Manganoan deerite and calderitic garnet from high-pressure metamorphic Fe–Mn-rich quartzites on Andros Island, Greece

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Abstract

Calderitic garnet and manganoan deerite have been found in Al-poor, Fe-Mn-rich quartzites associated with metabasic schists on the island of Andros, Cycladic blueschist belt, Greece. Calderitic garnet (30–45 mole % calderite, 55–70 mole % andradite, 0–2 mole % spessartine) occurs in paragenesis with quartz, rhodonite, rhodochrosite, Ni–Mn-bearing magnetite (2–20 mole % trevorite, 6–12 mole % jacobsite, 73–91 mole % Fe_3O_4), baryte, and orthite. Deerite is associated with quartz, garnet (rich in spessartine, almandine, and andradite), phengite, aegirine, magnetite (containing up to 12 mole % jacobsite), and crossite/riebeckite. Deerite contains 33.0–34.4 wt. % SiO_2, 0.53–5.5 wt. % TiO_2, 0.09–0.31 wt. % Al_2O_3, 11.9–33.9 wt. % MnO, 17.5–44.2 wt. % FeO_{tot}, and 1.5–2.8 wt. % MgO. MnO contents correspond to 29–77 cation % Mn^{2+} per total R^{2+} cations. Deerites from Andros are thus closer to the hypothetical end-member mangano-deerite, $Mn_{12}^{2+}Fe_6^{3+}Si_{12}O_{40}(OH)_{10}$, than any other analysis of deerite so far published.

KEYWORDS: deerite, garnet, calderite, Andros, Greece.

Introduction

THE iron-rich silicate deerite, $(Fe^{2+},Mn^{2+},Mg,Fe^{3+},Ti^{4+},Al,V^{3+})_{18}Si_{12}(O,OH)_{50}$, has been reported from several occurrences in blueschist-type rocks from the Franciscan and Shuksan terranes, U.S.A., the Alps, Corsica, Turkey, the Aegean, and New Caledonia (see list of occurrences in Muir Wood, 1979). Corresponding to a blueschist-type environment, Langer *et al.* (1977) and Lattard and Schreyer (1981) experimentally found a high-pressure, low- to medium-temperature stability field for deerite. In addition, the formation of deerite appears to be restricted to relatively reduced, Al-poor, Fe–Mn-rich metasediments probably derived from hydrothermal metalliferous sediments rich in Fe–Mn oxyhydroxides and/or smectites (Muir Wood, 1982; Reinecke *et al.*, 1985).

Chemically similar metasediments may contain Al-poor garnet enriched in the end-member calderite, $Mn_3^{2+}Fe_2^{3+}(SiO_4)_3$ (list of occurrences and chemical data in Lattard and Schreyer, 1983). In their experimental study Lattard and Schreyer (1983) showed that pure calderite is stable only at relatively high pressure. However, solid solution of calderite with andradite and spessartine as commonly found in natural calderitic garnets enlarges the stability field of calderitic garnets towards higher temperatures and lower pressures (cf. Lattard and Schreyer, 1983).

This paper reports on two new occurrences of deerite and calderitic garnet in magnetite-bearing quartzites metamorphosed under blueschist-facies conditions on the neighbouring islands of Andros and Tinos, Cycladic blueschist belt, Greece.

Geology

On the island of Andros, deerite and calderitic garnet were discovered in a layer of Fe-rich, Al-poor quartzites, about 2 to 3 m thick, on top of greenschists near Sagarianis, central Andros. The Fe-rich quartzites mainly consist of massive to thin layered aegirine–magnetite-rich quartzites containing layers and crosscutting veins rich in crossite/riebeckite. Rarely, yellow-brown fine-grained quartzites composed of garnet, quartz, and subordinate magnetite occur intercalated in the aegirine–magnetite quartzites.

In northern Tinos, deerite was found in two

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boulders of magnetite-crossite quartzite at the northern slope of the mountains extending a few kilometers north of Kardianí.

Metamorphic rocks in central Andros and northern Tinos possibly form part of the same tectonic unit of Mesozoic metasediments which underwent an Eocene blueschist-type metamorphism ($P > 10$ kbar, $T \simeq 450$-500 °C) and later Barrovian-type greenschist-facies overprint ($P \simeq 5$-6 kbar, $T \simeq 400$-500 °C) of upper Oligocene/lower Miocene age (Kohlmann, 1978; Altherr *et al.*, 1982; Melidonis, 1980; Reinecke, 1983, 1986).

