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GROWTH ZONED MANGANESE GARNET IN CHLORITOID, GRAPHITE SCHISTS NEAR MORLAIX, NORTH-WEST FRANCE

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Lower Devonian graphitic schists near Morlaix have the mineral assemblage, garnet + chloritoid + quartz + muscovite + chlorite + rutile + graphite + pyrite. Garnet and chloritoid grew after the firs5 and before the second foliation. Contoured composition maps of garnets reveal manganese-rich cores and sharp increases in iron close to the rims. Textural sector-growth is well-developed in the cores. Manganese garnet grew below biotite zone temperatures, promoted by the high rock Mn and by CO_2, CH_4 and H_2S in the fluid phase. The second foliation involved extensive pressure solution of quartz and dissolution of chloritoid and textural sector-growth ceased with this change in conditions.

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INTRODUCTION

This paper gives an account of the mineralogy, chemistry and textural relationships of a single outcrop of graphitic schists of the lower Devonian "Schistes carburés", which occurs at Roc'h C'hlaz, at the south end of Plage du Clouët, near Carentec, north-west of Morlaix. This rock has the mineral assemblage, garnet + chloritoid + quartz + muscovite + chlorite + rutile + graphite + pyrite. The mineral chemistry of chloritoid-bearing assemblages is now becoming better known (e.g. Wang and Spear, 1991) but additional information from different localities is always of potential interest. The garnets at this locality have spectacular textural sector-growth features which also justify description and discussion.

GEOLOGICAL SETTING

The area around Morlaix lies at a complex junction between three broad geological units (Figure 1). To the west, the Léon region is composed mainly of gneisses and schists intruded by Variscan granites (340-290 Ma). It has been proposed (see Le Corre *et al.,* 1989) that Leon constitutes a separate geological terrane with a Variscan history and with close geological affinities to southern Brittany. Further to the east of Morlaix, late Precambrian rocks and events predominate, with Brioverian metasediments and plutonic complexes deformed during the late Precambrian Cadomian orogeny. South of Morlaix, the North Armorican Shear Zone marks the northern boundary of the central Brittany region, within which both Brioverian and Lower Palaeozoic rocks show mainly the effects of Variscan deformation and metamorphism (Hanmer *et al.,* 1982). Between these three units, around Morlaix and extending west towards Landivisiau and east to Baie de St Michel en Grève, there is an area of lower Devonian metasedimentary rocks (Cabanis *et al.,* 1974) and resting on these is a sequence of metasedimentary rocks which make up the lower Carboniferous Morlaix Basin (Cabanis *et al.,* 1979).

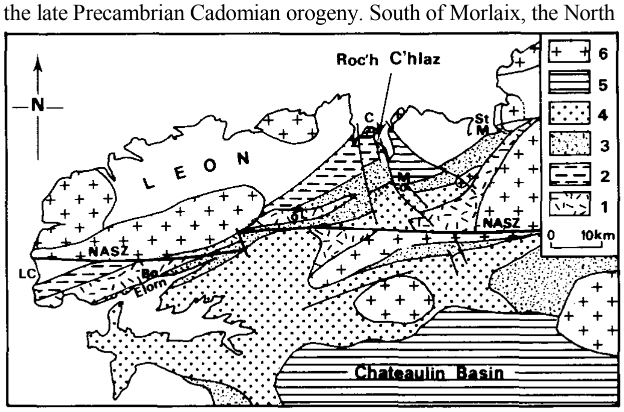


Figure 1: Geological sketch map of north-west Brittany, France (after Cabanis 1974). Place names:- B: Brest: C. Carentec; L; Landivisiau; LC: Le Conquet; M: Morlax; St M St Michel-en-Grève. NASZ: North Armorican Shear zone.
Key:- 1: Gneiss de Brest; 2: Le Conquet Schists; 3: *Brioverian Supergroup; 4: Palaeozoic, mainly Devonian sedimentary rocks; 5: Carboniferous of Chateaulin and Morlaix; Variscan granites.*

