A preliminary study of the structure, stratigraphy and metamorphism of some contact rocks of the western Andes, near the Quebrada Venado Muerto, Peru

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The sequence and structure of the volcanic rocks of a small area lying within the main belt of plutons of the Peruvian Andes were mapped and are here described. Metamorphic zoning of the calcareous aureole minerals was shown to be similar to that described elsewhere, e.g. wollastonite, diopside, hornblende with increasing distance from the contact. The mineral assemblages and their spatial and textural character indicate rapid heating of the aureole, with only a short time at maximum temperatures. The complex mineralogy in individual rocks is interpreted in terms of changing physical conditions during the thermal event. The sequential assemblages are the result of changes in activity of CO_2, H_2O and Fe^{3+} in particular.

1. Introduction

The work described here was undertaken as a preliminary study of the volcanic envelope which surrounds the complex chain of plutons forming the coastal batholith situated along the Andes in Peru. Generally the plutons of the western Cordillera separate a group of coastal volcanics from those to the east but in the area studied, along the Quebrada Venado Muerto, there is a break in the plutonic chain and the volcanics extend continuously from east to west. The area selected thus allows us to see the volcanics on either side of the batholith and to study the structure of the envelope across the batholith.

The area is also suitable for demonstrating the relationship of the metamorphic aureole to the plutonic bodies. Previously the sharp marginal contacts and small size or possible absence of an aureole has been emphasised. The metamorphic aureole visible in the field is of very limited extent and in many places there are no visible metamorphic effects even close to the contacts. New metamorphic mineral assemblages can nevertheless be recognised in thin section and it is apparent that the aureole effects extend out a considerable way from the contacts. Representative samples from the main lithologies of the area have allowed us to describe these new metamorphic assemblages and to map their spatial relations.

The data allows an estimate of the temperatures reached and the rate of heating and cooling of the envelope rocks. We believe that the nature of the aureole is of importance in understanding the mode of intrusion of the plutons, and that only an integration of the aureole geology with the geology and petrology of the batholith can give a complete picture of the mechanism of emplacement.

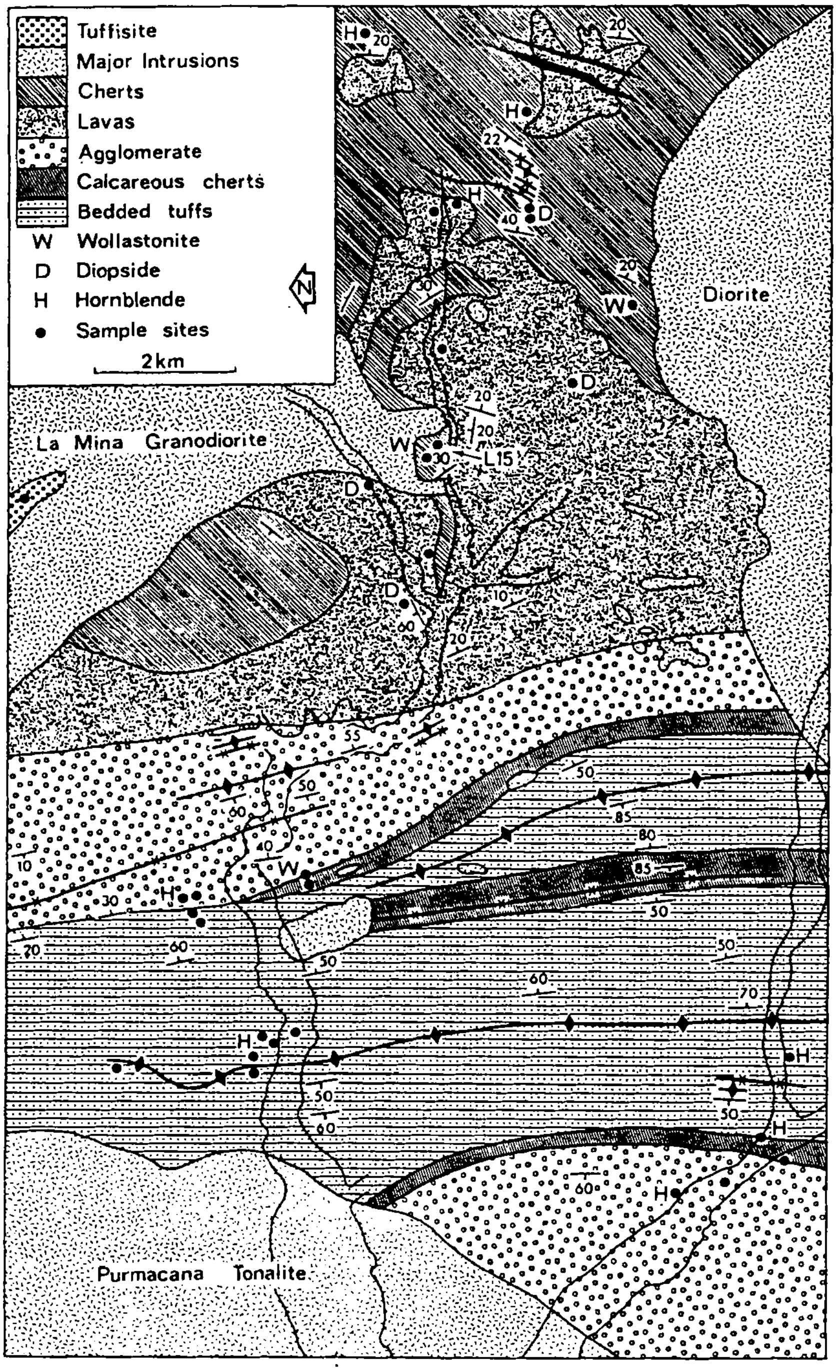

Fig. 1. Geological map of the area around the Quebrada Venado Muerto, Ancash Province, Peru. W—represents wollastonite bearing mineral assemblages, D—diopside bearing assemblages, E—epidote bearing assemblages. L15 is locality 15 with zoned garnets.

2. General geology of the area

The western Andes in Peru consist mainly of volcanics of Cretaceous and Tertiary age (Wilson 1963), intruded by the batholith.

A large area of the batholith in the Departments of Lima and Ancash has recently been described by Cobbing and Pitcher (in press). The area of approximately 200 sq. km. described here lies along the Quebrada Venado Muerto which is situated in the northern part of the area described by Cobbing and Pitcher (1972 in press).

Generally the batholith separates the coastal volcanics from those to the east, but in the Q. Venado Muerto there is a break in the plutonic chain and volcanics extend continuously from east to west. The volcanics here are cut by several large intrusions: in the west is the Purmacana Tonalite, in the north a tongue of La Mina Granodiorite while to the south there is an extension of a diorite mass (Fig. 1). These intrusions were mapped and described by Cobbing and Pitcher (*op. cit.*).