Deerite quartzite

Deerite is present in amounts of less than 1 vol.% in magnetite ± hematite-bearing layers. It forms black needles, up to about 500 μm long and 20 μm across, enclosed in quartz in subparallel orientation or as radiating bundles. Deerite textures are very similar to those described by Muir Wood (1979). Whereas larger crystals are opaque in thin section, tiny crystals are strongly pleochroic from olive-brown to almost opaque (parallel to needle axis). The mineral association of the deerite-bearing samples is:

quartz-aegirine-magnetite-spessartine-almandine garnet-crossite/riebeckite-deerite ± hematite ± phengite ± apatite.

Deerite is observed exclusively as inclusions armoured in quartz and may be therefore considered as relic not in textural equilibrium with the matrix assemblage consisting of aegirine + garnet + magnetite + Na-amphibole. Hematite has been formed as a late alteration product replacing deerite and magnetite, but is also present as individual grains beside magnetite in some samples. Rare albite and narrow rims of blue-green Ca-Na amphibole around crossite/riebeckite may reflect a partial reequilibration of the high-pressure assemblages during the greenschist-facies overprint.

Selected microprobe analyses of deerite and associated garnet, aegirine, and magnetite in one sample analysed are presented in Table 1. The deerite analyses were recalculated to 30 cations and their Fe^{3+}/Fe^{2+} ratios obtained assuming 90

Table 1 Selected mineral analyses from deerite-bearing aegirine-magnetite quartzite And 79/293 and rhodonite-magnetite-garnet quartzite And 83/23

sample	79/293				79/293	79/293	79/293	83/23				83/23	83/23	83/23			
	deerite				gar	aeg	mag	garnet				rhod	rhchr	magnetite			
SiO_2	33.4	33.0	33.9	33.9	37.3	54.4	-	34.1^{b}	34.2	33.9	34.4	46.4^{b}	-	$-^{b}$	$-^{b}$	-	-
TiO_2	5.5	2.1	1.0	0.53	0.14	-	-	-	-	-	-	-	-	-	-	-	-
Al_2O_3	0.13	0.15	0.22	0.31	18.1	4.3	-	0.27	0.44	0.08	0.10	-	-	-	-	-	-
Fe_2O_3	11.8^{c}	19.0^{c}	21.7^{c}	20.7^{c}	-	26.9^{d}	98.4^{d}	29.8^{d}	29.7^{d}	29.7^{d}	29.9^{d}	-	-	89.4^{d}	89.8^{d}	93.7^{d}	91.3^{d}
FeO_{tot}	17.5	42.7	41.2	38.9	13.2	-	-	-	-	-	-	4.7	0.4	-	-	-	-
MnO_{tot}	33.9	11.9	16.9	17.3	25.1	0.22	3.7	17.9	15.1	18.0	13.5	42.1	47.2	2.2	1.8	3.4	2.3
NiO	-	-	-	-	-	-	-	-	-	-	-	-	-	5.9	6.2	0.6	3.9
MgO	2.03	2.07	1.47	1.81	0.07	0.7	-	-	-	-	-	0.30	1.5	-	-	-	-
CaO	-	-	-	-	5.7	1.5	-	17.5	19.6	17.3	21.3	5.6	8.5	-	-	-	-
Na_2O	-	-	-	-	-	13.7	-	-	-	-	-	-	-	-	-	-	-
H_2O^{a}	4.20	4.18	4.29	4.23	-	-	-	-	-	-	-	-	-	-	-	-	-
Total	96.66	96.10	98.98	96.98	99.61	101.72	102.1	99.57	99.04	98.98	99.20	99.10	57.6	97.5	97.8	97.7	97.5
Si	11.92	11.84	11.84	12.03	3.05	1.99	-	3.00	3.01	3.01	3.01	1.00	-	-	-	-	-
Al	0.06	0.06	0.09	0.13	1.74	0.19	-	0.03	0.05	0.01	0.01	-	-	-	-	-	-
Ti^{4+}	1.48	0.57	0.26	0.14	0.01	-	-	-	-	-	-	-	-	-	-	-	-
Fe^{3+}	3.15	5.13	5.70	5.53	0.25	0.74	2.00	1.97	1.96	1.98	1.97	-	-	2.00	2.00	2.00	2.00
Fe^{2+}	2.07	7.68	6.34	6.01	0.65	-	0.88	-	-	-	-	0.09	0.01	0.73	0.74	0.87	0.79
Mn^{2+}	10.25	3.62	5.00	5.20	1.74	0.01	0.12	1.34	1.12	1.35	1.00	0.77	0.77	0.08	0.06	0.12	0.08
Ni	-	-	-	-	-	-	-	-	-	-	-	-	-	0.19	0.20	0.02	0.13
Mg	1.08	1.11	0.77	0.96	0.01	0.04	-	-	-	-	-	0.01	0.04	-	-	-	-
Ca	-	-	-	-	0.50	0.06	-	1.65	1.85	1.65	2.00	0.13	0.18	-	-	-	-
Na	-	-	-	-	-	0.97	-	-	-	-	-	-	-	-	-	-	-
Σ	30.01	30.01	30.00	30.00	7.95	4.00	3.00	7.99	7.99	8.00	7.99	2.00	1.00	3.00	3.00	3.01	3.00
gross %					4.4			-	-	-	-						
pyr %					0.3			-	-	-	-						
alm %					22.6			-	-	-	-						
andr %					12.8			55.3	62.2	55.1	67.3						
spess %					59.9			1.4	2.3	0.4	0.5						
cald %					-			43.3	35.5	44.5	32.2						