Cabanis (1974) gives a useful account of the structure and metamorphic history of the Morlaix area and recognises two main phases of deformation in the Devonian and Carboniferous rocks. The first phase produced a strong foliation, generally parallel to bedding. Folds associated with this deformation are rare but when seen are small scale, recumbent isoclinal folds trending 160 to 170°. The second phase of deformation produced the obvious folding in the rocks and is associated with a strain slip cleavage. These folds are slightly overturned to the north-west and trend about 060° and plunge 20 to 30° north-east. The metamorphic grade of the rocks around Morlaix is of the lower greenschist facies chlorite zone. The common assemblage in the metasediments is quartz + albite + muscovite + chlorite and in beds of suitable composition chloritoid occurs. All these minerals, except chloritoid, were formed during the first phase of deformation. Chloritoid intersects the first foliation and is deformed by the second deformation and hence grew statically between the two deformations with a possible further generation of chloritoid after the second deformation (Cabanis, 1975). Cabanis (1982) shows that the chloritoid only occurs in iron-rich rocks which contain excess aluminium above that required for muscovite and chlorite. Cabanis (1974) mapped a zonal sequence (chlorite, biotite, andalusite) of prograde metamorphism to the north-west of Morlaix and also noted locations where chloritoid, garnet and staurolite occur.

PLAGE DU CLOUET LOCALITY

The sample locality is at the south end of the Plage du Clouët, 2 km south-east of Carentec and about 8 km, north-west of Morlaix. Access is east down a lane at the junction of the D73 and D173 roads. Roc'h C'hlaz forms the high ground at the coast and is the site of a disused and very overgrown small quarry. The dominant cleavage strikes 060° and dips steeply to the south- east. The rock is black to dark grey in colour but there are some bands, 0.1 to 0.5 m thick, which are picked out by their rusty staining and greater resistance to weathering. These layers probably reflect original compositional differences and are now mainly

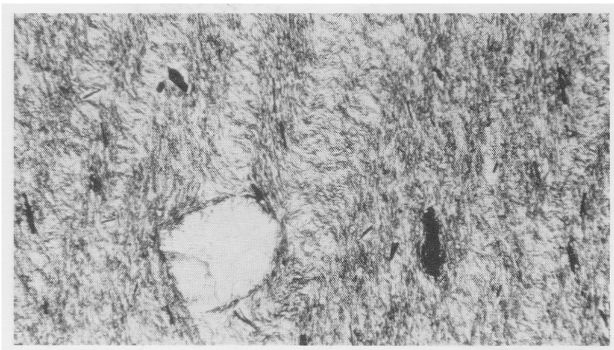


Figure 2: MC10A. Pressure solution striping associated with the second deformation giving rise to quartz- (Q), and phyllosilicate- (P) rich domains. The P-domains form the limbs of folds and the Q-domains the hinge zones. Garnet is about 1 mm in diameter.

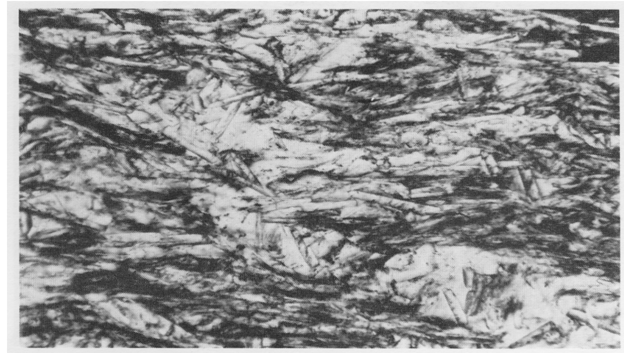


Figure 3: MC10A. Chloritoid as elongate, moderate relief prisms (up to 0.1 mm) shows fairly random orientation in the more leucocratic portions of the rock.

made up of pyrite, quartz and 1 to 2 mm euhedral garnets. The largest and most abundant garnets, up to 5 mm in size occur in the dark slates on either side of these pyrite-rich bands. The euhedral garnets are very pale pink in colour and even in hand-specimen may be seen to contain symmetrically arranged intergrowths. Observations in this paper are concentrated on three particular rocks, MC6, MC9 and MC10A from a series collected in and around the quarry.

PETROGRAPHY

MC6: This rock has a grain size of 0.1 to 0.3 mm and an assemblage of garnet + chloritoid + quartz + muscovite + chlorite + rutile + graphite + pyrite. No biotite is present. Mineral proportions are difficult to estimate with rocks of such a fine grain size, but it is clear that there are sufficient phyllosilicate minerals present for the rock to be classed as a pelite. The garnets are generally euhedral and 2 to 3.5 mm in size and are distributed in clusters throughout the rock without any obvious preferential distribution. Two foliations are present. The first is defined mainly by the shape orientation of muscovite and chlorite grains up to 0.3 mm long. Sometimes a grain shape orientation of quartz is also preserved between the phyllosilicates with single flat-sided narrow grains of quartz less than 0.1 mm in length. The domains where the first foliation is dominant are about 1 mm wide and up to 10 mm long before they taper out. They are separated by narrow more continuous, but anastomosing, zones up to 0.4 mm wide, composed of phyllosilicates which are extremely dark in appearance because they are choked with inclusions of graphite and opaque minerals. These dark phyllosilicate bands are in the limbs of asymmetric microfolds of the first cleavage.

