

Deerite from Papua New Guinea

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Abstract

Deerite in two meta-ironstones from Papua New Guinea coexists with quartz-albite-riebeckite-dannemorite-magnetite-spessartine-stilpnomelane-apatite-Ca/Mn carbonates and quartz-albite-crossite-ilmenite-spessartine-stilpnomelane-apatite respectively. Geochemical comparisons in the system FeO-MnO-MgO suggest that the P.N.G. deerites most closely resemble Franciscan types. However, the metamorphic assemblages more closely resemble Alpine types indicating metamorphism close to the lower P - T limit of deerite stability. Consistent differences in whole-rock and internal oxidation ratios between the two specimens suggest that f_{O_2} may be important in determining deerite chemistry. A redox equation is suggested linking changes in deerite internal oxidation ratio with variable OH content.

KEYWORDS: deerite, Papua New Guinea, oxygen fugacity.

Introduction

THE relatively rare hydrous iron silicate deerite (Agrell *et al.*, 1965) has been described from a number of localities around the world (see Muir Wood, 1979). Its occurrence appears to be limited to rocks of the glaucophane-lawsonite schist and associated transitional facies. This is consistent with experimental work by Langer *et al.* (1977) and Lattard and Schreyer (1981) which has suggested that under geological conditions its stability is limited to high pressure and low temperature. Its rarity has been attributed to the unusual combination of iron-rich chemistry and metamorphic grade required for its formation. This paper records the first occurrence of the mineral in Papua New Guinea.

Setting

The deerites occur in float blocks from Madi creek (Specimen 7008) 1 km WNW of Kokoda government headquarters (Lat 8° 53' S Long 147° 44' E) and Iora Creek (Specimen 7137) some 22 km south of Kokoda. Both localities are in the Northern province of Papua New Guinea. The area is very rugged and is covered by dense tropical rain forest. Exposure is rare and most specimen collecting is done in the creeks. Madi and Iora Creeks drain the Emo Metamorphic member of the Owen Stanley Metamorphics which form the mountainous spine of the Papuan peninsula. The Emo Meta-

morphics structurally underlie the Papuan Ophiolite Complex and are separated from it by a major thrust fault, the Owen Stanley Fault (Davies, 1971). The Emo Metamorphics are dominantly metabasites containing glaucophane and sparse lawsonite suggesting glaucophane-lawsonite-schist facies metamorphism (Davies, 1971; Pieters, 1978). Davies (1980) suggested that metamorphism occurred in the Eocene in a north-easterly-facing subduction zone prior to obduction of the ophiolite. Subsequent uplift and erosion exposed the ophiolite-metabasite complex at the surface. No detailed petrological and geochemical work has been done on these rocks.

Petrography

Specimen 7008 contains the assemblage deerite-quartz-albite-riebeckite-dannemorite-magnetite-spessartine-stilpnomelane-apatite-CaMn carbonates with secondary tirodite. Specimen 7137 contains deerite-quartz-albite-crossite-ilmenite-spessartine-stilpnomelane-apatite and secondary chlorite. The hand specimens are strikingly banded on a 2 mm scale, comprising alternating pink and black layers with some pale-coloured pods and layers. The pink bands are composed mostly of densely-packed zoned spessartine subhedra up to 25 μ m across (e.g. Sp 69.1 And 13.1 Gr 11.0 Alm 6.3 Py 0.5 in 7008 and Sp 41.2 Alm 38.0 Gr 10.9 And 9.1 Py 0.4 Uv 0.4 in 7137) with scattered porphyroblastic alkali amphiboles, iron-oxides and albite. The darker bands contain greater concentrations of

