Deerite from Ile de Groix, Brittany, France

K. DUDEK

Academy of Mining and Metallurgy, Institute of Geology and Mineral Deposits, Al. Mickiewicza 30, 30–059 Krakow, Poland

AND

J. R. KIENAST

Laboratoire de Pétrologie Métamorphique, U.A.727, Universite P. et M. Curie, 4 place Jussieu, 75252 Paris Cedex 05, France

Abstract

Deerite has been found in layers of Fe-rich metasediments, metamorphosed under conditions of blueschist to eclogite facies ($T = ca.\ 480\,°C$). Geochemical comparisons with other deerites described in the literature show that the Ile de Groix deerites most closely resemble the Mn-poor, alpine type, and Sifnos deerites. The P–T conditions of the Ile de Groix metamorphism do not conform with the stability field of deerite. In the assemblages examined here deerite seems to be a relic from earlier stages of prograde metamorphism.

KEYWORDS: deerite, metamorphism, Brittany, France

Introduction

THE hydrous iron-rich silicate, deerite, $(Fe^{2+},Mn,Mg)_{12}(Fe^{3+},Ti,Al)_6Si_{12}O_{40}(OH)_{10}$, was first described by Agrell et al. (1965) from Laytonville Quarry, California, USA. Since then, occurrences of this mineral have been reported from about twenty localities throughout the world (see Langer et al., 1977; Muir Wood, 1979; Vernié et al., 1986), always from blueschist-type metamorphic rocks.

Experimental work on the stability field of deerite (Langer et al., 1977; Lattard and Schreyer, 1981) demonstrates that it can be stable only in very low-temperature, high-pressure environments. Moreover, the formation of deerite is restricted to Fe–Si-rich metasediments (Muir Wood, 1979; Reinecke, 1987). In the literature deerites have been described in assemblages indicating very different oxygen fugacities; this is most probably due to the large variability in chemical composition of the mineral. Each particular deerite seems to be stable only in a relatively narrow range of f_{O_2} conditions (Lattard and Schreyer, 1981; cf. Vernié et al., 1986, and Reinecke, 1987).

This paper reports on the occurrence of deerite in Fe-rich metacherts from Ile de Groix, Brittany, France. It is of particular interest, in that the Ile de Groix series has been metamorphosed at temperatures higher than any of the deerite-bearing sequences so far described.

Geology

Ile de Groix, situated about 10 km from the south coast of Brittany (Fig. 1), represents emerged part of NW–SE elongated metamorphic belt (Audren and Triboulet, 1984). This belt, covering an area of about 40 × 10 km, consists of rocks formed under high-pressure and low- or medium-temperature conditions (blueschist and eclogite facies). Geochronological investigations (Peucat and Cogné, 1977; Peucat, 1986) indicate that high-pressure metamorphism took place around 420–400 Ma ago. Ile de Groix and Bois de Cené (Vendée, some 150–200 km SE) provide the only evidence for this type of metamorphism in the entire Variscan fold-belt of Western Europe.

The Ile de Groix complex is made up of a series of metapelites intercalated with metabasic rocks. Petrological studies (Makanjuola and Howie, 1972; Kienast and Triboulet, 1972; Triboulet, 1974; Carpenter, 1976; Djro, 1983) reveal that glaucophane-schist facies metamorphism was followed by retrogression in the greenschist facies.
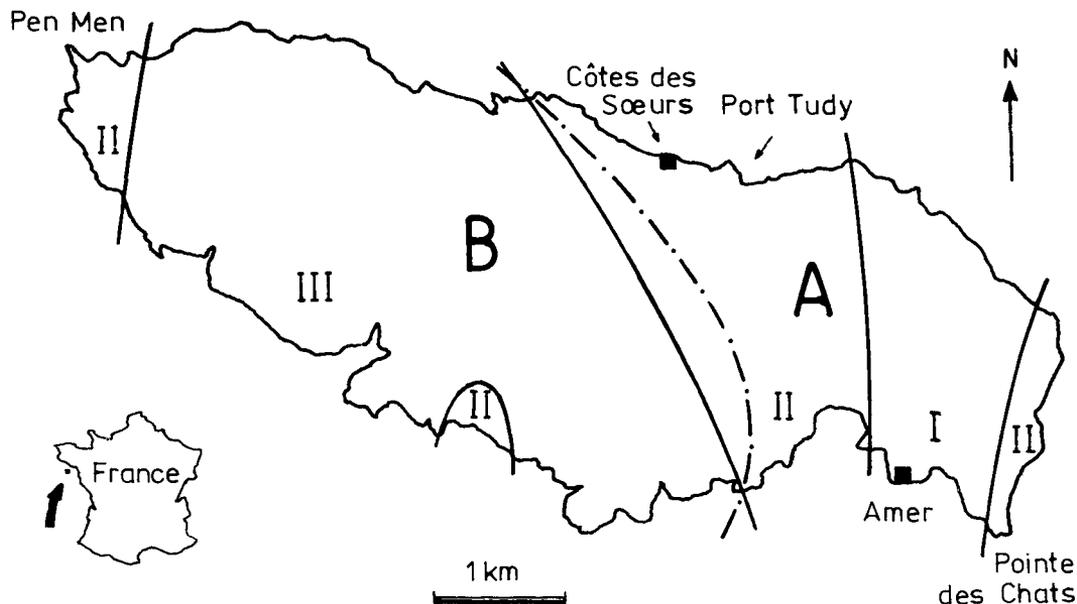
FIG. 1. Sketch-map of Ile de Groix showing location of the samples (squares). I, II, III—metamorphic zones according to Triboulet (1974) (separated by solid line). A and B—metamorphic zones according to Carpenter (1976) and Quinquis (1980) (dash-dotted line).