Chloritoid is typically about 0.1 mm long with an aspect ratio of 5:1. It is usually colourless with moderate relief but occasionally shows slight very pale gray pleochroism. It has low first order interference colours and some grains are simply twinned. In the earlier cleavage domains the chloritoid prisms do not have a strongly preferred orientation parallel to the first foliation. Some grains are at a high angle to the first foliation. No examples were observed of the ends of chloritoid grains that had undergone dissolution against the first cleavage. It seems reasonable to suppose that the chloritoid grew after the development of the first cleavage, but the graphite inclusions within the chloritoid grains do not appear to preserve any preferred orientation. Some chloritoid grains with their long axes at a high angle to the second cleavage have clearly undergone pressure solution and have been reduced to diamond shapes. Rutile needles occur throughout the rock and are 0.2 to 0.3 mm long with an aspect ratio of about 10:1. Chlorite flakes often grow from the sides of the rutile needles. In reflected light intergrowths of pyrite within the rutile may be seen and partial breakdown of rutile to titanite.

The second cleavage is wrapped around the garnets and areas where earlier fabrics may he preserved occur in the protected regions of lower strain either side of the garnets. Because of the extensive development of the second cleavage, it is difficult to see the relationship between the first cleavage and the garnets. It appears that some garnet edges abut directly at right angles to the first cleavage, but there is very little evidence for orientated inclusion trails related to the first cleavage having been preserved within the garnets, even at the edge of growth sectors. The inclusions within the garnet are related to the sectorial growth of the garnets. However, most of the garnets have several rims of a different form of growth, with alternations of dusty graphite and clearer garnet developed parallel to the crystal faces. The most reasonable explanation is that the main period of garnet growth occurred between the development of the first and second cleavages. Pyrite is both distributed throughout the rock as isolated grains about 0.1 mm in size and also occurs concentrated at the edge of garnet porphyroblasts, along with graphite and sometimes also along cracks developed in the garnet.

MC10A: The mineral assemblage is the same as for MC6 but the average grain size is rather finer. There are three main differences which are immediately apparent:-

(i) The garnets are very few in number and they are smaller, being 1 mm or less in size. Also they rarely have any well developed textural sector- zoning.

(ii) There is often a pronounced regular striping, composed of quartz-rich and phyllosilicate-rich domains about 0.5 mm wide, associated with the second foliation (see Figure 2). The quartz-rich domains are in the hinges of microfolds of the first foliation and quartz grains tend to be equidimensional in shape, the phyllosilicate-rich domains make up the limbs. Both chloritoid and rutile needles appear to have been rotated into the orientation of the second cleavage. Some phyllosilicate-rich domains within which the first cleavage has been completely overprinted are tens of millimetres wide, and in these regions there are often relics of chloritoid at a high angle to the second cleavage and these have undergone extreme pressure solution (Figure 4). Build-ups of residues of included graphite may be seen close to the tips of the chloritoid and these together with the change to diamond shapes from the original elongate prism shape, indicate that the removal of chloritoid by pressure solution has been considerable. It is also notable that chloritoid grains with their long axes parallel to the second cleavage tend to be thinner and longer (up to 0.25 mm long with aspect ratios of greater than 10:1), than those associated with first cleavage domains. Either there has been selective preservation, or there has been some continued growth of chloritoid during the formation of the second cleavage.

(iii) The graphite content is less than that of MC6. Graphite is still common but it does not form the extreme concentrations visible in the phyllosilicates of MC6.

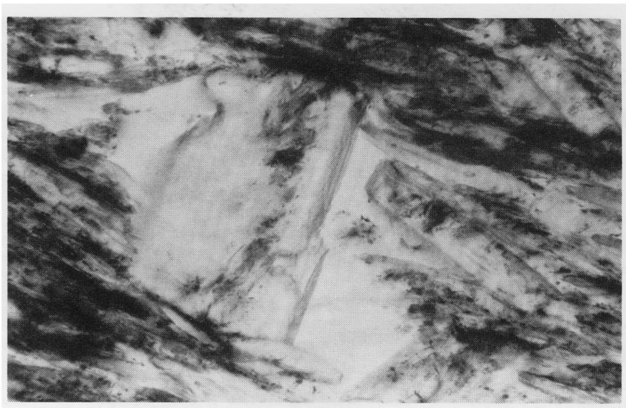


Figure 4: MC10A. Close-up view of chloritoid prism (0.14 mm long) at a high angle to the second foliation. The ends of the prism have been dissolved away by pressure solution processes. Note graphite inclusions and the much narrower chloritoid prism sub-parallel to the second foliation.