The volcanics of western Peru can be referred to two major groups; a lower Casma Group separated by an unconformity from an upper Calipuy Group. The Calipuy Group is only found to the east of the batholith and was not present in the area mapped. The Casma Group is a sequence of eugeosynclinal volcaniclastic sediments, lavas and massive tuffs, which according to the limited fossil evidence is partly or wholly of Albian age.

2a. Structure

The westward dip of the coastal volcanics of the Casma Group and the flat lying or eastward dip of the volcanics east of the plutons suggests that the plutons are intruded into a broadly anticlinal structure (Cobbing and Pitcher *op. cit.*). The major structure seen along the Quebrada Venado Muerto is anticlinal and might represent the core of the large scale anticline. The anticlinal axis is exposed in an approximately medial position in relation to the adjacent batholith. The most westerly rocks in the area dip westwards while Casma Group rocks, 3 km east of the batholith, dip eastwards.

Although the overall structure is anticlinal there are many smaller open, tight, or occasionally isoclinal folds. The style of folding is determined largely by the lithology and presumably the competence of the sequence. The massive lavas are not seen to be involved in any tight folding and usually have dips less than 30°. The tuffs and agglomerates are deformed into open folds with angular hinges and limbs which usually dip up to an angle of 60°–70°. The bedded cherts have in places been folded into tight to isoclinal folds with steeply inclined axial planes and sometimes slight overturning of one limb. Although the main anticlinal axis is nearly horizontal and can be traced for several miles many of the smaller folds have plunge culminations and appear to be periclines developed on the limbs of the major fold. Folding can be seen to be restricted to certain horizons notably where tight folds in the bedded cherts in the east of the area die out upwards so that the upper part of the chert succession dips gently east. Similarly tight folds in the agglomerates seen on the north side of the Q. Venado Muerto become reduced to low undulations at a higher level. The differential deformation of different lithological units may well have facilitated fracture in the more competent rocks and at least have provided some space for intrusion into the anticline.

2b. Metamorphism

There is relatively little evidence in the field in this area for a metamorphic aureole around the plutons. The main effect recognisable is epidotisation of the lavas and sometimes the calcareous cherts up to one kilometre from the nearest major intrusion. Otherwise garnets about 1 mm diameter were recognised in only one exposure which was of calcareous cherts within 50 m of a pluton margin. However, specimens collected from many localities throughout the area show that the effects of metamorphism are widespread, and the mineralogy is complex.

3. Stratigraphic succession

Cherts and interbedded lavas (top not seen), c. 500 m.
Lavas with subordinate cherts, c. 1000 m.
Agglomerates with associated bedded tuffs, c. 500 m.
Calcareous cherts, 0–100 m.
Bedded tuffs, 1150 m +.

3a. Bedded tuffs

The core of the main anticline is in massive dark grey porphyritic andesites which are part of a thick sill. The bedded tuffs lie above the sill and are well exposed on both limbs of the anticline. The tuffs vary from coarse to fine and are usually bedded in units more than one metre thick. All the lamination observed was parallel to the set boundary and grading was recorded from only one place. There is no evidence of sorting and reworking of the tuffs by currents which suggests the succession may have been deposited in a considerable depth of water, and at least below wave base.

The tuffs are composed of lava clasts and crystals. The clasts are commonly aphanitic and vesicular, but some contain felspar microlites and some are porphyritic. The lava clasts compare closely in petrology with the lavas higher in the succession except that yellow-green hornblende is more common in these clasts. The crystals are mainly andesine and lesser amounts of colourless pyroxene or green to yellow hornblende. There is a widespread alteration of the plagioclase and some of the lava clasts are altered to green hornblende and some is uralitised to a pale green fibrous hornblende. Other metamorphic effects are described in later sections of the paper.

3b. The calcareous cherts

This formation is seen on the south side of the Q. Venado Muerto where it is folded into a tight slightly overturned syncline and is exposed again, dipping eastwards, on the flank of the complementary anticline. The syncline and anticline do not cross the Q. Venado Muerto, and neither do the Calcareous Cherts, which are possibly cut out by faulting.

The rocks are buff or cream coloured well banded calcareous cherts. The banding is generally parallel with the strike of the formation but locally the banding is involved in very irregular folds a few metres in amplitude which bear no relationship to the regional folding.

The banding in the chert appears to be the result of slight differences in the coarseness of the texture, or in other cases to calcareous bands. The textural differences of the lamination is accentuated where metamorphism has resulted in the growth of new minerals.

3c. Agglomerates with associated bedded tuffs

Massive lapilli tuffs and agglomerates occur interbedded particularly near the base. The massive agglomerates are not clearly graded or sorted, but the field characters are insufficiently clear to determine whether the rocks were formed by fall from an ash cloud or from subaqueous flows.

The difference between the rocks of this formation and those of the underlying bedded tuffs is mainly one of grain size for the petrological characters are very similar.

3d. Lavas

Massive greenish-grey to dark grey lavas succeed the agglomerates with a sharp contact. Many horizons within the lava succession are markedly vesicular and these may delineate successive flows. At a few horizons poorly developed pillows with associated chert are seen. Silicification in the form of veins and nodules has locally altered the lavas, and the sequence is veined with epidote particularly near to intrusions where the lavas are darker grey. Interbedded banded chert horizons are thin and lenticular near the base of the formation but form thicker units towards the top where they are commonly considerably folded and contorted.

The lavas can be aphanitic with small lath shaped felspars, which may be hopper crystals, with a few andesine and pyroxene phenocrysts or they can be almost holocrystalline andesine, pyroxene rocks. In the latter the andesine is relatively small and lath shaped while the pyroxene occurs interstitially but also as large phenocrysts.

Although most lavas contain primary pyroxene occasional rocks have a green-yellow hornblende which also appears to be primary and many rocks show alteration of pyroxene to hornblende. Vesicles in the lavas are filled with calcite, chlorite or zeolites.

Close to the contact with La Mina Granodiorite the lavas become banded parallel with the vertical contact and are hornfelsed. The rocks have a dark green to mid-green hornblende, diopside and plagioclase in an equigranular mosaic sharing excellent triple junctions. Similar banded hornfelsed elsewhere have been interpreted as arising from the hornfelsing of mylonitic contacts.

3e. The upper cherts

There is no sharp contact between the cherts and the underlying lavas as these are interbedded for a few hundred metres. The main part of the chert succession consists of white and black banded cherts, the latter often weathering a rusty brown. Interbedded are thin, fine to coarse bedded tuffs and occasional thick massive tuffs which are slightly graded at their top. The top of the chert formation is not seen in the area mapped but the cherts are shown to continue some 3 km east of the plutons.

The banded cherts frequently contain fine tuffaceous material, particularly small felspars. Small patches of calcite and epidote are very common together with a very fine brown formless mineral.