Mineral analyses were carried out with the automated CAMEBAX microprobe at the TU Berlin (ZELMI). Analytical conditions are 15 kV, 30 nA for deerite, garnet, aegirine, rhodonite, and rhodochrosite, and 20 kV, 20 nA for magnetite. Used standards are synthetic TiO_2, Al_2O_3, MgO, Ni-metal, Mn-metal, and natural hematite, wollastonite (Si, Ca), and albite (Na). Raw data were corrected by the ZAF procedure. Deerite analyses were recalculated to 30 cations and 90 charges, aegirine to 4 cations and 6 charges, garnet to 12 oxygens, rhodonite to 3 oxygens, rhodochrosite to 1 oxygen, and magnetite to 3 cations and 8 charges. Fe^{2+} in garnet 79/293 was calculated from $Fe^{3+} = 2.00 - Al - Ti^{4+}$ and $Fe^{2+} = Fe_{tot} - Fe^{3+}$ per 12 oxygens; a = calculated by stoichiometry (10 (OH) and 40 oxygens); b = garnet, rhodonite, and magnetite analysed in close contact in sample 80/23. Ni could not be detected in garnet, rhodonite, and rhodochrosite of sample 83/23; c = Fe_2O_3 content recalculated on a basis of 30 cations and 90 charges; d = total Fe given as Fe_2O_3.

charges in the formula $(Fe^{2+},Mn^{2+},Fe^{3+},Al,Ti^{4+},Mg)_{18}Si_{12}O_{40}(OH)_{10}$ (cf. Muir Wood, 1979). Although individual grains are generally homogeneous, deerites from different parts of the section vary strongly in chemical composition (Table 1, Fig. 1). The concentrations of TiO_2, Al_2O_3, and SiO_2 are within the compositional range of deerites reported from the classical localities in the western U.S.A. (Agrell *et al.*, 1965; Langer *et al.*, 1977; Muir Wood, 1979, 1982; Brown, 1974), from the western Alps (Agrell and Gay, 1970; Bocquet and Forette, 1973), and from the Cycladic blueschist belt (Schliestedt, 1978, 1980). However, the MgO and particularly the MnO contents of the deerites from Andros are considerably higher and the FeO_{tot} contents are lower than in published analyses. A plot of R^{2+} cations in Fig. 1 shows limited substitution of Fe^{2+} and Mn^{2+} by Mg, but shows considerable $Mn^{2+}Fe^{2+}_{-1}$ substitution up to 77 cation % Mn^{2+} per total R^{2+} cations.

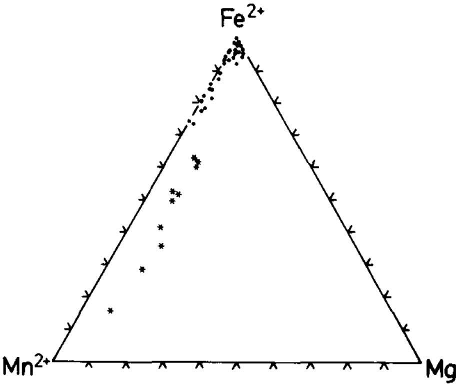

FIG. 1. Compositional variation of Mn^{2+}, Fe^{2+}, and Mg (mole %) in deerites. In microprobe analyses, Fe^{2+} was calculated from FeO^{tot} on a basis of 30 cations and 90 charges. Asterisks = deerites in sample 79/293 from Andros; dots = published analyses (Agrell *et al.*, 1965; Agrell and Gay, 1970; Bocquet and Forette, 1973; Brown, 1974; Muir Wood, 1979; Langer *et al.*, 1977; Schliestedt, 1978, 1980).