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alkali amphiboles and iron oxides. In 7008 the amphibole is riebeckite and in 7137 crossite; both contain abundant garnet inclusions. In 7008 the Mn-rich amphiboles dannemorite and tirodite occur in equivocal textural relationships. Some grains appear to be primary whilst others occur in a reaction relationship with riebeckite. Preliminary study of the geochemistry of the two textural types suggests that the dannemorite [$Mg/(Mg + Fe^{2+}) < 0.5$] is primary whilst the tirodite [$Mg/(Mg + Fe^{2+}) > 0.5$] is secondary after riebeckite. The iron oxides are almost pure magnetite in 7008 and mangan-ilmenite with up to 6 mole% Fe_2O_3 in 7137. The pale-coloured pods and layers are composed mainly of quartz with some calcium manganese carbonates (parakutnahorite, mol% Ca 69.4, Mn 24.6, Fe 3.4, Mg 2.4, Zn 0.19) in 7008. Both rocks contain stilpnomelane which is slightly altered to chlorite in 7137. Apatite is also present in both rocks.

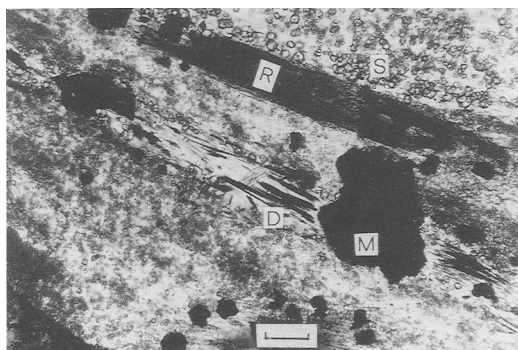


FIG. 1. Photomicrograph of 7008 showing main minerals and banding. D = deerite, M = magnetite, R = riebeckite, S = spessartine. Bar scale = 50 μ m.

The deerite occurs as sparse dark brown acicular to lath-like crystals (Fig. 1) associated with the quartz-rich layers. In 7008 the crystals are up to 125 μ m in length. In 7137 they are smaller, up to 100 μ m, and satisfactory analyses were difficult to obtain. In thin quartzose layers the needles are aligned along the banding though in thicker quartzose pods the mineral may grow randomly as inclusions within the quartz. In one part of the rock the mineral occurs as inclusions within the carbonate. In both specimens the deerite has been observed in mutual contact with garnet, alkali amphibole and iron oxide. The grains shows strong absorption though pleochroism from black-brown to dark red-brown is apparent. Finer needles within the quartz are honey-coloured and may easily be confused with rutile.

Chemistry

Whole rock and mineral chemistry data are presented in Table 1. Mineral chemistry was determined using a Link 860-500 E.D.S. system attached to a Jeol JXA 50A electron microprobe using an accelerating voltage of 20 kV, a beam current of 1 nA and a livetime of 100 seconds. Corrections were made using Link ZAF4/FLS software. Fe^{3+} values were determined by charge balance. Whole-rock FeO values were obtained by HF digestion and titration with standardised potassium dichromate solution. Notable features of the whole-rock chemistry are the high Fe and Mn contents. The whole-rock geochemistry suggests that the rocks may have been siliceous ironstones interbedded with the basalts and enriched in exhalative Mn and Fe of volcanogenic origin (Worthing and Bennett, in prep.).

Two analyses of the deerites from each rock are presented in Table 1. Microprobe traverses along the length of crystals revealed slight compositional variations, the two analyses representing the extremes of this variation. The analyses are normalised to 45 oxygens with Fe^{2+} and Fe^{3+} calculated by charge balance on the basis of 30 cations. The ideal formula of deerite requires 12 Si on the basis of 30 cations and 45 oxygens but natural deerites tend to have values in excess of 12. Muir Wood (1979) suggested that the discrepant values may be due to variations in hydroxyl content and octahedral cation vacancies. All the Si values quoted in Table 1 are higher than the ideal formula, though all except the second analysis for 7137, fall within the range quoted by Muir Wood (1979). The deerites in 7137 are very small and microprobe analyses were difficult to obtain, thus this high Si values may be due in part to contamination by adjacent quartz.