3f. Minor intrusions

Although some areas of the envelope close to the plutons are riddled with dykes in this particular area dykes are quite infrequent and the only major dykes are in the east of the area.

There are however a number of sills and their frequency may be underestimated as it is not easy to distinguish sills from lava flows. The sills which have been investigated are holocrystalline andesine, hornblende rocks, sometimes with large ore grains. The andesine is in large rectilinear crystals and the hornblende occurs as large interstitial crystals. Pale green to yellow hornblende is altered to pale green or blue-green hornblende.

Associated with the dykes in the east of the area there are intrusive breccias. A large breccia body also occurs cutting the La Mina Granodiorite. The breccia mass occurs as a vertical body which is apparently a pipe. The breccias are mainly massive and structureless but some show a horizontal bedding.

4. Metamorphic minerals

Samples representative of each formation, were collected from over forty localities within the area (Fig. 1). The metamorphic minerals described below are uniformly fine grained and are usually only detectable in thin section. The minerals are related to three separate plutons but the mineral assemblages and their distribution relative to the pluton margins is similar in each case. It has therefore not been necessary to describe the aureole assemblages separately.

4a. Wollastonite

Wollastonite occurs in two calcareous cherts from localities within 300 m of a pluton contact (Fig. 1). The wollastonite forms coarse bladed, radial groups of crystals, commonly twinned and is associated with diopside, idocrase, garnet and sphene. It appears to have crystallised early in the aureole metamorphism, and rocks containing it are quite markedly made over to new aureole assemblages.

4b. Diopside

Diopside is present in calcareous cherts and lavas from eight localities, which are all within 1500 m of the intrusions. It occurs as small rounded crystals, blebs, or aggregates which overprint the groundmass but also commonly occurs within scapolite and plagioclase where it may be associated with garnet. Sometimes the diopside is seen to be replaced by hornblende.

4c. Garnet

Garnet was found in calcareous rocks from two localities close to major plutons. It occurs as small individual euhedral grains or aggregates in the fine grained rocks, and as coarse layered aggregates in the coarser grained rocks. Some garnets have a zonal structure with a core and outer corona; this is often absent in the very small crystals, while in the large aggregates there are more complex structures with sometimes three or more concentric zones of euhedral garnet.

Symmetrical zonal structures are well developed in a small number of garnets from the impure calcareous chert; the core is yellow-brown or occasionally bright yellow green in colour and isotropic, while the outer zone is colourless and birefringent (Pl. 7a). X-ray powder analysis revealed the garnet to be grossular. The yellow colour is typical of grossular while the colourless rim suggests grossular with iron and manganese less than 2% (Deer, Howie and Zussman, Vol. 1, 1962 p. 96). It is not clear from the microprobe work which of these elements is responsible for the colour. A banded

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Plate 7

a Granular garnet with dark coloured cores in plates of scapolite, × 50.

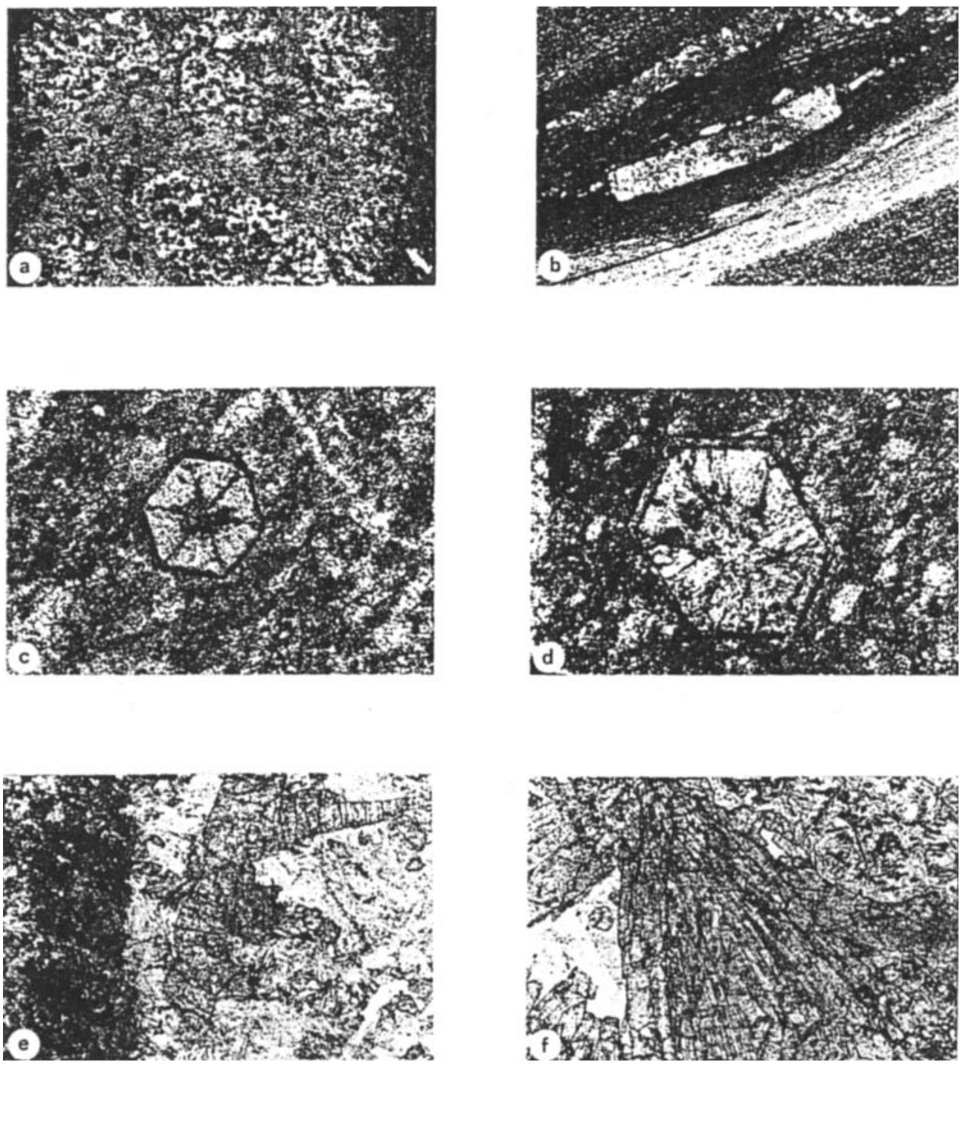
b Bioclastic fragment in fine grained chert-carbonate rock, containing garnet (high relief), and scapolite (right hand corner), × 12.

c Garnet from locality 15, showing well developed inclusion pattern along sector joins, × 100.

d Garnet from locality 15, showing a distinct rim and small tubular inclusions at right angles to the crystal faces, × 100.

e Clinozoisite, in a vesicle with a dark rim, overgrowing radiating tremolite, × 50.

f Radial clinozoisite in a vesicle, × 50.


a
b
c
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calcareous chert from locality 15 is made up of thin layers of epidote, calcite and garnet alternating with quartzose layers. Occasional bioclastic fragments contain garnet with epidote scapolite and idocrase (Pl. 7b). The garnet is large and often shows the euhedral zoned form described above, as well as more complex forms with three zones, of which the intermediate is yellow in colour. Again the X-ray analysis revealed only grossular.