MC9: This sample deserves special mention for the textures preserved within it. This rock is similar to MC6 in characteristics. It occurs adjacent to a quartz and pyrite-rich layer and contains clusters of garnets up to 5 mm in diameter, with very well developed growth sector-zoning. Many of the garnets have mica cleavage domes (Ferguson *et al.,* 1980; Rice and Mitchell, 1991) on a number of crystal faces. These arcuate accumulations of `inert' minerals, often muscovite and graphite in the case of garnet-forming reactions, are the result of mechanical displacement of matrix grains by a growing porphyroblast.

MINERAL AND ROCK CHEMISTRY

Electron microprobe analyses were carried out at the Department of Earth Sciences, Cambridge. Selected analyses are given for garnet, chlorite and chloritoid in Table 1. The chlorites are normal iron-magnesium types with about equal proportions of iron and magnesium. They are manganese-poor with less than 5% of sites occupied by manganese. The chloritoids are iron-rich with minor magnesium and again less than 5% of sites are occupied by manganese. There is little difference between the analyses for MC6 and MC10A for these minerals. Garnet shows considerable compositional zoning in Fe and Mn but little variation in Mg and Ca and there are significant differences in the range of garnet compositions between MC6 and MC10A.

TABLE 1: Representative analyses and atomic proportions for garnet cores and rims, chlorite (Chl.) and chloritoid (Ct.) in MC6 and MC10A.

	MC6				MC10A			
	Garnet		Chl.	ct.	Garnet		Chl.	ct.
	Core	Rim			Core	Rim		
MgO	0.67	1.18	12.82	2.54	1.02	1.28	13.5	2.57
Al_2O_3	21.18	21.38	23.63	41.13	21.37	21.03	23.92	41.01
SiO_2	37.57	38.00	25.28	25.92	38.91	37.45	25.16	25.62
CaO	5.62	4.32	-	-	4.12	3.34	-	-
MnO	15.48	8.15	0.36	1.00	11.08	9.96	0.34	1.11
FeO	19.98	27.36	25.96	22.84	25.71	26.66	25.21	22.28
Sum	100.50	100.39	88.05	93.43	102.21	99.72	88.13	92.58
Oxygen	24	24	28	24	24	24	28	24
Mg	0.16	0.28	4.00	0.62	0.24	0.31	4.19	0.62
Al	4.01	4.03	5.85	7.84	3.97	4.01	5.88	7.88
Si	6.03	6.08	5.30	4.20	6.13	6.06	5.25	4.18
Ca	0.97	0.74	-	-	0.70	0.58	-	0.02
Mn	2.11	1.11	0.06	0.14	1.48	1.37	0.06	0.15
Fe	2.68	3.66	4.55	3.10	3.39	3.10	4.40	3.04
Sum	16.05	15.90	19.76	15.90	15.91	15.43	19.78	15.89