The $P-T$ conditions and the subdivision of the prograde metamorphic sequence are still controversial. On the basis of metabasic assemblages, Triboulet (1974) distinguished three zones (Fig. 1): I = eclogite facies zone (8.5 kbar, 530 °C); II = glaucophane–epidote–garnet facies zone (8 kbar, 500 °C); III = greenschist facies zone (7.5 kbar, 470 °C). Carpenter (1976) recognized two contrasting areas: A, $P = 8 \pm 1.5$ kbar, $T = 400 \pm 50$ °C; and B, $P = 6.5$–8 kbar, $T < 400$ °C. The principal difference between these two areas is a lack of garnets in the metabasites of zone B. According to Quinquis (1980), Carpenter's isograd of garnet in metabasic rocks has a structural significance as well; the higher-grade zone A (eastern part of the island) seems to lie above the lower-grade zone B.

The most common rocks of Ile de Groix series are mica schists. Intercalated with these are metabasic rocks, chiefly greenschists, amphibolites, blueschists and eclogites. The thickness of the metabasic intercalations varies from a few centimetres to several tens of metres.

Among the metabasic rocks of the eastern part of Ile de Groix (zone A according Carpenter and Quinquis) garnet glaucophanites (assemblage: glaucophane–garnet–pyroxene–epidote) and am-

phibolites (glaucophane–blue–green amphibole–epidote–garnet) are the most common. Scarce outcrops of eclogites, abundant in jadeitic pyroxenes, have been reported as well (Triboulet, 1974; Carpenter, 1976). Metapelites of this zone are represented by heterogeneous, quartzophengitic mica schists with chloritoid, chloritoid + garnet, or chloritoid + garnet + glaucophane. All these assemblages can contain such accessory minerals as quartz, phengite, chloritoid (metabasites), epidote, albite, tourmaline (mica schists) and biotite, stilpnomelane, apatite, sphene, rutile, and opaques (both groups of rocks).

West of the garnet isograd, the metabasites of zone B are represented by greenschists, amphibolites and prasinites. Except for lack of garnet, the abundance of the blue–green amphibole barroisite (more abundant than glaucophane) is of major importance. The typical assemblages are: (1) blue–green amphibole–glaucophane–epidote–chlorite and (2) albite–epidote–chlorite–blue–green amphibole. The most common assemblage in the mica schist of this zone is: quartz–phengite–chloritoid–stilpnomelane–chlorite.

Apart from the rock types listed above, less common assemblages occur on Ile de Groix as

well. Minor outcrops of epidotites, garnetites, talc–actinolite schists, serpentinites, and quartzites have been reported, e.g. by Carpenter (1976) and Audren and Triboulet (1986). Small intercalations of black and pink banded metacherts are relatively rare, but this rock type will be given more attention, as it proved to contain deerite.

Sample description

The investigated specimens of garnet glaucophanites and deerite-bearing metacherts have been collected at Cotes des Soeurs and Amer, both situated in the higher-grade zone A (Fig. 1). Garnet glaucophanites from Cotes des Soeurs (GX-1) and Amer (GR-15) have been examined in order to compare the mineral chemistry of the metabasic rocks and metacherts, and to determine the P–T conditions of metamorphism. Deerite-bearing metacherts (GX-10, IG-2), found only at Cotes des Soeurs, occur as horizons several centimetres thick in dark-blue garnet glaucophanites. The metacherts are strikingly banded on a scale of several millimetres to 2 centimetres, comprising alternating black and pink bands. The pink bands are composed mainly of garnet and quartz, whereas the black bands contain greater concentrations of iron oxides and amphiboles. Specimen GX-10 contains the assemblage: garnet–quartz–amphibole–pyroxene–magnetite–ilmenite–deerite–pyrite. Specimen IG-2 contains garnet–quartz–amphibole–magnetite–hematite–deerite.

Idiomorphic porphyroblasts of garnet (almandine) are very common in both dark and pink bands. Pyroxene, present only in specimen GX-10, is a xenoblastic aegirine–augite. Amphiboles, of variable chemical composition, occur as prisms or needles. The most common is blue–green barroisite, but blue amphiboles and zoned crystals with blue cores and pale blue or blue–green rims are present as well. Colourless Fe–Mg amphibole, belonging to the cummingtonite series has been detected in one of the examined specimens.

Deerite (Fig. 2) occurs as very fine (up to 0.8 mm long; average 0.1 mm), almost black needles disseminated in quartz or as anhedral, opaque inclusions (on average 0.2 mm long). It is always entirely enclosed in another mineral, quartz, garnet or amphibole. Almost all the anhedral grains are surrounded by thin rims of hematite, which indicates destabilization of the deerite.

Millimetre-sized euhedral or subhedral crystals of magnetite are very abundant in dark bands and sparsely distributed in the pink bands. Ilmenite, detected only in specimen GX-10, appears as very fine (<0.1 mm long) opaque needles scattered in

a quartz matrix. Scarce inclusions of this mineral are observed in garnet cores. Hematite appears either as inclusions, in garnet, or as thin rims encircling crystals of deerite and magnetite. Scarce, needle-shaped hematites are most probably pseudomorphs after deerite. Small amounts of pyrite are visible in dark bands of specimen GX-10.