In another sample from locality 15, euhedral garnet occurs in a calcite groundmass, with a dark very fine grained dust of unknown mineralogy. This sample was studied in some detail because of some intriguing textural features (Fig. 2). The garnet occurs as very numerous small euhedral crystals, 500 to 50 microns in diameter, which all have a beautiful symmetrical zonation (Pl. 7d). The core is birefringent, sector twinned and contains many unoriented inclusions sometimes very large in size, usually of calcite and unidentifiable fine dark material. Inclusions are common along the sector joins and also more rarely (see also Harker 1932 and Powell 1966) as parallel arrangements at right angles to the crystal face (Pl. 7c and d, and Fig. 2). Surrounding the core is a zone, usually about a quarter or less the radius of the core, of clearer birefringent garnet, also twinned, but showing fewer inclusions than the core (Fig. 2). Sometimes the core-corona boundary is full of very small inclusions. Immediately away from the join, the garnet is often irregularly coloured a strong yellow or yellow-brown, which fades towards the outer edge of the crystal.

This garnet is unusual in that on X-ray analysis the separated material was seen to be made up of two distinct garnets, andradite and grossular; this was confirmed by the micro-probe analysis. In the X-ray powder photograph the grossular lines were seen to be very sharp while those of the andradite were quite diffuse. This could well be the result of a marked change in composition across the rim as inferred from the colour variation and shown in the micro-probe scanning picture. The colour of andradite is related to the Mn and Ti contents (Deer, Howie and Zussman, Vol. 1, 1962 p. 92), and the micro-probe scanning pictures (Pl. 8) clearly indicate that the irregular colour zoning is associated with the decrease in Ti content across the rim. Microprobe traces across the garnets (Fig. 3) also show that MnO is concentrated in the grossular rather than in andradite. The rim values reach up to 30% Fe_2O_3 which is that of a rather pure andradite (Deer, Howie and Zussman, Vol. 1, 1962 p. 90). The Fe_2O_3 in the grossular is about 3%. The MnO is fairly consistent at about 1% in the grossular and 0·25% in the andradite. The age relationships of garnet are not very clear although it is often euhedral and small and appears to overprint the groundmass and some of the thermal minerals.

4d. Idocrase

Idocrase is found in the same localities as the garnet and is most often intimately associated with it, either surrounding garnet or in triangular areas between large grains. It frequently shows fine zoning and grey-green birefringence colours. The age relations appear quite consistent; it is after garnet.

4e. Scapolite

Scapolite occurs mainly in the calcareous cherts and occasionally in the tuffs in which it forms large plates which appear to be late, as they include much granular garnet and diopside. It replaces felspar, and is associated with epidote and idocrase (Pl. 7b).

4f. Hornblende

Hornblende of various types occurs in 15 of the 40 rocks studied. It is present in the

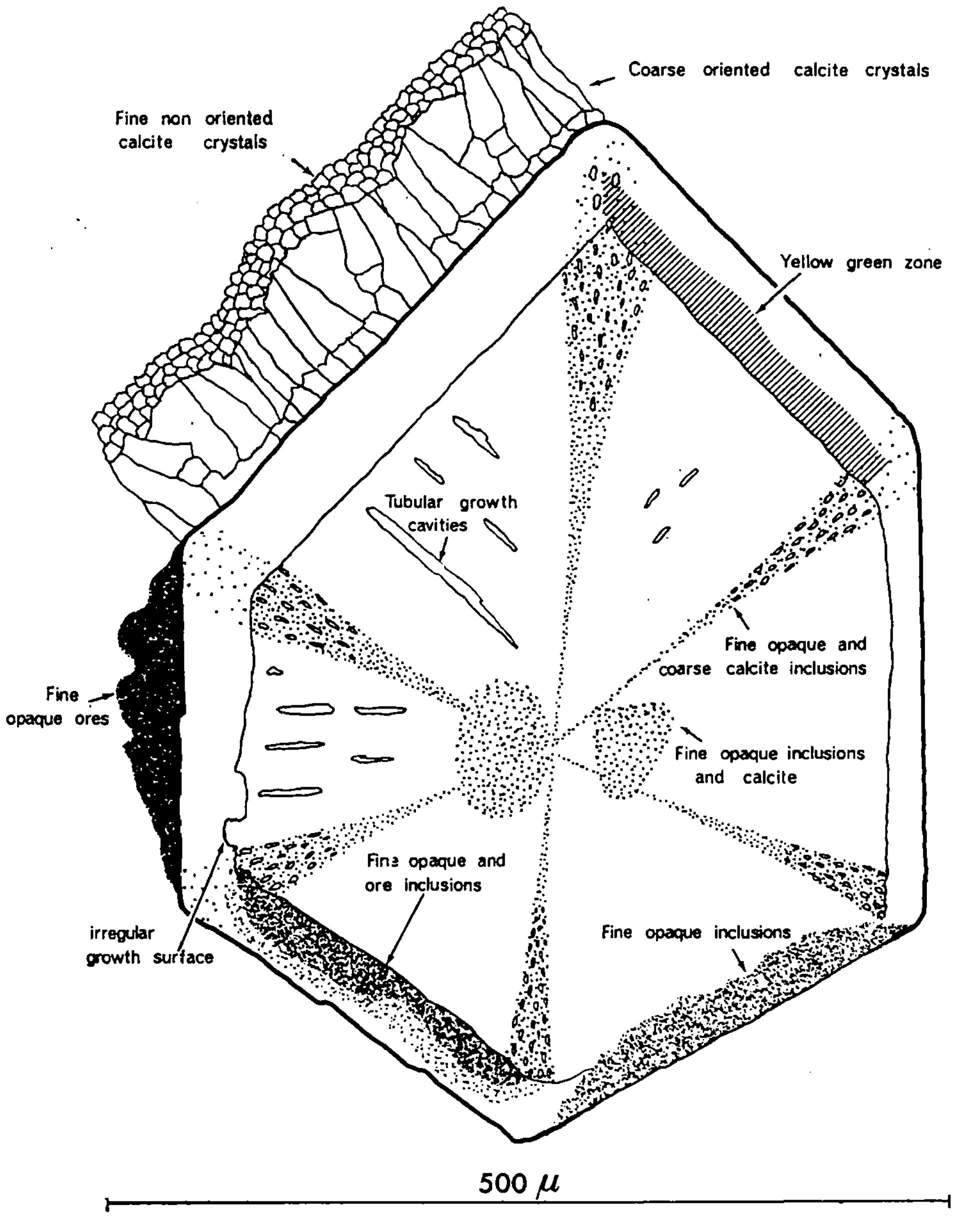


Fig. 2. Composite drawing of the andradite grossular garnet from an impure limestone from locality 15.