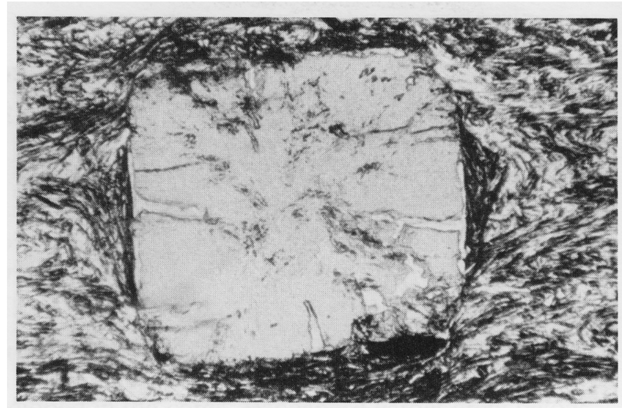


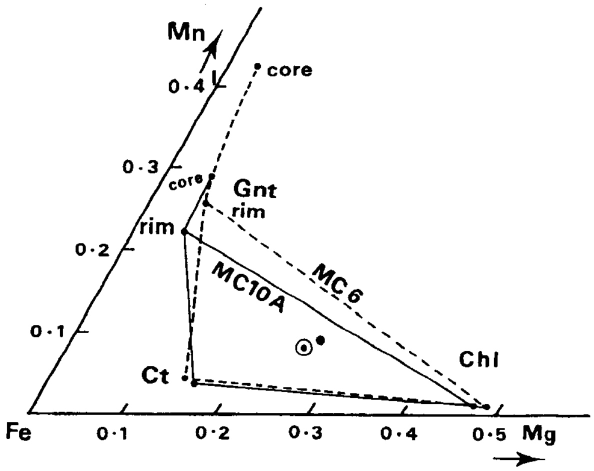
Figure 5: MC9. [001] section through rhombic dodecahedron of garnet (edge 1 mm) with possible mica cleavage dome preserved in the pressure shadow on the right hand face.

The cores of the garnets of MC6 are manganese-rich, with the spessartine, almandine, grossularite and pyrope molecules present in approximately the proportions, 0.35: 0.45: 0.15: 0.05. The same proportions in the cores of the garnets in MC10A are approximately, 0.25: 0.55: 0.15: 0.05. That is they have about 25% less manganese and 25% more iron. However the garnet rims in each rock have similar compositions with the proportions 0.2: 0.65: 0.1: 0.05. The mineral compositions are plotted on a triangular diagram of the atomic proportions of Mn, Fe and Mg in Figure 6. Tie lines join the chlorite and chloritoid with the rim compositions of the coexisting garnets. The range of garnet compositions between core and rim are also shown. Wang and Spear (1991) found comparable mineral compositions in the assemblage garnet + chlorite + chloritoid + biotite + muscovite + quartz in metapelites of a Barrovian sequence from the tri-state area of the Taconic Range, USA.

The bulk rock compositions for MC6 and MC10A are very similar. Partial analyses by x-ray fluorescence spectroscopy on glass fusion discs by D. J. Rowe at the University of Portsmouth are given in Table 2. The rocks are very closely similar in composition, but it should be noted that MC6 has 0.73 weight per cent MnO (0.57% Mn), whilst MC10A has only 0.48 weight per cent MnO (0.37% Mn), that is MC6 is about 50% richer in Mn. Symmes and Ferry (1992) suggest that the average range of Mn content in pelites is between 0.01 and 0.04 weight per cent and that the presence of this amount of Mn is critical in determining the stability of garnet during metamorphism. MC10A and MC6 would be classed as extremely enriched in Mn and both would be expected normally to stabilise the growth of garnet at lower temperatures than an average pelitic composition. In Figure 7 the bulk rocks are plotted on an AKNF diagram, which shows that they conform to the commonly accepted criterion for chloritoid-bearing rocks that they are more aluminous than is required to form muscovite and chlorite. MC10A only just plots within the muscovite, chloritoid, garnet, chlorite triangle. The rocks are also relatively alkali-poor and iron-rich. The muscovite in MC6 is almost pure muscovite, with very little phengitic substitution.

TABLE 2: Partial chemical analyses of rocks MC6 and MC10A.

	MC6	MC10A		MC6	MC10A
SiO_2	53.36	53.56	K_2O	2.37	1.59
Al_2O_3	24.14	25.96	TiO_2	1.05	1.11
FeO(T)	8.21	8.67	MnO	0.73	0.48
MgO	2.20	1.22	P_2O_5	0.08	0.08
CaO	1.23	1.10	LoI	5.60	4.89
Na_2O	1.01	1.04	Sum	99.98	99.70



gure 6: Triangular plot of atomic proportions of Mn, Fe and Mg in whole rock and coexisting mineral phases. Gnt: garnet; Chl: chlorite; Ct: chloritoid. Bulk rock compositions, black dot: MC10A; circle with black dot: MC6.

ZONING OF THE GARNETS

Examples of textural sector-zoning in garnets have been described in a number of recent papers (Andersen, 1984; Andrews and Power, 1984; Burton, 1986; Rice and Mitchell, 1991) and the general features are now well known. Essentially the garnets are assumed to grow by addition of 'layers' to each crystal face. Thus each face may be considered as the base of a pyramid, with the apices originating at the centre of the crystal. Each pyramidal sector must also grow sideways as the face grows larger. Inclusions often mark the plane along which sectors impinge laterally. Quartz intergrowths grow as rods with their long axes normal to the crystal face. The mechanism of formation of these structures has been the subject of considerable discussions (Andersen 1982; Burton 1986; Rice and Mitchell 1991). However, these two features, the definition of sector boundaries by inclusions and the geometry of the quartz rods, together with any euhedral crystal faces, yield valuable information about the orientation of slices cut through a garnet grain. Tracy (1982) reviewed chemical zoning in metamorphic minerals and it seems that very often information on the exact orientation of the mineral slice analysed has not been available. This information is essential if any real interpretation of the variations in chemical composition are to be attempted.