Rock chemistry

The bulk chemical compositions of the examined samples of deerite-bearing metachert (GX-10) and garnet glaucophanites (GX-1, GR-15) are presented in Table 1. Specimen GX-1 is a metabasic rock intercalated with deerite-bearing metacherts. Specimen GR-15, collected at Amer, is

Table 1. Chemical analyses of deerite-bearing metachert (GX-10) and associated garnet glaucophanites (GX-1, GR-15). FeO and Fe2O3 determined by wet analysis, other oxides by X-ray fluorescence (XRF). Analyst N. Vassard.

sample	GX-10	GX-1	GR-15
SiO2	53.42	54.50	47.75
TiO2	0.88	1.70	3.13
Al2O3	9.44	13.05	14.06
Fe2O3	10.31	5.66	6.74
FeO	14.61	7.94	8.63
MnO	0.25	0.21	0.23
MgO	2.27	4.94	4.72
CaO	6.05	8.54	9.10
Na2O	0.77	2.95	4.18
K2O	0.08	0.13	0.26
P2O5	0.14	0.20	0.31
H2O	1.13	0.91	1.05
total	99.35	100.73	100.16

an example of the most common garnet glaucophanites from the eastern, higher-grade metamorphic zone of Ile de Groix.

A notable difference in iron content between the metabasites and metachert mainly results from large amounts of magnetite in the latter. As metacherts are relatively poor in pyroxenes and amphiboles, the contents of sodium, calcium, magnesium and alumina are higher in metabasites.

Mineral chemistry

All minerals were analysed with a CAMEBAX electron microprobe at the University Paris VI. The accelerating voltage was 15 kV and beam current 10 nA. Standards used were natural silicates except for Fe, Mn, Ti, which were estimated with Fe_2O_3 and $MnTiO_3$. Counting times were between 10 and 20 s. Garnet and oxide analysis corrections were made using Philibert–Tixier ZAF method, and Fe^{3+} values were determined by charge
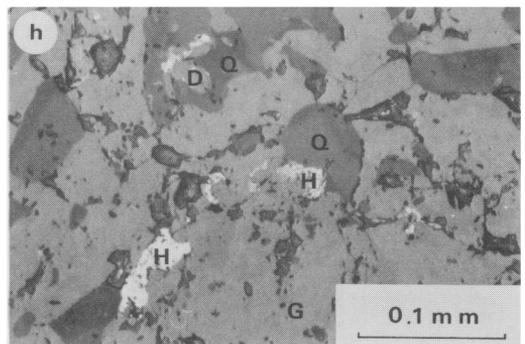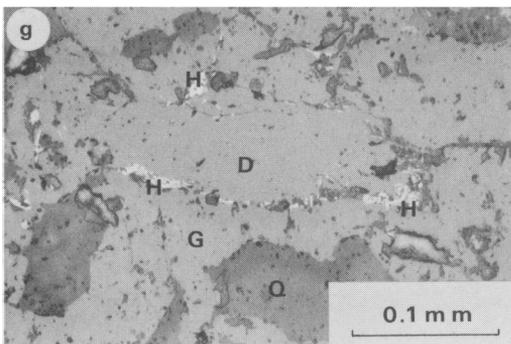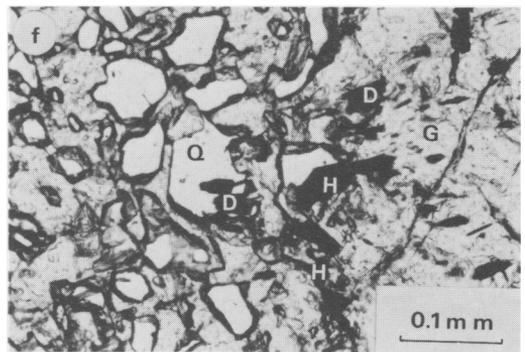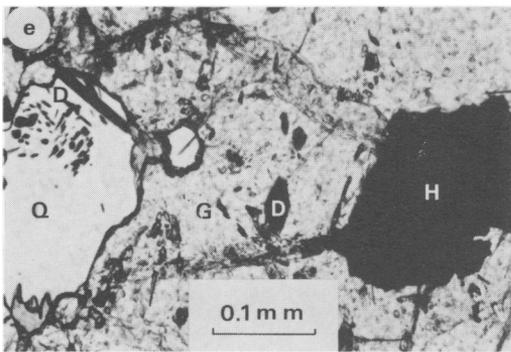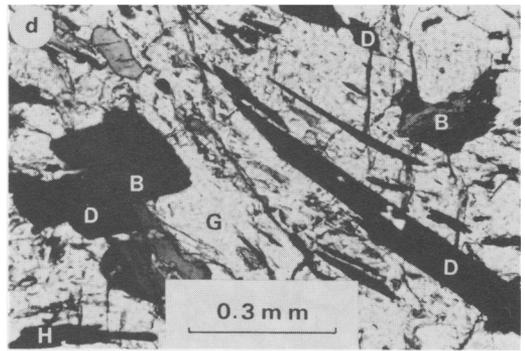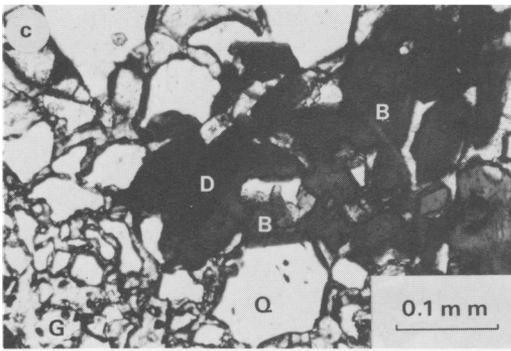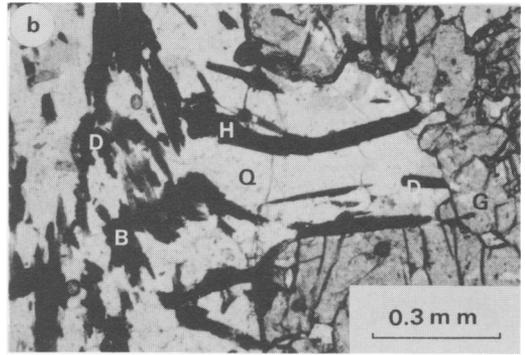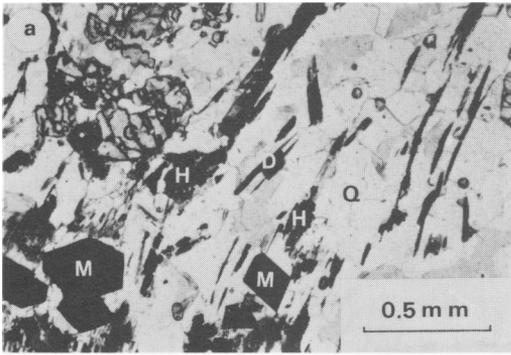
FIG. 2. Thin section photomicrographs, showing deerite crystals, *a* and *b* disseminated in quartz matrix, and *c–h* included in garnet. D—Deerite, M—Magnetite, H—Hematite, G—Garnet, B—Barroisite, Q—Quartz. *a–f* were taken in plane polarized light and *g, h*, in reflected light.
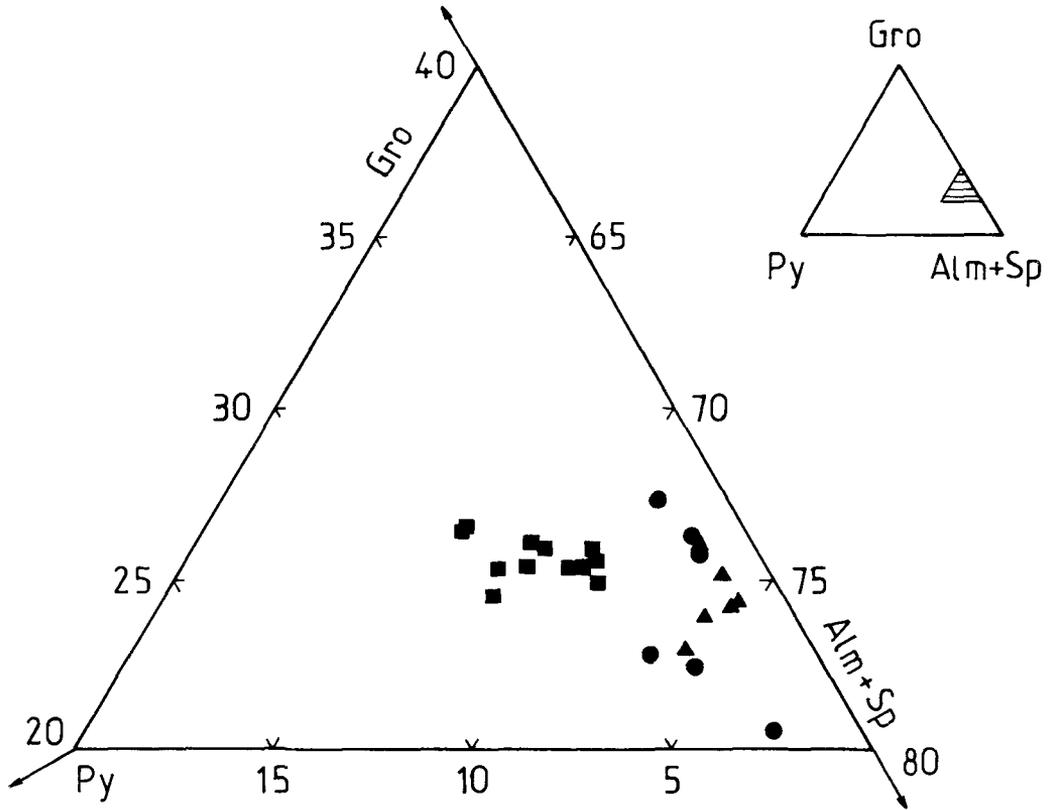
FIG. 3. Composition of garnets in a grossular–almandine + spessartine–pyrope diagram. Squares—GR-15, tri-angles—IG-2, circles—GX-10.