lavas, agglomerates and tuffs, but only occasionally in the cherts. It varies in colour from a dark green, almost khaki-yellow, to a rather typical blue-green variety which is sometimes surrounded by a green hornblende, and also to a pale almost colourless variety. It occurs as individual crystals, as fibrous rims to diposide, as fine veins, as alteration of igneous pyroxene, and as colourless radiating crystals in vesicles. In some of the lavas it is present as fine felts of radiating crystals which are very pale green and appear to be actinolite, but X-ray analysis suggested it is structurally similar to the coarser blue-green hornblende which is also present (cf. Binns 1965). In one rock green hornblende occurs as laths growing in altered igneous felspars (andesine) with a fine dentate texture. The relation to diopside is well shown in a lava where diopside occurs as a late growth inside an igneous felspar phenocryst and has an overgrowth of blue-green hornblende followed by green-brown hornblende. These occurrences indicate the crystallization sequence: plagioclase (igneous)→diopside→hornblende.

4g. Epidote

Epidote *s.l.* is common in the calcareous cherts, lavas and agglomerates and it may also occur in the bedded tuffs. It occurs as coarse plates and layered structures in laminae of the cherts, and as late filaments running through the rocks. It is made up of about equal amounts of green pleochroic epidote and colourless clinozoisite, either of which may enclose the other.

In contrast the lavas frequently contain radial or granular, cored clinozoisite in the vesicles (Pl. 7f), and bladed green epidote partially replacing original phenocrysts of felspar. Rarely, clinozoisite replaces tremolite in vesicles, cutting across the tremolite crystals at high angles (Pl. 7e).

4h. Stilpnomelane

Stilpnomelane is a fairly common mineral in some of the bedded tuffs and cherts. It is frequently of small amount and often fringes the ore and felspars. The areal distribution is uneven, but it tends to lie away from the pluton contacts. It also occurs along late fractures in the rock where it is a strong brown-yellow colour and has low birefringence.

5. Metamorphic assemblages

Some difficulty was encountered when analysing the mineral parageneses. Firstly, the rocks, particularly the cherts are very fine grained and identification of some of the aureole minerals was difficult. In many cases X-ray powder analysis was used to confirm the optical identifications. Secondly, the pre-metamorphic assemblages were only partially made over to the new thermal assemblages, so that polyphase assemblages are common. Thirdly, the new metamorphic minerals were not formed at the same time. The assemblages, which are not necessarily in equilibrium are listed below in order of increasing distance from the contact.

Plate 8

Electron microprobe scanning pictures of two garnets from locality 15:

a Electron picture of garnet (i)

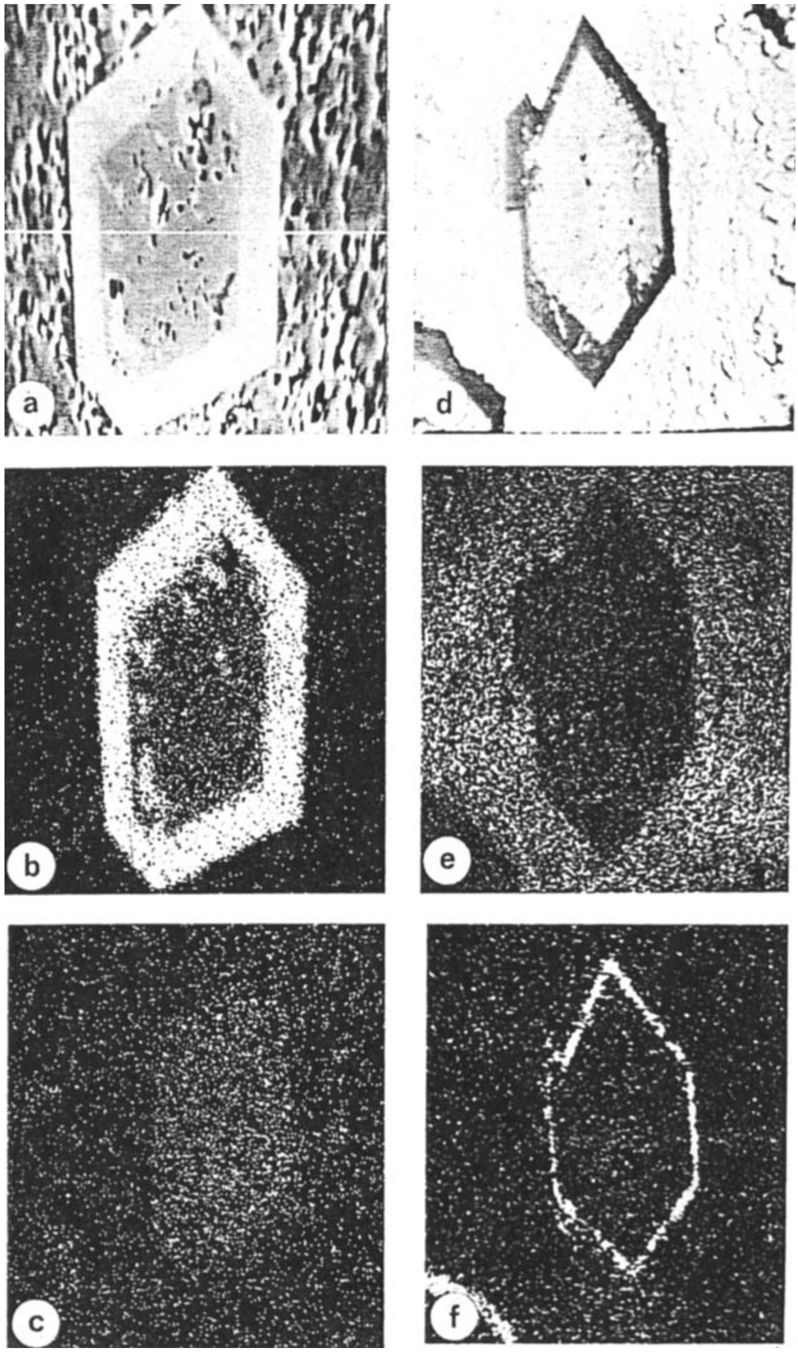
b X-ray picture showing the distribution of Fe;

c X-ray picture showing the distribution of Mn;

d Electron picture of garnet (ii);

e X-ray picture showing the distribution of Ca;