The garnets in MC6 (Figures 8 and 9) show excellent examples of the main features of the phenomenon of textural sector-growth, which has not been described previously from this locality. The garnets are generally euhedral and may be shown to have a simple and consistent rhombic dodecahedral habit. Thus sections with a recognisable symmetry may be selected for chemical analysis. Composition maps for a number of garnet grains in several different samples have been made. The maps have been contoured by visual estimation, using the additional assumption that contours are likely to be parallel to the crystal faces, as wherever this could be tested it was found to be true. All the maps conform to the general features described here for two particular identifiable geometric sections through garnets in rock MC6. The results for garnet MC6.1 based on 68 analyses are shown in Figure 8. This section is interpreted as a central section through the garnet nearly parallel to [110] so that a crystallographic axis is the central east-west line defined by sector boundaries, with faces normal to the page as the top and bottom edges. Note that the other four edges at either side are intersections of faces that are not normal to the page and actually slope both towards the viewer and the centre of the crystal. Composition contours are regular and similarly spaced for both iron and manganese. As manganese decreases from the core towards the margin, iron increases. There is a dramatic change in spacing of the contours at the margin of the garnet, where the sector-growth texture ceases and is replaced by a rim of garnet with bands of inclusions parallel to the crystal faces. Manganese rapidly falls in concentration and iron rises. Garnet MC6.3 is a more complicated cross-section (Figure 9). It has four sides and is nearly square. The quartz rods associated with these faces appear to be very continuous and to lie in the plane of the page so the faces must be normal to the page. The only sections through a dodecahedron that would give these relationships would be of the form [001]. It is also clear that the section does not go through the centre of the crystal, because traces of four further sectors, making up an X-shape, may be observed. Again the composition contours are remarkably regular and confirm the previous finding of a manganese-rich core and a rapid increase in iron near the rim.

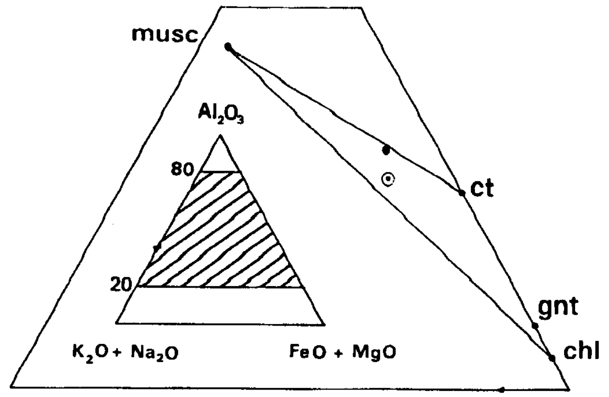


Figure 7: AKNF plot showing MC6 (circle with black dot) and MC10A (black dot) bulk rock compositions are iron-rich and alkali-poor and sufficiently aluminium- rich to plot above the chlorite-muscovite join. must: muscovite; gnt: garnet; ct: chloritoid; chl: chlorite.

PROPOSED METAMORPHIC HISTORY

The metamorphic history of the rocks may be summarised as follows:-

(i) Development of the first cleavage with the growth of muscovite and chlorite.

(ii) Static growth of manganese-rich cores to the garnets in MC6 at low temperatures below those of the biotite zone.

(iii) Chloritoid growth after first cleavage.

(iv) Beginning of growth of more iron-rich rims to garnets and formation of mica cleavage domes.

(v) Microfolding and formation of second cleavage, pressure solution forms Q - P domains and dissolution of chloritoids giving additional iron for growth of garnet rims.