Fig. 2A shows a plot of published deerite analyses (Brown, 1974; Schliestedt, 1978; Muir Wood, 1979), together with the P.N.G. specimens, in the system FeO-MnO-MgO. Franciscan deerites tend to be richer in MnO than Alpine types, reflecting the oceanic Fe-Mn-rich sedimentary facies of the Franciscan. The P.N.G. samples most closely resemble the Franciscan types, being characterised by higher MnO values, but they differ in that they contain significantly higher levels of MgO. In this respect they resemble manganiferous deerites from the Cycladic blueschists of Greece which contain from 1.5 to 2.8% MgO (Reinecke, 1987). Evidence of whole-rock chemical control is suggested by the differing compositions of the P.N.G. samples (Fig. 2A). A higher whole-rock MnO in 7008 is reflected in higher MnO values in the deerites.

Although the P.N.G. deerites are chemically similar to the Franciscan types, the metamorphic

Table I. Whole rock and mineral chemistry

Wt% Oxide	Rock 7008	Rieb	Dan	Mag	Garnet	Stilp	---Deerite---		Rock 7137	Cross	Ilm	Garnet	Stilp	---Deerite---	
SiO ₂	56.47	52.97	51.77	0.74	36.47	47.33	34.98	35.54	65.09	55.19	0.31	36.81	49.71	35.78	36.70
TiO ₂	0.27	0.00	0.00	0.01	0.40	0.00	4.63	1.46	0.42	0.07	52.14	0.22	0.03	5.20	4.37
V ₂ O ₅	nd	nd	nd	0.29	nd	nd	0.28	0.13	nd	nd	0.18	nd	nd	0.82	0.38
Al ₂ O ₃	4.08	1.63	0.95	0.21	17.92	5.32	0.00	0.24	8.14	6.89	0.02	18.67	6.11	0.21	0.29
Cr ₂ O ₃	nd	0.04	0.04	0.00	0.00	0.00	0.01	0.02	nd	0.00	0.00	0.13	0.05	0.00	0.00
Fe ₂ O ₃	13.57	14.71	19.86*	66.56	4.26	-	7.97	15.60	4.07	7.48	0.33	2.94	-	4.82	5.33
FeO	8.85	16.17	19.86*	30.83	2.94	17.78*	34.50	31.12	9.98	16.08	38.27	16.71	27.29*	44.20	44.36
MnO	6.52	1.20	14.71	0.89	29.71	9.41	9.32	9.21	3.48	0.11	8.46	17.77	2.39	2.10	1.93
MgO	1.76	3.75	9.20	0.06	0.13	7.16	1.08	1.76	1.56	4.73	0.22	0.09	4.28	0.63	0.80
CaO	3.88	0.43	0.79	0.00	8.24	0.29	0.00	0.00	2.48	0.19	0.00	6.94	0.18	0.00	0.00
Na ₂ O	1.32	6.61	0.48	nd	nd	0.14	nd	nd	1.91	7.33	nd	nd	0.00	nd	nd
K ₂ O	0.02	0.00	0.00	nd	nd	0.80	nd	nd	0.04	0.01	nd	nd	0.53	nd	nd
P ₂ O ₅	0.73	nd	nd	nd	nd	nd	nd	nd	0.49	nd	nd	nd	nd	nd	nd
NiO	nd	0.20	0.31	0.21	nd	0.11	0.00	0.13	nd	0.19	0.00	nd	0.10	0.00	0.07
ZnO	nd	nd	nd	0.00	nd	nd	0.15	0.11	nd	nd	0.09	nd	nd	0.00	0.00
Total	97.47	97.71	98.11	99.80	100.07	88.34	92.92	95.32	97.66	98.27	100.02	100.28	90.67	93.76	94.43
Cations															
Oxygens		23	23	4	12	22	45	45		23	3	12	22	45	45
Si	-	7.981	7.959	0.028	2.984	7.512	12.620	12.483	-	7.976	0.008	3.004	7.693	12.793	12.987
Ti	-	0.00	0.000	0.000	0.025	0.000	1.257	0.386	-	0.007	0.987	0.014	0.003	1.398	1.163
V	-	nd	nd	0.009	nd	nd	0.080	0.035	-	nd	0.004	nd	nd	0.236	0.107
Al	-	0.290	0.172	0.010	1.729	0.994	0.000	0.100	-	1.173	0.001	1.797	1.115	0.087	0.120
Cr	-	0.005	0.004	0.000	0.000	0.000	0.002	0.005	-	0.000	0.000	0.008	0.006	0.000	0.000
Fe ³⁺	-	1.668	-	1.923	0.262	-	2.164	4.122	-	0.813	0.006	0.181	-	1.297	1.472
Fe ²⁺	-	2.037	2.553*	0.990	0.201	2.359*	10.410	9.142	-	1.944	0.805	1.141	3.532*	13.215	13.129
Mn	-	0.153	1.916	0.029	2.059	1.265	2.848	2.740	-	0.013	0.180	1.229	0.313	0.636	0.579
Mg	-	0.843	2.108	0.004	0.016	1.694	0.579	0.921	-	1.018	0.008	0.011	0.988	0.338	0.423
Ca	-	0.069	0.130	0.000	0.722	0.050	0.000	0.000	-	0.029	0.000	0.607	0.029	0.000	0.000
Na	-	1.931	0.143	nd	nd	0.043	nd	nd	-	2.055	nd	nd	0.000	nd	nd
K	-	0.000	0.000	nd	nd	0.163	nd	nd	-	0.001	nd	nd	0.104	nd	nd
P	-	nd	nd	nd	nd	nd	nd	nd	-	nd	nd	nd	nd	nd	nd
Ni	-	0.024	0.038	0.006	nd	0.014	0.000	0.036	-	0.002	0.000	nd	0.013	0.000	0.020
Zn	-	nd	nd	0.000	nd	nd	0.040	0.030	-	nd	0.002	nd	nd	0.000	0.000
Total		15.001	15.023	2.999	7.998	14.094	30.000	30.000		15.051	2.001	7.992	13.796	30.000	30.000