f X-ray picture showing the distribution of Ti.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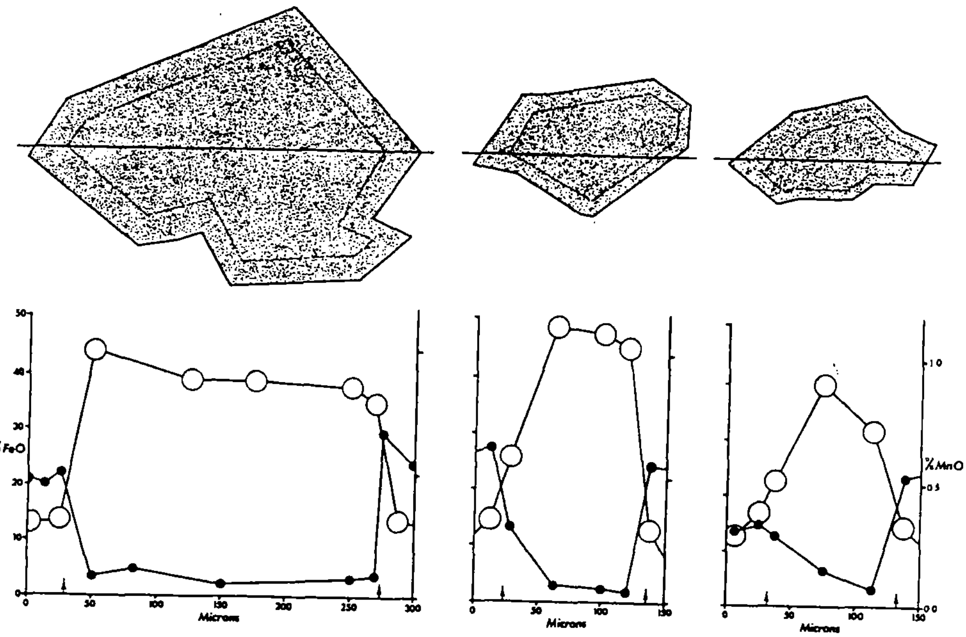

Fig. 3. Electron microprobe traces for Mn and Fe across 3 garnets, in a rock from locality 15. The diameter of the circles on the probe trace indicate the counting precision. The weight per cent of the elements analysed is uncorrected for absorption etc.

epidote+chlorite
grossular+scapolite
grossular
epidote+grossular+scapolite+idocrase
grossular+idocrase+wollastonite+diopside
scapolite+idocrase+wollastonite+diopside
hornblende+diopside
hornblende+epidote+scapolite+wollastonite+diopside
hornblende+epidote+scapolite+diopside
hornblende+epidote+diopside
hornblende+diopside+stilpnomelane
hornblende+diopside
hornblende
hornblende+chlorite
epidote
hornblende+epidote+chlorite
hornblende+scapolite
stilpnomelane

The above assemblages may also include varying amounts of pre-metamorphic minerals such as calcite, quartz, plagioclase, pyroxene and sphene etc.

The textural evidence is limited but it is probable that there is a mineral sequence, and that some minerals grew together i.e. wollastonite-diopside and epidote-hornblende; but it is by no means certain. All that can be said is that the hydrous minerals in general (hornblende and epidote) seem to postdate the anhydrous minerals (diopside and wollastonite). A similar sort of sequence occurs in space as well as in time for the minerals garnet, diopside and wollastonite occur close to the granodiorite contact, while hornblende, epidote and stilpnomelane all occur well away from the contacts, as well as close to the contact (Fig. 1). In a simple way the sequence is similar to that described by Eskola (1922) i.e. hornblende, diopside, wollastonite in order of increasing temperature and closeness to the contact.

6. Metamorphism and stability of the minerals

6a. Idocrase

The phase relations between grossular and idocrase are rather interesting and have been discussed at some length by Ito and Arem (1970). They found that the stability ranges of both minerals overlap considerably at medium pressures and temperatures (1·5 kb and 450–600°C) and transitions of one mineral to the other are not likely to be due to PT changes, but rather the transition grossular to idocrase might result from a rise in the activity of H_2O with a consequent decrease in CO_2 activity. Although there is no evidence for zoning in space of garnet and idocrase, as has been demonstrated elsewhere, there is a zoning in time and it is likely that the crystallization sequence grossular→idocrase is due to a change in the composition of the vapour phase with time. Such an explanation would indicate a high initial CO_2 activity which would stabilise grossular followed by an increasing relative H_2O content in the vapour phase during the metamorphism (see Ito and Arem 1970). This explanation fits in well with the general reactions postulated here with regard to anhydrous phases appearing before hydrous phases. Indeed this is what might be expected in a calcareous sequence on metamorphism. Initially the CO_2 activity would be high and during later reactions the CO_2 would decrease relative to the H_2O activity (cf. Turner 1968 p. 60).

6b. Hornblende

The interrelations of the hornblendes in the rocks studied are complex. But certain features are clear, viz. blue-green hornblende is earlier than green or brown-green hornblende (see also Wiseman 1934; Binns 1965). Binns (1965) found that high titanium and low ferric iron correlated with brown-green colour, while blue-green correlates with high ferric iron and low titanium.

The change in colour does not appear to be the result of an increase in temperature during the crystallization of hornblende (cf. Binns 1965) as the distribution of hornblendes showing this colour sequence is sporadic. Examination of the two lavas which showed the most pronounced colour zoning in hornblende (blue-green→green→green-brown) indicate an initial igneous assemblage including pyroxene and sphene. The pyroxenes are now rimmed with green and green-blue hornblende and the sphene is markedly altered. We think the early thermal hornblende crystallized from titanium poor pyroxene and /or glass, and during this time the breakdown of the refractory sphene did not occur. When sphene entered the reaction the hornblende became relatively Ti rich and changed to a green or green-brown colour.

6c. Diopside

The presence of diopside closer to the contact than hornblende and extending further away than wollastonite is consistent with general thermochemical data (Turner 1968 p. 152), assuming a temperature gradient away from the contact.

6d. Wollastonite

Wollastonite is the common high-temperature mineral found in metamorphosed quartz-calcite-dolomite rocks (Turner 1968). In the Peruvian rocks it is confined to the contacts and is absent in diopside bearing rocks away from the contact. This may be taken as evidence that although some overlap is probable, wollastonite and diopside formed at different temperatures, at moderate CO_2 pressures rather than isothermally. Turner (1968 p. 224) suggests the wollastonite-diopside assemblage may occur in the hornblende hornfels facies very close to the contact, due to the higher temperature or due to a local low P_{CO_2} value resulting from water vapour expulsion from the crystallizing magma. The relative importance of these two mechanisms will be discussed later.

6e. Grossular and andradite

Although all the garnets show variable birefringence, only the andradite-grossular garnets show sector twinning and the systematically arranged inclusions described earlier. The birefringence of the grossular core and the rim as well as the twinning is almost certainly due to the rapid growth rate (Harker 1932 p. 82) which must result from the rapid heating of the aureole rocks. Twinned nuclei grow more rapidly than untwinned nuclei and twinning increases with the supersaturation (Spry 1969 p. 68).