balance. Analyses of pyroxenes, amphiboles and deerites were recalculated with special pro-grammes, taking into account charge balance and site occupancies.

Garnet. The garnets from both garnet glauco-phanites and metacherts are almandine-rich (Table 2, Fig. 3). They show a normal zonation with decreasing Mn content and slightly increas-ing Fe and Mg content from the core to the rim (Fig. 4). The garnets from glaucophanites are somewhat more abundant in Mg (3.87–8.25% of pyrope) than the garnets from deerite-bearing rock (1.11–3.98% of pyrope).

Pyroxene. The pyroxenes are relatively homo-geneous chloromelanites in the glaucophanites, and aegirine-augites in the metacherts (Fig. 5).

Amphibole. Structural formulae have been determined with a programme written by C. Mevel. The method has been discussed by Robin-son *et al.* (1982). Assuming 23 oxygens per struc-tural unit, the cation sum is normalized as follows: (1) total silicon to 8; (2) total cations (exclusive of Ca, Na, K) to 13; (3) total cations (exclusive of Na, K) to 15; (4) total cations (exclusive of K) to 15; and (5) total cations to 16. Fe^{3+} is then estimated by charge balance. The validity of the results was checked with the formula proposed by Papike *et al.* (1974). For the analysed amphi-boles, this formula led us to choose as the most accurate the calculations with total cations norma-lized to 13 (option (2) above).

