept manganese more readily.

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