Fe³⁺ calculated by charge balance

nd = not determined

* Total iron as FeO

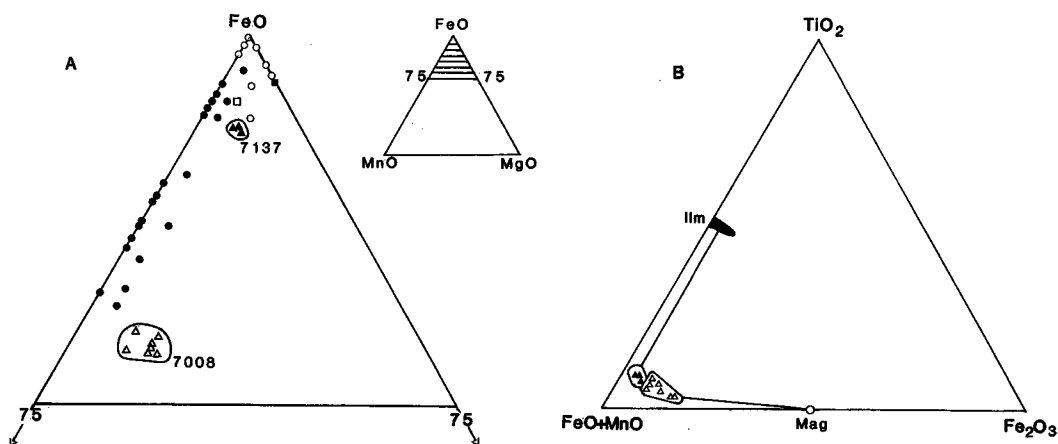


FIG. 2A. Composition of deerites in the system FeO-MnO-MgO: closed circles Franciscan types, open circles Alpine types (Muir Wood, 1979); closed square (Schliestedt, 1978); open square (Brown, 1974). P.N.G. deerites: open triangles 7008, closed triangles 7137. FIG. 2B. Compositions of magnetite, mangano-ilmenite and deerite in the system TiO₂-(FeO+MnO)-Fe₂O₃. Tie-lines join coexisting minerals. Deerite ornament as in 2A; both diagrams Mol% oxide.