Compositional variations of the analysed amphiboles are shown in Fig. 6a–d. A plot of Ca *vs.* Na (Fig. 6a) indicates relatively low occupancy of site A in blue and blue–green amphiboles. The Na content in the vacant site is maximal (up to 0.3 cation per unit) in glaucophanes (Table 2). The broad variability in Al^{IV} in barroisites is remarkable (Fig. 6b). The Al^{IV} content varies from 1.52 to 0.24 cations per unit. The poorest

Table 2. Electron microprobe analyses of minerals. Total iron as FeO.

sample	garnets			pyroxenes		deerites				amphiboles				
	GR-15 core	IG-2 core	IG-2 rim	GR-15	GX-10	GX-10	GX-10	IG-2	IG-2	GX-10	GX-10	IG-2	IG-2	IG-2
SiO_2	36.43	36.45	36.87	54.48	53.23	33.07	33.19	33.82	33.31	56.24	47.91	49.05	52.59	51.42
TiO_2	0.17	0.02	–	0.03	0.02	5.02	3.61	1.22	0.14	0.08	0.21	0.12	0.01	–
Al_2O_3	20.34	19.46	20.02	7.68	3.56	0.66	0.50	0.89	0.66	8.56	5.35	7.25	5.51	0.09
Cr_2O_3	–	0.05	0.06	–	–	0.07	–	0.05	–	–	–	–	–	–
FeO	28.77	26.59	32.85	11.57	16.82	52.42	53.07	54.68	55.12	16.52	27.21	24.49	25.57	32.70
MnO	3.71	6.95	0.10	0.03	–	0.50	0.14	0.51	0.04	–	0.18	0.01	0.01	0.02
MgO	1.05	0.31	0.77	5.93	5.89	0.59	0.82	0.86	0.95	7.76	5.25	6.31	4.69	11.67
CaO	9.50	8.65	8.07	11.27	13.99	0.09	0.07	0.01	0.01	1.14	7.04	4.65	1.47	0.54
Na_2O	0.02	0.04	–	8.02	6.10	0.03	–	0.03	0.02	6.55	3.13	5.50	7.10	0.03
K_2O	–	–	–	–	–	–	0.07	–	–	0.04	0.22	0.19	0.03	–
total	99.99	98.52	98.74	99.01	99.61	92.45	91.47	92.07	90.25	96.89	96.50	97.57	96.98	96.47
oxygens	24	24	24	6	6	45	45	45	45	23	23	23	23	23

Cations — garnets, pyroxenes, deerites:

	garnets GR-15 core	garnets IG-2 core	garnets IG-2 rim	pyroxenes GR-15	pyroxenes GX-10	deerites GX-10	deerites GX-10	deerites IG-2	deerites IG-2
Si	5.91	6.00	6.03	1.99	1.99	11.96	12.09	12.18	12.22
Al	3.89	3.78	3.86	0.33	0.16	0.28	0.22	0.38	0.29
Ti	0.02	–	–	–	–	1.36	0.99	0.33	0.04
Cr	–	0.01	0.01	–	–	0.02	–	0.01	–
Fe^{3+}	–	0.17	0.07	0.26	0.31	3.08	3.67	4.62	5.22
Fe^{2+}	3.90	3.49	4.43	0.09	0.22	12.77	12.50	11.84	11.69
Mn	0.51	0.97	0.01	–	–	0.15	0.04	0.16	0.01
Mg	0.25	0.08	0.19	0.32	0.33	0.32	0.45	0.46	0.52
Ca	1.65	1.53	1.41	0.44	0.56	0.04	0.03	–	–
Na	0.01	0.01	–	0.57	0.44	0.02	–	0.02	0.01
K	–	–	–	–	–	–	0.03	–	–
total	16.14	16.04	16.01	4.00	4.01	30.00	30.02	30.00	30.00

Cations — amphiboles:

	GX-10	GX-10	IG-2	IG-2	IG-2
Si	7.97	7.32	7.28	7.82	7.97
Al	0.03	0.68	0.72	0.18	0.02
	8.00	8.00	8.00	8.00	7.99
Al	1.39	0.28	0.55	0.78	–
Ti	0.01	0.02	0.01	–	–
Cr	–	–	–	–	–
Fe^{3+}	0.47	1.08	1.05	0.88	–
Fe^{2+}	1.49	2.40	1.99	2.30	4.24
Mn	–	0.02	–	–	–
Mg	1.64	1.20	1.40	1.04	0.76
	5.00	5.00	5.00	5.00	–
Mg	–	–	–	–	1.94
Ca	0.17	1.15	0.74	0.23	0.09
Na	1.80	0.85	1.26	1.77	–
	1.97	2.00	2.00	2.00	2.03
Na	–	0.08	0.32	0.28	0.01
K	0.01	0.04	0.04	0.01	–

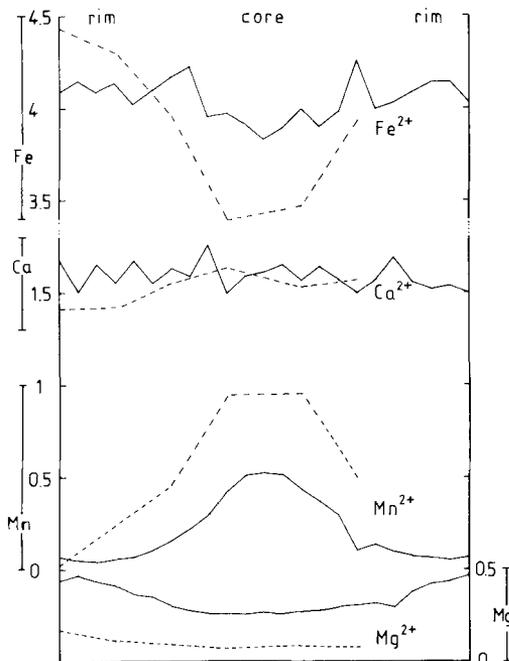in silicon are dark green crystals occurring as inclusions in garnets. Glaucophanes, common in metabasites, and scarce in metacherts, fall en-tirely in the glaucophane field (Fig. 6c), but in all analyses the Fe^{2+} content is relatively high. Blue amphibole from specimen IG-2 is crossite. Fig. 6d shows a miscibility gap between blue–green and colourless amphiboles in this sample.