The formation of the inclusions appears to be as follows. The parallel fine "inclusions" at right angles to the crystal faces are due to a sheet mechanism acting at slightly higher supersaturation than that required for sheet growth. Under such conditions the crystallographic corners of individual sheets may grow faster than edges which will "infill more or less completely" (Smith 1963 p. 62). Successive sheets will preserve long tube-like inclusions under suitable supersaturation and constant growth rate.

When these inclusions were viewed at very high magnification they were seen to be of uneven rod like forms with rounded, closed ends. No mineral species could be identified and we think they are rod like liquid inclusions which in some cases have been reconstituted to minerals. Such structures are indicative of a supersaturation below that required by dendritic growth.

The inclusion patterns along the internal sector planes are the regular growth inclusions due to rapid growth (Harker 1932), which tended to preserve in part the pre-existing rock fabric and minerals. We think that the growth is again due to the postulated sheet mechanism, and that the inclusions occur in sector lineage boundaries (Smith *op. cit.*). The boundaries can be recognised by a general alignment of inclusions in corner extension lines and in this respect may be distinguished from completed dendrite forms (Smith 1963 p. 60). Clearly the width of these boundaries will be a function of the growth rate and may tend to increase in size probably due to the added effect of the previous layer. The result would be a curved wedge form opening outwards with relatively fast growth rates. This suggestion is similar to that of Rast (1965) for the analogous structure in chiastolite in that increased growth rate is postulated for the corners which therefore tends to include more of the matrix. It does not however involve dendritic growth or an alternation of supersaturation conditions.

The dark coloured layer, with fine inclusions immediately outside the grossular core is similar to that shown by Powell (1966) in two phase garnet from Morar. In the garnet from Morar a distinct hiatus was thought to have occurred before the rim was crystallized on the earlier core (Atherton and Edmunds 1966). However there is no evidence in the aureole rocks studied of polyphase metamorphism. Nonetheless the garnet shows a marked change in composition in the outer zone, which must have been associated with an increase in growth rate as indicated by the small average size of the inclusions in the zone parallel to the growth faces (Smith *op. cit.*).

Table 1. Chemical analysis of metamorphosed limestone

	Soluble fraction (in 1:2 Hcl)	*whole rock*
CaO	41·7	
MgO	0·142	
MnO	0·144	
Fe_2O_3	0·13	1·43
FeO	—	0·17

Both sets of analyses were done in duplicate; the soluble fraction made up about 75 % by weight of the specimen. Analysis expressed in terms of the total rock. Analysts R. Raiswell (soluble fraction), M. S. Brotherton (whole rock).

Grossular and andradite are interesting because their stabilities are particularly sensitive to O_2 and H_2O pressures. The general association of andradite with highly oxidised rocks was demonstrated by Huckenholz and Yoder (1971) and suggests a more oxidized environment during andradite growth than during grossular growth. This is confirmed by the experimental data (*op. cit.*).

Considering the sample with the two garnets, the conditions must initially have been such that there was a relatively high CO_2 activity as might be expected in calcareous metasediments (Table 1) so that grossular formed. The activity ratio CO_2/Fe^{3+} decreased as decarbonation slowed and andradite was stabilized. The restriction of andradite+grossular to one rock next to rocks with grossular only, suggests that the oxidising environment when andradite grew was a local phenomena and not due to a pervasive fluid phase. The chemical analysis of the rock is compatible with such an explanation as the oxidation ratio is very high (Table 1). The garnet appears to have grown in the following manner. The rock was very rapidly heated such that garnet crystallized under highly supersaturated conditions as evinced by the numerous small crystals. At this stage the CO_2 activity was high due to the decarbonation of the limestone and grossular was the stable phase. The stablization of grossular rather than andradite was also partly determined by kinetic factors such as the "slow" diffusion of Fe^{3+} to the nucleating sites. The relatively slow diffusion of Fe^{3+} compared to Ca^{2+} may well be due to the immediate availability of $CaCO_3$, which makes up 75% by weight of the rock, to a nucleation site, or more likely the rate controlling process was the breakdown reaction of the Fe^{3+} phase compared to the decarbonation reaction. Growth of grossular was very rapid as shown by the inclusion patterns and twinning, and would deplete the local environment in the grossular molecule, but it would increase the local Fe^{3+} concentration around the garnet tending to enhance the transition to andradite which appears to have been the stable equilibrium phase for the total rock system. The patchy distribution of titanium in the andradite rim is a further indication of the rapid growth rate, so that the surfaces of the individual faces were not in equilibrium with themselves. Inhomogeneities in the local environment due to the nonhomogeneous distribution and alteration of the phases breaking down (iron—titanium oxides) could therefore be responsible for the patchiness. This model is similar to that proposed for the production of the zonal structure in hornblende, although in the case of the garnets the Fe and Ti activities initially increased together, but the titanium activity must have decreased towards the garnet edge.

In the other garnet bearing rocks twinning is absent and the garnet is often isotropic. Growth in these calcareous cherts appeared to be under less supersaturated conditions, although the colour zoning which is sometimes complex suggests a similar type of change in the local environment occurred over the crystallization interval.

6f. Epidote

Clinozoisite surrounded by green epidote is common although the opposite may also occur. A similar colour-zoning was noted by Miyashiro and Seki (1958) in basic rocks of the Bessi district and was thought to be due to retrograde effects with decreasing temperature of metamorphism. The formation of epidote from a calcium rich plagioclase at low grade is almost certainly due to an increase in the activity of Fe^{3+} relative to Al^{3+}, and an increase in the activity of H_2O. An increase of Fe^{3+} over Al^{3+} activity during the metamorphism is also seen in the change from clinozoisite to epidote shown in the bioclastic fragment.

6g. Scapolite

Rocks with scapolite typically contain diopside, wollastonite, and garnet; a characteristic association in upper amphibolite facies rocks. The scapolite in the calcareous cherts is bedded and we think it is not metasomatic but formed from the sediments (see Hietanen 1967). The X-ray analysis showed it to be meionitic in composition which tends to confirm this. The scapolite in the tuff is also considered to be formed from locally derived material, for scapolitization is not extensive in the volcanic rocks.

6h. Stilpnomelane

This is a common late mineral in the basic rocks, and is often indicative of late stage low temperature metamorphism. The variety seen in these rocks is ferristilpnomelane (Hutton 1956) suggesting a late fluid phase with a high activity of Fe^{3+}.

7. Conclusions

1. The rocks in the field show very little effect of the metamorphism and even in thin section they show only partial alteration to the new thermal assemblages. Very large numbers of small crystals of garnet, diopside etc. indicate that nucleation occurred under high supersaturation conditions, and twinning and inclusion patterns in the garnet indicate very rapid growth rates. We conclude that the aureole was very rapidly heated and had a short time at maximum temperature, and therefore the rocks had little chance to equilibriate.