Millimeter-sized garnets in the deerite-bearing quartzite have compositions rich in spessartine, almandine, and andradite (Table 1). Aegirine compositions are typically in the range 64–82 mole % acmite, 8–20 mole % jadeite, and 6–12 mole % augite (including rhodonite). Magnetite shows significant solid solution towards jacobsite (Table 1).

Calderite–andradite–garnet quartzite

The fine-grained garnet quartzites show a subparallel banding of quartz-rich layers, less than one millimeter thick, alternating with layers rich in yellow-brown garnet ± aegirine ± magnetite. Rarely, lenses of rose coloured rhodonite–rhodochrosite ± garnet-bearing rock are enclosed in the quartzite. The mineral assemblages of the garnet quartzite are:

(i) quartz + garnet + rhodonite + rhodochrosite + magnetite ± baryte ± orthite,

and

(ii) quartz + garnet + aegirine + hematite.

The subhedral garnets which are yellow coloured in thin section and typically 5–100 μm in diameter, occur irregularly distributed in the equigranular quartz matrix. Rhodonite forms poikiloblasts, 100–500 μm across, including quartz, rhodochrosite, and magnetite. There are no indications of a greenschist-facies overprint on the garnet quartzite assemblages.

Selected mineral analyses from one sample are shown in Table 1. Garnets show unusual Al-poor compositions. Assuming Fe_{tot} and Mn_{tot} as Fe^{3+} and Mn^{2+}, respectively, cation totals of Mn^{2+} + Ca and Fe^{3+} + Al satisfy the constraints of the garnet formula. The analysed garnets typically contain 30–45 mole % calderite, 55–70 mole % andradite, and 0.4–2.3 mole % spessartine, and thus are almost binary andradite–calderite solid solutions. Rhodonite has a rather uniform composition, typically 77–81 mole % $MnSiO_3$, 5.4–8.5 mole % $FeSiO_3$, 0.8–1.1 mole % $MgSiO_3$, and 12.4–14.2 mole % $CaSiO_3$. Rhodochrosite is enriched in Ca and Mg and is depleted in Fe^{2+} relative to coexisting rhodonite (Table 1). Magnetite is unusually rich in Ni and Mn (0.6–6.2 wt. % NiO and 1.7–3.4 wt. % MnO in different homogeneous grains; Table 1). Recalculated to Fe_3O_4, jacobsite, $MnFe_2O_4$, and trevorite, $NiFe_2O_4$, magnetite solid solutions range from 1.9–20.2 mole % trevorite, 5.9–11.5 mole % jacobsite, and 73.1–90.8 mole % Fe_3O_4.

Discussion

Except for rhodonite, the assemblage calderitic garnet + rhodonite + magnetite observed in Al-poor quartzites on Andros corresponds to the reaction assemblage calderite$_{ss}$ + pyroxmangite$_{ss}$ + magnetite$_{ss}$ occurring in experiments aimed at determining the stability of calderite garnet in the system Fe-Mn-Si-O at the f_{O_2} of the hematite-magnetite buffer (Lattard and Schreyer, 1983). For a given *P*, *T*, and f_{O_2}, the presence of pyroxmangite/rhodonite$_{ss}$ + magnetite$_{ss}$ buffers the calderite solid solution in garnet at a maximum value according to the reaction:

$$\underset{\text{pyroxenoid}}{18\,MnSiO_3} + \underset{\text{magnetite}}{4\,Fe_3O_4} + \underset{\text{oxygen}}{O_2} = \underset{\text{calderite}}{6\,Mn_3^{2+}Fe_2^{3+}Si_3O_{12}}. \quad (1)$$

The extrapolation of the experimentally determined high-pressure, high-temperature stability curve to lower temperatures indicates that pure calderite should be stable at about 9 kbar at 400 °C and at about 13 kbar at 500 °C (Lattard and Schreyer, 1983). Calderitic garnets in the assemblage garnet + rhodonite + magnetite from Andros, however, contain only up to 45 mole % calderite, although the physical conditions of the regional high-*P*, low-*T* metamorphism might have been close to or even within the stability field of pure calderite.