Deerite. Structural formulae have been calculated on the basis of 45 oxygens with a programme written by P. Vernié. The amount of Fe^{3+} has been estimated by converting as much Fe^{2+} as necessary to achieve charge balance (30 cations,

FIG. 4. Zoning profile of garnets. Solid line—GX-15, dashed line—IG-2. Cation scale for structural formulae based on 24 oxygens.
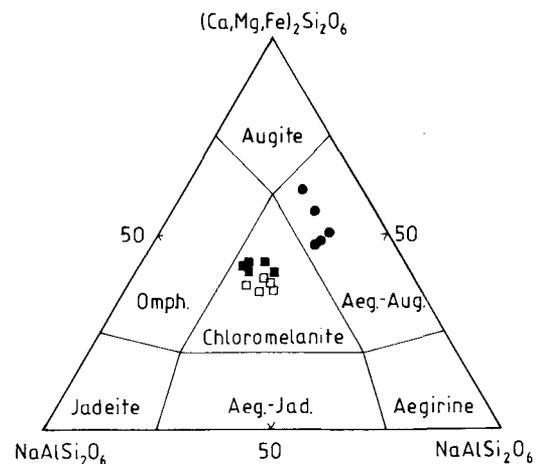
FIG. 5. Composition of pyroxenes in the diagram jadeite–aegirine–others. Squares—GR-15, circles—GX-10. Open symbols—pyroxenes included in garnets.
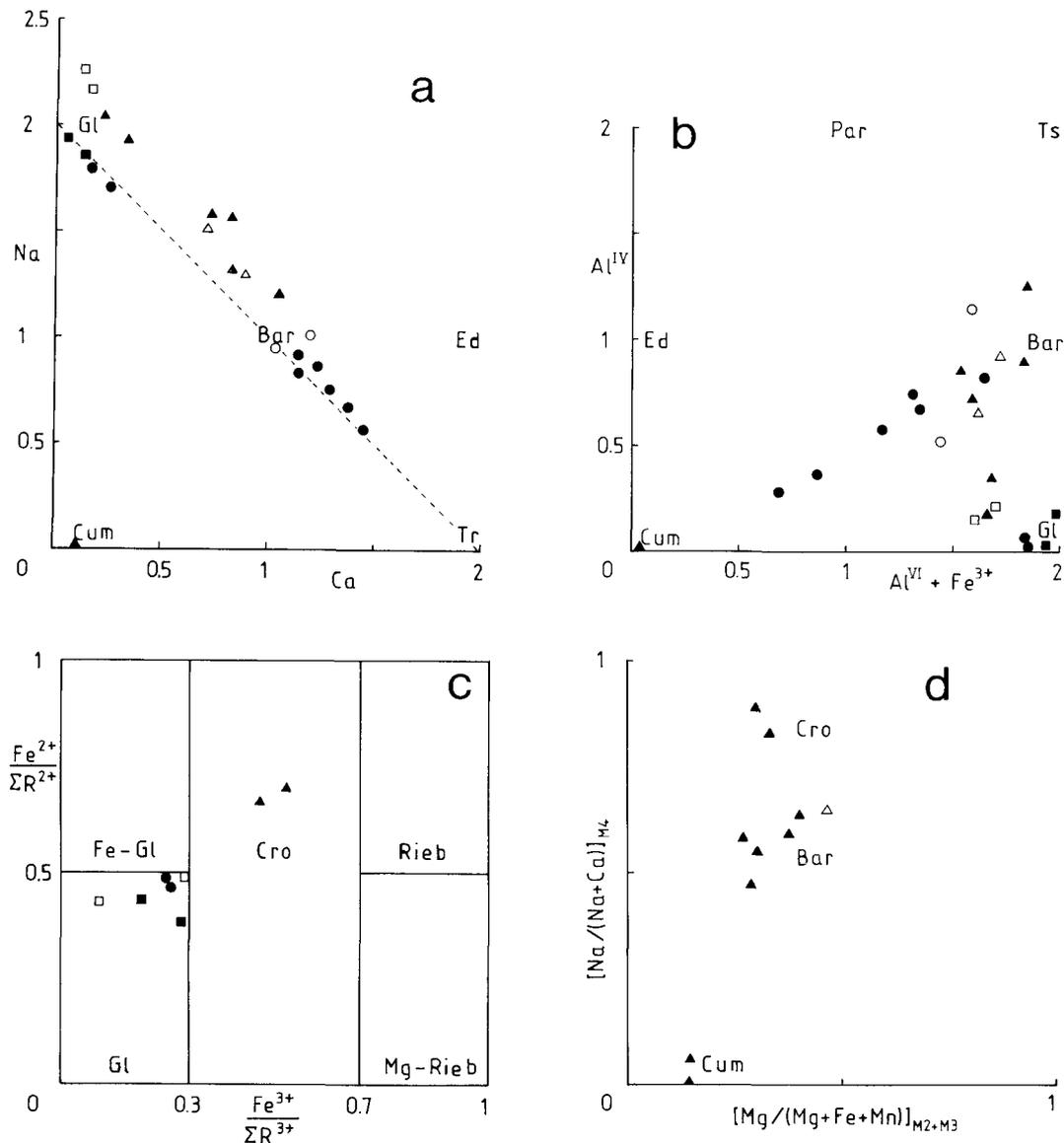
FIG. 6. Composition of amphiboles in: (*a*) Ca *vs.* Na diagram; (*b*) Al^{IV} *vs.* $Al^{VI} + Fe^{3+}$ diagram; (*c*) Fe^{2+}/R^{2+} *vs.* Fe^{3+}/R^{3+} diagram; and (*d*) $[Na/(Na + Ca)]_{M4}$ *vs.* $[Mg/(Mg + Fe + Mn)]_{M2+M3}$ diagram. Squares—GR-15, triangles—IG-2, circles—GX-10, open symbols—amphiboles included in garnets. Gl–Glaucophane, Bar–Barroisite, Ed—Edenite, Cum—Cummingtonite, Tr—Tremolite, Par—Pargasite, Ts—Tschermakite, Cro—Crossite, Rieb—Riebeckite.