2. The minimum estimated width of an aureole is 5 km, while the width of the batholith in the area studied is 25 km. It should be noted however that the batholith probably lies not far below the surface in the area studied.

3. The metamorphism is of hornblende hornfels facies grade (Turner 1968).

4. The minerals show a sequence of crystallization in a given rock which can be partly elucidated i.e. idocrase is later than grossular and hornblende is after diopside. A complete sequence including all the minerals could not be determined due to the small grain size, small modal amounts, and metastable persistence of some premetamorphic phases. These results indicate that any extended discussion based on assemblages found in a given rock could be perilous unless the textural and spatial evidence are adequate and consistent. Thus fixes of P_{H_2O}, P_{CO_2}, P, and T are not possible with the present data except in a crude manner. The lack of pelitic assemblages allows of no cross-checking.

5. The mineral sequence in space is essentially that of Eskola (1922); wollastonite, diopside, hornblende. Scapolite, grossular and idocrase tend to go with wollastonite, and epidote with hornblende.

6. The presence of andradite rims to grossular, and clinozoisite surrounded by green epidote suggest that the rock fluids became more oxidizing. However, the time

sequence is not so clear in all cases and sometimes the first epidote to grow is green, Furthermore, in the case of hornblende which appears to be earlier than epidote in some rocks, the earliest hornblendes were Fe^{3+} rich and the later ones poor in Fe^{3+}. This suggests to us that it was the local environment which determined the oxidation rather than external sources (see also Kerrick 1970). The variations may well be due to the relative ease of breakdown of the pre-metamorphic Fe^{3+} and Ti containing phases. The occurrence of the andradite+grossular and grossular only in adjacent rocks confirms the hypothesis above.

7. The late minerals in the aureole are hydrous phases, and the early minerals are anhydrous phases e.g. idocrase after grossular. Clearly the relative activity of water increased during the period of crystallization. However, it should be emphasized that there is no evidence indicating that the activity of water was determined by the magma or other external source.

8. The conclusions regarding the PT conditions during thermal metamorphism follow Kerrick's (1970) argument on the contact metamorphism of the calcareous rocks of the Sierra Nevada, which closely resemble the rocks from Peru. Grossular (Gr_{90} An_{10}) in the assemblage grossular-quartz is stable from 530°–600°C at 1 to 2 kb (*op. cit.*). The occurrence of clinozoisite well away from the contact and probably later than grossular (cf. Kerrick 1970) suggests crystallization with increasing water rich fluid phases and/or lower temperatures. The schematic isobaric equilibrium diagram of Kerrick (*op. cit.*) shows the grossular+quartz field is bounded by nearly isothermal curves so that the transition to clinozoisite+quartz appears to involve essentially a decrease in temperature. The apparent restriction of grossular+quartz to a rather narrow range of temperature and in the presence of a water rich fluid is apparently inconsistent with the evidence of Ito and Arem (1970) who suggested grossular is favoured by a high CO_2 activity. The occurrence of wollastonite in bands with little or no calcite, near to the contact and associated with calcite+quartz+grossular bands, is consistent with the temperature estimates above and suggests the presence of wollastonite is due to the high temperature, and a local moderately high P_{H_2O}/P_{CO_2} ratio. The presence of hornblende further away from the contact than diopside is taken to indicate that temperature is the main factor. As Kerrick (1970) points out the flat nature of the reaction curve,

$$\text{tremolite} + 3\ \text{calcite} + 2\ \text{quartz} \rightleftharpoons 5\ \text{diopside} + 3CO_2 + H_2O$$

indicates temperature is the dominant factor, rather than a change in the P_{H_2O}/P_{CO_2} ratio in the fluid phase. The sequence in space (wollastonite, diopside, hornblende) therefore is largely a result of the thermal gradient.

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References

ATHERTON, M. P. and EDMUNDS, W. M. 1966. An electron microprobe study of some zoned garnets from metamorphic rocks. *Earth Planet. Sci. lett.* **1**, 185.

BINNS, R. A. 1965. The mineralogy of metamorphosed basic rocks from the Willyama Complex, Broken Hill district, New South Wales. Pt. I, Hornblendes. *Min. Mag.* **35**, 306.

COBBING, E. J. and PITCHER, W. S. 1972. The Coastal Batholith of Central Peru. *Q. J. geol. Soc. Lond.* (in press).

DEER W. A., HOWIE, R. A. and ZUSSMAN J. 1962. *Rock forming minerals. Vol.* 1 Longmans, London.

ESKOLA P. 1922. On contact phenomena between gneiss and limestone in western Massachusetts *J. Geol.* **30**, 265.

HARKER, A. 1932. *Metamorphism.* Methuen, London.

HIETANEN, A. 1967. Scapolite in the Belt Series in the St. Joc Clearwater region Idaho. *Geol. Soc. Am. Spec. Pap.* 68.

HUCKENHOLZ, H. G. and YODER, H. S. 1971. Andradite stability in Air at 1 atm, O_2 up to 30kb, and H_2O+O_2 up to 20kb, total pressure. *Annual rep. Director Geophys Lab.* 1969–1970, 182.

HUTTON, C. O. 1956. Further data on the stilpnomelane mineral group. *Am. Mineral.* **41**, 608.

ITO, J. and AREM. J. E. 1970. Idocrase: synthesis, phase relations and crystal chemistry. *Am. Mineral.* **55**, 880.

KERRICK, D. M. 1970. Contact metamorphism in some areas of the Sierra Nevada, California. *Geol. Soc. Am. Bull.* **81**, 2913.

MIYASHIRO, A. and SEKI, Y. 1958. Enlargement of the composition field of epidote and piemontite with rising temperature. *Am. J. Sci.* **256**, 423.

POWELL, D. 1966. On the preferred crystallographic orientation of garnet in some metamorphic rocks. *Min. Mag.* **35**, 1094.

RAST, N. 1965. Nucleation and growth of metamorphic minerals. In W. S. Pitcher and G. S. Flinn (Ed.) *Controls of metamorphism.* Geol. J. Spec. Issue No. 1. Oliver and Boyd, Edin.

SMITH, F. G. 1963. *Physical Geochemistry.* Addison. Wesley, Mass.

SPRY, A. 1969. *Metamorphic Textures.* Pergamon Press, Oxford.

TURNER, F. J. 1968. *Metamorphic Petrology.* McGraw Hill Book Company, New York.

WILSON, J. J. 1963. Cretaceous stratigraphy of Central Andes of Peru. *Bull. Am. Ass. Petrol. Geol.* **47**, 1.

WISEMAN, J. D. H. 1934. The Central and southwest Highland epidiorites. *Q. J. geol. Soc. Lond.* **90**, 354.

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