assemblages more closely resemble the Alpine types which commonly contain riebeckite and magnetite (e.g. Bocquet, 1971; Schliestedt, 1978). Magnetite is absent from the Franciscan assemblages and riebeckite is not stable. Based on the phase relationships of minerals believed to have been involved in deerite-forming reactions, Muir Wood (1979) placed the low-pressure stability of deerite to 4 kbar at 200 °C and 6 kbar at 300 °C. This is in reasonable agreement with low-pressure extrapolations by Lattard and Schreyer (1981) based on high-pressure experimental studies on ferri-deerite. The presence of magnetite and the high activity of Na suggested by the occurrence of riebeckite in 7008 suggests that the P.N.G. samples were formed close to these lower P - T conditions (Muir Wood, 1979). The Franciscan assemblages appear to have formed under somewhat higher P - T conditions.

Role of f_{O_2}

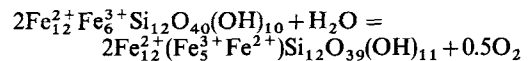
Chopin (1978), in a study of Alpine manganeseiferous cherts metamorphosed in the blueschist facies, described juxtaposed layers with reduced and oxidised assemblages. He concluded that the intrinsic oxygen fugacity of each layer dated back to the sedimentary origin of the rocks. This implies a very low oxygen mobility during metamorphism. Okay (1979) has suggested that alkali amphiboles may be used as f_{O_2} indicators. A plot of the alkali amphiboles in 7008 and 7137 relative to Okay's f_{O_2} isopleths suggests that 7008 was metamorphosed under higher f_{O_2} than 7137. The presence of magnetite in 7008 suggests metamorphism below the hematite-magnetite buffer. The upper f_{O_2} - T stability of ilmenite lies below the hematite-magnetite buffer (Rumble, 1976) but there is a wide f_{O_2} - T field in which the two minerals can coexist. However, ilmenite can indicate a lower f_{O_2} than magnetite.

Study of the mineralogy and textures in the metabasites associated with the Papuan deerite-bearing rocks suggests that there was no lateral change in metamorphic grade across the zone from which they were derived (Worthing, in prep.). Thus

the recognition of consistent differences in mineralogical and chemical parameters in 7008 and 7137 which may be controlled by redox reactions may provide data on the possible role of f_{O_2} in controlling deerite chemistry under isophysical conditions.

Table 2 shows internal oxidation ratios $[\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})]$ for the main iron-bearing phases in each rock. In each case the values are higher for 7008 than for 7137. Whole-rock oxidation ratios have a similar relative relationship. In the case of deerite, Fe^{3+} calculations based on charge balance should be viewed with caution in view of the high Si values which may in part be due to analytical error, particularly in the case of 7137. High Si values will decrease the amount of Fe^{3+} determined by calculation. However, the consistent difference in whole-rock and internal oxidation ratios for other phases shown in Table 2 suggests that in the case of the deerites, the differences in internal oxidation ratio are real. These differences are illustrated in Fig. 2B which shows the composition of deerites and iron oxides in the system TiO_2 - $(\text{FeO} + \text{MnO})$ - Fe_2O_3 . Deerites in the riebeckite-magnetite-bearing assemblage (7008) are richer in Fe_2O_3 than those in the crossite-ilmenite-bearing assemblage (7137). The differences in whole-rock and internal oxidation ratios outlined above are consistent with metamorphism under different conditions of f_{O_2} . They suggest that f_{O_2} may be an important variable in the determination of deerite chemistry.

Reinecke (pers. comm.) has suggested a possible redox reaction which relates deerite internal oxidation ratio to changes in OH content:



Muir Wood (1979) has suggested differences in OH content as one possible explanation of the high Si content in deerite microprobe analyses. This reaction links such variations to variable f_{O_2} during metamorphism.

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Table 2. Oxidation ratios

$\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$	7008	7137
Alkali amphibole	0.465	0.313
Garnet	0.419	0.066
Deerite	0.229	0.088
Whole-rock oxidation ratio	74.49	43.35

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