total charge = 90). Table 2 presents four analyses of deerites from the specimens examined. Fig. 7 shows a plot of some published deerite analyses (Worthing, 1987; Reinecke, 1987; former data recalculated by Vernié *et al.*, 1986), together with those from Ile de Groix. The ideal formula of

deerite requires 12 Si per unit, but microprobe analyses recalculated to 30 cations often reveal this value to be higher. According to Muir Wood (1979) it can be caused by variations in the hydroxyl content and octahedral cation vacancies. In the deerites examined here, the Si content varies
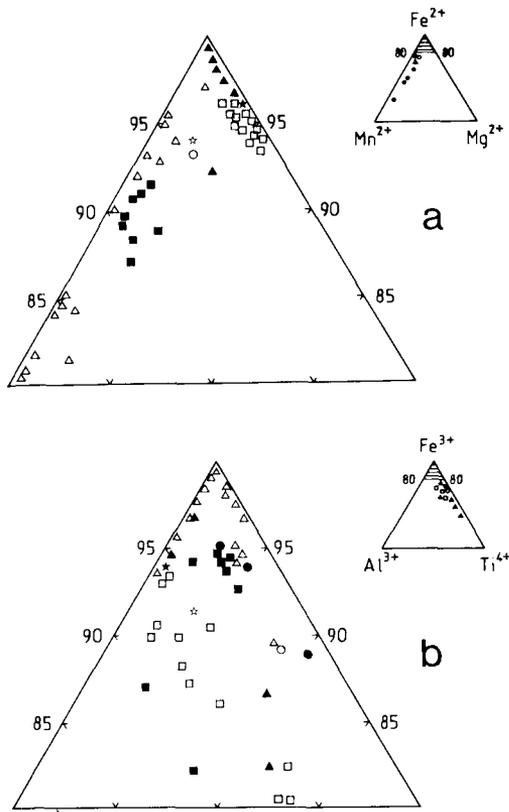
FIG. 7. Composition of deerites in: (*a*) Fe^{2+}-Mg-Mn diagram; (*b*) Fe^{3+}-Al-Ti diagram. Open triangles—Franciscan iron formation (Muir Wood, 1979), closed triangles—Alpine formations (Agrell and Gay, 1979; Bocquet and Forette, 1973; Dal Piaz and Molin, 1978; Muir Wood, 1979), open asterisks—Shuksan Unit (Brown, 1974), closed asterisks—Sifnos (Schliestedt, 1978), open squares—Ile de Groix (Kienast, 1983; this study), closed squares—Corsica (Vernié *et al.*, 1986), open circles—Papua New Guinea (Worthing, 1987), closed circles—Andros (Reinecke, 1987).

FIG. 8. Composition of Ile de Groix deerites on an Fe^{3+} *vs.* $Fe^{2+} + Ti^{4+}$ diagram. Triangles—IG-2, circles—GX-10, open symbols—deerites included in garnets.

between 11.91 and 12.29 cations per unit, so the deviation from the theoretical value is less than 3% (Muir Wood reports *ca.* 5% extra silicon in deerites from Franciscan Formation and Shuksan Unit). The Ile de Groix samples most closely resemble deerites from Sifnos (Schliestedt, 1978) and some of the Alpine Formations. The low Mn (<0.2 Mn^{2+} cation per unit) in deerites included in garnets, and the virtual lack of Mn in deerites free from garnets distinguishes the Ile de Groix deerites from those from the Franciscan Formation, Corsica, Papua, New Guinea, and manganoan deerites from Andros. The substitutions of
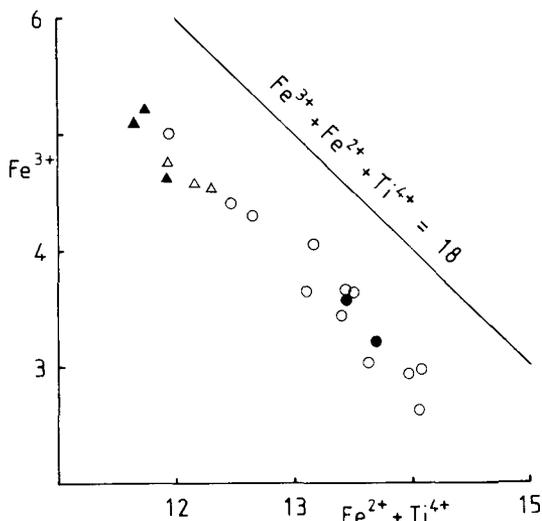
Mg (0.3–0.8 Mg cation per unit) and Al (0.2–0.4 Al cation per unit) are comparable with most other deerites. The content of Ti (up to 1.43 Ti^{4+} cation per unit) is most probably due to substitution $2Fe^{3+} = Ti^{4+} + Fe^{2+}$ (Fig. 8). The discrepancy between the values obtained from analyses and the line $Fe^{3+} + Fe^{2+} + Ti^{4+} = 18$ is due to Al and Mg substitutions (average 0.3 and 0.6 cation per unit respectively) and cation vacancies. The last can be compensated by silicon contents greater than in the ideal formula (average 12.2 cations per unit). Due to significant substitution of Ti the Ile de Groix deerites are very similar to Alpine deerites, those from Sifnos are very poor in titanium. Other elements known from the literature to substitute in deerite are chromium, vanadium and zinc. In the Ile de Groix deerites, Cr and V are below the detection level and Zn is present only in traces (0.01–0.04 wt.% ZnO, i.e. <0.01 Zn^{2+} cation per unit).