This discrepancy may result from: (i) uncertainties in extrapolating the experimental data to much lower *P* and *T*; (ii) the presence of additional components (Ni, Ca, and Mg) lowering the activities of $MnSiO_3$ in rhodonite and Fe_3O_4 in magnetite so that the garnet must not have the maximum calderite content predicted from the experimental data; and (iii) the influence of a variable f_{O_2} on the location of reaction (1) in the *P*–*T* field. For instance, a lower f_{O_2} than that of the hematite-magnetite buffer, at which the experiments of Lattard and Schreyer (1983) were carried out, places reaction (1) at a higher equilibrium pressure (at constant *T*).

Although the physical conditions of high-pressure metamorphism on Andros have been favourable for the high-pressure polymorph of $MnSiO_3$, pyroxmangite (Maresch and Mottana, 1976), only rhodonite is present in all samples investigated. Apparently, the preferred incorporation of Ca in rhodonite relative to pyroxmangite stabilizes rhodonite effectively towards higher pressures (cf. Maresch and Mottana, 1976; Chopin, 1978). The change in the slope of reaction (1) resulting from the presence of rhodonite instead of pyroxmangite is probably small, because the ΔS and ΔV of the rhodonite–pyroxmangite transition is small (Navrotsky and Coons, 1976).

The microprobe analyses of deerites from Andros reveal unexpected high Mn contents suggesting that a manganese end member of deerite, $Mn_{12}^{2+}Fe_6^{3+}Si_{12}O_{40}(OH)_{10}$, may exist. This represents a new phase in the system $MnSiO_3$–Fe_2O_3–H_2O which is also relevant to equilibria among pyroxmangite/rhodonite, hematite, and calderite similar to those discussed above. Fig. 2 shows two possible enantiomorphic configurations of univariant reactions around the invariant point which were constructed with the assumption that all dehydration reactions [(Px), (Hem), and (Cald)] have a positive d*P*/d*T* slope and that the slope of the reaction (MnDe), (H_2O) (calderite = pyroxmangite + hematite) is similar to that of the experimentally investigated breakdown of calderite (Lattard and Schreyer, 1983). Both configurations predict that for a Mn-rich bulk composition, calderite and manganoan deerite may coexist at high pressures if there is some H_2O present in the rock. So far, however, the assemblage deerite + calderitic garnet (+ quartz ± pyroxenoid ± hematite/magnetite) which would yield informa-

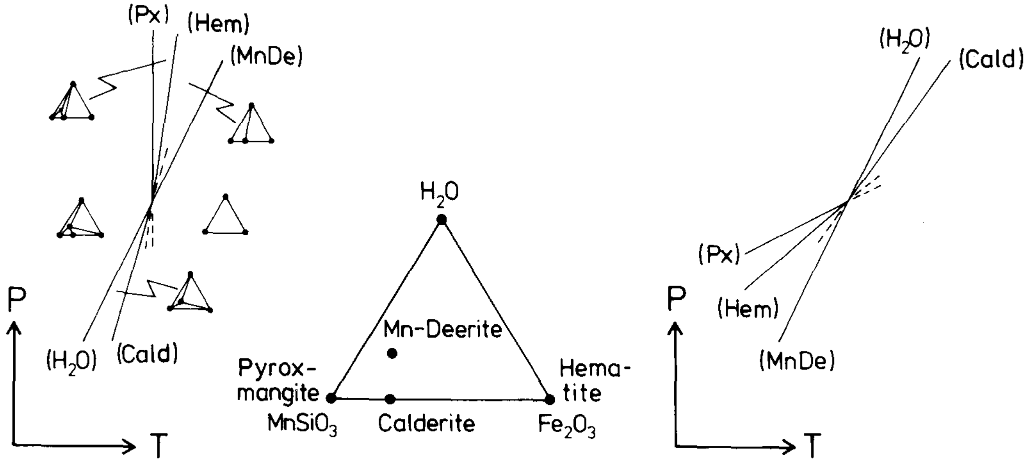

FIG. 2. Chemographic relations between calderite (Cald), pyroxmangite (Px), mangano-deerite (Mn-De), hematite (Hem), and H_2O in the system $MnSiO_3$–Fe_2O_3–H_2O. Further explanations in the text.

tion about cation partitioning between minerals in natural, chemically more complex systems, has not been found in blueschist-facies rocks.

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