DISCUSSION

No previous record of growth sector-zoned garnet occurring with chloritoid has been traced in the literature. The occurrence of chloritoid in north-west France is not uncommon. Paradis *et al.* (1983) record its presence in Lower Palaeozoic rocks east of Brest and also identify pyrophyllite as one of the precursor minerals. Hanmer *et al.* (1982) give a map of localities where chloritoid has been found in central Brittany and Le Corre (1969) gives a detailed account of chloritoid in Ordovician rocks close to Rennes. Chloritoid requires rocks of a restricted and specialised chemical composition, high in aluminium, low in alkalis and with a high Fe/(Fe + Mg) ratio. Marine clay with a volcanogenic component is one possible parent rock type. The graphite in the occurrence near Morlaix presumably comes from degraded plant materials as the age of these rocks was established from spores in a lower grade outcrop near the hospital in Morlaix (Cabanis *et al.,* 1974).

The cores of the Morlaix garnets are considerably more manganese

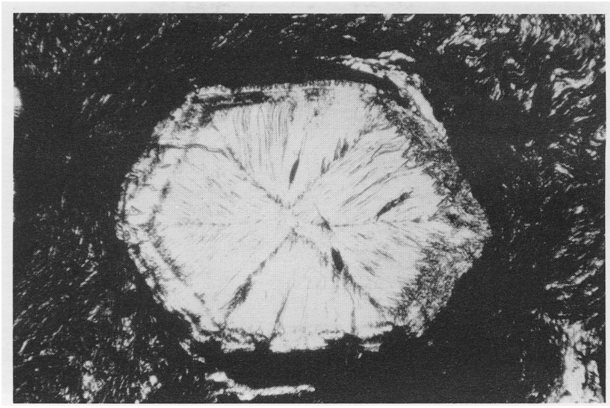


Figure 8a: MC6.1 Rhombohedral garnet (about 3 mm wide). Central section cut close to [110]. Six sector boundaries are picked out by graphite concentrations. Quartz intergrowth rods grow normal to [110] faces. The small "island" at the centre of the crystal is the tip of a vertical growth sector. This establishes that the section is not cut exactly through the centre of the crystal where the apices of all growth pyramids meet.

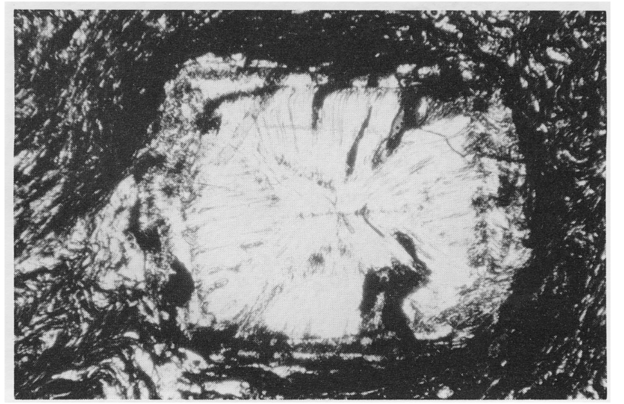


Figure 9a: MC6.3 Near square section through rhombohedral garnet (about 3 mm wide) close to parallel with [001]. This is not a central section because the four sectors normal to the well developed [110] faces are not the only growth sectors seen. There are also narrow slices through four other growth sectors.

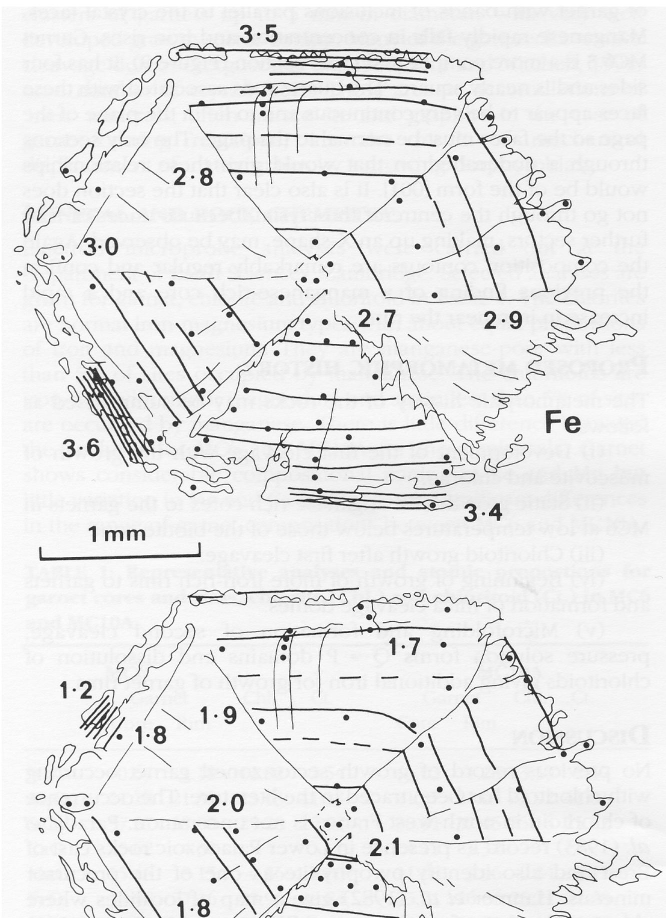


Figure 8b: Composition maps for the garnet, MC6.1, for iron and manganese concentrations in cations per 24 oxygens. 68 black dots are the sites of electron probe analyses.