P–T conditions of metamorphism

Previous estimations of the *P–T* conditions of the Ile de Groix metamorphism were made by Triboulet (1974) and Carpenter (1976). Triboulet evaluated pressure from the jadeite content of pyroxenes (Essene and Fyfe, 1967) and temperature from different studies on mineral stability fields (Velde, 1967, 1970; Kienast and Triboulet, 1972). Carpenter calculated pressure from the activity of jadeite in pyroxenes (Ganguly, 1973)
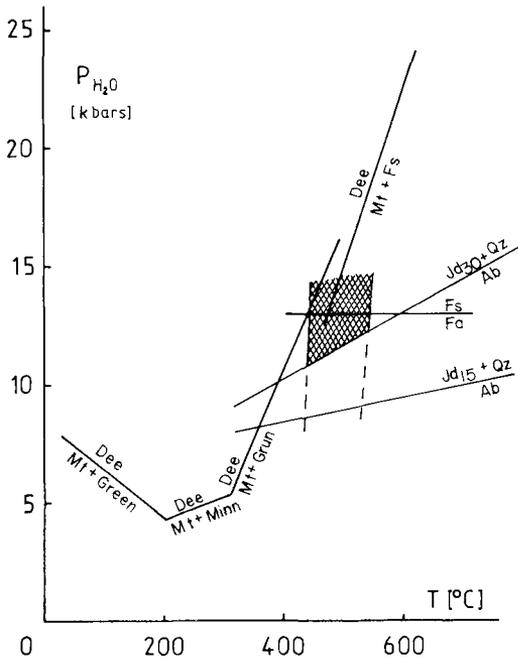
FIG. 9. The *P–T* conditions of Ile de Groix metamorphism (shaded area) compared with the stability field of deerite (after Muir Wood, 1979, simplified). Dee—Deerite, Mt—Magnetite, Green—Greenalite, Minn—Minnesotaite, Grun—Grunerite, Fs—Ferrosilite, Fa—Fayalite, Jd—Jadeite, Qz—Quartz, Ab—Albite.

and temperature from the Fe–Mg partitioning between coexisting garnet and clinopyroxene (Raheim and Green, 1974). The same methods were applied in this study, but calculations were made on the basis of calibrations by Holland (1980) and Ellis and Green (1979).

P–T conditions of prograde metamorphism have been calculated from microprobe analyses of clinopyroxenes and garnets from samples GX-10 (metachert, Cotes des Soeurs) and GR-15 (garnet glaucophanite, Amer). As both contain clinopyroxenes and quartz but no albite, the albite breakdown curve (Fig. 9) marks only the minimum pressure. The discrepancy between curves

calculated from glaucophanite (curve Jd_{30}) and from metachert (curve Jd_{15}) is due to different composition of pyroxenes (jadeite content, see Fig. 5) in the samples examined. Assuming that Fe–Si-rich metacherts are undersaturated in sodium (Table 1), the pressure indicated by curve Jd_{30}, minimum 10.5 kbars, seems to be more realistic. The values of temperature, shown by curves of Fe–Mg exchange equilibria, are very similar for both examined samples; 480 ± 50 °C.

Conclusions

The pressure calculated in this study differs considerably from Triboulet's and Carpenter's estimation (Table 3). As in all studies the activity of jadeite was assumed to be equal to 30, the discrepancy results from different modes of calculation. In addition, Carpenter assumed coexistence of clinopyroxene and quartz with albite in equilibrium, whereas we did not observe such an assemblage. The values of temperature obtained here are close to Triboulet's estimations and somewhat higher than the temperature calculated by Carpenter.

Comparison of the *P–T* conditions of metamorphism, together with the stability field of deerite (Fig. 9), reveals that deerites from Ile de Groix do not fall into this field. The most probable explanation of this discordance is that the Ile de Groix deerite is a relic from earlier stages of the prograde metamorphism. The following observations favour this hypothesis: (1) all the investigated deerites are included in minerals of the high-pressure typomorphic paragenesis (garnet, quartz or amphibole); (2) deerites are often surrounded by fine rims of hematite; and (3) scarce needle-shaped pseudomorphs of hematite after deerite occur in quartz and in garnets. Observations (2) and (3) clearly denote the destabilization of deerite. We assume that it is a metastable phase, not at equilibrium with the matrix assemblage.

Acknowledgements

Table 3. Conditions of prograde metamorphism of Ile de Groix series.

	Triboulet (1974)	Carpenter (1976)		this study
zone I	8.5 kb, 530 C	zone A	8±1.5 kb, 400±50 C	>10.5 kb, 480 ±50 C
zone II	8 kb, 500 C			
zone III	7.5 kb, 470 C	zone B	6.5 – 8 kb, <400 C	not determined

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