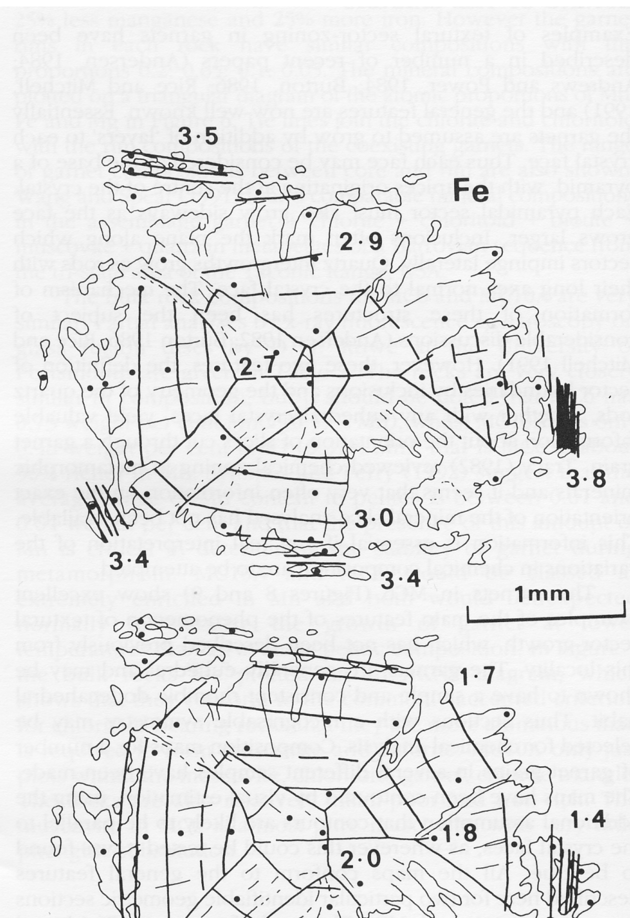


Figure 9b: Composition maps for the garnet, MC6.3, for iron and manganese concentrations in cations per 24 oxygens. 40 black dots are the sites of electron probe analyses.

rich than either the garnets Andersen (1984), or Burton (1986), studied from Norway. Wang and Spear (1991) in a detailed study of garnets in pelitic rocks from the Taconic Range, USA, describe manganese garnet occurring at a lower grade than the biotite zone in a Barrovian sequence, but even this garnet is not quite so manganese-rich as the Morlaix samples. Unfortunately the Morlaix mineral assemblage, with no biotite or plagioclase and rutile rather than ilmenite and hematite, is not conducive to quantitative temperature estimates. So only a qualitative judgement may be made. Spear and Cheney (1989) comment that the temperature and pressure of formation of minerals will be depressed from those of experimental or theoretical assessments based on a fluid phase of pure water, by dilution of the water by other components, so that it seems fairly certain that the manganese-rich cores formed at quite low temperatures. With rise in temperature the composition of the garnet crystallising became more iron-rich. There is also textural evidence for a change in the mobility of quartz. The Q - P fabric must have involved dissolution and transport of quartz (and chloritoid) in the fluid phase. Burton (1986) argued that the quartz rod intergrowths in the garnets resulted from limited diffusion of quartz, because of lower solubility of quartz in a fluid composed of CO_2 and CH_4 derived from graphite together with H_2O and H_2S. The changes in growth habit and composition of the garnet may be linked to a change in composition of the fluid phase, possibly by influx of water accompanying deformation.

It is interesting to speculate what caused the differences in metamorphic history of the two rocks, MC6 and MC10A, collected from within a few metres of each other. Was the difference in manganese content sufficient to cause the manganese garnets to grow at an early stage in the history of one rock and not the other? Or were the relative abundances of graphite an important factor? Or was it neither of these but a difference in the access of external fluids that caused the differences?

ACKNOWLEDGEMENTS

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